

Final

Phase I Groundwater Sampling Field Sampling Workplan

University of California, Berkeley
Richmond Field Station, Richmond, California

April 15, 2010

Prepared for
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University of California, Berkeley
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Prepared by



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April 15, 2010

Barbara J. Cook, P.E.
Acting Assistant Deputy Director
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Department of Toxic Substances Control
Attention: Lynn Nakashima
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Dear Ms. Cook:

The University of California, Berkeley (UC Berkeley), prepared this Final Field Sampling Workplan (FSW) in response to the California Environmental Protection Agency, Department of Toxic Substances Control (DTSC), Site Investigation and Remediation Order No. IS/E-RAO 06/07-004. In November 2008, UC Berkeley prepared a Current Conditions Report (CCR) for DTSC to provide a comprehensive summary of current conditions at the Richmond Field Station (RFS) and to identify data gaps that warrant additional characterization or evaluation at the RFS. Section 5.3.1 of the Order requires preparation of a FSW to conduct site investigations to address these data gaps.

This Final FSW outlines a site-wide field investigation strategy which differs from the approach proposed in the February 27, 2009 Draft FSW. UC Berkeley staff and consultants have worked closely with DTSC staff in revising the text, tables, figures, and appendices of the Draft FSW. The document was edited to address DTSC's written comments on the Draft FSW, dated April 15, 2009 and December 1, 2009. Additional comments were also received in a meeting with DTSC staff on October 27, 2009.

Given the broad scope of activities necessary to address the data gaps identified in the CCR, the planned field investigations will be conducted in five temporal phases (Phases I through V), as endorsed by DTSC at a meeting on December 19, 2008. Phase I of the investigations will begin with the implementation of a site-wide groundwater sampling investigation. This approach, agreed upon by UC and DTSC during the October 27, 2009 working meeting, will determine overall groundwater characteristics and confirm or deny the presence of any unknown groundwater contamination issues. The proposed Phase I investigation will focus on the shallow and intermediate groundwater zones.

An assessment of potential adverse impacts to groundwater quality is the focus of the Phase I investigation. The Final FSW incorporates the Phase I Field Sampling Plan (FSP) and includes the approach and rationale for the facility-wide groundwater investigation. The sampling strategies for subsequent Phases II through V will be determined based on the findings of the Phase I investigation. The Phase II through V investigations will include soil, soil-gas, and other sampling strategies to resolve specific data gaps outlined in the FSW, as well as any new data gaps indicated by results of the Phase I groundwater investigation. The sampling strategies for the Phase II through V investigations will be proposed through planning documents similar to this FSW and will include site-specific background and history, purpose for sampling, data quality objectives, sample locations, site-screening level methodology, and chemicals of potential concern.

The objectives of the phased investigations are to (1) identify potential risks to public health and the environment and (2) prioritize and implement response actions using removal actions and operable units, if appropriate, based on the relative potential risks at the site. Site- and chemical-specific methodologies for identifying and applying background concentrations and screening levels will be developed in concurrence with DTSC following the receipt and review of groundwater analytical data, as agreed by UC Berkeley and DTSC at the meeting on October 27, 2009.

Although we continue to be constrained by the stark realities of the state budget, UC Berkeley is pleased to be working closely with DTSC to move forward on this important project.

If you have questions, please contact me at (510) 642-4848 or gjhaet@berkeley.edu.

Sincerely,

A handwritten signature in black ink, appearing to read 'G. Haet', with a long horizontal line extending to the right.

Greg Haet
Associate Director

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ACRONYMS AND ABBREVIATIONS

AST	Aboveground storage tank
BAPB	Biologically active permeable barrier
Bay Trail	East Bay Regional Parks District's Bay Trail
bgs	Below ground surface
CCR	Current Conditions Report
COC	Chemical of concern
COPC	Chemical of potential concern
CSM	Conceptual site model
CSV	Cherokee Simeon Ventures I, LLC
DQO	Data quality objectives
DTSC	Department of Toxic Substances Control
EPA	U.S. Environmental Protection Agency
FPL	Forest Products Laboratory
FSP	Field Sampling Plan
FSW	Field Sampling Workplan
HSP	Health and Safety Plan
IDW	Investigation-derived waste
MCL	Maximum contaminant level
MS/MSD	Matrix spike/matrix spike duplicate
NAWQC	National Ambient Water Quality Control
OSHA	Occupational Safety and Health Administration
Order	DTSC Site Investigation and Remediation Order No. IS/E-RAO 06/07-004
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PG&E	Pacific Gas & Electric
PID	Photoionization detector
QAPP	Quality Assurance Project Plan
QC	Quality control
RAO	Remedial action objective
RI/FS	Remedial Investigation/Feasibility Study
RFS	Richmond Field Station
SVOC	Semivolatile organic compound
TCRA	Time-critical removal action
TDS	Total dissolved solids

ACRONYMS AND ABBREVIATIONS (continued)

Tetra Tech	Tetra Tech EM Inc.
TPH	Total petroleum hydrocarbons
TPH-e	Total extractable petroleum hydrocarbons
TPH-p	Total purgeable petroleum hydrocarbons
UC	University of California
VOC	Volatile organic compound
WTA	Western Transition Area
WTL	Wood treatment laboratory

1.0 PROJECT DESCRIPTION

The University of California (UC), Berkeley, prepared this Field Sampling Workplan (FSW) in response to the California Environmental Protection Agency, Department of Toxic Substances Control (DTSC), Site Investigation and Remediation Order No. IS/E-RAO 06/07-004 (Order). In response to the Order, UC Berkeley prepared a Current Conditions Report (CCR) ([Tetra Tech EM Inc. \[Tetra Tech\] 2008](#)). The final CCR, dated November 21, 2008, provided a comprehensive summary of current conditions at the Richmond Field Station (RFS) in accordance with the DTSC Order, including the 96 acres of upland and 13 acres of tidal marsh and transition habitat. The RFS is an academic teaching and research facility, located adjacent to the San Francisco Bay and 6 miles northwest of the UC Berkeley Central Campus. RFS has been used primarily for large-scale engineering research since 1950.

The CCR identified data gaps that warrant additional characterization or evaluation at the RFS. Section 5.3.1 of the Order requires preparation of a FSW to conduct site investigations in order to address these data gaps. The objective of the site sampling is to address data gaps to complete a final remediation investigation report and baseline health risk assessment. Given the broad scope of activities necessary to address the data gaps identified in the CCR, the planned field investigations will be conducted in five temporal phases (Phases I through V), as approved by DTSC at a meeting on December 19, 2008. Phase I of the investigations will begin with the implementation of a site-wide groundwater sampling investigation. This approach, agreed upon by UC and DTSC, will determine overall groundwater characteristics and confirm or deny the presence of any unknown groundwater contamination issues. The proposed Phase I investigation will focus on the shallow and intermediate groundwater zones. The FSW outlines the sampling strategy for Phase I. The sampling strategies for Phases II through V will be proposed through planning documents similar to this FSW—field sampling plans (FSP)—and will include site-specific background and history, purpose for sampling, data quality objectives (DQO), sample locations, site-screening level methodology, and chemicals of potential concern (COPC). Future FSPs will reference methodologies and protocols presented in this FSW.

1.1 FIELD SAMPLING WORKPLAN COMPONENTS

This section describes the elements of the FSW. The FSW is a facility-wide document that includes two appendices: a facility-wide planning Quality Assurance Project Plan (QAPP), and a facility-wide Health and Safety Plan (HSP). The FSW is also intended to serve as the Phase I FSP and will address the approach of and rationale for the facility-wide groundwater investigation. Site-specific FSPs, outlining investigation Phases II through V, will be prepared after completion of Phase I. The scope of these sampling plans is not yet defined; however, the site-specific FSPs will address data gaps not resolved by groundwater sampling, and will introduce soil and soil gas (if necessary) investigations at the RFS. Together, the FSW, QAPP, HSP, and FSPs will meet the intended purpose of the FSW as defined in the DTSC Order.

1.1.1 Field Sampling Workplan

The FSW is intended for use as the first planning document in a series that will outline field, laboratory, and data reporting efforts associated with sampling and reporting to address the data gaps at RFS. The FSW outlines the site-wide project background, objectives, conceptual site model (CSM), roles and responsibilities, and schedule for investigating RFS. The FSW also acts as the FSP for Phase I; therefore, the FSW includes remedial action objectives (RAO), site-

specific background and history, purpose for sampling, DQOs, and an outline of the sampling strategies, which includes sample locations, rational, depths and sampling COPCs.

1.1.2 Quality Assurance Project Plan

The QAPP (Appendix A) establishes criteria for data quality assurance and control, and serves as a reference for facility-wide activities such as field data collection and sample analysis. The QAPP includes a brief history and background of RFS, quality assurance objectives, sampling procedures, sample handling protocols, laboratory procedures, data validation and reporting, internal quality review, performance monitoring, data evaluation and assessment procedures, quality assurance reporting, and laboratory certification. The QAPP includes project organization and responsibilities with respect to sampling and analysis.

The DTSC approval of the QAPP will enable the RFS project team to prepare site-specific FSPs that incorporate by reference the facility-wide QAPP for data quality and sample collection, ensuring consistent quality throughout the project. As FSPs for subsequent phases are prepared, if new sample collection methods are recommended, the QAPP will be revised or amended to include all applicable information.

1.1.3 Health and Safety Plan

The HSP (Appendix B) assesses the type, risk level, and severity of hazards for the project, and identifies safe work practices and appropriate personal protective equipment for site personnel in accordance with California and Federal Occupational Safety and Health Administration (OSHA) standards. The HSP includes a brief site history and background, chemicals of potential concern, a description of standard work practices, hazard assessment, and health and safety requirements. HSP addenda will be submitted with the FSPs and will include a summary description of the project including the duration of planned activities, personnel requirements, the extent to which subcontractors will be used, and all available information regarding contaminants and conditions present at the area being investigated.

1.1.4 Field Sampling Plans

FSPs will identify the site-specific data gaps, and data collection approaches and activities to successfully complete each subsequent phase of the site investigations. The sampling strategies for Phases II through V have not yet been determined but will be developed based on the findings of the Phase I investigation. The Phase II through V investigations will include soil and soil-gas sampling strategies to resolve specific data gaps outlined in the CCR, as well as any remaining groundwater data gaps apparent from results of the Phase I groundwater investigation. The scopes for Phases II through V will also be determined by DTSC and UC Berkeley site prioritization. Each FSP will include site-specific background and history, purpose for sampling, DQOs, sample locations, site-screening levels, and chemicals of potential concern. Each FSP will reference the facility-wide QAPP (Appendix A) for general sampling procedures and data collection protocols applicable to all data collection at RFS.

1.2 PHYSICAL SETTING

The RFS is located at 1301 South 46th Street, Richmond, California, along the southeastern shoreline of the City of Richmond on the San Francisco Bay and northwest of Point Isabel (see [Figure 1](#)). It consists of upland areas developed for academic teaching and research activities, an upland remnant coastal terrace prairie, a tidal salt marsh, and a transition zone between the upland areas and marsh. Between the late 1800s and 1948, several companies, including the California Cap Company, manufactured explosives at the RFS. In 1950, The UC Regents purchased the property from the California Cap Company. UC Berkeley initially used the RFS for research for the College of Engineering; later, it was also used by other campus departments.

In this FSW, the RFS is described in terms of types of habitat because future uses and potential receptors vary by the type of habitat available. Three habitat type areas have been identified at RFS: (1) the Upland Area, (2) the Transition Area, and (3) the Western Stege Marsh (see [Figure 2](#)).

The Upland area consists of 96 acres of land bounded by Meade Street to the north, South 46th Street to the east, the Transition Area to the south, and Meeker Slough and Regatta Boulevard to the west. The Transition Area occupies approximately 5.5 acres and is bounded to the north by the Upland Area at the location of a buried, former seawall that is believed to have been the edge of the historic mudflats, and to the south by Western Stege Marsh at the 5-foot elevation upper extent of the marsh (National Geodetic Vertical Datum 29). The Transition Area is believed to consist entirely of artificial fill placed on historic mudflats. Western Stege Marsh occupies approximately 7.5 acres and is bounded by the Transition Area to the north, the RFS connector trail to the East Bay Regional Park District Trail (Bay Trail) and Eastern Stege Marsh to the east, the Bay Trail to the south, and Meeker Slough and Marina Bay housing development to the west (see [Figure 2](#)).

1.3 HISTORY

Between the 1880s and 1948, prior to UC ownership, the California Cap Company operated facilities on portions of the RFS property for manufacture of blasting caps, shells, and explosives ([UC Berkeley 1973](#)). Two small companies, the U.S. Briquette Company and the Pacific Cartridge Company, are presumed to have operated on a portion of the RFS property.

By 1920, the California Cap Company was the only remaining explosives manufacturer on site. Operations of the California Cap Company plant included manufacturing explosives (primarily mercury fulminate), shells, and blasting caps; testing explosives; and storing explosives ([URS Corporation 1999](#)). All components of the blasting caps were manufactured on site, including explosives, shells, copper containers, tin boxes, paper cartons, and insulated wire.



Richmond Field Station
University of California, Berkeley

FIGURE 1 SITE LOCATION MAP

Field Sampling Workplan



- Bay Trail
- Meeker Slough
- Western Stage Marsh
- Transition Area (Including Bulb)
- Upland
- Property Boundary
- Approximate Property Boundary

Notes:
 EBRPD East Bay Regional Parks District
 EERC Earthquake Engineering Research Center
 EPA Environmental Protection Agency
 NRLF Northern Regional Library Facility
 RFS Richmond Field Station



Richmond Field Station
University of California, Berkeley

FIGURE 2 SITE MAP

Field Sampling Workplan

In October 1950, the California Cap Company property was purchased by UC with the agreement that the California Cap Company would remove all hazardous materials from the property. However, subsequent site observations and testing revealed the presence of hazardous materials on RFS. For example, several explosions reportedly occurred between 1950 and 1953 during a controlled burn for clearing. These explosions likely were associated with residual chemicals used by the California Cap Company. Previous investigations in the test pit and explosive storage area identified a detection of explosives at a concentration close to the detection limit ([URS Corporation 2000](#)).

The RFS was initially established by UC Berkeley for large-scale engineering research that required significant space and resources that were not available on UC Berkeley's central campus in downtown Berkeley. Studies more suited to an off-campus location included research on solid waste and sewage, transportation and lighting studies, and beach erosion modeling ([McGauhey 1974](#)). Research projects have been and are conducted under the supervision of professors from numerous UC Berkeley colleges and departments. Current research activities are conducted by the College of Engineering, the College of Natural Resources, Art Practice, the Center for Tissue Engineering, Earthquake Engineering, the Institute for Transportation Studies, the Center for Occupational and Environmental Health's Ergonomics Program, the Northern Regional Library Facility, and others. The research is performed by graduate students, professors, and researchers, supplemented by support staff and technicians ([UC Berkeley 2006](#)).

In addition to UC Berkeley-related operations, the UC Regents have leased space to non-UC Berkeley tenants. Current tenants include the U.S. Environmental Protection Agency (EPA) Region 9 Laboratory; Schlumberger, Inc.; The Watershed Project; and Stratacor, Inc. In 1989, UC management estimated that 250 to 300 people worked at the RFS ([Ensco Environmental Services, Inc. 1989](#)). Current staffing remains at around 300 people.

Many of the RFS buildings historically housed (and currently house) offices, laboratories, warehouses, and workshops used to support engineering projects ([UC Berkeley 2006](#)). Many of the buildings used by the California Cap Company were torn down when UC Berkeley purchased the RFS property, but some buildings still remain—including two buildings that were formerly homes and several buildings used for a laboratory, offices, and storage. In a few cases, RFS moved buildings to new locations on the property ([UC Berkeley 2006](#)). A summary of historical academic research and teaching activities associated with the RFS is presented in the final CCR ([Tetra Tech 2008](#)).

2.0 SUMMARY OF PREVIOUS INVESTIGATIONS AND DATA GAPS

Section 2 presents a summary of previous investigations performed at RFS. Sampling results documented through November 21, 2008, are presented in detail in the CCR ([Tetra Tech 2008](#)).

2.1 SUMMARY OF PREVIOUS SITE INVESTIGATIONS

Numerous extensive investigations at the RFS have focused on known and suspected sources and their contaminants. These investigations have included characterization of soil, sediment, surface water, groundwater, and indoor air quality. This section is a summary of the previous investigations as presented in the CCR ([Tetra Tech 2008](#)), and therefore specific references are not presented in this document. Specific sampling locations, chemicals, and results are reported in the reference documents identified in the CCR.

2.1.1 Soil Investigations in the RFS Upland Area

Soil samples collected from the Upland Area have been analyzed primarily for metals and polychlorinated biphenyls (PCB), and on a more limited basis for pesticides, semivolatile organic compounds (SVOC), volatile organic compounds (VOC), explosives, and total petroleum hydrocarbons (TPH). Soil and groundwater samples were also collected in the former Research Well Field area, located in the central portion of the RFS Upland Area, to determine the presence or absence of radionuclides.

Remediation activities performed in the Upland Area in 2004 consisted of excavating soil at locations where elevated concentrations of metals and PCBs had previously been identified. The remediated portions of the Upland Area were backfilled with clean soil after excavation. Another small area near the former Forest Products Laboratory (FPL) Wood Treatment Laboratory (WTL) area was excavated and backfilled with clean soil in October and November 2007.

Additionally, between 2007 and 2010, soil samples have been collected in numerous areas to assess construction worker exposure and waste disposal requirements for a number of completed or planned small utility installation, building renovation, and proposed research equipment installation projects. The only known remaining portions of the Upland Area with elevated concentrations of concentrations of concern (COC) in soil are near the former California Cap Company Mercury Fulminate Plant and isolated areas of pyrite cinders.

2.1.2 Soil Investigations in the RFS Transition Area

The eastern portion of the Transition Area was remediated during several phases between 2002 and 2003, and the areas were backfilled with clean soils and sediments. The western portion of the Transition Area, including a feature known as “the Bulb”, consists of historical fill material from unknown sources that were placed onto the former tidal mudflat and has not been subject to remediation. Soil samples collected in the western portion of the Transition Area have been analyzed for metals, pesticides, and PCBs. The highest concentrations of chemicals detected in soil in the Transition Area were found primarily in subsurface samples in the sediments of the former tidal mudflat beneath the upland fill material.

2.1.3 Investigation of the Off-Site Areas to the North and East

As described in the CCR, the RFS is bordered by other properties containing former and current industrial operations. To evaluate whether historic industrial operations at bordering properties had impacted RFS, soil samples were collected from the northern off-site property area for PCB analysis. Samples were also collected from the eastern off-site property area at five locations for analyses for metals and pesticides.

2.1.4 Investigations in Western Stege Marsh

Remediation of the eastern portion of the Western Stege Marsh was performed in two phases in 2002 and 2003. The remediation activities in the marsh included excavation of sediments down to clean, stiff, tan clay, followed by backfilling with clean bay mud. As a result of the completed remediation activities, an extensive area of pollutant source material and most of the contaminated sediments present in the eastern portion of the Western Stege Marsh were removed. Remediation activities performed in 2004 consisted of excavating sediment to widen an existing channel and to create a new channel in the north-central portion of Western Stege Marsh. Following the remediation activities, sediment samples collected from the eastern portion of Western Stege Marsh have been submitted for analysis of metals, PCBs, and pesticides.

2.1.5 Backfill Soils and Sediment

Numerous samples have been collected from the soil and sediment that were used as clean backfill in the areas previously remediated at the RFS. Remediation performed between September 2002 and November 2004 proceeded under oversight of the San Francisco Bay Regional Water Quality Control Board. DTSC oversaw the time-critical removal actions (TCRA) in the vicinity of the former FPL WTL and two locations in the Western Transition Area (WTA) that occurred in October 2007 and October 2008, respectively.

2.1.6 Surface Water Investigations

As part of the project's Groundwater, Surface Water, and Sediment Monitoring Plan, surface water samples have been collected biannually from three locations in Western Stege Marsh and one at the Meeker Slough Bay Trail bridge near the Marina Bay Housing Development from 2006 through the present ([Blasland, Bouck, and Lee 2004](#)). As part of the plan, stormwater runoff samples were collected during rain events in November 2006, April 2007, January 2008, December 2008, March 2009, and October 2009 from five locations: the Eastern Storm Drain outfall, the Western Storm Drain outfall, Meeker Culvert, Meeker Tidal Creek, and at the Meeker Slough Bay Trail bridge.

2.1.7 Groundwater Investigations

Three groundwater zones (shallow, intermediate, and deep) have been identified at RFS; however, most of the groundwater data for RFS has been obtained from the shallow groundwater zone, with approximately 110 samples collected from 95 locations. Shallow zone samples were analyzed for metals, VOCs, pesticides, and PCBs. Metals were the most frequent target analytes, with only a small percentage of samples analyzed for other groups of chemicals. Four groundwater samples were collected from the intermediate zone in three locations along the

eastern property boundary, and three groundwater samples were collected in the deep zone from three locations in the Research Well Field area.

In addition, Cherokee Simeon Venture I, LLC (CSV) began the Lot 1 pilot injection study in the spring of 2010, which includes a portion of RFS in the vicinity of Building 478. The pilot study is being conducted under the oversight of DTSC. The Lot 1 pilot injection study includes installing injection wells, piezometers, and monitoring wells for the purpose of injecting fluids into groundwater to pilot test groundwater treatment technologies and to collect groundwater elevations and samples.

2.2 DATA GAPS

The CCR ([Tetra Tech 2008](#)) identified data gaps that warrant additional characterization or evaluation at the RFS (see [Figure 3](#)). The data gaps are identified as areas where a contaminant release is suspected or where site-specific data are not available to confirm that no contaminant release has occurred. This section summarizes the specific data gaps identified in the CCR. The FSW is intended to act as the Phase I FSP and addresses the approach and rationale for the facility-wide groundwater data gaps investigation. The Phase II through V investigations will include utility, soil, and soil-gas sampling strategies to resolve specific data gaps outlined below, as well as any new data gaps indicated by results of the Phase I groundwater investigation.

The data gaps have been categorized according to three primary sources of concern: (1) soil, (2) groundwater, and (3) utilities. Investigation strategies presented in Section 4 of this FSW are specific for the site-wide groundwater investigation only. However, UC Berkeley understands that future investigation phases may address multiple sources, media, and pathways, depending on initial sampling results. For example, if contaminant releases are detected in groundwater, a soil or soil-gas investigation may be warranted.

2.2.1 Soil

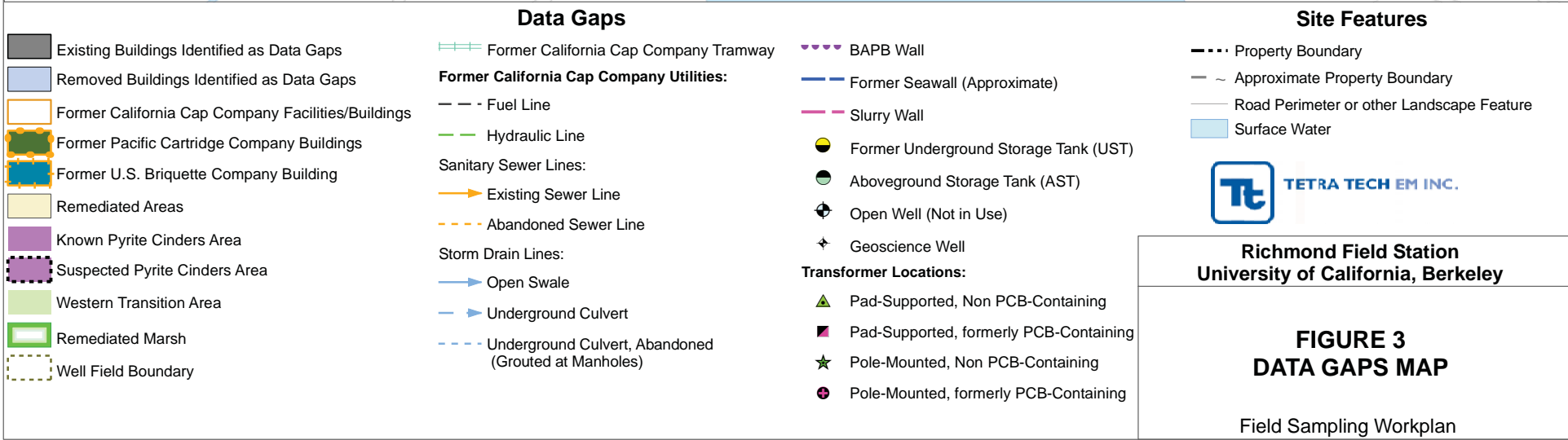
Soil data gaps identified in the CCR are generally related to possible surface or near-surface spills associated with historical and current activities at RFS.

Current and Historical Research Facilities. Many current and historical research facilities used or stored hazardous chemicals at RFS. Although no other sources indicate previous spills in these facilities, limited or no sampling has occurred in these areas. These areas include the earthquake engineering facilities at Buildings 420 and 421, and multiple other activities at Buildings 102, 110, 111, 112, 113, 114, 117, 118, 121, 125, 138, 150, 151, 158, 175, 177, 197, 278, 280A, 280B, 450, 460, 470, 474, 478, 480, and 482. In addition, spills have been reported in the vicinity of Building 120 and the RFS Corporation Yard; and these areas are also included as data gaps, as no site-specific data are available for these two areas to confirm or deny if releases have occurred there.

Aboveground Storage Tanks (AST). ASTs are present at various locations at RFS. The ASTs are in good condition, and there have been no reports of releases from the ASTs; however, no site-specific data are available for the vicinity of the tanks to confirm or deny whether releases have occurred there.



Notes:
 1-Some locations are approximate.
 2-PCB Polychlorinated biphenyls



PCB-Containing Transformers. Previously, PCB-containing transformers have been present on the RFS property. These transformers have either been replaced or retrofitted. Some of the transformers were retrofitted on their pads, and some were stored with other electrical equipment on a concrete pad in the northern portion of Building 280B. While there are no records of PCB leaks or spills, samples will be collected in the areas where the former PCB-containing transformers were located, retrofitted, or stockpiled to confirm or deny releases have occurred.

Western Transition Area. The Bulb area, located in the WTA, was identified as a data gap based on an historical interview with a former UC employee who claimed debris may have been dumped in this area. This area has been investigated using Geoprobe borings and a magnetic survey. The magnetometer showed a strong anomaly southwest of the concrete pad in the Bulb. This area will be further investigated to determine the source of the anomaly and to confirm or invalidate the possibility of buried debris. In 2008, a TCRA was performed in two locations (Subareas I and II) of the western portion of the Bulb to remove a small volume of ash and debris with detected concentrations of PCBs. During excavation of WTA Subarea II, debris including miscellaneous laboratory glassware was noted in excavated soils and excavation sidewalls. After DTSC approval, sample locations and excavation extents were surveyed then the two excavation areas were lined with clear, 6 mil plastic and were backfilled with clean soils ([Tetra Tech 2009](#)).

California Cap Company Operations. The former operations of the California Cap Company have been identified as a data gap. Specifically, the former California Cap Company Test Pit and Dry House were identified as areas where explosions may have occurred during California Cap Company operations. No site-specific characterization data for explosive residues are available for these areas.

In addition, no site-specific characterization data are available for the California Cap Company's tram lines. The construction, use, maintenance, or history of releases along the former tram lines is not known.

Other Former Operations. The U.S. Briquette Company and Pacific Cartridge Company have been identified on historical Sanborn maps from 1912 and 1916 as operating on the property when it was owned by the California Cap Company. No site-specific characterization data are available for the areas where these companies reportedly operated.

Western Stege Marsh. Although the eastern portion of Western Stege Marsh has been remediated, additional information is needed to determine if the surface water and sediment concentrations in the native marsh pose a significant risk to human and ecological receptors.

2.2.2 Groundwater

Groundwater data gaps identified in the CCR are related to general comments regarding limited hydrogeologic and groundwater data at RFS, as well as several site-specific data gaps.

Site-Wide Groundwater Conditions. Additional data are needed to evaluate general hydrogeologic information for the shallow, intermediate, and deep groundwater zones in various areas across RFS. This includes collecting general hydrogeologic information (groundwater elevations and lithology) to generate a hydrogeologic model, and groundwater quality data (chemical concentrations, total dissolved solids [TDS] concentrations, metals bioavailability data, etc.).

Northeastern Property Boundary. Additional data are needed for characterizing groundwater near Building 478. Shallow-zone groundwater containing VOCs has been identified in the vicinity of the adjacent Campus Bay Site Lot 1 removal action conducted by CSV in summer 2008.

Eastern Property Boundary. Additional data are needed to characterize the shallow, intermediate, and deep groundwater zones along the portion of the RFS/Campus Bay property boundary between the area south of the Building 478 area and the southern end of the slurry wall, where metals, pesticides, and VOCs have been identified in groundwater.

The Biologically Active Permeable Barrier (BAPB) wall. The effectiveness of the portion of the BAPB wall located on the RFS property has yet to be assessed, and additional information is needed to characterize groundwater quality in the shallow and intermediate zones in that vicinity.

Engineering Geosciences Well Field. The Geosciences Well Field, installed in the 1980s, has been and continues to be used primarily for research on borehole-to-surface electrical resistivity to accurately map subsurface groundwater flow. No site-specific characterization data are available for these wells.

Western Transition Area. Groundwater conditions are unknown at the WTA, including the southern portion of the Western Storm Drain line where metals (cadmium, copper, mercury, nickel, and zinc) and PCBs may be present at elevated concentrations.

2.2.3 Utilities

The CCR identified data gaps related to possible transport of contaminants through or along utility lines throughout the RFS. These utility lines, including current and former sanitary sewer and storm drain lines operated by UC Berkeley and the California Cap Company, and former hydraulic and fuel lines used by the California Cap Company, may have served as preferential pathways for contaminants to migrate across the RFS. Contaminants may be present in the lines or in nearby soil and groundwater as a result of direct releases from the lines or transport of contaminants to the storm drains via stormwater. Cinder material was previously found to have been used as backfill, therefore, a potential exists for contamination to soil or groundwater from backfill material.

3.0 CONCEPTUAL SITE MODEL

This section presents a summary of the CSM for RFS; a detailed analysis appears in the CCR (Tetra Tech 2008). The CSM is based on historical operations, sources for chemical releases, and current environmental data, all of which are presented in the CCR. The CSM describes possible migration of potential contaminants through the primary pathways in soil, water, and utilities. In addition, possible exposure pathways to both human and ecological receptors via transporting media are described.

3.1 SOURCES, MIGRATION PATHWAYS, AND EXPOSURE

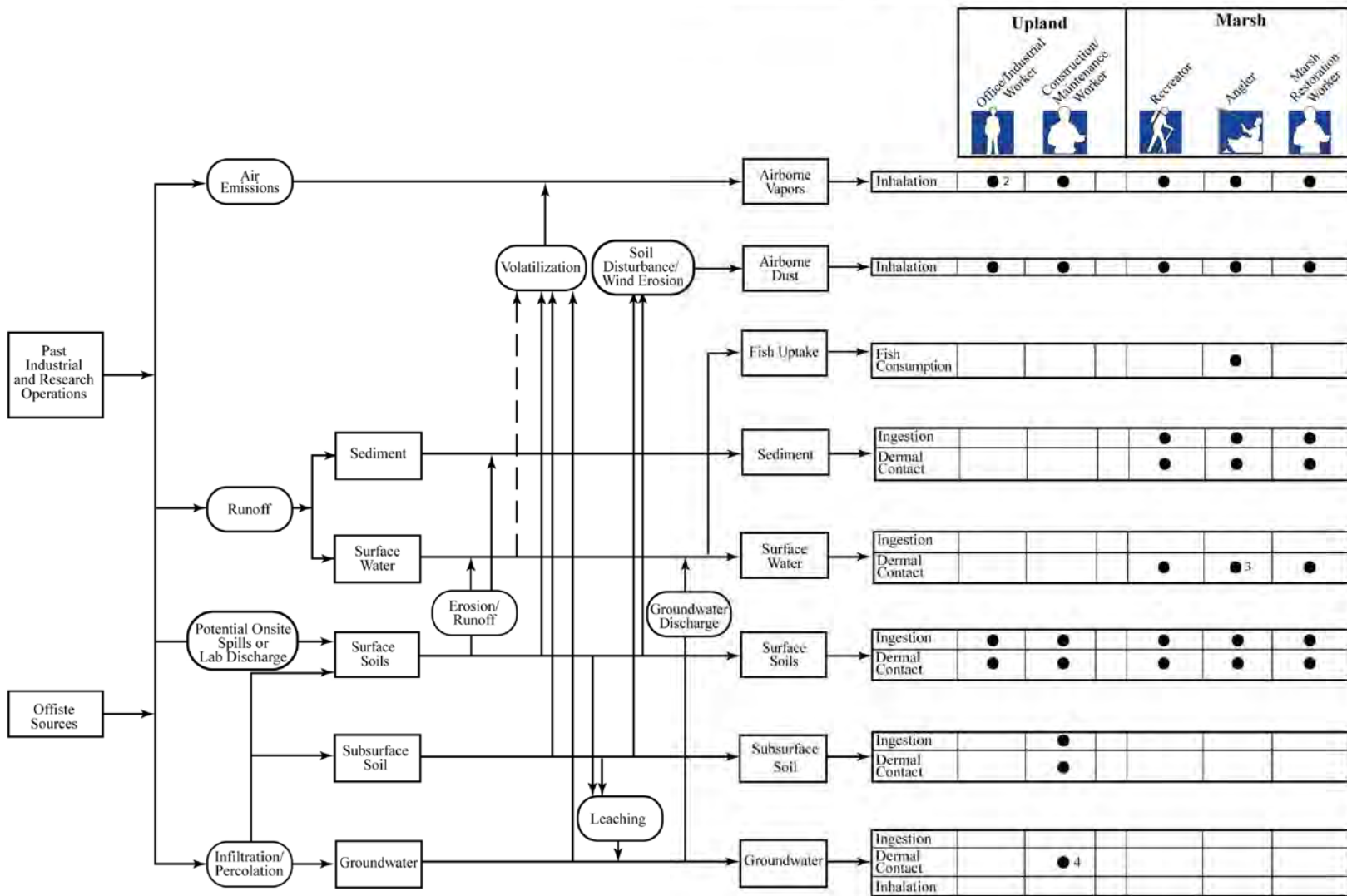
Possible sources of contamination include past industrial operations by the California Cap Company, past manufacturing operations at the adjacent former Zeneca site, current and historical research-related activities, and possibly industrial operations from current or former neighboring properties such as the Bio-Rad Laboratories, the former Pacific Gas & Electric facility, the former Liquid Gold facility, the former Kaiser Shipyard, and other activities in the area that is now the Marina Bay housing development (Tetra Tech 2008). On-site potential sources are discussed above in Section 2.2, Data Gaps.

On- and off-site sources may have affected the RFS in three primary ways: (1) direct release of chemicals to soils and sediments at the RFS; (2) transport of chemicals onto the RFS and into the marsh and slough areas via surface water overland flow, storm drain and sanitary sewer flows, and groundwater transport; and (3) possible influx of contaminants from the San Francisco Bay. A depiction of the sources, migration pathways, and possible receptors is shown on Figures 4 and 5.

A complete exposure pathway from the contaminated medium to the potential receptors must exist in order for exposure to humans or ecological receptors to occur. The following potential primary chemical migration pathways at RFS will be evaluated:

- Leaching from soil to groundwater by infiltrating precipitation or as a result of fluctuating groundwater levels
- Migration from groundwater to surface water through direct discharge
- Direct dermal contact with surface soil, subsurface soils, and surface water
- Ingestion of soil, subsurface soils, and surface water
- Inhalation of vapors from soil or groundwater sources
- Wind entrainment of dust-size particles from surface soils to the atmosphere or to surface water
- Transport of soil or sediment to surface water with overland flow of stormwater
- Transport of contaminants throughout the site via underground utility corridors
- Sediment transport within the marsh from tidal, wind, and wave action.

POTENTIAL PRIMARY SOURCE(S)	PRIMARY RELEASE MECHANISM(S)	SECONDARY SOURCES(S)	SECONDARY RELEASE MECHANISM(S)	MIGRATION PATHWAY(S)	EXPOSURE ROUTES	POTENTIAL HUMAN RECEPTORS
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- 1 Hikers, bikers, joggers (children and adults).
2 Indoor vapor exposure also possible.
3 Assumes children and adults may contact surface water.
4 Assumes contact with shallow groundwater during excavation activities.

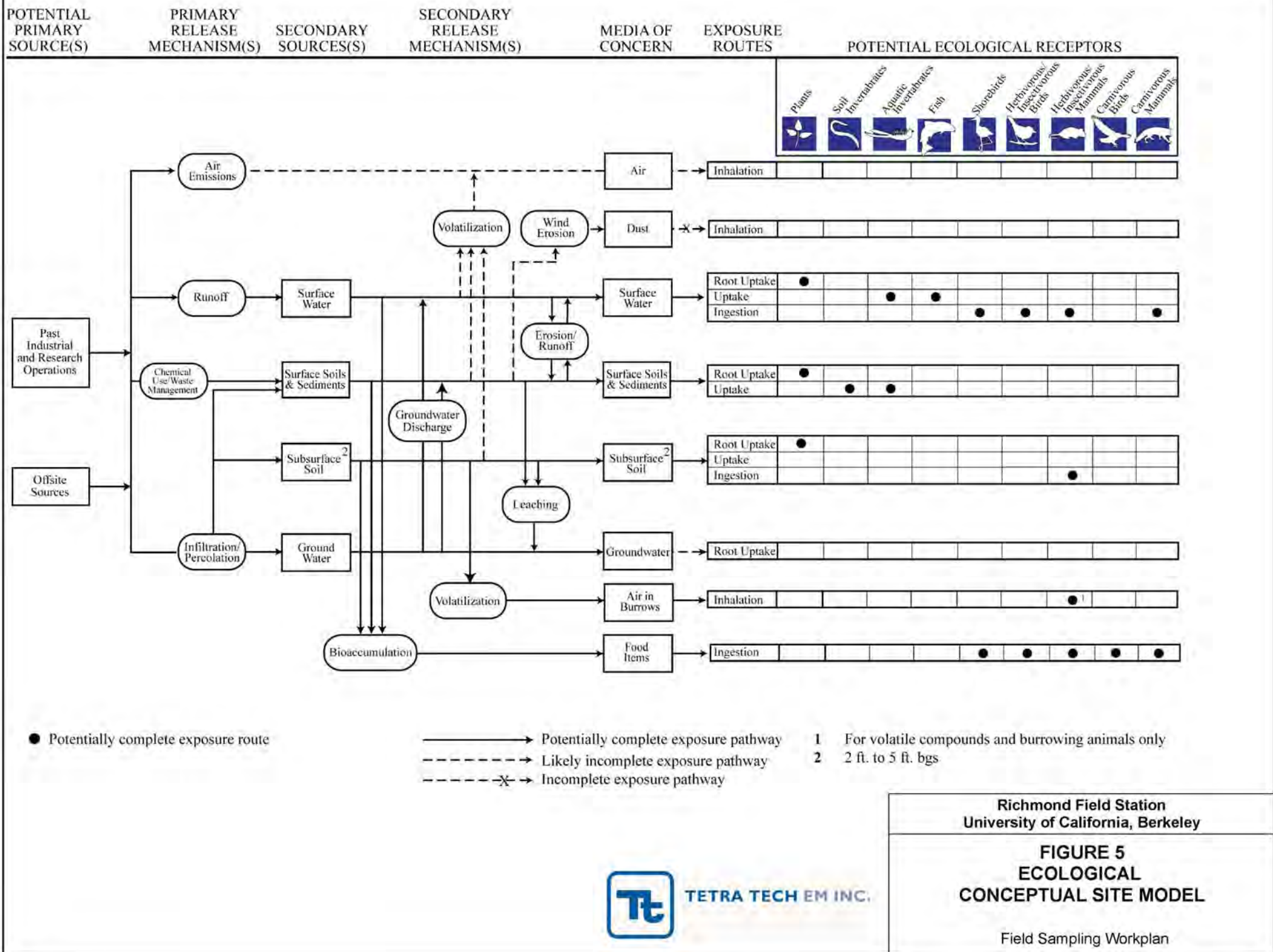


TETRA TECH EM INC.

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FIGURE 4 HUMAN HEALTH CONCEPTUAL SITE MODEL

Field Sampling Workplan



Both humans and wildlife use the Upland Area, Transition Area, and Western Stege Marsh areas of RFS, and thus may be exposed to chemicals in soils, sediments, groundwater, and surface water. The primary human receptors that may be exposed to the remaining chemicals at RFS include UC Berkeley researchers and employees, RFS staff, RFS tenants, visitors to the Bay Trail and RFS connector trail, and workers planting and weeding in the marsh. Most workers would be exposed only to surface soils from dust or incidental contact and any potential volatilization. Construction workers performing intrusive activities could be exposed to chemicals present in deeper soils. Visitors are likely to be exposed only to dust emitted from RFS surface soils and incidental contact with surface soils.

Native and non-native plants are present in all of the RFS habitats and provide roosting and foraging habitat for many species. Some special-status plant and animal species are present on the RFS, including populations of the Federally listed endangered California clapper rail (*Rallus longirostris obsoletus*) which are restricted to San Francisco Bay estuaries and marshes. They are known to reside year-round at the RFS and breed from February to late August, using both the Marsh and a small portion of the marsh edge Upland Area for nesting sites and cover

3.2 SOIL MIGRATION AND EXPOSURE

Metals and PCBs are the most prevalent of the COCs that have been identified in surface and subsurface soils at RFS. Pesticides and SVOCs have also been identified in some locations. PCBs and pesticides typically have a slow rate of adsorption and desorption between sedimentary particles and surrounding water. They tend to migrate very little from their initial release point and are not likely to leach from surface soils to subsurface soils and groundwater. VOCs and SVOCs have low sorption capacities so they may not be retained in the soil. These organic compounds tend to leach into the underlying groundwater or volatilize into the soil gas.

Behaviors of metals in soils are influenced by the geochemical environment. Factors that determine the geochemical environment include soil pH, oxidation-reduction potential, presence of adsorbents, presence of complexing agents, and concentrations of other elements. In addition to these chemical processes, physical processes such as the amount of precipitation infiltration (leaching) can also influence the fate of metals. The geochemical environment in the Upland Area soils of the RFS is conducive to sorption of metals. The soil in the tidal marsh prior to remediation possessed geochemical characteristics that could have contributed to the migration of metals into groundwater and tidal slough. However, the tidal marsh currently has a geochemistry that tends toward reducing the solubility of metals, increasing the likelihood that the metals remain sorbed in the soils.

Leaching

The primary mechanism of migration of chemicals from surface soil to subsurface soil and shallow groundwater at the RFS is most likely through leaching by infiltrating precipitation. As a result of increased precipitation during the wet season (December through March), the water table is expected to be higher in the winter than during the dry season (April through November). Increased leaching of chemicals may occur during the wet season due to increased infiltration and increased groundwater contact with chemicals in soil. The pH and alkalinity of the infiltrating precipitation relative to the soil solution or porewater in sediment can also exert an influence on leaching. However, leaching of contaminants from surface soils to subsurface soils and groundwater is assumed to be a small factor in the overall on-site migration of contaminants due to the chemical and physical properties of both the soil and contaminants at RFS.

Adsorption to Sediment

Most contamination in the surface soils at the RFS occurring from a spill assumedly would have migrated little from its original release point, considering the presumed contaminants at RFS and properties of the on-site soils. PCBs and pesticides strongly adsorb to soil particles and are not readily leached. The degree of metals adsorption depends on the geochemical environment, which at the RFS is conducive to soil sorption. For these reasons, any releases of contaminants to the surface soils at RFS are assumed to have remained near the ground surface. A subsection of [Section 3.3](#) discusses migration of contaminants due to physical transportation of sediments to which they are adsorbed.

Potential Exposure to Human Receptors

On-site workers, such as office workers and researchers, may go outside and walk portions of the RFS and may also conduct projects or testing outdoors. As a consequence of outside activities, people may contact surface soils, resulting in dermal (skin) contact with chemicals in soils. Direct soil contact could also result in incidental ingestion of chemicals in the soils that may adhere to hands. In March 2008, the [California Department of Public Health](#) and the federal Agency for Toxic Substances and Disease Registry released a [Public Health Assessment](#) (PHA) for the RFS. The PHA concluded that outside of the fenced former mercury fulminate plant area there is no evidence that working in Uplands Area is hazardous. The PHA states that “walking on the ground at the RFS would not expose people to contaminants at levels of health concern.”

On-site workers may also be involved with or employed as site maintenance workers. These workers could perform landscaping or building maintenance activities, including simple construction in support of research projects. These types of workers may have more opportunity for soil contact (such as incidental soil ingestion and dermal contact with soil) or contact with soil vapors (resulting in inhalation of soil vapors). Construction activities could also result in contact with deeper soils and possibly shallow groundwater, resulting in incidental ingestion of subsurface soils and dermal contact with soils and groundwater. Although construction activities presumably would occur for a shorter period, these exposures may be higher than for other on-site workers. RFS on-site maintenance staff receive the 40-hour OSHA Hazardous Waste Operations and Emergency Response training (with annual 8-hour refresher courses), and UC Berkeley has implemented a Job Safety Analysis procedure and developed an interim soil management plan to ensure that on-site maintenance workers and contractors follow protocols for safe handling of soil at the RFS. In addition, UC Berkeley developed an on-line training system for all on-site workers to inform them of the history, COPCs at the site, prohibitions on digging in soil and impacting sensitive ecological habitats (such as the California clapper rail habitat), and general health and safety practices at the RFS.

Potential Exposure to Ecological Receptors

All ecological receptors are subject to potential dermal contact with any contaminants in the soil on site. Grasses, shrubs, and trees could be exposed to contaminants through root uptake of soil and sediment. Invertebrates can take up contaminants in soil by osmosis and ingestion of sediment and prey. Birds and mammals can be exposed to contaminants through ingestion of dirt on the plant surface and through cleaning and grooming.

Migration of soluble contaminants in water potentially occurs in all three zones of groundwater, surface water, and sanitary sewers (Section 3.4). Migration also occurs through transport and deposition of contaminants adsorbed to soil sediments that are eroded by stormwater runoff.

Groundwater

Groundwater underlying the RFS exists in three separate zones: shallow, intermediate, and deep. The overall hydrology at the site is currently unknown, but most groundwater flow is assumedly in the general south-southwest direction towards the San Francisco Bay. Contamination of groundwater could occur through leaching of contamination down through surface and subsurface soils into the shallow groundwater zone. Although the soil conditions are more favorable for sorption, contamination of groundwater with VOCs, metals, and pesticides has been identified in the groundwater along the eastern property boundary. Tetrachloroethylene, trichloroethylene, and *cis*-1,2-dichloroethylene have been identified in the shallow groundwater located near the RFS and Campus Bay property boundary in the vicinity of RFS Building 478. Because they are soluble in groundwater, these solvents are more mobile than metals and they also may readily volatilize from groundwater to soil gas, depending on soil types.

Migration of chemicals from groundwater to surface waters may occur if groundwater discharges to the San Francisco Bay; however, the rate of discharge is expected to be low because of the low permeability of the predominant soils at RFS.

Surface Water and Sediment Transport

Many contaminants, such as metals and hydrophobic organic compounds, readily adsorb to clay and silt-sized sediment particles. Therefore, an often dominant transport mechanism for these chemicals in the aquatic environment is movement of sediment particles. If surface sediments are eroded and suspended in the water column, they can be transported through surface water runoff and storm drains into the tidal marsh. Once in the marsh, contaminants adsorbed to sediments can be moved by tidal action or waves and deposited in areas of reduced speed.

Three processes primarily act to transport suspended sediments in the RFS region:

- Tidal exchange of sediments through the marsh and sloughs. Tidal exchange is responsible for sediment exchange to and from the central San Francisco Bay. The net flux of sediments depends on conditions in the marsh and sloughs, sediment load in the central San Francisco Bay, and seasonal events.
- Delivery of sediments to the marsh and sloughs by upland runoff
- Wind and wave activity from the San Francisco Bay. Wind and waves generally mobilize sediments through the San Francisco Bay. The net effect of this mobilization can both deliver sediment from the San Francisco Bay and remove sediment from the shoreline regions.

The interplay of these processes is seasonally dependent, but no site-specific data are available to definitively determine the magnitude or relative contribution of each process.

Potential Exposure to Human Receptors

On-site workers that are outside during a storm event may contact surface water runoff, possibly resulting in dermal contact or incidental ingestion of soluble or suspended contaminants. On-site workers involved with landscaping, building maintenance, or simple construction could come in dermal contact with shallow groundwater. Persons occupying buildings or on-site workers who may come in contact with groundwater or work in trenches could be exposed to inhalation of vapors from volatilization of contaminated groundwater. Recreation activities such as hiking or bird watching along public access paths also pose possibility of dermal or incidental ingestion of surface waters. Anglers are potentially more at risk for dermal contact and incidental ingestion of surface waters. Moreover, this group of receptors could be exposed to chemicals that originate in sediments or surface water, accumulate in the food chain, and ultimately are taken up by fish in this portion of the bay.

Potential Exposure to Ecological Receptors

All ecological receptors are subject to potential dermal contact with any contaminants in the water on site. Small plants could be exposed to contaminants through root uptake of sediment and surface water, while shrubs and trees can extend roots down several feet to reach shallow groundwater. Aquatic and benthic invertebrates, as well as fish, can take up contaminants in water by osmosis and ingestion of detritus, suspended sediment, and prey. Birds and mammals can be exposed to contaminants through ingestion of surface water.

3.4 MIGRATION ALONG UTILITIES AND EXPOSURE

On- and off-site stormwater drainage systems likely contributed to transport of contaminants to the RFS upland and marsh areas. The configuration of the Western Storm Drain line from eastern and northern off-site properties that discharged into the marsh has changed over the years. Prior to construction of the City of Richmond Wastewater Treatment Plant in the 1950s, the Western Storm Drain line appears to have been the primary sewer line in the area, conveying stormwater and sewage (including industrial wastes) from an undelineated upstream area of the City of Richmond directly to the western portion of Western Stege Marsh and Meeker Slough. After the City of Richmond Wastewater Treatment Plant was constructed, the line continued to be used by the City of Richmond as a sanitary sewer overflow line until the northern portion of the line was disconnected from the City of Richmond's sanitary sewer system by UC Berkeley in 2004.

In addition, a historic sanitary sewer line traversed the former tidal mudflat area. This sanitary sewer line drained the eastern portion of the California Cap Company, and later RFS, and portions of the former Stauffer site and Harbor Front properties to the north and east of the former Stauffer site. A large portion of this sanitary sewer line was removed during remediation activities in 2003 and replaced with a new section of sanitary sewer line that is now located further north of the former sanitary sewer line orientation and only drains building at RFS.

These drainage systems possibly facilitated transport of soluble contaminants throughout the RFS. Contaminants adsorbed to eroded sediment suspended in runoff could have been conveyed through these sewers as well. Also, contaminants located in the subsurface soil but not originating from the sewers may have migrated along the material used as backfill for the lines. Despite confirmation that the storm drain previously discharged directly into the tidal marsh, it is unknown whether any of the contaminants migrated from the sewers into the surrounding soil and groundwater due to breaks or leaks in the lines.

Hydraulic and fuel oil lines originally installed by the California Cap Company run throughout the RFS. During their time of operation, these lines may have leaked fuel oil into the surrounding subsurface soil and groundwater. Contaminants in the subsurface soil, if present, may have migrated along the backfill material.

Potential Exposure to Human Receptors

On-site workers who may enter or perform maintenance on the utility lines could have dermal contact or incidental ingestion of contaminants. All other exposure pathways for human receptors are the same as those listed above for soil and water.

Potential Exposure to Ecological Receptors

The exposure pathways for all ecological receptors are the same as those listed above for soil and water.

4.0 SITE INVESTIGATION APPROACH

This section describes the overall strategy and technical approaches to address the data gaps identified in the CCR (Tetra Tech 2008) and summarized in Section 3.0. The RAOs, site investigation strategy, facility-wide DQOs, and schedules for field events and data review are presented below.

4.1 REMEDIAL ACTION OBJECTIVES

Section 5.1.2 of the Order presents the RAOs for the site, which are as follows:

- The reasonably foreseeable future land use of the site is commercial/educational and open space. Therefore, RAOs for contaminated media shall be developed that are protective of adults and children in a commercial/education scenario and as recreational users of open space.
- Western Stege Marsh is a sensitive habitat for the endangered California clapper rail. Therefore, RAOs for contaminated media shall be developed that are protective of endangered and threatened species that have been identified at the site, and their habitat.
- The coastal terrace prairie is a sensitive habitat for native grasses and forbs. Therefore, RAOs for contaminated media shall be developed that are protective of sensitive species and their habitat.

Data collected during the FSW field activities will be used to support these RAOs through incorporation in the upcoming risk assessment and remedial investigation report.

4.2 GENERAL SITE STRATEGY, PRIORITIZATION, AND DATA EVALUATION

The purpose of the overall site investigation at RFS is to identify immediate or potential risks to public health and the environment, in order to prioritize and implement response actions, as stated in Section 5.1.1 of the Order. The Order states that site priorities should be developed and modified through the course of the investigations. This section presents the site prioritization strategy for implementation of the overall site investigation.

4.2.1 Strategy

The investigation strategy has been designed to confirm or deny the presence of primary contaminant sources identified as data gaps within the CCR. These would be primary sources of possible contaminants in soil, groundwater, and former and current utilities. The investigation is organized by the primary sources:

Groundwater Data Gaps. The possible presence of contaminants in groundwater at RFS has been identified as a data gap. Potential sources include contamination from off-site sources as well as potential contamination from previous site activities that may have leached from soil or utility lines to groundwater. The groundwater data gap will be

addressed in Phase I of the data gap investigation to confirm or deny the presence of contamination that would imply complete pathways to groundwater from either soil or utility lines. This data gap will be investigated through collection of groundwater samples from piezometers that will be drilled and completed at strategic locations throughout the RFS. Phase I is intended to develop a hydrogeologic model of the site and to improve the understanding of overall site-wide groundwater quality. The results of the Phase I sampling will be evaluated to determine subsequent additional sampling locations, if necessary. If analytical results support the presence of an unidentified source, additional soil or soil-gas sampling may be conducted after consultation with DTSC.

Soil Data Gaps. The possible presence of contaminant spills or releases has been identified as a data gap. Soil data gaps will be investigated through characterization of near-surface and subsurface soils throughout the RFS. Investigation of soil data gaps will occur in Phases II through V. Sampling strategies, including sampling locations and potential contaminants of concern, will be addressed in upcoming FSPs. Prioritization of soil data gaps and investigation areas will be addressed with DTSC and UC Berkeley input, as well as results from the Phase I groundwater investigation.

Utility Data Gaps. The possible presence of contaminant spills or releases through former and current utilities at RFS has been identified as a data gap. The utilities data gap will first be investigated in Phase I through placement of piezometers near utility lines, where possible, to sample for potential contamination. FSPs for subsequent phases will address soil and soil-gas sampling to resolve data gaps outlined in the CCR, as well as any new data gaps initiated by results from the Phase I groundwater investigation. If contamination is identified in groundwater samples at levels that warrant additional work, further investigation may be proposed—including passive or active soil gas sampling or soil sampling. Assuming contamination could still exist in soil or soil gas if not detected in groundwater, further investigation, including sample locations and potential contaminants of concern, will be addressed in subsequent FSPs.

4.2.2 Prioritization

The CCR identified data gaps that warrant additional characterization or evaluation at the RFS. Given the broad scope of activities necessary to address these data gaps, the planned field investigations will be divided into manageable-sized study areas in a phased approach, thus enabling UC Berkeley to accelerate the investigation of data gaps ranked as higher priorities. The approach also allows for field investigations to coincide with work constraints in the Western Stege Marsh and Transition Area where no activities may occur between February 1 and August 31 because of the California clapper rail breeding season.

The proposed investigation strategy will be conducted in five temporal phases (Phases I through V), as approved by DTSC at a meeting on December 19, 2008. Phase I of the investigations will begin with the implementation of a site-wide groundwater investigation. This approach, proposed by UC Berkeley and agreed to by DTSC, will determine overall groundwater characteristics (TDS, gradient, etc.) and confirm or deny the presence of any significant groundwater contamination concerns. The proposed investigation will focus on the shallow (to approximately 20 feet below ground surface [bgs]) and intermediate (to approximately 40 feet bgs) groundwater zones.

Once the results from the Phase I investigation sampling activities have been received, UC Berkeley and DTSC will review them, and UC Berkeley will propose any follow-up sampling locations to DTSC, as appropriate. If necessary, any issues discovered will be added to the list of data gaps and addressed in a following phase of investigation. UC Berkeley recognizes that contamination may be present in soil which may not be identified through the proposed facility-wide groundwater investigation; therefore, site-specific sampling strategies for soil and utility data gaps outlined in [Section 2.2](#) will be included in upcoming FSPs. The proposed scope for each subsequent phase may change based on updated sampling information. Schedule updates will be presented with each subsequent FSP.

4.2.3 Data Evaluation

The objectives of the phased site investigations are to identify immediate or potential risks to public health and the environment, and prioritize and implement response actions using removal actions and operable units, if appropriate, based on the relative potential risks at the site. As a first step in determining immediate or potential risk, groundwater sampling data obtained during Phase I will be evaluated to either confirm or deny the release of a hazardous substance, as defined in the DTSC Order. Site- and chemical-specific soil screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of groundwater analytical data, as agreed by UC Berkeley and DTSC at the meeting on October 27, 2009. For Phases II through V, screening values will be developed within each subsequent FSP in concurrence with DTSC. Screening levels will be developed so that confirmation or invalidation of a release of hazardous substance can be determined.

4.3 SCHEDULE

This section establishes the procedures for document submittals, reviews, and schedule changes for implementing the scope of work under the Order. UC Berkeley will implement the planning activities, field investigations, and report preparation in accordance with the schedule, as shown on [Figure 6](#).

4.3.1 Document Submittal and Review

UC Berkeley is responsible for preparing and distributing documents to DTSC on or before the corresponding deadline. Both parties may determine that specific documents require additional or less time than the specified review period and alter the review schedule accordingly. UC Berkeley will be available to DTSC during the review periods to respond informally to questions and comments on draft documents.

At or before the close of the DTSC review periods, DTSC will transmit its written comments to UC Berkeley. Both parties will meet prior to 15 calendar days of the close of the review period to discuss comments.

Following the close of the review periods, UC Berkeley will give full consideration to all DTSC and other government agency comments, and will revise any reports to address DTSC written comments.

4.3.2 Changes to Schedule

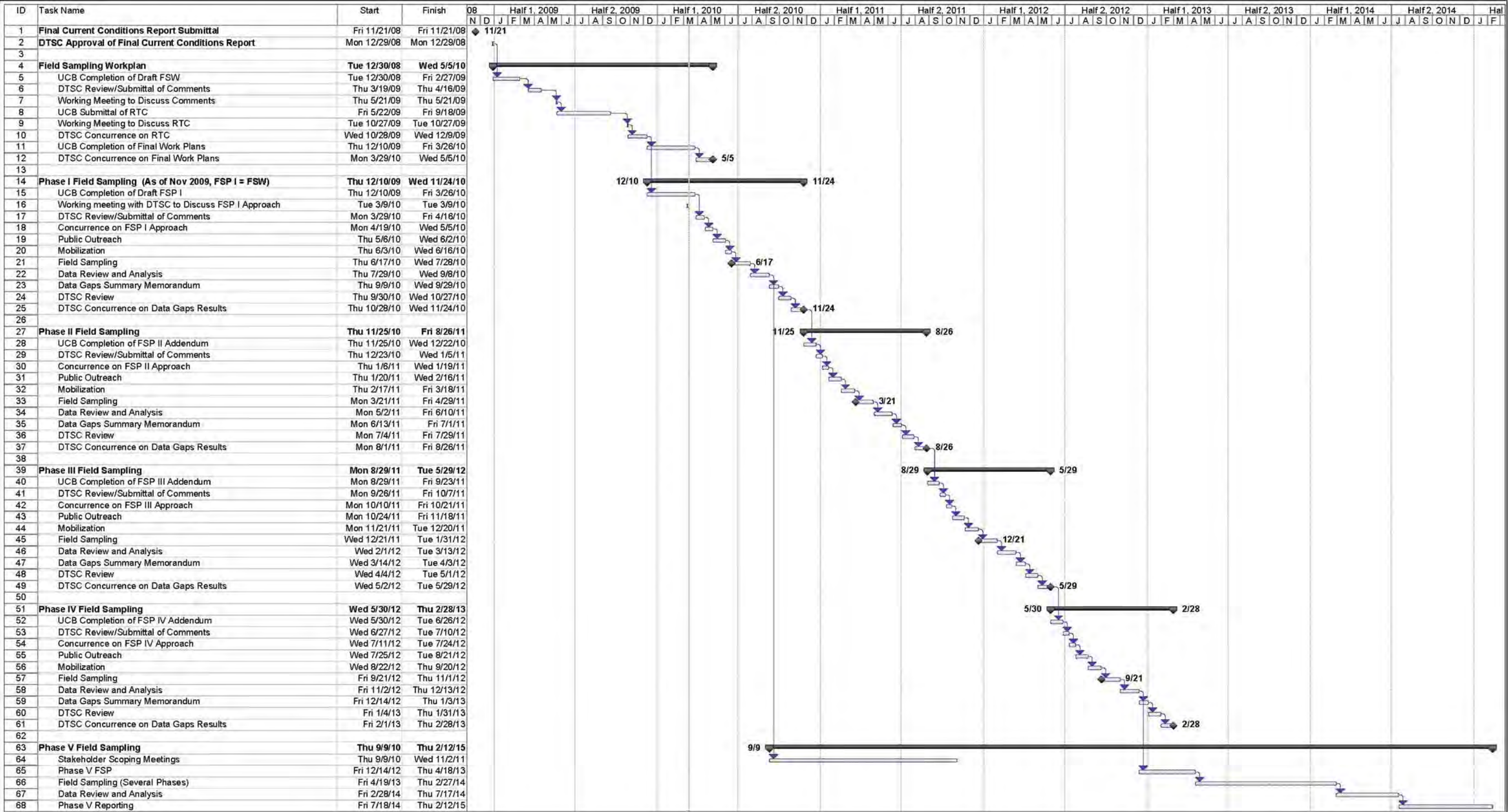
The schedule for implementing field programs and report preparation depends on UC Berkeley and DTSC concurrence regarding the scope of the field program or response to comments for a report. UC Berkeley may request an extension of any deadline for good cause. UC Berkeley will identify the length and cause of the extension requested.

If DTSC grants the extension, UC Berkeley will extend the affected timetable and deadline or schedule accordingly. If DTSC does not concur in the requested extension, it will include an explanation of the basis for its position.

4.3.3 Documentation

Monthly Summary Reports, which are prepared by UC Berkeley in accordance with Section 6.3 of the Order, will include a description of any schedule changes and the reasons for such changes.

UC Berkeley will issue as-needed revisions to [Figure 6](#) for any schedule changes. Items that are critical-path dependent will be updated in the event of any schedule change. Updated schedules for ensuing field investigation phases will be provided with each corresponding FSP.



Richmond Field Station
University of California, Berkeley

FIGURE 6
PROJECT SCHEDULE

Field Sampling Workplan



5.0 PHASE I GROUNDWATER SAMPLING DESIGN

This section discusses the purpose of the facility-wide groundwater investigation, groundwater DQOs, and sampling process design.

5.1 PURPOSE OF INVESTIGATION

Groundwater was identified as the focus of the Phase I investigation to address concerns that off-site or previous on-site activities may have seriously impacted groundwater quality. The overall hydrology at the site is currently unknown, but groundwater flow is assumed in the general south-southwest direction towards the San Francisco Bay. Contamination of groundwater can occur through leaching of contamination down through surface and subsurface soils into the shallow groundwater zone. Although the soil conditions are more favorable for sorption, contamination of metals and pesticides in the groundwater is known along the eastern property boundary.

A site-wide groundwater sampling approach will provide an overview of chemical concentrations across the RFS site. This will allow UC Berkeley to recognize possible complete pathways of potential contamination from soil or utilities to groundwater via leaching and focus investigation in later phases on these areas. Based on review of the data gaps described in [Section 2.2](#), sampling locations have been specified at strategic locations across the RFS in order to determine potential impacts from previous site activities, as well as to understand the groundwater gradients across the RFS.

Once sampling results from the Phase I sampling activities have been received, results will be reviewed by UC Berkeley and DTSC, and specifications of additional locations for subsequent sampling may occur. If contamination is discovered, the findings will be included within an updated list of data gaps and addressed in a following phase of investigation.

5.2 GROUNDWATER DATA QUALITY OBJECTIVES

DQOs are intended to help ensure collection of data appropriate for support of defensible decisions. The DQO process is a seven-step iterative approach to prepare plans for environmental data collection activities. It is a systematic approach for defining the criteria that a data collection design should satisfy, including when, where, and how to collect samples or measurements; determination of tolerable decision error rates; and the number of samples or measurements that should be collected ([EPA 2006](#)). The seven steps for DQO development are defined in the QAPP (Appendix A, Section 3.1). The DQOs for the Phase I groundwater investigation are outlined below. DQOs for surface and subsurface soil, and potential soil gas investigations will be defined in subsequent FSPs.

Step 1: State the Problem.

- Additional characterization of the groundwater at RFS is needed to develop a hydrogeologic model of the site and to improve understanding of overall groundwater quality.
- Additional characterization of groundwater is needed to improve understanding of groundwater quality for specific locations of known or possible contamination.

- If contaminants are present in shallow groundwater, exposure to both human and ecological receptors is possible.

Step 2: Identify the Goals of the Study

- What is the general hydrogeology at RFS?
- What is the prevailing hydraulic gradient of the groundwater at RFS?
- Are metals, PCBs, VOCs, SVOCs, polycyclic aromatic hydrocarbons (PAH), pesticides, or other contaminants present within the study area in quantities or concentrations that would require inclusion of the area into the remedial investigation/feasibility study (RI/FS)?
- Are metals, PCBs, VOCs, SVOCs, PAHs, pesticides, or other contaminants present within the study area in quantities or concentrations that would require remedial action?
- Are metals, PCBs, VOCs, SVOCs, PAHs, pesticides, or other contaminants present within the study area in quantities or concentrations that would require an immediate response?
- If contamination is present, is it migrating either on site or off site within any of the groundwater zones?

Step 3: Identify Information Inputs

- Information from historical documents
- Interviews of current and former employees
- Previously conducted sampling locations and concentrations
- Boring logs and depth-to-water measurements
- Concentrations in groundwater of metals, PCBs, PAHs, VOCs, SVOCs, pesticides, and other contaminants measured using appropriate EPA SW-846 Methods

Step 4: Define the Boundaries of the Study

- The Phase I study area is all groundwater located within the property boundaries of the RFS.
- The shallow groundwater zone is primarily of interest, with secondary data collection to occur within the intermediate zone in order to determine flow directions (laterally and vertically)
- Horizontal expansion of the study area may be necessary to investigate potential groundwater plumes if contamination is found present in the first round of groundwater sampling.
- No temporal boundaries are imposed upon this investigation.

Step 5: Develop the Decision Rules

- The data provided by this investigation will be reviewed by UC Berkeley and DTSC. Once all the data have been received, the decision making parties will proceed with evaluation of lines of evidence to determine if either no further action or further investigation is warranted.

- If an area is recommended for further investigation, one or several of the following may occur: further data evaluation or data gap sampling (either by further groundwater sampling or expansion of the lateral or vertical boundary of the study area to subsurface or surface soils), inclusion in the RI/FS, or immediate consideration for interim remedial action.

Step 6: Specify Performance or Acceptance Criteria

- The screening levels will be established after data have been received and reviewed by UC Berkeley and DTSC. The screening levels will be developed through evaluation of several sets of values, including but not limited to, National Ambient Water Quality Control values (NAWQC), state or federal maximum contaminant levels (MCL), and other risk-based values.

Step 7: Optimize Design for Obtaining Data

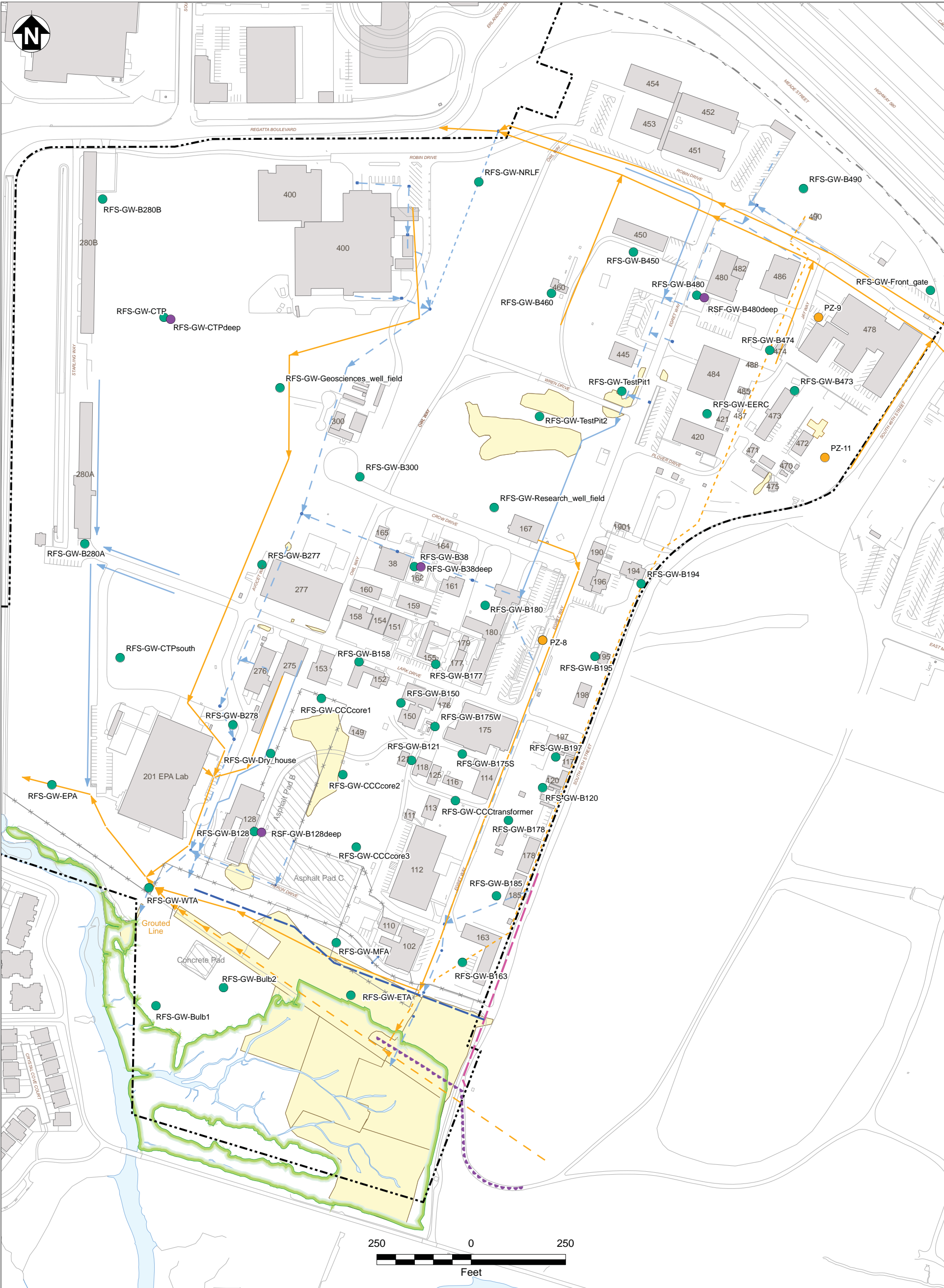
- Groundwater data gaps will be addressed through collection of groundwater samples collected from 51 piezometers (see [Figure 7](#)).
- Following receipt and review of the laboratory results from either the groundwater or future soil investigations, any additional groundwater sampling—if deemed necessary—will proceed using the same methodology.

5.3 SAMPLING PROCESS DESIGN

The sampling strategy for Phase I consists of drilling, completing, and sampling 51, 2-inch diameter completed piezometers throughout the RFS, as well as sampling three existing CSV-installed piezometers (see [Figure 7](#)). Groundwater samples will be analyzed for dissolved metals, pesticides, PCBs, SVOCs, total extractable petroleum hydrocarbons (TPH-e), total purgeable petroleum hydrocarbons (TPH-p), PAHs, and VOCs. In addition, water levels and water quality parameters such as TDS, dissolved oxygen, pH, oxidation-reduction potential, specific conductance, and temperature, will be measured at each location. Certain locations include additional analytes based on site history. Rationales for groundwater sampling locations, depths, and proposed analyses are presented in Tables 1 and 2. Sampling locations were strategically placed across the RFS based on review of the data gaps and previous investigation data. The intent of this sampling is to determine potential impacts from previous site activities, as well as to identify groundwater gradients across the RFS.

Four piezometers, completed in the intermediate groundwater horizon (at approximately 40 feet bgs), will only be used to record groundwater elevation and to sample for TDS, dissolved oxygen, pH, oxidation-reduction potential, specific conductance, and temperature. These piezometers are not proposed for chemical sampling during Phase I. Water level measurements will be used to determine the hydrogeologic gradient between the upper and lower aquifers. If the gradient is found to be upward, and if no contamination is found in the upper groundwater zone, no contamination would be suspected in lower zones. If the gradient is downwards, and contamination is discovered, further sampling will be proposed in intermediate or lower groundwater zones.

An estimated 10 piezometers will be proposed for a year of quarterly monitoring to assess the seasonal effects on the hydraulic gradients in the shallow groundwater zone at the RFS. Specific locations will be specified with concurrence from DTSC after review of analytical results.



Existing Buildings

Asphalt/Concrete Pads

Remediated Areas

Surface Water

Marsh Boundary

Property Boundary

Approximate Property Boundary

Roads and Other Landscape Features

Fenceline

Biologically Active Permeable Barrier Wall

Former Seawall (Approximate)

Slurry Wall

Storm Drain Lines:

Open Swale

Underground Culvert

Underground Culvert, Abandoned (Grouted at Manholes)

Sanitary Sewer Lines:

Existing Sewer Line

Removed Sewer Line

Abandoned Sewer Line

Proposed new piezometer locations (20ft bgs)

Proposed new piezometer locations (40ft bgs)

Zeneca's PZ-8, PZ-9, and PZ-11

Tt

TETRA TECH EM INC.

Richmond Field Station

University of California, Berkeley

FIGURE 7

GROUNDWATER SAMPLING

LOCATIONS

Field Sampling Workplan

Note:

bgs

ft

below ground surface

feet

2010-3-12 V:\Misc_GIS\Richmond_Field_Station\Projects\Field_Sampling_Workplan\groundwater FSP\GW_sampling.mxd T\EMI-SF CF

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Table 1 – Groundwater Sample Rational

Location ID	Data Gap Addressed	Sampling Strategy
RFS-GW –Front_Gate	The alleged pesticide spill by front gate needs further investigation.	Collect a shallow groundwater sample from a piezometer installed near the front gate and submit for a full suite of analytes, potentially with low detection levels for pesticides. This sample will provide information on the groundwater conditions at the northeast corner of the property, along the property boundary, north of B478.
RFS-GW-B490	Sewer line from B490 to former digester ponds	Collect a shallow groundwater sample near the upstream end of the former line near B490 to help determine potential impacts to groundwater from the line, as well as to help determine hydraulic gradients in the northern area of the property.
RFS-GW-NRLF	Sanitary sewer lines and off-site impacts	This sample will provide information about hydraulic gradient along the northern end of the property, as well as about potential impacts from off-site sources (PG&E), or the City of Richmond's sanitary sewer lines that traverses the northern portion of the RFS.
RFS-GW-B280B	PCB-containing transformers were historically stockpiled at B280B	Collect a shallow groundwater sample near the area where PCB-containing materials were formerly stored.
RFS-GW-CTP	Investigation of site-wide hydrology	Collect a shallow groundwater sample to provide information about the hydraulic gradient in this area of the property and provide data to evaluate potential impacts from off-site contamination.
RFS-GW-CTPdeep	Investigation of the intermediate groundwater zone for gradient	Install and complete adjacent piezometers in the upper and intermediate groundwater zones. Collect water level measurements to determine if there is a vertical hydraulic gradient between these zones. Samples will not be collected for laboratory analysis during the first round of sampling.
RFS-GW-B450	Former transportation studies machine shop	Collect a shallow groundwater sample from the area south of the building to evaluate potential impacts from previous site activity.
RFS-GW-B460	UC Berkeley chemical storage, California Cap Company stored vehicles here	Collect a shallow groundwater sample from the area south of the building to evaluate potential impacts from previous site activity.
RFS-GW-B480	B482, asphalt testing building needs to be investigated for SVOCs and metals	Collect a groundwater sample from the area southeast of the asphalt testing building and materials storage area to evaluate potential impacts to shallow groundwater from previous site activity.
RFS-GW-B480deep	Investigation of the intermediate groundwater zone for gradient	Install and complete adjacent piezometers in the upper and intermediate groundwater zones. Collect water level measurements to determine if there is a vertical hydraulic gradient between these zones. Samples will not be collected for laboratory analysis during the first round of sampling.
PZ-9	Characterize area west of B478 for evidence of contamination	Collect a shallow groundwater sample from this piezometer (installed by Zeneca in 2006 on the RFS site as part of their property boundary investigation) to evaluate potential impacts to shallow groundwater from previous activity and to provide information about the hydraulic gradient in this area.

Location ID	Data Gap Addressed	Sampling Strategy
RFS-GW-B474	B474 formerly and currently used for chemical storage	Collect a groundwater sample from the drainage area to the southwest of the building to evaluate for potential impacts to shallow groundwater from previous site activity.
RFS-GW-B473	Former PCB-containing transformer location	Collect a groundwater sample from the area where the transformers were formerly located to evaluate for potential impacts to shallow groundwater from previous site activity.
RFS-GW-Test_Pit1	Former Test Pit area	Collect a groundwater sample from the area north of the former test pit to evaluate for potential impacts to shallow groundwater from historical California Cap Company activities. Perchlorates, PAHs, and explosives residue will be added to the list of target analytes for sample analyses.
RFS-GW-Test_Pit2	Former Test Pit area, and California Cap Company tram line	Collect a groundwater sample from the area south of the former test pit to evaluate for potential impacts to shallow groundwater from historical California Cap Company activities. This sample also represents an area where a portion of the California Cap Company tram line was located; therefore, perchlorates, PAHs, explosives residue, and creosote will be added to the list of target analytes for sample analyses.
RFS-GW-EERC	The earthquake engineering building has been used to store hydraulic oil	Collect a groundwater sample from the courtyard area of the earthquake engineering building to evaluate for potential impacts to shallow groundwater from previous site activities as well as for potential impacts from the two current ASTs.
RFS-GW-Geosciences_well_field	Geosciences well field	Collect a groundwater sample to evaluate general shallow groundwater quality in the area of the Geosciences Well Field.
RFS-GW-B300	Geosciences well field and former chemical storage area	Collect a groundwater sample from the area in the vicinity of B300 and Geosciences Well Field to evaluate shallow groundwater quality in the area of the Geosciences Well Field and to evaluate potential impacts from chemical storage in B300.
RFS-GW- Research_well_field	Research well field	Collect a groundwater sample from the area of the former Research Well Field to evaluate potential impacts to groundwater from historical activities related to the former research well field.
PZ-11	Property boundary	Collect a groundwater sample and water level measurements from piezometer PZ-11 that was recently installed by CSV on the RFS site as part of their Lot 1 pilot injection study. The analytical results and groundwater level results will be used evaluate groundwater conditions and the hydraulic gradient along the property boundary.
RFS-GW-B280A	B280A formerly used for chemical storage	Collect a groundwater sample from the area south of Building 280A to evaluate potential impacts to shallow groundwater from former chemical storage in the building and the current AST.
RFS-GW-B277	Former PCB containing transformer location	Collect a groundwater sample in the in the area west of B277 to evaluate potential impacts to shallow groundwater from the PCB-containing transformers formerly located here. Results of the groundwater sample will also be used to evaluate potential impacts to shallow groundwater from the nearby sanitary sewer line.

Location ID	Data Gap Addressed	Sampling Strategy
RFS-GW-B38	This sample lies in the former California Cap Company Blasting Cap Area.	Collect groundwater samples in the vicinity of B38 to assess potential impacts to the shallow groundwater zone as a result of historical California Cap Company operations.
RFS-GW-B38deep	Investigation of the intermediate groundwater zone for gradient	Install and complete adjacent piezometers in the upper and intermediate groundwater zones. Collect water level measurements to determine if there is a vertical hydraulic gradient between these zones. Samples will not be collected for laboratory analysis during the first round of sampling.
RFS-GW-B194	Property boundary	Collect a groundwater sample and water level measurements in the area southeast of B194 to assess potential impacts to the shallow groundwater zone as a result of the current AST and provide general information about groundwater quality and hydraulic gradients along the eastern property boundary.
RFS-GW-B180	GW information in the core of the field station	Collect a groundwater sample and water level measurements in the vicinity of B180 to assess potential impacts to the shallow groundwater zone as a result of historical California Cap Company operations.
PZ-8	Groundwater flow and direction across the field station	Collect a shallow groundwater sample from this piezometer (installed by Zeneca in 2006 on the RFS site as part of their property boundary investigation) to evaluate potential impacts to shallow groundwater from previous activity and to provide information about the hydraulic gradient in this area.
RFS-GW-B195	This shed has been used for chemical storage; this location is also along the property boundary	Collect a groundwater sample in the area of B195 to assess potential impacts to the shallow groundwater zone as a result of past site activities and provide general information about groundwater quality and hydraulic gradient along the eastern property boundary.
RFS-GW-B177	This location is in the core of the field station – there is also an unused well southwest of the building	Collect a groundwater sample and water level measurements in the area of B195 to assess potential impacts to the shallow groundwater zone as a result of past site activities and provide general information about groundwater quality and the hydraulic gradient in the interior portion of RFS.
RFS-GW-B158	B151 and B158 have both been identified as data gaps	Collect a groundwater sample and water level measurements in the area of B151, 152, 154, and 158 to assess potential impacts to the shallow groundwater zone as a result of past site activities and provide general information about groundwater quality and the hydraulic gradient in the interior portion of RFS.
RFS-GW-CTPsouth	Groundwater flow and direction across the field station	Collect a groundwater sample and water level measurements in the area northwest of the EPA Region 9 laboratory to assess potential impacts to the shallow groundwater zone as a result of past site activities and provide general information about groundwater quality and the hydraulic gradient in the western portion of RFS.
RFS-GW-B278	B278 was previously used for chemical storage	Collect a groundwater sample and water level measurements in the area where B278 was formerly located to assess potential impacts to the shallow groundwater zone as a result of past California Cap Company site activities and provide general information about groundwater quality and the hydraulic gradient in the western portion of RFS.

Location ID	Data Gap Addressed	Sampling Strategy
RFS-GW-CCCcore1	The locations of impacts from California Cap Company operations are not certain; therefore, these three samples are placed in the core areas of activities.	Collect a groundwater sample and water level measurements in the area south of B153 to assess potential impacts to the shallow groundwater zone as a result of past California Cap Company site activities and provide general information about groundwater quality and the hydraulic gradient in the western portion of RFS.
RFS-GW-B150	B150 was previously used for chemical storage	Collect a groundwater sample and water level measurements in the area west of B150 to assess potential impacts to the shallow groundwater zone as a result of segments of the former California Cap Company tram line and a hydraulic line that were located in this portion of the site.
RFS-GW-B175W	Location of a previously PCB-containing transformer	Collect a groundwater sample and water level measurements in the area west of B175 to assess potential impacts to the shallow groundwater zone as a result of previous site activities including a formerly PCB-containing transformer.
RFS-GW-B175S	Two former shallow production water wells are located south of B175 and also the B175 parking lot area has been identified as a data gap	Collect a groundwater sample and water level measurements in the area south of B175 to assess potential impacts to the shallow groundwater zone as a result of site activities.
RFS-GW-B197	B197 and fuel pump island were previously used for chemical and waste oil storage	Collect a groundwater sample and water level measurements in the area south of B197 to assess potential impacts to the shallow groundwater zone as a result of past site activities (including impacts from the Corporation Yard, light vehicle maintenance, the current AST, or a former UST) and provide general information about groundwater quality and the hydraulic gradient in the eastern portion of RFS.
RFS-GW-B120	The courtyard of B120 has been identified as a data gap	Collect a groundwater sample and water level measurements in the area south of B120 to assess potential impacts to the shallow groundwater zone as a result of past site activities (including chemical storage and light vehicle maintenance) and provide general information about groundwater quality and the hydraulic gradient in the eastern portion of RFS.
RFS-GW-CCCtransformer	This is the location of a California Cap Company transformer house (as identified from a Sanborn map)	Collect a groundwater sample and water level measurements in the area northeast of B113 to assess potential impacts to the shallow groundwater zone as a result of the reported, but unsubstantiated, location of the California Cap Company transformer house
RFS-GW-B121	B121 and B118 have both been identified as data gaps	Collect a groundwater sample and water level measurements in the area between B118 and B121 to assess potential impacts to the shallow groundwater zone as a result of past site activities.
RFS-GW-CCCcore2	The locations of impacts from California Cap Company operations are not certain; therefore, these three samples are placed in the core areas of activities.	Collect a groundwater sample and water level measurements in the open grass field located north of the former California Cap Company Mercury Fulminate Plant to assess potential impacts to the shallow groundwater zone as a result of past California Cap Company activities and provide general information about groundwater quality and the hydraulic gradient in the south central portion of RFS.
RFS-GW- Dry_house	Former California Cap Company Dry House explosion area	Collect a groundwater sample and water level measurements in the area of the former California Cap Company Dry House where a reported explosion occurred. Perchlorates, PAHs, and explosives residue will be added to the list of target analytes that the groundwater samples will submitted for laboratory analysis.

Location ID	Data Gap Addressed	Sampling Strategy
RFS-GW-EPA	The soil pile west of the EPA lab has been identified as a data gap	Collect a groundwater sample in the area west of the EPA Region 9 laboratory to assess potential impacts to the shallow groundwater zone due the presence of cinders that were placed as bedding material along the sanitary sewer line. Will also collect water level measurements to calculate hydraulic gradients in the western portion of the site.
RFS-GW-B128	The locations of impacts from California Cap Company operations are not certain; therefore, these three samples are placed in the core areas of activities.	Collect groundwater samples in the vicinity of B128 to assess potential impacts to the shallow groundwater zone as a result of historical California Cap Company operations
RFS-GW-B128deep	Investigation of the intermediate groundwater zone for gradient	Install and complete adjacent piezometers in the upper and intermediate groundwater zones. Collect water level measurements to determine if there is a vertical hydraulic gradient between these zones. Samples will not be collected for laboratory analysis during the first round of sampling.
RFS-GW-CCCcore3	The locations of impacts from California Cap Company operations are not certain; therefore, these three samples are placed in the core areas of activities.	Collect a groundwater sample and water level measurements in the open grass area located north of the former California Cap Company Mercury Fulminate Plant to assess potential impacts to the shallow groundwater zone as a result of past California Cap Company activities and provide general information about groundwater quality and the hydraulic gradient in the south central portion of RFS.
RFS-GW-B178	The RFS Corporation Yard storage area has been identified as a data gap	Collect a groundwater sample and water level measurements in the central portion of the Corporation Yard to assess potential impacts to the shallow groundwater zone as a result of past site activities and provide general information about groundwater quality and the hydraulic gradient in the southeastern portion of RFS.
RFS-GW-B185	The RFS Corporation Yard storage area has been identified as a data gap	Collect a groundwater sample and water level measurements in the southern portion of the Corporation Yard to assess potential impacts to the shallow groundwater zone as a result of past site activities and provide general information about groundwater quality and the hydraulic gradient in the southeastern portion of RFS.
RFS-GW-B163	The former US Briquette Co has been identified as a data gap	Collect a groundwater sample and water level measurements in the parking lot area of B163 to assess potential impacts to the shallow groundwater zone as a result of past site activities including the former US Briquette Co and provide general information about groundwater quality and the hydraulic gradient in the southeastern portion of RFS.
RFS-GW-WTA	The transition area has been identified as a data gap	Collect a groundwater sample and water level measurements in the western portion of the WTA to assess potential impacts to the shallow groundwater zone as a result of California Cap Company activities and from cinders that were placed as bedding material along the sanitary sewer lines that connect together at a nearby manhole and provide general information about groundwater quality and the hydraulic gradient in the southeastern portion of RFS.
RFS-GW-MFA	The former mercury fulminate plant has been identified as a data gap	Collect a groundwater sample and water level measurements in the area south and downgradient of the north of the former California Cap Company Mercury Fulminate Plant to assess potential impacts to the shallow groundwater zone as a result of past California Cap Company activities and provide general information about groundwater quality and the hydraulic gradient in the south central portion of RFS.

Location ID	Data Gap Addressed	Sampling Strategy
RFS-GW-ETA	The transition area has been identified as a data gap	Collect a groundwater sample and water level measurements in the eastern portion of the WTA to assess potential impacts to the shallow groundwater zone as a result of California Cap Company activities and from the Southern Sanitary Sewer lines that formerly traversed the southern portion of the RFS and provide general information about groundwater quality and the hydraulic gradient in the southeastern portion of RFS.
RFS-GW-Bulb1	During the WTA TCRA excavation, incidental debris was discovered in this area	Collect a groundwater sample in the southwestern portion of the Bulb area to assess potential impacts to the shallow groundwater zone as a result of past site activities and from the disposal of miscellaneous site debris. Will also collect water level measurements to calculate the hydraulic gradient in the in this portion of the RFS.
RFS-GW-Bulb2	The magnetic anomaly detected in the bulb has been identified as a data gap	Collect a groundwater sample in the northeastern portion of the Bulb area to assess potential impacts to the shallow groundwater zone as a result of past site activities and in the area of the magnetic anomaly that was identified. Will Also collect water level measurements to calculate the hydraulic gradient in the in this portion of the RFS.

Notes:

AST	Above ground storage tank
B	Building
CTP	Costal terrace prairie
EERC	Earthquake engineering research center
EPA	Environmental Protection Agency
ETA	Eastern transition area
GW	Groundwater
ID	Identification
MFA	Mercury fulminate area
NRLF	Northern research library facility
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
PG&E	Pacific Gas and Electric
RFS	Richmond Field Station
SVOC	Semivolatile organic compounds
TCRA	Time critical removal action
UC	University of California
UST	Underground storage tank
WTA	Western transition area

TABLE 2 – SAMPLE REGISTER

GROUNDWATER SAMPLES																		
Analysis			TPH-P (EPA Method 8015B modified)	VOCs (EPA Method 8260B)	TPH-E (EPA Method 8015B modified)	SVOCs (EPA Method 8270C)	Metals (EPA Method 6020A/7400 series)	PAH (EPA Method 8270-SIM)	PCB (EPA Method 8082)	Pesticides (EPA Method 8081A)	Perchlorates (EPA Method 314)	explosive residue (EPA Method 8330)	TDS (EPA Method 160.1)	pH	DO	ORP	Temperature	SC
Sample Container			2 40mL Amber VOA vials with HCl	2 40mL Amber VOA vials with HCl	1 Liter Amber	1 Liter Amber	500mL Poly with HNO3	1 Liter Amber	1 Liter Amber	1 Liter Amber	250mL poly	1 Liter Amber	250mL poly	in field	in field	in field	in field	in field
Holding Time			14 Days	14 Days	14 Days	7/40 days	Metals – 6 Months (except Mercury – 28 Days)	7/40 days	7/40 days	7/40 days	28 days	7/40 days	7 days					
Point Location ID	Sample ID	Depth (feet bgs)																
RFS-GW-Front-Gate	RFSGWFG01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B490	RFSGWB49001	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-NRLF	RFSGWLBNL01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B280B	RFSGWB280B01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-CTP	RFSGWCPT01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-CTPdeep	RFSGWCPTD01	20 - 40											X	X	X	X	X	X
RFS-GW-B450	RFSGWB45001	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B460	RFSGWB46001	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B480	RFSGWB48001	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B480deep	RFSGWB480D01	20 - 40											X	X	X	X	X	X
PZ-9	RFSGWPZ901	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B474	RFSGWB47401	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B473	RFSGWB47301	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-Test_Pit1	RFSGWTP101	10 - 20	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
RFS-GW-Test_Pit2	RFSGWTP201	10 - 20	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
RFS-GW-EERC	RFSGWEERC01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-Geosciences_Well_Field	RFSGWGEO01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B300	RFSGWB30001	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-Research_well_field	RFSGWRWF01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
PZ-11	RFSGWPZ1101	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B280A	RFSGWB280A01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B277	RFSGWB27701	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B38	RFSGWB3801	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B38deep	RFSGWB38D01	20 - 40											X	X	X	X	X	X
RFS-GW-B194	RFSGWB19401	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B180	RFSGWB18001	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
PZ-8	RFSGWPZ801	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B195	RFSGWB19501	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B177	RFSGWB17701	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B158	RFSGWB15801	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-CTPsouth	RFSGWCPTS01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B278	RFSGWB27801	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-CCCcore1	RFSGWCCC101	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B150	RFSGWB15001	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X

TABLE 2 – SAMPLE REGISTER

GROUNDWATER SAMPLES																		
Analysis			TPH-P (EPA Method 8015B modified)	VOCs (EPA Method 8260B)	TPH-E (EPA Method 8015B modified)	SVOCs (EPA Method 8270C)	Metals (EPA Method 6020A/7400 series)	PAH (EPA Method 8270-SIM)	PCB (EPA Method 8082)	Pesticides (EPA Method 8081A)	Perchlorates (EPA Method 314)	explosive residue (EPA Method 8330)	TDS (EPA Method 160.1)	pH	DO	ORP	Temperature	SC
Sample Container			2 40mL Amber VOA vials with HCl	2 40mL Amber VOA vials with HCl	1 Liter Amber	1 Liter Amber	500mL Poly with HNO3	1 Liter Amber	1 Liter Amber	1 Liter Amber	250mL poly	1 Liter Amber	250mL poly	in field	in field	in field	in field	in field
Holding Time			14 Days	14 Days	14 Days	7/40 days	Metals – 6 Months (except Mercury – 28 Days)	7/40 days	7/40 days	7/40 days	28 days	7/40 days	7 days					
Point Location ID	Sample ID	Depth (feet bgs)																
RFS-GW-B175W	RFSGWB175W01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B175S	RFSGWB175S01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B197	RFSGWB19701	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B120	RFSGWB12001	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-CCCtransformer	RFSGWCCCT01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B121	RFSGWB12101	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-CCCcore2	RFSGWCCC201	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-Dry_house	RFSGWDH01	10 - 20	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
RFS-GW-EPA	RFSGWEPA01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B128	RFSGWB12801	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B128deep	RFSGWB128D01	20 - 40											X	X	X	X	X	X
RFS-GW-CCCcore3	RFSGWCCC301	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B178	RFSGWB17801	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B185	RFSGWB18501	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-B163	RFSGWB16301	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-WTA	RFSGWWTA01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-MFA	RFSGWMFA01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-ETA	RFSGWETA01	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-Bulb1	RFSGWBULB101	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X
RFS-GW-Bulb2	RFSGWBULB201	10 - 20	X	X	X	X	X	X	X	X			X	X	X	X	X	X

TABLE 2 – SAMPLE REGISTER

QC SAMPLES																		
Analysis			TPH-P (EPA Method 8015B modified)	VOCs (EPA Method 8260B)	TPH-E (EPA Method 8015B modified)	SVOCs (EPA Method 8270C)	Metals (EPA Method 6020A/7400 series)	PAH (EPA Method 8270-SIM)	PCB (EPA Method 8082)	Pesticides (EPA Method 8081A)	Perchlorates (EPA Method 314)	explosive residue (EPA Method 8330)	TDS (EPA Method 160.1)	pH	DO	ORP	Temperature	SC
Sample Container			2 40mL Amber VOA vials with HCl	2 40mL Amber VOA vials with HCl	1 Liter Amber	1 Liter Amber	500mL Poly with HNO3	1 Liter Amber	1 Liter Amber	1 Liter Amber	250mL poly	1 Liter Amber	250mL poly	in field	in field	in field	in field	in field
Holding Time			48 hrs	14 days	14 Days	7/40 days	Metals – 6 Months (except Mercury – 28 Days)	7/40 days	7/40 days	7/40 days	28 days	7/40 days	7 days					
Point Location ID	Sample ID																	
Water IDW	RFSWIDW01 - XX	1 per drum of IDW water	analysis will be based on disposal criteria															
Soil IDW	RFSSIDW01 - XX	1 per drum of IDW soil	analysis will be based on disposal criteria															
MS/MSD*	Same as original sample		X	X	X	X	X	X	X	X			X	X	X	X	X	X
MS/MSD*	Same as original sample		X	X	X	X	X	X	X	X			X	X	X	X	X	X
MS/MSD*	Same as original sample		X	X	X	X	X	X	X	X			X	X	X	X	X	X
Field Replicate	Add "D" to end of original sample ID		X	X	X	X	X	X	X	X			X	X	X	X	X	X
Field Replicate	Add "D" to end of original sample ID		X	X	X	X	X	X	X	X			X	X	X	X	X	X
Field Replicate	Add "D" to end of original sample ID		X	X	X	X	X	X	X	X			X	X	X	X	X	X
Field Replicate	Add "D" to end of original sample ID		X	X	X	X	X	X	X	X			X	X	X	X	X	X
Field Replicate	Add "D" to end of original sample ID		X	X	X	X	X	X	X	X			X	X	X	X	X	X
Trip Blank	RFSGWTB01 - XX	1 per shipping container containing volatile samples	X	X														
Equipment Rinsate	RFSGWER01 - XX	1 per day per type of non-disposable sampling equipment	X	X	X	X	X	X	X	X			X	X	X	X	X	X
Source Water Blank	RFSGWSW01 - XX	1 per source of decontamination water	X	X	X	X	X	X	X	X			X	X	X	X	X	X
Temperature Blank	RFSGWTemp01 - XX	1 per shipping container															X	

Notes:

Holding Times Listed time is to preservation/extraction by the lab.
*MS/MSD Use the same sample number and triple the number of containers (bottles) per sample.
Preservation All samples must be put on ice in coolers after collection and shipped to the lab maintaining a temperature of 4°Q- 2°C.

bgs	Below ground surface	PCB	Polychlorinated biphenyl
DO	Dissolved oxygen	QC	Quality control
EPA	U.S. Environmental Protection Agency	SC	Specific conductance
HCl	Hydrochloric acid	SVOC	Semivolatile organic compound
ID	Identification	TDS	Total dissolved solids
IDW	Investigation derived waste	TPH-E	Total petroleum hydrocarbons - extractable
mL	Milliliter	TPH-P	Total petroleum hydrocarbons - purgeable
MS/MSD	Matrix spike/matrix spike duplicate	VOA	Volatile organic analysis
ORP	Oxidation-Reducton potential	VOC	Volatile organic compound
PAH	Polycyclic aromatic hydrocarbon		

5.3.1 Sampling Methods

All groundwater samples will be collected from completed 2-inch diameter piezometers installed using direct-push technology suitable for collecting groundwater samples. Standard information for planning and conducting field sampling for Phase I, such as piezometer installation, borehole logging, field equipment calibration and maintenance, sample collection methodology, sample packaging and documentation, has been outlined in the QAPP.

Use of real-time screening methods such as a membrane interface probe (MIP) are not proposed during Phase I, as these are most effective in determining chemical delineation within known contamination, and less effective as a screening or site discovery technique. The goal of the Phase I sampling is to develop a base-line hydrogeologic model and to improve the understanding of overall site-wide groundwater quality; therefore, real-time screening methods are not proposed. Real-time screening may be considered during a subsequent sampling phase if the need for detailed and robust chemical delineation is required.

All locations will be logged for site lithology characterization and screened using a photoionization detector (PID). If VOCs are detected by the PID, the location will be flagged for future soil sampling. [Table 2](#) provides specific sampling and analysis information to assist the field crew during field activities, including sample identification numbers for the various sampling locations and a summary of the test methods to be ordered for each sample. Decontamination and management of investigation-derived waste (IDW) from sampling activities will be addressed during sampling. Information for methods and procedures for decontamination and IDW handling can be found in the QAPP.

5.3.2 Analytical Methods and Quality Control

The groundwater samples will be submitted for analysis using the analytical methods shown on [Table 2](#). Samples for chemical analysis will be submitted to California state-certified laboratories pre-approved by UC Berkeley and DTSC. Additional descriptions of the analytical methods, including the selection of analytical laboratories and project analytical requirements, can be found in the QAPP, as outlined below.

To assess the quality of field data, field quality control (QC) samples will be collected and analyzed as listed in [Table 2](#). Laboratory QC samples will also be analyzed in accordance with referenced analytical method protocols to ensure laboratory procedures are conducted properly and the quality of the data is known. Testing, inspection, and maintenance procedures for field equipment are also critical for accurate data collection. Procedures for these QC practices are explained in the QAPP.

Table 3 – QAPP Reference Locations

Preparation for Field Activities	Reference Section in QAPP
Utility Clearance	Section 4.12
Health and Safety Plan (HSP)	See Appendix B, HSP
Analytical Methods	Section 7.2
Analytical Laboratory Selection	Section 7.4
Analytical Requirements	Section 7.3 and Table A-13
Field Sampling	
Chain-of-Custody Requirements	Section 5.4
Geoprobe/Push Technology	Section 4.1.4.1
Hollow Stem Auger	Section 4.1.4.2
Management of Investigation-Derived Waste	Section 4.11
Decontamination	Section 4.10
Field Quality Control Samples	
Equipment Rinsate Samples	Section 4.9 and 3.2.2
Source Water Blank	Section 4.9 and 3.2.2
Temperature Blanks	Section 4.9 and 3.2.2
Trip Blanks	Section 4.9 and 3.2.2
Laboratory Quality Control Samples	
Method Blanks	Section 3.2.2
Matrix Spike and Matrix Spike Duplicates (MS/MSD)	Section 3.2.2
Laboratory Control Samples	Section 3.2.2
Surrogate Standards	Section 3.2.2
Field Equipment Testing, Inspection and Maintenance	
Calibration of Field Equipment	Section 6.1
Maintenance of Field Equipment	Section 11.1

6.0 PROJECT ROLES AND RESPONSIBILITIES

This section presents key staff and responsibilities. Additional project organization information pertaining to sampling and laboratory quality is presented in the QAPP.

Table 4 – Richmond Field Station Roles and Responsibilities

Name and Affiliation	Roles	Responsibilities
Greg Haet (UC Berkeley Office of Environment, Health & Safety)	Project Coordinator	Directs environmental health and safety compliance of the project. Receives notices, comments, approvals, and related communications from DTSC and forwards them to Respondents' representatives. Reports to and interacts with the DTSC for all Order tasks and/or public outreach.
Gwojen Fung (UC Berkeley Capital Projects)	Project Manager	Manages contracts, schedules, and budgets. Authorizes work to proceed.
Karl Hans (UC Berkeley Office of Environment, Health & Safety)	Project Scientist/ On-Site EH&S Coordinator	UC on-site environmental health and safety project coordinator at the Richmond Field Station. Assists in managing the project and in reporting to and interacting with the DTSC and Respondents. Reviews all submittals and notifications to DTSC and other agencies for quality and completeness.
Jason Brodersen, P.G. (Tetra Tech EM Inc.)	Project Consultant/Project Geologist	Provides direction and supervision of hazardous waste site cleanup work. Provides expert advice on environmental management during investigation and remediation phases of the project. Primary author and coordinator of completion Order required reports and other technical deliverables.
Gene Barry, P.E. (4LEAF, Inc.)	Project On-Site Coordinator	Performs construction management and oversight duties during various construction phases of the project and other on-site activities. Assists the project consultant and project coordinators in managing project information and data and completion of project deliverables.
Anthony Garvin (UC Office of the General Counsel)	Respondent Representatives	Provide input to and receive input from Project Coordinator regarding project management, task completion, and DTSC interaction.
Brian Spiller (Zeneca)		
John Edgcomb (Edgcomb Law Group- Zeneca/Bayer CropScience)		
Bill Marsh (Edgcomb Law Group- Zeneca/Bayer CropScience)		

7.0 REFERENCES

- Agency for Toxic Substances and Disease Registry. 2008. "Public Health Assessment Evaluation of Exposure to Contaminants at the University of California, Berkeley, Richmond Field Station." March 13.
- Blasland, Bouck & Lee, Inc. 2004. "Groundwater, Surface Water, and Sediment Monitoring Plan, Subunit 2, Meade Street Operable Unit, University of California, Berkeley, Richmond Field Station, Richmond, California." December.
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- University of California, Berkeley (UC Berkeley). 1973. *Sanitary Engineering Research Laboratory News Quarterly*. Volume XXIII, No. 2. Richmond, California. April.
- UC Berkeley. 2006b. Interview regarding Richmond Field Station (RFS) Operational History. Between Scott Shackleton, Karl Hans, Larry Bell, and Greg Haet, UC Berkeley; and Julia Vetromile and Leslie Lundgren, Tetra Tech EM Inc. November 14.
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- URS Corporation. 1999. "Final Field Sampling and Analysis Plan and Tiered Risk Evaluation, University of California, Berkeley, Richmond Field Station." December 10.
- URS Corporation. 2000. "Field Sampling and Analysis Results, University of California Berkeley, Richmond Field Station/Stege Marsh." December.

ATTACHMENT 1
RESPONSE TO COMMENTS



Linda S. Adams
Secretary for
Environmental Protection



Department of Toxic Substances Control

Maziar Movassaghi
Acting Director
700 Heinz Avenue
Berkeley, California 94710-2721



Arnold Schwarzenegger
Governor

April 15, 2009

Mr. Greg Haet
Associate Director, Environmental Protection
Office of Environment, Health & Safety
University of California, Berkeley
317 University Hall #1150
Berkeley, California 94720-1150

Dear Mr. Haet:

The Department of Toxic Substances Control (DTSC) received the Field Sampling Workplan (FSW), Appendix A: Quality Assurance Project Plan, and Appendix B: Health and Safety Plan for the University of California Richmond Field Station (RFS), Richmond, California. The plans, dated February 27, 2009, were prepared by Tetra Tech EM, Inc. for the University of California. The purpose of the FSW is to describe the general facility-wide strategy and protocols for the field investigations that will fill the identified data gaps and allow characterization of the site. Separate site-specific field sampling plan addenda will be submitted in the future for the various investigation areas that will include background and historical information, specific data quality objectives, sampling locations, analytical methods, etc. DTSC received comments from the Richmond Southeast Shoreline Area Community Advisory Group and has taken their comments into consideration when preparing this letter. DTSC support staff has reviewed the report and their comments are enclosed along with the following comments:

General Comment:

1. The use of Multi-Increment Sampling (MIS) has not been approved by DTSC for site characterization or risk assessment purposes. Therefore, at this time reference to MIS should be removed from all documents and replaced with standard soil sampling methods.

Field Sampling Workplan:

1. Page 12, Section 3.1, Sources, Migration Pathways, and Exposure:
 - a. Inhalation of vapors from soil or groundwater sources needs to be added to the text as a potentially complete exposure pathway as identified in Figure 3 (Conceptual Site Model).
 - b. The potential for contaminated backfill material in utility corridors should also be identified as a potential source of contamination to soil and groundwater in the Conceptual Site Model as cinder material was previously found to have been used as backfill. Section 4.3.3, Utility Data Gaps should also be revised to include the potential for contaminated backfill in utility lines.
 - c. This section states that the former Liquid Gold facility may have been a possible source of contamination to the RFS. Due to the distance of the Liquid Gold facility to the RFS, a brief rationale for this statement should be included. Additional rationale should also be included in the appropriate future site-specific field sampling plan(s).
2. Page 15, Section 3.2, Exposure to Human Receptors: This section should include inhalation of soil vapors from soil as a potential exposure pathway.
3. Page 17, Section 3.3, Exposure to Human Receptors: This section should include that inhalation of vapors from volatilization of contaminated groundwater may also be a potential exposure pathway to persons occupying buildings and to workers that may come in contact with groundwater or work in trenches.
4. Page 19, Section 4.2, Strategy, Prioritization, and Data Evaluation: This section should also include an investigation strategy for the possible presence of soil vapors from a soil and/or groundwater sources.
5. The rationale used to identify the prioritization of the investigation areas, other than habitat areas, should be included.
6. Page 25, Section 4.3.1, Soil Data Gaps: Revisions to this section are needed as the depth of initial sampling is being limited to the upper two feet of soil. For example, in areas where the former California Cap Company operated, known hazardous waste storage areas, and in the Western Transition Area where dumping was known to have occurred, deeper soil sampling is warranted.
7. Page 27, Section 4.3.2, Groundwater Data Gaps, Step 2: Please include as one of the goals of the study a determination whether contaminants are migrating from the RFS to off-site locations.

Appendix A, Quality Assurance Project Plan (QAPP)

The QAPP needs to be revised to include specific standard operating procedures (SOPs) for the investigation methods that are most likely to be used at the site. Anticipated laboratory analytical methods along with a list of chemicals that will be reported, sample size, holding times, preservative, etc. should be included.

1. Page A-14, Section 3.2.1, Sensitivity: The last sentence of this section is unclear and needs to be revised. Please explain what the laboratory detection limit and laboratory method reporting limits are, and why it is acceptable to use the laboratory method reporting limit. Previously, quantitation limits and detection limits were discussed. This comment also applies to Page A-154, Section 7.3, Reporting Limits.
2. Page A-15, Section 3.2.2, Precision and Accuracy:
 - a. The default frequency for laboratory blanks and spike blanks should be a minimum of once for every batch of samples, or type of matrix, or 20 samples, whichever is more frequent.
 - b. Temperature blanks need to be added to Table A-2 as part of the Field QC requirements, and included in Section 4.9, Field Quality Control Samples.
3. Page A-17, Section 3.2.4, Completeness: The criteria that will be used to establish the degree of completeness needs to be included. A minimum percentage for each type of matrix should be included.
4. Page A-18, Section 4.0, Sampling Procedures: Utility clearances and specific types of permits that are required prior to sampling should be identified in this section. The description should also include lead times required to obtain permits and clearances.
5. Page A-23, Section 4.1.2, Soil Sampling for Volatile Organic Compounds:
 - a. DTSC's November 2004 guidance document for implementation of Method 5035 should be reviewed and incorporated into this section and referenced in Section 4.1.29.
 - b. This section needs to include a discussion regarding the collection and analysis of high and low concentration VOC samples. Collection of low concentration soil samples in vials that contain methanol is not appropriate for samples analyzed with closed system purge and trap equipment. It should also be noted that the use of methanol as a preservative and extraction solvent introduces a significant dilution factor that will raise the method quantitation level beyond the operating range of the low concentration direct purge and trap. The high concentration method is used for samples with VOC concentrations greater than 200 ug/kg.
 - c. This section needs to contain a discussion regarding packaging and transportation of vials used to transport samples. For example, VOAs need to be transported upright in the ice chest.

- d. The criteria for acceptance of vials containing methanol needs to be included. Vials containing methanol should be weighed a second time in the field on the day they are to be used. Vials containing methanol that are found to have lost a reduction in weight of greater than 0.05 grams should not be used. Also, vials should not be submitted for analysis if the preservative has spilled or splashed from the vial.
 - e. Additional tared and preserved vials should be available in the field due to the potential for rejecting vials.
 - f. It should be specified that the tared weight of each vial is to include the weight of the sample label.
 - g. If the preservative is added to the vial in the field, the analytical laboratory should be contacted to determine if a magnetic stirring bar needs to be placed in the vial prior to sample collection.
6. Page A-24, Section 4.1.2.2, Sampling Protocol 2: It should be specified in this section that the surrogate, matrix spikes and internal standards are only added to the vials after the sample is added to the vial, and will be done by the analytical laboratory.
 7. Page A-25, Section 4.1.2.4, Field Weighing: The field balance needs to be checked at least daily and against an appropriate reference weight. Also, please explain and provide a reference indicating why a weight accuracy of 0.1 grams is acceptable. DTSC's November 2004 guidance for implementation of Method 5035 recommends an accuracy of 0.05 grams and that it is achievable in the field.
 8. Page A-26, Section 4.1.2.5, Presence of Carbonates: Please provide the reference demonstrating that a holding time of unpreserved EnCore samples of 7 or 14 days does not result in a loss of VOCs.
 9. Page A-67, Section 4.3.2.12.1, Deciding When to Filter: The decision to filter groundwater samples should also include an evaluation of who the receptor is and how that receptor will come into contact with the groundwater. For example if the receptor may come into direct contact with groundwater, filtering may not be recommended.
 10. Page A-79, Soil-Gas Sampling: This section should be updated to reflect the current state of practice of soil gas sampling. For example continuous soil gas sampling and post-run tubing methods are no longer accepted due to the recognized difficulty in sealing the space between the drive rod and borehole. The actual zone that is being sampled therefore cannot be determined, and there is a greater potential for ambient air leakage.
 11. Page A-85, Table A-5, Summary of Vapor Intrusion Analytical Methods: Because analytical methods have not been certified for soil gas analysis, the laboratory

Mr. Greg Haet
April 15, 2009
Page 5

Standard Operation Procedures will need to be submitted for approval prior to analysis.

12. Page A-109, Section 4.11, Management of IDW: Please add to this section that waste determined to be a hazardous waste must be disposed within 90 days of generation. In addition, personal protective equipment and other waste that is grossly contaminated with a known hazardous substance should not be disposed in the facility trash receptacle. The waste should be stored in a container and disposed at a proper off-site facility to prevent exposure to unauthorized personnel.

If you have any questions regarding this letter, please contact Lynn Nakashima of my staff at (510) 540-3839.

Sincerely,

A handwritten signature in black ink, appearing to read 'Barbara J. Cook', with a long horizontal line extending to the right.

Barbara J. Cook, P.E.
Performance Manager
Brownfields and Environmental Restoration Program – Berkeley Office

Enclosures

cc: See next page

Mr. Greg Haet
April 15, 2009
Page 6

cc: Mr. Mark Vest
Geologic Services Unit
Department of Toxic Substances Control
8800 Cal Center Drive
Sacramento, CA 95826-3200

Dr. James Eichelberger
Human and Ecological Risk Division
Department of Toxic Substances Control
8800 Cal Center Drive
Sacramento, CA 95826-3200

Dr. Kimiko Klein
Human and Ecological Risk Division
Department of Toxic Substances Control
700 Heinz Avenue
Berkeley, CA 94710

Mr. Eric Brocales
Office of Human Capital and Workplace Innovation
Health and Safety Branch
Department of Toxic Substances Control
700 Heinz Avenue
Berkeley, CA 94710



Linda S. Adams
Secretary for
Environmental Protection



Department of Toxic Substances Control


Maureen F. Gorsen, Director
700 Heinz Avenue
Berkeley, California 94710-2721



Arnold Schwarzenegger
Governor

MEMORANDUM

TO: Lynn Nakashima
Senior Hazardous Substances Scientist
Cleanup Program-Berkeley

FROM: Eric Brocales 
Associate Industrial Hygienist
Office of Human Capital and Workplace Innovation (OHCWI)
Health and Safety Branch (HSB)

DATE: April 1, 2009

SUBJECT: University of California, Berkeley, Richmond Field Station
Health and Safety Plan
PCA Code: 11050 Site Number: 201605-00

BACKGROUND

The Cleanup Program-Berkeley requested the HSB to review the Health and Safety Plan (HASP) for the remediation activities at the University of California, Berkeley, Richmond Field Station (Site) in Richmond, California. The Site is located at 1301 South 46th Street, Richmond, CA.

DOCUMENT REVIEWED

The HSB reviewed the HASP for the remediation activities at the Site. The HSB received the plan on March 17, 2009.

GENERAL COMMENTS

The Department of Toxic Substances Control (DTSC) reviewed the HASP for compliance with appropriate State and Federal Health and Safety Regulations. An industrial hygienist from the HSB may perform a field audit in order to confirm the implementation of the provisions and specifications presented in the HASP.

The DTSC is unable to foresee all the health and safety hazards in the work place by the review of the submitted plan. Continuous surveillance of the work-site and

creation of an effective health and safety program by the employer will reduce work place injuries and reduce liability.

In the event that this HASP does not cover a contractor or sub-contractor, they must submit their own HASP to DTSC for review. If the scope of work changes significantly, (an unanticipated chemical, physical, or biological hazard is discovered or introduced to the site), then the new hazard must be addressed in an addendum to this HASP and submitted to DTSC for review.

The final site HASP must be available at all times for on-site personnel to reference. In utilizing the site HASP, field staff must be able to obtain sufficient information to compile an accurate assessment of the site safety issues associated with every job function.

The HSB review of this HASP is not a guarantee that it will be properly and safely implemented. HASP implementation is the employer's responsibility. The acceptance is limited to concurrence that all the required elements of a safety plan are present.

SPECIFIC COMMENTS

HSB's review finds the submitted HASP deficient in providing sufficient information to assess the hazards. The HASP appears to be lacking and/or has incomplete key elements.

1. **KEY PERSONNEL AND RESPONSIBILITIES.** In Section 2.1, PROJECT PERSONNEL, please provide information identifying key personnel who at a minimum, have the responsibility and authority to perform the following functions:
 - a. Be present at all times during site operations.
 - b. Have the authority to enforce the HASP and stop operations if personnel or community safety and health may be jeopardized.
 - c. Evaluate monitoring data to make field decisions regarding safety and health.
2. **WORK PLAN.** In Section 3.3, PLANNED ACTIVITIES, HSB is aware that UCRFS will be submitting separate sampling plans for the Site activities covered in the remedial work plan, however please ensure that each addendum is included in the final HASP, and at a minimum includes a summary description of the project, including but not limited to: the duration of planned activities, personnel requirements, and the extent to which subcontractors will be used. In addition, please provide a summary of the information regarding known or suspected hazardous waste disposal on-site, the waste(s) location, physical state, chemical characteristics, and the range of concentrations found to date by matrix

(soil, water, air).

3. **JOB HAZARD ANALYSIS/SUMMARY.** In Section 8, SITE-SPECIFIC HAZARD EVALUATION, please provide the following details:
 - a. The best information available regarding the contaminants and conditions present at the site.
 - b. Approximate duration of the operation and each task.
4. **EMPLOYEE TRAINING.** In Section 5.0, TRAINING REQUIREMENTS, the HASP should state that the employee training program is in compliance with CCR 5192(e).
5. **PERSONAL PROTECTION.** In Section 6.0, PERSONAL PROTECTION REQUIREMENTS, The body of the HASP should state that the Personal Protective Equipment program is in accordance with 8 CCR 5192(g).
6. **MEDICAL SURVEILLANCE PROGRAM.** In Section 7.1, HEALTH MONITORING REQUIREMENTS, please verify and state in the body of the HASP that the health monitoring program is in accordance with 8 CCR 5192(f).
7. **AIR SURVEILLANCE.** In Section 8, ENVIRONMENTAL MONITORING AND SAMPLING, please provide additional information regarding:
 - a. When air monitoring levels would indicate the expansion(s) of exclusion zone. In addition, provide the rationale for how each action level was derived.
 - b. The specific make and model of instrument(s) selected for use.
 - c. The relative response factors for the instrument of choice must be incorporated into any action level(s) derived for the site.
8. **SITE CONTROL.** In section 9.0, SITE CONTROL, please verify and state in the body of the HASP that the site control measures are in accordance with CCR 5192(d).
9. **SPILL CONTAINMENT.** A discussion regarding a spill containment plan shall be incorporated as a separate section in the body of the HASP. The spill containment program must meet the requirements of 8 CCR 5192(j).
10. **SANITATION.** Please describe the provisions that will be made to ensure proper sanitation facilities are available for site personnel, including but not limited to:
 - a. Adequate washing facilities such as soap, water, towels and where appropriate showers.

- b. Toilets and other sanitary facilities in numbers which will reasonably handle the projected number of personnel.
- c. Adequate stocks of potable water, provided in sanitary containers.

11. **ILLUMINATION.** Please include a section discussing how minimum illumination shall be provided for site personnel. The plan shall be in accordance with the requirements of 8 CCR 5192(m).

If all planned field activities are to be conducted during daylight hours and not within any structures at the site, please state as such.

CONCLUSIONS

The HASP must follow and contain the specific content and procedural elements as indicated in the Department of Toxic Substances Control guidance document and be resubmitted for further review. HSB recommends consulting a safety professional to complete the Health and Safety Plan.

In addition, the HASP must comply with 8 CCR, 5192: "Health and Safety for Hazardous Waste Operations and Emergency Response" as well as other appropriate State and Federal Health and Safety Regulations. Please note that in addition to the requirements of this section, the employer is also responsible for the implementation of an Illness and Injury Prevention program, which is required by the 8 CCR, 1509 and 3203.

The HSB is available to discuss the necessary revisions and approach. Thank you for the opportunity to review this document. Should questions arise regarding this review and/or related issues, please contact Eric Brocales at (510) 540-3953.

PEER REVIEW BY:



Kathleen Yokota-Wahl
Senior Industrial Hygienist



Linda S. Adams
Secretary for
Environmental Protection



Department of Toxic Substances Control


Maziar Movassaghi
Acting Director
8800 Cal Center Drive
Sacramento, California 95826-3200



Arnold Schwarzenegger
Governor

MEMORANDUM

TO: Lynn Nakashima
Site Mitigation and Brownsfields Reuse Program
Geology, Permitting and Corrective Action Branch
Department of Toxic Substances Control (DTSC)
Cypress, CA 90630

FROM: J. Michael Eichelberger, Ph.D. 
Staff Toxicologist
Human and Ecological Risk Division (HERD)

DATE: April 14, 2009

SUBJECT: DRAFT FIELD SAMPLING WORKPLAN, UNIVERSITY OF CALIFORNIA,
BERKELEY RICHMOND FIELD STATION, RICHMOND, CALIFORNIA

PCA: 11050 SITE CODE: 201605-00

Background

The University of California Richmond Field Station is located on former industrial land and consists of 96-acres of uplands and 13-acres of tidal marsh and marsh edge habitat. Industrial use of the uplands, particularly for the manufacture of blasting caps containing mercury fulminate, has been documented as early as the 1870's and continued until 1950 when the University of California purchased the property for use as a research facility. Documented releases of chemicals of potential ecological concern (COPECs) including metals, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs) have been reported. An ecological risk evaluation of the uplands and West Stege Marsh were completed in 2001. Several remedial measures have been implemented since 2002, and include, but are not limited to, treatment and transport to the adjacent Zeneca property of mercury-

Lynn Nakashima

4/14/2009

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contaminated soils, installation of a biologically active permeable barrier and excavation and removal of contaminated sediments from a portion of West Stege Marsh, and backfilling with clean fill to restore California clapper rail habitat. The site includes upland habitats including rare coastal prairie and wetlands consisting of saltwater marsh. This memorandum is in response to the DTSC project manager request for technical review of ecological issues related to the Draft Field Sampling Workplan.

Document Reviewed

HERD reviewed "Draft Field Sampling Workplan, University of California, Berkeley Richmond Field Station, Richmond, California" prepared by Tetra Tech EM Inc. (Oakland, California) and dated February 27, 2009, hereafter referred to as the work plan. HERD received the report in March, 2009 for review.

Scope of the Review

The report was reviewed for scientific content related to ecological risk assessment. Grammatical or typographical errors that do not affect the interpretation of the text have not been noted.

General Comments

1. HERD does not believe the work plan contains sufficient information to determine if the sampling approach is adequate to assess nature and extent of contamination relative to potential hazards to ecological receptors. Screening levels for ecological receptors are not listed. Since the report represents an overall approach to sampling for all five sampling phases, it should provide all of the information common to all. Screening levels, the references to these screening levels, appropriate chemical analytical methods and associated detection limits below the ecological screening levels should be presented for each of the chemical constituents to be assessed. For ecological risk assessment purposes, sampling and analysis should be conducted to the No Observable Adverse Effect Level, please see Specific Comments 6 and 7 below.
2. HERD is concerned that Multi-incremental Sampling will not adequately support ecological risk assessment needs. It will certainly not be adequate for sediments where individual sample locations represent total exposure to sedentary marine benthic invertebrates. Average concentrations calculated for individual Areas of Concern (AOC), that are larger than the home range of terrestrial species such as the shrew, may not adequately represent actual exposure.

SPECIFIC COMMENTS

1. Page 13, Figure 3, Conceptual Site Model. The Conceptual Site Model is not complete, only a partial list of exposure pathways to ecological receptors is depicted. There is neither graphical representation of contaminant transport to

sediments nor the transfer of sediment contaminants up the food chain. There is some representation of trophic transfer from surface water but it is too small to interpret and is incomplete. Likewise exposure to terrestrial ecological receptors is also only partially represented. There is no representation of potential exposure pathways to invertebrates or food chain pathways from plants and invertebrates to vertebrate receptors. HERD believes for clarity it would be useful to separate the conceptual site models for human health and ecological receptors into separate figures.

2. Page 15, Section 3.2, Adsorption to Sediment. The sentence "*PCBs and pesticides are strongly adsorbed to soil particles and are not readily leached*" is not entirely accurate and needs to be clarified. HERD would agree that PCBs readily adsorb to soil particularly those that are more highly chlorinated, however PCBs can readily migrate down in the soil horizon if organic solvents are present. Also, not all pesticides bind tightly to soil. For example, aldicarb, atrazine and carbaryl are all examples of pesticides that readily leach in soils. The work plan needs to clarify which pesticides it is referring to when stating that they do not leach.
3. Page 15, Section 3.2, Exposure to Ecological Receptors. This section is not well organized and written. The text indicates that grasses, shrubs and trees are not exposed to contaminants through the "*root uptake of soil and sediment.*" There is no uptake of soil and sediment by plants. Soil and sediment are complex media containing many different components. What is accurate to say is that plants can take up contaminants present in soil and sediment. Generally, the majority of the exposure of birds and mammals is through the diet, not through ingestion of soil 'dirt' on plant leaves or through grooming or preening .
4. Page 17, Section 3.3, Exposure to Ecological Receptors. Please see specific comment 3 above.
5. Page 21, Table 1: Site Prioritization and Page 22, Figure 4, Soil Investigation Areas. Figure 4 delineates where Phase I Sampling is to occur but it is not clear where the specific areas within Phase I listed in Table I are located. Table I lists four primary soil sources: 1a) IA1-1 Building 478; 2a) IA1-2 East Meadow; 3a) IA1-3 Corporation Yard; 4a) IA1-4 U.S. Briquette Company, five groundwater source areas: 1b) GW1: Building 478 Area; 2b) GW2 Building 120 Area; 3b) GW3 Property Boundary; 4b) GW4 Biologically Active Permeable Barrier Wall (BAPB); and 5b) GW5 Site-wide Groundwater, and a separate utilities source are identified as UT1 Select Utility Locations. With the exception of the BAPB, none of the primary sources are identifiable in Figure 4. It is also unclear why the BAPB, a structure constructed to impede downgradient movement of site related Chemicals of Potential Ecological Concern (COPECs) to Western Stege Marsh is considered a 'Primary Source.' Neither the 'Approximate Property Boundary' nor the 'Property Boundary' shown in the Figure 4 legend, are identifiable on the figure. The figure should be modified to show the primary sources, secondary

sources and the property boundary as indicated in the legend. HERD notes that Figure A-3 Physical Features Map in Appendix A identifies buildings 478 and 120 but does not identify other features such as the U.S. Briquette Company, East Meadow, Corporation Yard, or utility locations.

6. Page 23, Section 4.2.3, Data Evaluation, Decision I Levels. The report fails to describe Ecological Soil Screening Levels as a Decision I Level. This needs to be rectified in the report. Please provide a reference for soil screening levels. Given that Western Stege Marsh is being remediated and reclaimed to support California clapper rail habitat, the use of Effects Range Median (ER-M) is not warranted. Protection for endangered and threatened species needs to be at the level of the individual. Sampling to the ER-M will not provide sufficient protection to the clapper rail.
7. Page 23, Section 4.2.3, Data Evaluation, Detection II Levels. Please explain how Decision II Levels will be applied to ecological receptors, none are mentioned in the report. HERD fundamentally disagrees with the approach presented in the unnamed table on page 23. For site characterization purposes, sampling needs to be conducted to determine nature and extent to the 'No Effect Level.' This is particularly important for the sediments of Western Stege Marsh. Sampling needs to be conducted with detection limits set to a value lower than the No Effect Screening Level. Since the work plan offers no information regarding how Decision II Levels would apply to ecological receptors, only to human receptors, HERD assumes that, as written, sampling could occur at levels not protective of ecological receptors.
8. Page 25, Section 4.3.1, Soil Data Gaps, Step 4: Define the Boundaries of the studies. HERD does not believe the work plan has provided sufficient documentation to justify limiting initial sampling to the depth of 2 feet. Location of each specific chemical constituent within the soil horizon is, as the report points out, dependent on multiple factors, some related to the soil, others to the chemical itself, and also potential soil disturbance subsequent to the release. The UC Richmond Field Station historically has been used for many purposes and the potential for movement of soils due to site activities and potentially from grading due to past remedial efforts is apparent. HERD believes that sampling should be conducted at multiple depths. For ecological purposes a logical soil sampling strategy would include surface soil to a depth of 6 inches, samples between two and three feet and deep samples at 6 feet.
9. Page 25, Section 4.3.1, Soil Data Gaps, Step 5: Develop Decision Rules. HERD does not believe that if a chemical is detected at concentrations below Decision I Levels that it can be assumed that a release has not occurred as stated in the report. It is appropriate to state that chemicals are below a level that reasonably would be considered to pose a hazard to receptors. The work plan should be revised accordingly.

Lynn Nakashima

4/14/2009

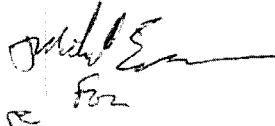
5

10. Page 26, Section 4.3.1, Soil Data Gaps, Step 6: The report needs to be more specific about the screening levels, neither soil or sediment screening levels are mentioned. Inorganic background concentrations should be approved by the DTSC Geological Services Unit and should be used as the determinant for establishing inorganic COPECs.

Conclusions

HERD does not believe that Multi-incremental Sampling is necessarily the best method for conducting site investigation at the UC Richmond Field Station. Compositing samples from an AOC do not provide sufficient information to evaluate certain receptors such as benthic invertebrates or species with smaller home ranges than the AOC. HERD disagrees that detected concentrations of a chemical below the screening level indicates that there has not been a release. This reference in the work plan should be deleted. Sampling for site characterization purposes should be to the No Effect Level and all methods with their references and detection limits appropriate to the screening levels should be presented in the work plan. The conceptual site model should be reworked to accurately represent exposure pathways to ecological receptors. The report should be revised to reflect the comments in this memorandum and resubmitted to HERD for review.

Reviewed by: James M. Polisini, Ph.D.
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Department of Toxic Substances Control



Linda S. Adams
Secretary for
Environmental Protection

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Arnold Schwarzenegger
Governor

MEMORANDUM

TO: Lynn Nakashima
Senior Hazardous Substances Scientist
Brownfields and Environmental Restoration Program
Berkeley Office

FROM: Mark Vest, CEG *Mark Vest*
Senior Engineering Geologist
Geologic Services Unit
Sacramento Office

REVIEWED BY: Kate Burger, PG, PhD *Kate Burger*
Senior Engineering Geologist
Geologic Services Unit
Sacramento Office

DATE: April 13, 2009

SUBJECT: GSU REVIEW OF FIELD SAMPLING WORKPLAN, UNIVERSITY OF CALIFORNIA, BERKELEY, RICHMOND FIELD STATION, RICHMOND, CALIFORNIA AND FIELD SAMPLING WORKPLAN: APPENDIX A, QUALITY ASSURANCE PROJECT PLAN, UNIVERSITY OF CALIFORNIA, BERKELEY, RICHMOND FIELD STATION, RICHMOND, CALIFORNIA

Project: 201286/11050-00

GRE:0810246/ESTOR:WR20001124

Activity Requested

In response to your request, the Geological Services Unit (GSU) has reviewed the subject documents. The Field Sampling Workplan (FSP) and Appendix A: Quality Assurance Project Plan (QAPP) were prepared by Tetra Tech EM Inc. for the University of California at Berkeley. When approved and finalized, the February 27, 2009 FSW and

QAPP will provide an overall approach for investigating the Richmond Field Station (RFS) for uncontrolled releases of hazardous substances. The following comments and recommendations are provided for your information and use. If you need more information regarding this matter, feel free to contact me at (916) 255-3692 or mvest@dtsc.ca.gov.

General Comments and Recommendations

1. As per requirements in the California Business and Professions Code (Sections 6735 and 7835), the FSP and QAPP should be signed and/or stamped by a California registered civil engineer and/or professional geologist indicating their responsibility for engineering and/or geologic content of the documents.
2. The FSP, QAPP, and pending FSP addenda should present sufficient detail such that sampling teams unfamiliar with the site could perform the same quality field investigation using the FSP and QAPP as references. In particular, the QAPP should be amended to include detailed Standard Operating Procedures (SOPs) for reasonably anticipated site investigation activities.

The SOPs should present concise, detailed written instructions for planning, conducting, and documenting routine investigation activities. Sampling procedures including personnel qualifications, equipment checklists, step-by-step procedures, and field forms should be included. Additional SOPs may be provided with the FSP addenda, as warranted. The SOPs should be signed by the Tetra Tech Quality Assurance/Quality Control manager, or equivalent.

3. Based on a review of literature on multi-incremental (MI)/decision unit (DU) sampling, it seems that the method can provide good estimates of mean concentrations within sampled grids (DUs) when applied correctly. Also, it is recognized that there are uncertainties associated with sample representativeness and associated decisions based on discrete samples. Because of growing interest in the sampling method, DTSC is participating in a review and assessment of MI/DU sampling that is being performed by the Interstate Technology & Regulatory Council (ITRC)¹. Unfortunately, the ITRC work is not scheduled to be completed until at least the end of this year. Therefore, DTSC should not accept MI/DU sampling for implementation on the RFS project.

¹ "ITRC is a state-led coalition working together with industry and stakeholders to achieve regulatory acceptance of environmental technologies. ITRC consists of 50 states, the District of Columbia, multiple federal partners, industry participants, and other stakeholders, cooperating to break down barriers and reduce compliance costs, making it easier to use new technologies, and helping states maximize resources. ITRC brings together a diverse mix of environmental experts and stakeholders from both the public and private sectors to broaden and deepen technical knowledge and streamline the regulation of new environmental technologies."

(<http://www.itrcweb.org/aboutITRC.asp>)

Specific Comments and Recommendations

4. Page 1 of the FSP contains a typographical error. The order number should be IS/E-RAO 06/07-004.
5. Page 20 of the FSP proposes *"Use of multi-incremental (MI)/decision unit (DU) sampling will be the primary technique to address the soil data gaps. MI/DU sampling has been developed as a sampling technique to greatly increase sample result confidence and identify possible spill areas"*.

Recommendation

- MI/DU sampling should not be approved by DTSC for implementation on the RFS project. Propose an alternate approach to address the soil data gaps.
6. Page 20 of the FSP proposes *"The requirement for subsurface sampling will be determined following review of near-surface sampling results"*. Contaminant releases at depth may not correlate with detectable results in near surface samples. For example, releases from subsurface utilities, under ground tanks, buried wastes, or discharges to dry wells are not likely to be detected in surface soil samples. Even historical discharges to the ground surface of volatile or very soluble compounds may not be detectable in surface soil samples. Grading activities may also prevent detection of historical surface releases.

Recommendation

- The proposal to use *"near-surface sample results"* as decision criteria for investigating releases at depth should not be approved. Also, "Near surface results" may not be an appropriate decision criteria for evaluating contaminant mobility and fate in shallow soils. Decision criteria for evaluating releases at depth and contaminant mobility/fate should be based on an appropriate conceptual site model of the potential release(s).
7. Pages 20 to 24 of the FSP propose *"Decision I Levels"* and *"Decision II Levels"* as a way to apply screening levels to detected contamination. According to the FSP, contaminants found at concentrations less than Decision Level I criteria would result in a no further action decision. Contaminant concentrations greater than Decision Level II criteria would result in more investigation, possibly including removal actions. The significance of concentrations detected between the two levels would be evaluated based on a lines-of-evidence methodology. These decision rules are also incorporated into the data quality objectives (DQOs) section of the FSP.

Recommendations

- Although the proposal to identify or develop numerical decision criteria within the FSP addenda is acceptable, the criteria should be applied carefully.

- The lines-of-evidence methodology should incorporate the nature of potential contaminant releases that are under investigation and the associated confidence in sampling locations. For example, sampling locations for potential releases from existing storage tanks or waste lines can be more confidently identified than sampling locations for spill areas related to poor housekeeping or other poorly documented historical practices.
- The Level I pass/fail decision criteria should be amended to apply a lines-of-evidence approach. As discussed above, in areas where historical activities and potential releases are not well documented, analytical results from one or two isolated, discrete samples may represent anything from the highest to the lowest concentrations in an area. In such a case, several surrounding samples should be completed to better understand what the discrete sample results represent.

8. Page 23 of the FSP proposes using *“National Drinking Water Maximum Contaminant Levels (MCL)”* as screening criteria.

Recommendation

- If MCLs are used as screening criteria, the lower of federal or state MCLs should be used.

9. Page 25 of the FSP proposes DQOs for soil investigation including *“Step 4: Define the boundaries of the Studies - All reasonably accessible surface soils located within the property boundaries of the RFS.”*

Recommendation

- The boundaries of the study should be expanded if contamination from the RFS is known or thought to have spread off the RFS property. This determination should be based on an appropriate conceptual site model as well as data collected under this FSP.

10. Page 25 of the FSP proposes DQOs for soil investigation including *“Step 5: Develop Decision Rules - If surface soil contaminants are detected at concentrations at or less than Decision I Levels, then the data confirms that there has not been a contaminant release and no further action is required.”*

Recommendation

- Level I decisions should incorporate a lines-of-evidence approach as recommended above. Detected concentrations from locations that are confidently expected to be within source or release area should be given more weight than concentrations from areas with little documentation or no obvious release mechanisms.

11. Page 25 of the FSP proposes DQOs for soil investigation including *“Step 5: Develop Decision Rules - If surface soil contaminants are detected as concentrations exceeding Decision II Levels, expand the vertical boundary of the study area to subsurface soils.”*

Recommendation

- The lateral boundaries may also be expanded in such a case.

12. Page 26 of the FSP proposes DQOs for soil investigation including *“Step 6: Specify performance or Acceptance Criteria - Use of MI/DU sampling will maximize the confidence of confirming or denying the presence of unacceptable hazardous concentrations at each site”* and *“Step 7: Optimize Design for Obtaining Data - The DUs will be sampled using MI sampling and the samples will be sent to the laboratory for analysis.”*

Recommendation

- The use of MI sampling has not been approved by DTSC for use on the RFS project. Alternate DQOs should be proposed.

13. Page 27 of the FSP proposes DQOs for ground water investigation including *“Step 2: Identify the Goals of the Study – What is the prevailing hydraulic gradient of the groundwater at RFS?”*

Recommendation

- The study should identify seasonal or other variations in groundwater flow conditions, in addition to the prevailing hydraulic gradient.

14. Page 27 of the FSP proposes DQOs for ground water investigation including *“Step 4: Define the boundaries of the Study – The study area is all groundwater located within the property boundaries of the RFS.”*

Recommendation

- The boundaries of the study should be expanded if contamination from the RFS is found to have spread off the RFS property, or if the conceptual site model suggests that releases may have extended off-site.

15. Page 28 of the FSP proposes DQOs for ground water investigation including *“Step 5: Develop the Decision Rules.”* Ground water quality including contaminant concentrations may vary seasonally. The variations can be significant resulting in decision criteria being exceeded only seasonally.

Recommendation

- Decision rules for ground water should be developed in the FSP addenda.

16. Page 27 of the FSP proposes DQOs for ground water investigation including *“Step 7: Optimize Design for Obtaining Data – Groundwater data gaps will be addressed through collection groundwater grab samples. Grab sample results will be evaluated to determine subsequent optimal placement of piezometers, if necessary.”*

Recommendations

- Simply collecting shallow grab water samples is not recommended. Prior to, or combined with, collecting shallow grab samples, the site hydrostratigraphy should be investigated to depths below initial target grab sample depths. This is needed to understand the hydrostratigraphic context of the grab samples and the overall site hydrogeology.
- Completing cone penetrometer surveys and, where VOCs may be present, membrane interface probe surveys are recommended. Such an approach will provide for high resolution stratigraphic and contaminant distribution data needed to support site characterization decisions (such as optimal placement of monitoring wells and/or piezometers).
- Please insure that the piezometers are designed such that they can provide representative ground water samples because ground water quality will need to be monitored over time to evaluate trends.

17. Pages 28 and 29 propose DQOs for utilities including sewers, fuel lines and hydraulic lines. Passive soil gas sampling is proposed to possibly be followed by active soil gas, soil, and/or ground water sampling. The FSP proposes sampling the main lines beginning at the southern (downstream) part of the site and moving towards building areas and laterals based on the main line results.

Recommendations

- Samples should be collected at the building areas (where lines leave the buildings) and where laterals connect to main lines even if main line samples do not exceed screening criteria.
- If release areas are identified based on detected VOCs, follow-up sampling and analysis should include non-VOC constituents. If no VOC release areas are identified, target areas for non VOCs should be identified based on other criteria.



Linda S. Adams
Secretary for
Environmental Protection



Department of Toxic Substances Control


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Arnold Schwarzenegger
Governor

MEMORANDUM

TO: Lynn Nakashima
Site Mitigation and Brownfields Reuse Program
700 Heinz Avenue, Suite 200
Berkeley, CA 90630

FROM: 
Kimiko Klein, Ph.D.
Staff Toxicologist
Human and Ecological Risk Division (HERD)

DATE: April 14, 2009

SUBJECT: Draft Field Sampling Workplan
UNIVERSITY OF CALIFORNIA, BERKELEY, RICHMOND FIELD STATION
PCA 11050 Site Code: 201605-00

Background

The University of California Richmond Field Station (UCRFS) is located on about 96 acres of former industrial upland and 56 acres of transition area, Western Stege Marsh, and the outboard area south of the bay trail. Industrial use of the uplands, including the manufacture of blasting caps containing mercury fulminate and a briquette company, has been documented as early as the 1870's and continued until 1950, when the University of California purchased the property for use as a engineering research facility. A human health and ecological risk evaluation of the uplands and West Stege Marsh were completed in 2001. Several remedial measures have been implemented since 2002, and include the treatment and transport to the adjacent Zeneca property of mercury contaminated soils, installation of a biologically active permeable barrier (PAPB), installation of a slurry wall between the Zeneca property and the USRFS, and excavation and removal of contaminated sediments from a portion of West Stege Marsh, and backfilling with clean fill to restore California clapper rail habitat. The Human and Ecological Risk Division (HERD) has been requested to provide technical support for this site.

Document Reviewed

The HERD reviewed a document entitled "Draft Field Sampling Workplan, University of California, Berkeley, Richmond Field Station, Richmond, California", dated February 27, 2009, and prepared by Tetra Tech EM Inc. for the Office of Environment, Health and Safety, University of California, Berkeley. This document includes two appendices: Appendix A Quality Assurance Project Plan, and Appendix B Health and Safety Plan. The HERD received this document around March 5, 2009.

General Comments

The HERD reviewed the draft workplan and both appendices. The field sampling workplan is an umbrella workplan for all site investigation activities that will take place. Field sampling addenda will be submitted for specific areas. Therefore, no chemical or area-specific approaches and methods are described, except for the stated preference for the use of multi-increment sampling (MIS) as the primary tool for soil characterization.

- A. Multi-increment sampling (MIS) strategy. The HERD has not yet reviewed or accepted data using this technique in any health risk assessment. In addition, the Department of Toxic Substances Control (DTSC) has not yet reviewed or approved the use of this technique for soil investigatory activities. However, the DTSC is currently participating in a review of this sampling strategy with the Interstate Technology and Regulatory Council (ITRC). Until significant issues are resolved regarding the appropriate use of the technique and the suitability of using MIS data in health risk evaluations, the HERD believes this sampling strategy should not be employed at this site. Some questions that need to be resolved include how or under what conditions this strategy may be acceptably used to characterize the release into the environment of volatile organic compounds (VOCs) or chemicals known to migrate in soil due to leaching, the appropriate design and use of this strategy for ecological risk evaluation, and how MIS data may be evaluated to obtain a statistically acceptable 95% upper confidence limit on a mean concentration.
- B. Appendix A Quality Assurance Project Plan. A large part of this appendix is a compendium of sampling procedures used in environmental site investigations and, thus, presumably represents the complete potential battery of techniques that may be used at any site. This appendix should be revised to include only those methods most likely to be utilized at this site and to remove those methods that are no longer widely used in site investigation or would not apply to this site.
- C. Appendix B Health and Safety Plan. The HERD reviewed only the environmental monitoring and sampling and ambient air monitoring sections and assumes that other DTSC staff have reviewed this appendix in depth.

The HERD has the following specific comments.

Specific Comments

1. Page 10 Section 2.2.1 Soil – Western Stege Marsh. Western Stege Marsh has been identified as a soil data gap, so more information will be collected to determine if surface water and sediment concentrations in the marsh pose risks to humans and ecological receptors. A) Please confirm that data to be collected will include the information necessary, such as wind and wave activity and tidal action exchange and recharge, to develop a site-specific fate and transport model for sediments and contaminants in the marsh. B) Please confirm that sampling will take place in the shallow, saturated zone beneath the depth of previous removal activities in the marsh.
2. Page 11 Section 2.2.2 Groundwater – The Biologically Active Permeable Barrier Wall, and Table 1 Site Prioritization. A) Table 1 lists specific groundwater priorities, identified as GW 1 through 8. A figure should be included that shows the approximate locations of these areas. B) Table 1 indicates that the biologically active permeable barrier (BAPB) will be investigated as GW4 in Phase I of the field sampling, but the soil BAPB area will be investigated as IA3-9 in Phase III. Please explain why these two closely associated areas are being investigated as separate units in different time periods.
3. Page 15 Section 3.2 Soil Migration and Exposure – Exposure to Human Receptors. This discussion of human exposure to environmental contaminants is restricted to workers, without consideration of potential human exposure in a residential scenario. Please confirm that a land use covenant will be in place to prohibit use of the site for residential purposes and that the human health risk assessment to be performed will support the use of such a land use covenant.
4. Page 19 Section 4.2 Strategy, Prioritization, and Data Evaluation – Soil Data Gaps. Soil data gaps are proposed to be addressed through multi-incremental sampling. The lack of soil VOC data on this site is a data gap that the HERD believes cannot be filled using multi-incremental sampling techniques. Where VOCs may be present in soil, the HERD recommends soil gas sampling to be performed.
5. Page 20 Section 4.2 Strategy, Prioritization, and Data Evaluation – Groundwater Data Gaps. Please confirm that the approaches to be used to fill the groundwater data gap will include those that will provide information on the groundwater hydrology of the site.
6. Page 21 Table 1 Site Prioritization; and, Page 22 Figure 4 Soil investigation Areas. A) Table 1 lists investigation areas using Arabic numerals, whereas Figure 4 lists

those areas using Roman numerals. For clarity, use one or the other. B) Figure 4 should be revised to include a brief descriptor for each soil investigation area.

7. Page 23 Section 4.2.3 Data Evaluation – Decision I Levels. Chemical concentrations measured in this proposed site investigation will be compared to generic human and ecological screening criteria. In addition, site data will also be compared to background concentrations where applicable. The general approach to be used to determine local background concentrations should be described in this workplan.
8. Page 23 Section 4.2.3 Data Evaluation – Decision II Levels. Chemical concentrations that are greater than their respective Decision I Levels will be compared to Decision II Levels. Decision II Levels are chemical screening concentrations that have been modified with site-specific parameters, such as “Tier II exposure concentrations”. Please define Tier II exposure concentrations.
9. Page 23 Section 4.2.3 Data Evaluation. The text states that areas with concentrations less than or equal to Decision I Levels will not be further investigated. The cumulative screening risk and hazard for all detected chemicals should be calculated before no further action is recommended for a particular area.
10. Page 25 Section 4.3.1 Soil Data Gaps – Step 4: Define the Boundaries of the Studies. Vertical expansion of study areas will take place if surface soils from zero to two feet below ground surface (bgs) are contaminated. For risk assessment purposes, it is necessary to have soil data down to ten feet bgs. For ecological receptors, it may be necessary to have soil data below two feet. For VOCs and chemicals known to be mobile in soils, sampling at depths below two feet will be necessary.
11. Page 25 Section 4.3.1 Soil Data Gaps – Step 5: Develop Decision Rules. A) These proposed decision rules do not address the frequency of detection of specific chemicals. In general, if a chemical is detected in less than or equal to five percent of samples, that chemical may be eliminated as a chemical of concern. B) If a known human carcinogen (an A carcinogen) is detected in only one sample, it must be evaluated in a health risk assessment. These rules would apply to those circumstances where multi-increment sampling will not be used.
12. Page 26 Section 4.3.1 Soil Data Gaps – Step 6: Specify Performance or Acceptance Criteria. Screening Levels will be based on background concentrations, unrestricted and commercial land use California Health Hazard Screening Levels (CHHSLs), and other risk-based values. These screening levels should include ecological screening criteria.

13. Appendix B Health and Safety Plan. Page B-71 Section 8.3 Ambient Air Monitoring.

This section summarizes the ambient air monitoring that will be performed during site investigation activities. A) The number of air monitoring stations and/or instruments that will usually be present should be included in this summary. B) The method/instruments to be used to determine upwind and downwind locations during a work day should also be described. C) Detection limits and fence line standards should be briefly discussed in this section.

14. Appendix B Health and Safety Plan. Page B-72 Section 8.4.2 Other Chemicals.

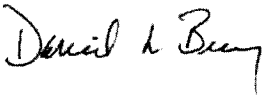
Engineering controls are proposed to control emissions of metals, polychlorinated biphenyls (PCBs) and pesticides. The text states that no other chemicals have been identified at this site that may require air monitoring. Site investigatory activities in the mercury fulminate area may require air monitoring instruments for mercury vapors, and this should be so stated.

Conclusions

This draft field sampling plan has very little detail with respect to the specific methods and approaches that will be used in the forthcoming site investigation. There are major deficiencies that must be addressed before the HERD can accept this workplan.

If you have further questions on this memorandum, please contact me at Kklein@dtsc.ca.gov or by telephone at 916 255 6643 or 510 540 3762.

Reviewed by:

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Human and Ecological Risk Division

cc: J. Michael Eichelberger, Ph.D.
Staff Toxicologist
Human and Ecological Risk Division

Mark Vest
Geologic Services Unit

Final Field Sampling Workplan
University of California, Richmond Field Station Site
April 15, 2010

Response to Comments
Department of Toxic Substances Control, April 15, 2009

April 15, 2010

Page 1 of 23

UC Berkeley Ref. No.	Draft FSW Page/ Sect No. (Final FSW Page/ Sect. No.)	DTSC Comment No.	DTSC Comment	UC Berkeley Response
1	General Comment (Final FSW p 2, Section 1.1.2)		The use of Multi-Incremental Sampling (MIS) has not been approved by DTSC for site characterization or risk assessment purposes. Therefore, at this time reference to MIS should be removed from all documents and replaced with standard soil sampling methods.	All references to MIS have been removed from the SOP and QAPP. The Final FSW states: "As FSPs for subsequent phases are prepared, if new sample collection methods are recommended, the QAPP will be revised or amended to include all applicable information."
2	FSW p 12, Section 3.1 (a. Final FSW p 13, Section 3.1 and p 17, Section 3.2 b. Final FSW p 12, Section 2.2.3)	BC FSW 1	Sources Migration Pathways, and Exposure: a. Inhalation of vapors from soil or groundwater sources needs to be added to the text as a potentially complete exposure pathway as identified in Figure 3 (Conceptual Site Model) b. The potential for contaminated backfill material in utility corridors should also be identified as a potential source of contamination to soil and groundwater in the Conceptual Site Model as cinder material was previously found to have been used as backfill. Section 4.3.3, Utility Data Gaps should also be revised to include the potential for contaminated backfill in utility lines. c. This section states that the former Liquid Gold facility may have been a possible source of contamination to the RFS. Due to the distance of the Liquid Gold facility to the RFS, a brief rationale for this statement should be included. Additional rationale should also be included in the appropriate future site-specific field sampling plan(s).	a. The CSM was revised to include inhalation of vapors from soil or groundwater sources as potentially complete exposure pathways. The Final FSW states: "These types of workers may have more opportunity for soil contact (such as incidental soil ingestion and dermal contact with soil) or contact with soil vapors (resulting in inhalation of soil vapors)." b. The CSM was revised to show potentially contaminated backfill material in utility corridors as a potential source of contamination to soil and groundwater. The FSW data gaps were revised to include the potential for contamination in utility line backfill. c. Aerial photos from the 1950s, prior to the construction of the Bay Trail rail spur and Stauffer Chemical landfill in the marsh, show a possible route of discharge from the former Liquid Gold site to Western Stege Marsh by the way of Baxter Creek. Therefore, the former Liquid Gold facility property will continue to be identified as a potential source area for contamination within Western Stege Marsh. This photograph is located at the end of the December 1 Response to Comments.
3	FSW p 15, Section 3.2 (Final FSW p 17, Section 3.2)	BC FSW 2	Exposure to Human Receptors: This section should include inhalation of soil vapors from soil as a potential exposure pathway.	The FSW was revised to state: "These types of workers may have more opportunity for soil contact (such as incidental soil ingestion and dermal contact with soil) or contact with soil vapors (resulting in inhalation of soil vapors)."
4	FSW p 17, Section 3.3 (Final FSW p 19, Section 3.3)	BC FSW 3	Exposure to Human Receptors: This section should include that inhalation of vapors from volatilization of contaminated groundwater may also be a potential exposure pathway to persons occupying buildings and to workers that may come in contact with groundwater or work in trenches.	The FSW was revised to state: "Persons occupying buildings or on-site workers that may come in contact with groundwater or work in trenches could be exposed to inhalation of vapors from volatilization of contaminated groundwater."

Final Field Sampling Workplan
University of California, Richmond Field Station Site
April 15, 2010

Response to Comments
Department of Toxic Substances Control, April 15, 2009

April 15, 2010

Page 2 of 23

UC Berkeley Ref. No.	Draft FSW Page/ Sect No. (Final FSW Page/ Sect. No.)	DTSC Comment No.	DTSC Comment	UC Berkeley Response
5	FSW p 19, Section 4.2 (Final FSW p 22, Section 4.2.1)	BC FSW 4	Strategy, Prioritization, and Data Evaluation: This section should also include an investigation strategy for the possible presence of soil vapors from a soil and/or groundwater sources.	The FSW was revised to state: "If contamination is identified in groundwater samples at levels that warrant additional work, further investigation may be proposed—including passive or active soil gas sampling or soil sampling. Assuming contamination could still exist in soil or soil gas if not detected in groundwater, further investigation, including sample locations and potential contaminants of concern, will be addressed in subsequent FSPs."
6	FSW p 25, Section 4.3.1 (Final FSW p 22, Section 4.2.1)	BC FSW 5	Soil Data Gaps: Revisions to this section are needed as the depth of initial sampling is being limited to the upper two feet of soil. For example, in areas where the former California Cap Company operated, known hazardous waste storage areas, and in the Western Transition Area where dumping was known to have occurred, deeper soil sampling is warranted.	The Final FSW states: "Soil data gaps will be investigated through characterization of near-surface and subsurface soils throughout the RFS. Investigation of soil data gaps will occur in Phases II through V. Sampling strategies, including sampling locations and potential contaminants of concern, will be addressed in upcoming FSPs."
7	FSW p 27, Section 4.3.2 (Final FSW p 27, Section 5.2)	BC FSW 6	Groundwater Data Gaps, Step 2: Please include as one of the goals of the study a determination whether contaminants are migrating from the RFS to off-site locations.	The FSW was revised to state: "If contamination is present, is it migrating either on site or off site within any of the groundwater zones?"
8	QAPP, General Comment (Final FSW, Attachment 2 and 3)		The QAPP needs to be revised to include specific standard operating procedures (SOPs) for the investigation methods that are most likely to be used at the site. Anticipated laboratory analytical methods along with a list of chemicals that will be reported, sample size, holding times, preservative, etc. should be included.	The FSW was revised to include specific SOPs for the groundwater investigation methods that are most likely to be used at the site, as well as laboratory analytical methods and a list of chemicals that will be reported, sample size, holding times, and preservatives.
9	QAPP p 14, Section 3.2.1 (Final QAPP p 14, Section 3.2.1)	BC QAPP 1	Sensitivity: The last sentence of this section is unclear and needs to be revised. Please explain what the laboratory detection limit and laboratory method reporting limits are, and why it is acceptable to use the laboratory method reporting limit. Previously, quantitation limits and detection limits were discussed. This comment also applies to Page A-1 54, Section 7.3, Reporting Limits.	<p>The QAPP was revised to clarify that the laboratory detection limits and laboratory method quantitation limits are the same number.</p> <p>The RFS project team will select analytical methods with sensitivities appropriate to the intended data use. Current, routinely used analytical methods will be specified such that matrix-specific method quantitation limits are lower than any contaminant concentrations of concern. If not possible to achieve laboratory method reporting limits less than the screening criteria, it is generally acceptable to use the laboratory quantitation limit for the chemical of concern, with concurrence from DTSC, unless reasonable grounds are established for pursuing non-routine methods.</p> <p>For Phase I, the laboratory detection limits for groundwater samples are outlined in a table following the laboratory analytical SOPs in Attachment 2 of the FSW.</p>

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10	QAPP p 15, Section 3.2.2 (Final QAPP p 15, Table A-2)	BC QAPP 2	Precision and Accuracy: a. The default frequency for laboratory blanks and spike blanks should be a minimum of once for every batch of samples, or type of matrix, or 20 samples, whichever is more frequent. b. Temperature blanks need to be added to Table A-2 as part of the Field QC requirements, and included in Section 4.9, Field Quality Control Samples.	a. The QAPP was revised to state that laboratory blanks and spike blanks will be analyzed once every batch of samples, type of matrix, or 20 samples, whichever is more frequent. b. The QAPP was revised to include temperature blanks as part of the field QC requirements.
11	QAPP p 17, Section 3.2.4 (Final QAPP p 17, Section 3.2.4)	BC QAPP 3	Completeness: The criteria that will be used to establish the degree of completeness needs to be included. A minimum percentage for each type of matrix should be included.	The QAPP was revised to clarify that the degree of completeness will be calculated by dividing the number of useable sample results by the total number of sample results. A minimum of 95 percent completeness per matrix type will be required for usable data.
12	QAPP p 18, Section 4.0 (Final QAPP p 102, Section 4.12)	BC QAPP 4	Sampling Procedures: Utility clearances and specific types of permits that are required prior to sampling should be identified in this section. The description should also include lead times required to obtain permits and clearances.	The QAPP was revised to include utility clearance procedures and permits required prior to sampling.

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13	QAPP p 23, Section 4.1.2 (Final QAPP p 23, Section 4.1.2)	BC QAPP 5	<p>Soil Sampling for Volatile Organic Compounds:</p> <p>a. DTSC's November 2004 guidance document for implementation of Method 5035 should be reviewed and incorporated into this section and referenced in Section 4.1.2.</p> <p>b. This section needs to include a discussion regarding the collection and analysis of high and low concentration VOC samples. Collection of low concentration soil samples in vials that contain methanol is not appropriate for samples analyzed with closed system purge and trap equipment. It should also be noted that the use of methanol as a preservative and extraction solvent introduces a significant dilution factor that will raise the method quantitation level beyond the operating range of the low concentration direct purge and trap. The high concentration method is used for samples with VOC concentrations greater than 200 ug/kg.</p> <p>c. This section needs to contain a discussion regarding packaging and transportation of vials used to transport samples. For example, VOAs need to be transported upright in the ice chest.</p> <p>d. The criteria for acceptance of vials containing methanol needs to be included. Vials containing methanol should be weighed a second time in the field on the day they are to be used. Vials containing methanol that are found to have lost a reduction in weight of greater than 0.05 grams should not be used. Also, vials should not be submitted for analysis if the preservative has spilled or splashed from the vial.</p> <p>e. Additional tared and preserved vials should be available in the field due to the potential for rejecting vials.</p> <p>f. It should be specified that the tared weight of each vial is to include the weight of the sample label.</p> <p>g. If the preservative is added to the vial in the field, the analytical laboratory should be contacted to determine if a magnetic stirring bar needs to be placed in the vial prior to sample collection.</p>	<p>a. The QAPP was revised to include DTSC's guidance for implementation of Method 5035.</p> <p>c. The QAPP was revised to include proper packaging of VOA samples.</p> <p>b, d, e, f, g. The QAPP was revised to remove all reference to methanol-preserved, discrete VOC soil samples.</p>

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14	QAPP p 24, Section 4.1.2.2	BC QAPP 6	Sampling Protocol 2: It should be specified in this section that the surrogate, matrix spikes and internal standards are only added to the vials after the sample is added to the vial, and will be done by the analytical laboratory.	The QAPP was revised to remove all reference to methanol-preserved, discrete VOC soil samples, thus eliminating the discussion of surrogate, matrix spikes, and internal standards.
15	QAPP p 25, Section 4.1.2.4	BC QAPP 7	Field Weighing: The field balance needs to be checked at least daily and against an appropriate reference weight. Also, please explain and provide a reference indicating why a weight accuracy of 0.1 grams is acceptable. DTSC's November 2004 guidance for implementation of Method 5035 recommends an accuracy of 0.05 grams and that it is achievable in the field.	The QAPP was revised to remove all reference to methanol-preserved, discrete VOC soil samples, thus eliminating the discussion of field weighing.
16	QAPP p 26, Section 4.1.2.5 (Final QAPP p 26, Section 4.1.2.5)	BC QAPP 8	Presence of Carbonates: Please provide the reference demonstrating that a holding time of unpreserved Encore samples of 7 or 14 days does not result in a loss of VOCs.	The QAPP was revised to include a reference for the holding times for samples collected with Encore samplers (or similar sampling device).
17	QAPP p 67, Section 4.1.2.12.1 (Final QAPP p 60, Section 4.3.2.12.1)	BC QAPP 9	Deciding When to Filter: The decision to filter groundwater samples should also include an evaluation of who the receptor is and how that receptor will come into contact with the groundwater. For example if the receptor may come into direct contact with groundwater, filtering may not be recommended.	Text has been amended to clarify that filtered groundwater samples will be collected for metals during initial characterization efforts. If a groundwater release is present in an area where a complete exposure pathway to a receptor is present, an unfiltered sample may be collected in consultation with DTSC.
18	QAPP p 79, Section 4.6	BC QAPP 10	Soil-Gas Sampling: This section should be updated to reflect the current state of practice of soil gas sampling. For example continuous soil gas sampling and post-run tubing methods are no longer accepted due to the recognized difficulty in sealing the space between the drive rod and borehole. The actual zone that is being sampled therefore cannot be determined, and there is a greater potential for ambient air leakage.	The QAPP includes current soil-gas sampling practices. The QAPP will be amended as necessary if any new soil-gas sampling methodologies are adopted by DTSC.

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19	QAPP p 85, Table A-5 (Final QAPP p 147, Section 7.4)	BC QAPP 11	Table A-5, Summary of Vapor Intrusion Analytical Methods: Because analytical methods have not been certified for soil gas analysis, the laboratory Standard Operation Procedures will need to be submitted for approval prior to analysis.	<p>The revised QAPP states: "The following criteria will be considered when evaluating contract laboratories:</p> <ul style="list-style-type: none"> • Quality assurance and quality control documents governing laboratory operations • Initial demonstration of proficiency results for all analysts on all methods performed • Standard operating procedures for the desired analyses" <p>If soil vapor collection is proposed in a subsequent sampling phase, these criteria for laboratory selection will be followed, and the SOP from the analytical laboratory will be included in the subsequent FSP for DTSC's review and acceptance.</p>
20	QAPP p 109, Section 4.11 (Final QAPP p 102, Section 4.11)	BC QAPP 12	Management of IDW: Please add to this section that waste determined to be a hazardous waste must be disposed within 90 days of generation. In addition, personal protective equipment and other waste that is grossly contaminated with a known hazardous substance should not be disposed in the facility trash receptacle. The waste should be stored in a container and disposed at a proper off-site facility to prevent exposure to unauthorized personnel.	The QAPP was revised to state that waste determined to be a hazardous waste will be disposed of within 90 days of generation. In addition, personal protective equipment and other waste that is grossly contaminated with a known hazardous substance will be stored in a container and disposed of at a proper off-site facility to prevent exposure to unauthorized personnel.
21	HSP, General Comment (Final HSP p B-5, Section 2.2)		In the event that this HASP does not cover a contractor or sub-contractor, they must submit their own HASP to DTSC for review. If the scope of work changes significantly, (an unanticipated chemical, physical, or biological hazard is discovered or introduced to the site), then the new hazard must be addressed in an addendum to this HASP and submitted to DTSC for review. The final site HASP must be available at all times for on-site personnel to reference. In utilizing the site HASP, field staff must be able to obtain sufficient information to compile an accurate assessment of the site safety issues associated with every job function.	<p>The HSP was revised to state, "In the event that this HSP does not cover subcontractor activities, the subcontractor will be responsible for completing a site-specific HSP and receiving all appropriate regulatory reviews and approvals from DTSC for its site-specific HSP."</p> <p>The HSP will be available at all times for on-site personnel to reference. The HSP contains sufficient information for field staff and subcontractors to compile an accurate assessment of the site safety issues associated with every job function.</p>

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22	HSP p 2, Section 2.1 (Final HSP p B-4, Section 2.1.2)	EB HSP 1	Project Personnel, please provide information identifying key personnel who at a minimum, have the responsibility and authority to perform the following functions: a. Be present at all times during site operations. b. Have the authority to enforce the HASP and stop operations if personnel or community safety and health may be jeopardized. c. Evaluate monitoring data to make field decisions regarding safety and health.	The HSP was revised to state, "The SSC will be present at all times during site operations to enforce the HSP and stop operations if personnel or community safety and health may be jeopardized, and to evaluate monitoring data to make field decisions regarding safety and health."
23	HSP p 10, Section 3.3	EB HSP 2	Planned Activities, HSB is aware that UCRFS will be submitting separate sampling plans for the Site activities covered in the remedial work plan, however please ensure that each addendum is included in the final HASP, and at a minimum includes a summary description of the project, including but not limited to: the duration of planned activities, personnel requirements, and the extent to which subcontractors will be used. In addition, please provide a summary of the information regarding known or suspected hazardous waste disposal on-site, the waste(s) location, physical state, chemical characteristics, and the range of concentrations found to date by matrix (soil, water, air).	The HSP addenda submitted with FSW addenda will include a summary description of the project including the duration of planned activities, personnel requirements, and the extent to which subcontractors will be used. Information regarding known or suspected hazardous waste disposal on site, the waste(s) location, physical state, chemical characteristics, and the range of concentrations found to date by matrix (soil, water, air) is presented in the Final Current Conditions Report.
24	HSP p 11, Section 4.0	EB HSP 3	Site-specific Hazard Evaluation, please provide the following details: a. The best information available regarding the contaminants and conditions present at the site. b. Approximate duration of the operation and each task.	The HSP addendum for site-specific sampling plans will include the available information regarding contaminants and conditions present at the area being investigated and approximate durations for the operation and tasks.
25	HSP p 61, Section 5.0 (Final HSP p B-62, Section 5.0)	EB HSP 4	Training Requirements, the HASP should state that the employee training program is in compliance with CCR 51 92(e).	The HSP was revised to state that the employee training program is in compliance with <i>California Code of Regulations</i> (CCR) Title 8, Section 5192(e).
26	HSP p 63, Section 6.0 (Final HSP p B-64, Section 6.1)	EB HSP 5	Personal Protective Requirements, The body of the HASP should state that the Personal Protective Equipment program is in accordance with 8 CCR 5192(g).	The HSP was revised to state that the Personal Protective Equipment program is in accordance with CCR Title 8, Section 5192(g).

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27	HSP p 68, Section 7.1 (Final HSP p B-69, Section 7.1)	EB HSP 6	Health Monitoring Requirements, please verify and state in the body of the HASP that the health monitoring program is in accordance with 8 CCR 51 92(f).	The HSP was revised to state that the health monitoring program is in accordance with CCR Title 8, Section 5192(f).
28	HSP p 70, Section 8.0 (Final HSP p B-71, Section 8.0)	EB HSP 7	Environmental Monitoring and Sampling, please provide additional information regarding: a. When air monitoring levels would indicate the expansion(s) of exclusion zone. In addition, provide the rationale for how each action level was derived. b. The specific make and model of instrument(s) selected for use. c. The relative response factors for the instrument of choice must be incorporated into any action level(s) derived for the site.	The HSP addendum for site-specific sampling plans will include relevant air monitoring requirements for individual sampling events.
29	HSP p 77, Section 9.0 (Final HSP p B-78, Section 9.0)	EB HSP 8	Site Control, please verify and state in the body of the HASP that the site control measures are in accordance with CCR 5192(d).	The HSP was revised to state that the site control measures are in accordance with CCR Title 8, Section 5192(d).
30	HSP, General Comment (Final HSP p B-86, Section 11.11)	EB HSP 9	A discussion regarding a spill containment plan shall be incorporated as a separate section in the body of the HASP. The spill containment program must meet the requirements of 8 CCR 5192(j).	The HSP has been revised to include a spill containment plan which meets the requirements of CCR Title 8, Section 5192(j).
31	HSP, General Comment	EB HSP 10	Please describe the provisions that will be made to ensure proper sanitation facilities are available for site personnel, including but not limited to: a. Adequate washing facilities such as soap, water, towels and where appropriate showers. b. Toilets and other sanitary facilities in numbers which will reasonably handle the projected number of personnel. c. Adequate stocks of potable water, provided in sanitary containers.	The HSP addenda will include information regarding the locations of sanitation facilities available for site personnel based on where a project is located. This information will include where site personnel can access adequate washing facilities, toilets and other sanitation facilities, and potable water.
32	HSP, General Comment (Final HSP p B-61, Section 4.2)	EB HSP 11	Please include a section discussing how minimum illumination shall be provided for site personnel. The plan shall be in accordance with the requirements of 8 CCR 51 92(m). If all planned field activities are to be conducted during daylight hours and not within any structures at the site, please state as such.	The HSP was revised to state that all activities will be conducted during daylight hours, and when conducted within buildings, proper illumination will be provided in accordance with the requirements of CCR Title 8, Section 5192(m).

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33	HSP General Comment	EG HSP GC	The HASP must follow and contain the specific content and procedural elements as indicated in the Department of Toxic Substances Control guidance document and be resubmitted for further review. HSB recommends consulting a safety professional to complete the Health and Safety Plan. In addition, the HASP must comply with 8 CCR, 5192: "Health and Safety for Hazardous Waste Operations and Emergency Response" as well as other appropriate State and Federal Health and Safety Regulations. Please note that in addition to the requirements of this section, the employer is also responsible for the implementation of an Illness and Injury Prevention program, which is required by the 8 CCR, 1509 and 3203.	The revised HSP will be submitted to DTSC as an appendix to the FSW for review.
34	FSW, General Comment (Final FSW p 23, Section 4.2.3)	ME FSW GC	HERD does not believe the work plan contains sufficient information to determine if the sampling approach is adequate to assess nature and extent of contamination relative to potential hazards to ecological receptors. Screening levels for ecological receptors are not listed. Since the report represents an overall approach to sampling for all five sampling phases, it should provide all of the information common to all. Screening levels, the references to these screening levels, appropriate chemical analytical methods and associated detection limits below the ecological screening levels should be presented for each of the chemical constituents to be assessed. For ecological risk assessment purposes, sampling and analysis should be conducted to the No Observable Adverse Effect Level, please see Specific Comments 6 and 7 below.	The Final FSW states: "The objectives of the phased site investigations are to identify immediate or potential risks to public health and the environment, and prioritize and implement response actions using removal actions and operable units, if appropriate, based on the relative potential risks at the site. As a first step in determining immediate or potential risk, groundwater sampling data obtained during Phase I will be evaluated to either confirm or deny the release of a hazardous substance, as defined in the DTSC Order. Site- and chemical-specific soil screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of groundwater analytical data, as agreed by UC Berkeley and DTSC at the meeting on October 27, 2009. For Phases II through V, screening values will be developed within each subsequent FSP in concurrence with DTSC. Screening levels will be developed so that confirmation or invalidation of a release of hazardous substance can be determined."
35	FSW, General Comment (Final FSW p 22, Section 4.2.1)	ME FSW GC	HERD is concerned that Multi-incremental Sampling will not adequately support ecological risk assessment needs. It will certainly not be adequate for sediments where individual sample locations represent total exposure to sedentary marine benthic invertebrates. Average concentrations calculated for individual Areas of Concern (AOC) that are larger than the home range of terrestrial species such as the shrew, may not adequately represent actual exposure.	All references to MIS have been removed from the SOP and QAPP. The scope of the FSW for Phase I does not include collection of soil samples and therefore does not include a discussion of ecological receptor areas. The Final FSW states: "Soil data gaps will be investigated through characterization of near-surface and subsurface soils throughout the RFS. Investigation of soil data gaps will occur in Phases II through V. Sampling strategies, including sampling locations and potential contaminants of concern, will be addressed in upcoming FSPs."

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36	FSW p 13, Figure 3 (Final FSW p 14 and 15, Figures 4 and 5)	ME FSW 1	The Conceptual Site Model is not complete, only a partial list of exposure pathways to ecological receptors is depicted. There is neither graphical representation of contaminant transport to sediments nor the transfer of sediment contaminants up the food chain. There is some representation of trophic transfer from surface water but it is too small to interpret and is incomplete. Likewise exposure to terrestrial ecological receptors is also only partially represented. There is no representation of potential exposure pathways to invertebrates or food chain pathways from plants and invertebrates to vertebrate receptors. HERD believes for clarity it would be useful to separate the conceptual site models for human health and ecological receptors into separate figures.	The FSW was revised to include separate conceptual site models to demonstrate human and ecological receptors and pathways.
37	FSW p 15, Section 3.2 (Final FSW p 22, Section 4.2.1)	ME FSW 2	Adsorption to Sediment. The sentence "PCBs and pesticides are strongly adsorbed to soil particles and are not readily leached" is not entirely accurate and needs to be clarified. HERD would agree that PCBs readily adsorb to soil particularly those that are more highly chlorinated; however PCBs can readily migrate down in the soil horizon if organic solvents are present. Also, not all pesticides bind tightly to soil. For example, aldicarb, atrazine and carbaryl are all examples of pesticides that readily leach in soils. The work plan needs to clarify which pesticides it is referring to when stating that they do not leach.	The Final FSW states: "Soil data gaps will be investigated through characterization of near-surface and subsurface soils throughout the RFS. Investigation of soil data gaps will occur in Phases II through V. Sampling strategies, including sampling locations and potential contaminants of concern, will be addressed in upcoming FSPs." Groundwater samples collected during Phase I sampling will be analyzed for PCBs and pesticides, as specified in Table 2 of the Final FSW.
38	FSW p 15, Section 3.2 (Final FSW p 17, Section 3.2)	ME FSW 3	Exposure to Ecological Receptors. This section is not well organized and written. The text indicates that grasses, shrubs and trees are not exposed to contaminants through the "root uptake of soil and sediment." There is no uptake of soil and sediment by plants. Soil and sediment are complex media containing many different components. What is accurate to say is that plants can take up contaminants present in soil and sediment. Generally, the majority of the exposure of birds and mammals is through the diet, not through ingestion of soil 'dirt' on plant leaves or through grooming or preening.	The FSW was revised to state: "All ecological receptors are subject to potential dermal contact with any contaminants in the soil on site. Grasses, shrubs, and trees could be exposed to contaminants through root uptake of soil and sediment. Invertebrates can take up contaminants in soil by osmosis and ingestion of sediment and prey. Birds and mammals can be exposed to contaminants through ingestion of dirt on the plant surface and through cleaning and grooming."
39	FSW p 17, Section 3.3 (Final FSW p 19, Section 3.3)	ME FSW 4	Exposure to Ecological Receptors. Please see specific comment 3 above.	The FSW was revised to state: "Aquatic and benthic invertebrates, as well as fish, can take up contaminants in water by osmosis and ingestion of detritus, suspended sediment, and prey. Birds and mammals can be exposed to contaminants through ingestion of surface water."

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40	FSW p 21 and 22, Table 1 and Figure 4 (Final FSW p 10 and 29, Figures 3 and 7)	ME FSW 5	<p>Figure 4 delineates where Phase I Sampling is to occur but it is not clear where the specific areas within Phase I listed in Table I are located. Table I lists four primary soil sources: 1a) IAI-I Building 478; 2a) IAI-2 East Meadow; 3a) IAI-3 Corporation Yard; 4a) IAI-4 US. Briquette Company, five groundwater source areas: 1b) GW1: Building 478 Area; 2b) GW2 Building 120 Area; 3b) GW3 Property Boundary; 4b) GW4 Biologically Active Permeable Barrier Wall (BAPB); and 5b) GW5 Site-wide Groundwater, and a separate utilities source are identified as UT1 Select Utility Locations.</p> <p>With the exception of the BAPB, none of the primary sources are identifiable in Figure 4. It is also unclear why the BAPB, a structure constructed to impede downgradient movement of site related Chemicals of Potential Ecological Concern (COPECs) to Western Stege Marsh is considered a 'Primary Source.' Neither the 'Approximate Property Boundary' nor the 'Property Boundary' shown in the Figure 4 legend, are identifiable on the figure. The figure should be modified to show the primary sources, secondary sources and the property boundary as indicated in the legend. HERD notes that Figure A-3 Physical Features Map in Appendix A identifies buildings 478 and 120 but does not identify other features such as the U.S. Briquette Company, East Meadow, Corporation Yard, or utility locations.</p>	The FSW was updated to contain a map which displays the data gaps identified in the Final Current Conditions Report (Figure 3). The FSW was also updated to contain a map which shows the sampling locations for the site-wide groundwater investigation (Figure 7). FSPs for individual phases of sampling will include specific areas of sampling, including sampling locations and suspected primary and secondary sources of contamination.
41	FSW p 23, Section 4.2.3 (Final FSW p 25, Section 4.2.3)	ME FSW 6	<p>Data Evaluation, Decision I Levels. The report fails to describe Ecological Soil Screening Levels as a Decision I Level. This needs to be rectified in the report. Please provide a reference for soil screening levels. Given that Western Stege Marsh is being remediated and reclaimed to support California clapper rail habitat, the use of Effects Range Median (ER-M) is not warranted. Protection for endangered and threatened species needs to be at the level of the individual. Sampling to the ER-M will not provide sufficient protection to the clapper rail.</p>	As stated in response to Ref. No. 34, site- and chemical-specific screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of the site-wide groundwater analytical data, as UC Berkeley and DTSC agreed during their meeting on October 27, 2009.

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42	FSW p 23, Section 4.2.3 (Final FSW p 23, Section 4.2.3)	ME FSW 7	Data Evaluation, Decision II Levels. Please explain how Decision II Levels will be applied to ecological receptors, none are mentioned in the report. HERD fundamentally disagrees with the approach presented in the unnamed table on page 23. For site characterization purposes, sampling needs to be conducted to determine nature and extent to the 'No Effect Level.' This is particularly important for the sediments of Western Stege Marsh. Sampling needs to be conducted with detection limits set to a value lower than the No Effect Screening Level. Since the work plan offers no information regarding how Decision II Levels would apply to ecological receptors, only to human receptors, HERD assumes that, as written, sampling could occur at levels not protective of ecological receptors.	As stated in response to Ref. No. 34, site- and chemical-specific screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of the site-wide groundwater analytical data, as UC Berkeley and DTSC agreed during their meeting on October 27, 2009.
43	FSW p 25, Section 4.3.1 (Final FSW p 22, Section 4.2.1)	ME FSW 8	Soil Data Gaps, Step 4: Define the Boundaries of the studies. HERD does not believe the work plan has provided sufficient documentation to justify limiting initial sampling to the depth of 2 feet. Location of each specific chemical constituent within the soil horizon is, as the report points out, dependent on multiple factors, some related to the soil, others to the chemical itself, and also potential soil disturbance subsequent to the release. The UC Richmond Field Station historically has been used for many purposes and the potential for movement of soils due to site activities and potentially from grading due to past remedial efforts is apparent. HERD believes that sampling should be conducted at multiple depths. For ecological purposes a logical soil sampling strategy would include surface soil to a depth of 6 inches, samples between two and three feet and deep samples at 6 feet.	As stated in the response to Ref. No 37, the scope of the FSW for Phase I does not include collection of soil samples and therefore does not include a discussion of the proposed methodology for collecting soil samples.
44	FSW p 25, Section 4.3.1 (Final FSW p 23, Section 4.2.3)	ME FSW 9	Soil Data Gaps, Step 5: Develop Decision Rules. HERD does not believe that if a chemical is detected at concentrations below Decision I Levels that it can be assumed that a release has not occurred as stated in the report. It is appropriate to state that chemicals are below a level that reasonably would be considered to pose a hazard to receptors. The work plan should be revised accordingly.	As stated in response to Ref. No. 34, site- and chemical-specific screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of the site-wide groundwater analytical data, as UC Berkeley and DTSC agreed during their meeting on October 27, 2009.

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45	FSW p 26, Section 4.3.1 (Final FSW p 23, Section 4.2.3)	ME FSW 10	Soil Data Gaps, Step 6: The report needs to be more specific about the screening levels, neither soil or sediment screening levels are mentioned. Inorganic background concentrations should be approved by the DTSC Geological Services Unit and should be used as the determinant for establishing inorganic COPECs.	As stated in response to Ref. No. 34, site- and chemical-specific screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of the site-wide groundwater analytical data, as UC Berkeley and DTSC agreed during their meeting on October 27, 2009.
46	FSW General Comment (Final FSW p 23, Section 4.2.3)	ME GC	HERD does not believe that Multi-incremental Sampling is necessarily the best method for conducting site investigation at the UC Richmond Field Station. Compositing samples from an AOC do not provide sufficient information to evaluate certain receptors such as benthic invertebrates or species with smaller home ranges than the AOC. HERD disagrees that detected concentrations of a chemical below the screening level indicates that there has not been a release. This reference in the work plan should be deleted. Sampling for site characterization purposes should be to the No Effect Level and all methods with their references and detection limits appropriate to the screening levels should be presented in the work plan. The conceptual site model should be reworked to accurately represent exposure pathways to ecological receptors. The report should be revised to reflect the comments in this memorandum and resubmitted to HERD for review.	All references to MIS have been removed from the SOP and QAPP. The scope of the FSW for Phase I does not include collection of soil samples and therefore does not include a discussion of ecological receptor areas. As stated in response to Ref. No. 34, site- and chemical-specific screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of the site-wide groundwater analytical data, as UC Berkeley and DTSC agreed during their meeting on October 27, 2009.
47	FSW/QAPP General Comment	MV FSW/ QAPP GC 1	As per requirements in the California Business and Professions Code (Sections 6735 and 7835), the FSP and QAPP should be signed and/or stamped by a California registered civil engineer and/or professional geologist indicating their responsibility for engineering and/or geologic content of the documents.	Section 7835 addresses all geologic reports, including the investigation of the soil or the earth's crust (by reference), and therefore the FSW will include a California Registered Geologist stamp and signature on the final document.

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48	FSW/QAPP/ HSP General Comment (Final FSW Attachments 2 and 3)	MV FSW/ QAPP/ HSP GC 2	The FSP, QAPP, and pending FSP addenda should present sufficient detail such that sampling teams unfamiliar with the site could perform the same quality field investigation using the FSP and QAPP as references. In particular, the QAPP should be amended to include detailed Standard Operating Procedures (SOPs) for reasonably anticipated site investigation activities. The SOPs should present concise, detailed written instructions for planning, conducting, and documenting routine investigation activities. Sampling procedures including personnel qualifications, equipment checklists, step-by-step procedures, and field forms should be included. Additional SOPs may be provided with the FSP addenda, as warranted. The SOPs should be signed by the Tetra Tech Quality Assurance/Quality Control manager, or equivalent.	The FSW was revised to include specific SOPs for the groundwater investigation methods that are most likely to be used at the site, as well as laboratory analytical methods and a list of chemicals that will be reported, sample size, holding times, and preservatives. The SOPs are signed by the Tetra Tech EM Inc. Quality Assurance Officer.
49	FSW General Comment (Final FSW p 2, Section 1.1.2)	MV FSW GC 3	Based on a review of literature on multi-incremental (MI)/decision unit (DU) sampling, it seems that the method can provide good estimates of mean concentrations within sampled grids (DUs) when applied correctly. Also, it is recognized that there are uncertainties associated with sample representativeness and associated decisions based on discrete samples. Because of growing interest in the sampling method, DTSC is participating in a review and assessment of MI/DU sampling that is being performed by the Interstate Technology & Regulatory Council (ITRC). Unfortunately, the ITRC work is not scheduled to be completed until at least the end of this year. Therefore, DTSC should not accept MIIDU sampling for implementation on the RFS project.	All references to MIS have been removed from the SOP and QAPP. The Final FSW states: "As FSPs for subsequent phases are prepared, if new sample collection methods are recommended, the QAPP will be revised or amended to include all applicable information."
50	FSW p 1, Section 1.0 (Final FSW p 1, Section 1.0)	MV FSW 4	Page 1 of the FSP contains a typographical error. The order number should be IS/E-RAO 06/07-004.	The FSW was corrected and now states, "Site Investigation and Remediation Order No. IS/E-RAO 06/07-004."

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51	FSW p 20, Section 4.2.1	MV FSW 5	<p>The FSP proposes <i>"Use of multi-incremental (MI)/decision unit (DU) sampling will be the primary technique to address the soil data gaps. MI/DU sampling has been developed as a sampling technique to greatly increase sample result confidence and identify possible spill areas"</i>.</p> <p>Recommendation:</p> <p>MI/DU sampling should not be approved by DTSC for implementation on the RFS project. Propose an alternate approach to address the soil data gaps.</p>	All references to MIS have been removed from the SOPs and QAPP.
52	FSW p 20, Section 4.2.1 (Final FSW p 22, Section 4.2.1)	MV FSW 6	<p>The FSP proposes <i>"The requirement for subsurface sampling will be determined following review of near-surface sampling results"</i>. Contaminant releases at depth may not correlate with detectable results in near surface samples. For example, releases from subsurface utilities, under ground tanks, buried wastes, or discharges to dry wells are not likely to be detected in surface soil samples. Even historical discharges to the ground surface of volatile or very soluble compounds may not be detectable in surface soil samples. Grading activities may also prevent detection of historical surface releases.</p> <p>Recommendation:</p> <p>The proposal to use <i>"near-surface sample results"</i> as decision criteria for investigating releases at depth should not be approved. Also, "Near surface results" may not be an appropriate decision criteria for evaluating contaminant mobility and fate in shallow soils. Decision criteria for evaluating releases at depth and contaminant mobility/fate should be based on an appropriate conceptual site model of the potential release(s).</p>	As stated in the response to Ref. No 37, the scope of the FSW for Phase I does not include collection of soil samples and therefore does not include a discussion of the proposed soil sample depths.

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53	FSW p 20-24, Section 4.2.3 (Final FSW p 23, Section 4.2.3)	MV FSW 7	<p>The FSP propose "<i>Decision I Levels</i>" and "<i>Decision II Levels</i>" as a way to apply screening levels to detected contamination. According to the FSP, contaminants found at concentrations less than Decision Level I criteria would result in a no further action decision. Contaminant concentrations greater than Decision Level II criteria would result in more investigation, possibly including removal actions. The significance of concentrations detected between the two levels would be evaluated based on a lines-of-evidence methodology. These decision rules are also incorporated into the data quality objectives (DQOs) section of the FSP.</p> <p>Recommendations:</p> <p>Although the proposal to identify or develop numerical decision criteria within the FSP addenda is acceptable, the criteria should be applied carefully.</p> <p>The lines-of-evidence methodology should incorporate the nature of potential contaminant releases that are under investigation and the associated confidence in sampling locations. For example, sampling locations for potential releases from existing storage tanks or waste lines can be more confidently identified than sampling locations for spill areas related to poor housekeeping or other poorly documented historical practices.</p> <p>The Level I pass/fail decision criteria should be amended to apply a lines-of-evidence approach. As discussed above, in areas where historical activities and potential releases are not well documented, analytical results from one or two isolated, discrete samples may represent anything from the highest to the lowest concentrations in an area. In such a case, several surrounding samples should be completed to better understand what the discrete sample results represent.</p>	As stated in response to Ref. No. 34, site- and chemical-specific screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of the site-wide groundwater analytical data, as UC Berkeley and DTSC agreed during their meeting on October 27, 2009.
54	FSW p 23, Section 4.2.3 (Final FSW p 23, Section 4.2.3)	MV FSW 8	<p>The FSP proposes using "<i>National Drinking Water Maximum Contaminant Levels (MCL)</i>" as screening criteria.</p> <p>Recommendation:</p> <p>If MCLs are used as screening criteria, the lower of federal or state MCLs should be used.</p>	As stated in response to Ref. No. 34, site- and chemical-specific screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of the site-wide groundwater analytical data, as UC Berkeley and DTSC agreed during their meeting on October 27, 2009.

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55	FSW p 25, Section 4.3.1 (Final FSW p 22, Section 4.2.1)	MV FSW 9	<p>The FSP proposes DQOs for soil investigation including "<i>Step 4: Define the boundaries of the Studies - All reasonably accessible surface soils located within the property boundaries of the RFS.</i>"</p> <p>Recommendation:</p> <p>The boundaries of the study should be expanded if contamination from the RFS is known or thought to have spread off the RFS property. This determination should be based on an appropriate conceptual site model as well as data collected under this FSP.</p>	As stated in the response to Ref. No 37, the scope of the FSW for Phase I does not include collection of soil samples and therefore does not include a discussion of the proposed boundaries of the soil investigation.
56	FSW p 25, Section 4.3.1 (Final FSW p 23, Section 4.2.3)	MV FSW 10	<p>The FSP proposes DQOs for soil investigation including "<i>Step 5: Develop Decision Rules - If surface soil contaminants are detected at concentrations at or less than Decision I Levels, then the data confirms that there has not been a contaminant release and no further action is required.</i>"</p> <p>Recommendation:</p> <p>Level I decisions should incorporate a lines-of-evidence approach as recommended above. Detected concentrations from locations that are confidently expected to be within source or release area should be given more weight than concentrations from areas with little documentation or no obvious release mechanisms.</p>	As stated in response to Ref. No. 34, site- and chemical-specific screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of the site-wide groundwater analytical data, as UC Berkeley and DTSC agreed during their meeting on October 27, 2009.
57	FSW p 25, Section 4.3.1 (Final FSW p 23, Section 4.2.3)	MV FSW 11	<p>The FSP proposes DQOs for soil investigation including "<i>Step 5: Develop Decision Rules - If surface soil contaminants are detected at concentrations exceeding Decision II Levels, expand the vertical boundary of the study area to subsurface soils</i> "</p> <p>Recommendation:</p> <p>The lateral boundaries may also be expanded in such a case.</p>	As stated in response to Ref. No. 34, site- and chemical-specific screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of the site-wide groundwater analytical data, as UC Berkeley and DTSC agreed during their meeting on October 27, 2009.

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58	FSW p 26, Section 4.3.1	MV FSW 12	<p>The FSP proposes DQOs for soil investigation including 'Step 6: <i>Specify performance or Acceptance Criteria - Use of MI/DU sampling will maximize the confidence of confirming or denying the presence of unacceptable hazardous concentrations at each site</i>' and 'Step 7: <i>Optimize Design for Obtaining Data – The DUs will be sampled using MI sampling and the samples will be sent to the laboratory for analysis.</i>' "</p> <p>Recommendation:</p> <p>The use of MI sampling has not been approved by DTSC for use on the RFS project. Alternate DQOs should be proposed.</p>	All references to MIS have been removed from the SOP and QAPP.
59	FSW p 27, Section 4.3.2 (Final FSW p 28, Section 5.3)	MV FSW 13	<p>The FSP proposes DQOs for ground water investigation including "Step 2: <i>Identify the Goals of the Study - What is the prevailing hydraulic gradient of the groundwater at RFS?</i>"</p> <p>Recommendation:</p> <p>The study should identify seasonal or other variations in groundwater flow conditions, in addition to the prevailing hydraulic gradient.</p>	The Final FSW states: "An estimated 10 piezometers will be proposed for a year of quarterly monitoring to assess the seasonal effects on the hydraulic gradients in the shallow groundwater zone at the RFS. Specific locations will be specified with concurrence from DTSC after review of analytical results."
60	FSW p 27, Section 4.3.2 (Final FSW p 27, Section 5.2, Step 4)	MV FSW 14	<p>The FSP proposes DQOs for ground water investigation including "Step 4: <i>Define the boundaries of the Study - The study area is all groundwater located within the property boundaries of the RFS.</i>"</p> <p>Recommendation:</p> <p>The boundaries of the study should be expanded if contamination from the RFS is found to have spread off the RFS property, or if the conceptual site model suggests that releases may have extended off-site.</p>	<p>The FSW was revised to state:</p> <ul style="list-style-type: none"> - The Phase I study area is all groundwater located within the property boundaries of the RFS. - The shallow groundwater zone is primarily of interest, with secondary data collection to occur within the intermediate zone in order to determine flow directions (laterally and vertically) - Horizontal expansion of the study area may be necessary to investigate potential groundwater plumes if contamination is found present in the first round of groundwater sampling.
61	FSW p 27, Section 4.3.2 (Final FSW p 28, Section 5.3)	MV FSW 15	<p>The FSP proposes DQOs for ground water investigation including 'Step 5: <i>Develop the Decision Rules.</i>' Ground water quality including contaminant concentrations may vary seasonally. The variations can be significant resulting in decision criteria being exceeded only seasonally.</p> <p>Recommendation:</p> <p>Decision rules for ground water should be developed in the FSP addenda.</p>	The Final FSW states: "An estimated 10 piezometers will be proposed for a year of quarterly monitoring to assess the seasonal effects on the hydraulic gradients in the shallow groundwater zone at the RFS. Specific locations will be specified with concurrence from DTSC after review of analytical results."

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62	FSW p 28, Section 4.3.2 (Final FSW p 39, Section 5.3.1)	MV FSW 16	<p>The FSP proposes DQOs for ground water investigation including <i>"Step 7: Optimize Design for Obtaining Data - Groundwater data gaps will be addressed through collection groundwater grab samples. Grab sample results will be evaluated to determine subsequent optimal placement of piezometers, if necessary."</i></p> <p>Recommendations:</p> <p>Simply collecting shallow grab water samples is not recommended. Prior to, or combined with, collecting shallow grab samples, the site hydrostratigraphy should be investigated to depths below initial target grab sample depths. This is needed to understand the hydrostratigraphic context of the grab samples and the overall site hydrogeology.</p> <p>Completing cone penetrometer surveys and, where VOCs may be present, membrane interface probe surveys are recommended. Such an approach will provide for high resolution stratigraphic and contaminant distribution data needed to support site characterization decisions (such as optimal placement of monitoring wells and/or piezometers).</p> <p>Please insure that the piezometers are designed such that they can provide representative ground water samples because ground water quality will need to be monitored over time to evaluate trends.</p>	<p>The Final FSW states: "All groundwater samples will be collected from completed 2-inch diameter piezometers installed using direct-push technology suitable for collecting groundwater samples. Standard information for planning and conducting field sampling for Phase I, such as such as piezometer installation, borehole logging, field equipment calibration and maintenance, sample collection methodology, sample packaging and documentation, has been outlined in the QAPP.</p> <p>Use of real-time screening methods such as a membrane interface probe (MIP) are not proposed during Phase I, as these are most effective in determining chemical delineation within known contamination, and less effective as a screening or site discovery technique. The goal of the Phase I sampling is to develop a base-line hydrogeologic model and to improve the understanding of overall site-wide groundwater quality; therefore, real-time screening methods are not proposed. Real-time screening may be considered during a subsequent sampling phase if the need for detailed and robust chemical delineation is required."</p>
63	FSW p 28, Section 4.3.3 (Final FSW p 22, Section 4.2.1)	MV FSW 17	<p>The FSW proposes DQOs for utilities including sewers, fuel lines and hydraulic lines. Passive soil gas sampling is proposed to possibly be followed by active soil gas, soil, and/or ground water sampling. The FSP proposes sampling the main lines beginning at the southern (downstream) part of the site and, moving towards building areas and laterals based on the main line results.</p> <p>Recommendations:</p> <p>Samples should be collected at the building areas (where lines leave the buildings) and where laterals connect to main lines even if main line samples do not exceed screening criteria.</p> <p>If release areas are identified based on detected VOCs, follow-up sampling and analysis should include non-VOC constituents. If no VOC release areas are identified, target areas for non VOCs should be identified based on other criteria.</p>	<p>As stated in the response to Ref. No 37, the scope of the FSW for Phase I does not include collection of soil samples and therefore does not include a discussion of the proposed methodology for soil screening criteria.</p> <p>The Final FSW states: "FSPs for subsequent phases will address soil and soil-gas sampling to resolve data gaps outlined in the CCR, as well as any new data gaps initiated by results from the Phase I groundwater investigation. If contamination is identified in groundwater samples at levels that warrant additional work, further investigation may be proposed—including passive or active soil gas sampling or soil sampling."</p>

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64	FSW General Comment	KK FSW GC A	Multi-increment sampling (MIS) strategy. The HERD has not yet reviewed or accepted data using this technique in any health risk assessment. In addition, the Department of Toxic Substances Control (DTSC) has not yet reviewed or approved the use of this technique for soil investigatory activities. However, the DTSC is currently participating in a review of this sampling strategy with the Interstate Technology and Regulatory Council (ITRC). Until significant issues are resolved regarding the appropriate use of the technique and the suitability of using MIS data in health risk evaluations, the HERD believes this sampling strategy should not be employed at this site. Some questions that need to be resolved include how or under what conditions this strategy may be acceptably used to characterize the release into the environment of volatile organic compounds (VOCs) or chemicals known to migrate in soil due to leaching, the appropriate design and use of this strategy for ecological risk evaluation, and how MIS data may be evaluated to obtain a statistically acceptable 95% upper confidence limit on a mean concentration.	All references to MIS have been removed from the SOP and QAPP.
65	QAPP General Comment	KK QAPP GC B	A large part of this appendix is a compendium of sampling procedures used in environmental site investigations and, thus, presumably represents the complete potential battery of techniques that may be used at any site. This appendix should be revised to include only those methods most likely to be utilized at this site and to remove those methods that are no longer widely used in site investigation or would not apply to this site.	The QAPP was revised to include only relevant sampling methods most likely to be used during the data gaps sampling investigation.
66	HSP General Comment	KK HSP GC C	Appendix B Health and Safety Plan. The HERD reviewed only the environmental monitoring and sampling and ambient air monitoring sections and assumes that other DTSC staff has reviewed this appendix in depth.	No response is necessary.

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67	FSW p 10, Section 2.2.1 (Final FSW p 22, Section 4.2.1)	KK FSW 1	Western Stege Marsh has been identified as a soil data gap, so more information will be collected to determine if surface water and sediment concentrations in the marsh pose risks to humans and ecological receptors. A) Please confirm that data to be collected will include the information necessary, such as wind and wave activity and tidal action exchange and recharge, to develop a site-specific fate and transport model for sediments and contaminants in the marsh. B) Please confirm that sampling will take place in the shallow, saturated zone beneath the depth of previous removal activities in the marsh.	As stated in the response to Ref. No 37, the scope of the FSW for Phase I does not include collection of soil samples and therefore does not include a discussion of the proposed methodology for collecting soil samples.
68	FSW p 11, Section 2.2.2 (Final FSW p 22, Section 4.2.1)	KK FSW 2	A) Table 1 lists specific groundwater priorities, identified as GW 1 through 8. A figure should be included that shows the approximate locations of these areas. B) Table 1 indicates that the biologically active permeable barrier (BAPB) will be investigated as GW4 in Phase I of the field sampling, but the soil BAPB area will be investigated as IA3-9 in Phase 111. Please explain why these two closely associated areas are being investigated as separate units in different time periods.	The Final FSW states: "The groundwater data gap will be addressed in Phase I of the data gap investigation to confirm or deny the presence of contamination that would imply complete pathways to groundwater from either soil or utility lines. This data gap will be investigated through collection of groundwater samples from piezometers that will be drilled and completed at strategic locations throughout the RFS." As stated in the response to Ref. No 37, the scope of the FSW for Phase I does not include collection of soil samples and therefore does not include a discussion of the proposed methodology for collecting soil samples.
69	FSW p 15, Section 3.2	KK FSW 3	Soil Migration and Exposure - Exposure to Human Receptors. This discussion of human exposure to environmental contaminants is restricted to workers, without consideration of potential human exposure in a residential scenario. Please confirm that a land use covenant will be in place to prohibit use of the site for residential purposes and that the human health risk assessment to be performed will support the use of such a land use covenant.	Institutional controls, such as a land use covenant, will be incorporated into any final remedy decisions. These controls will be consistent with the assumptions identified in the risk assessment and remedial investigation report.
70	FSW p 19, Section 4.2 (Final FSW p 22, Section 4.2.1)	KK FSW 4	Soil data gaps are proposed to be addressed through multi-incremental sampling. The lack of soil VOC data on this site is a data gap that the HERD believes cannot be filled using multi-incremental sampling techniques. Where VOCs may be present in soil, the HERD recommends soil gas sampling to be performed.	As stated in the response to Ref. No 37, the scope of the FSW for Phase I does not include collection of soil samples and therefore does not include a discussion of the proposed methodology for collecting soil or soil gas samples.
71	FSW p 20, Section 4.2 (Final FSW p 22, Section 4.2.1)	KK FSW 5	Please confirm that the approaches to be used to fill the groundwater data gap will include those that will provide information on the groundwater hydrology of the site.	The Final FSW states: "Phase I is intended to develop a hydrogeologic model of the site and to improve the understanding of overall site-wide groundwater quality."

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72	FSW p 21 and 22, Table 1 and Figure 4	KK FSW 6	A) Table 1 lists investigation areas using Arabic numerals, whereas Figure 4 lists those areas using Roman numerals. For clarity, use one or the other. B) Figure 4 should be revised to include a brief descriptor for each soil investigation area.	Table 1 and Table 4 have been removed since submittal of the Draft FSW.
73	FSW p 23, Section 4.2.3 (Final FSW p 23, Section 4.2.3)	KK FSW 7	Decision I Levels. Chemical concentrations measured in this proposed site investigation will be compared to generic human and ecological screening criteria. In addition, site data will also be compared to background concentrations where applicable. The general approach to be used to determine local background concentrations should be described in this workplan.	As stated in response to Ref. No. 34, site- and chemical-specific screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of the site-wide groundwater analytical data, as UC Berkeley and DTSC agreed during their meeting on October 27, 2009.
74	FSW p 23, Section 4.2.3 (Final FSW p 23, Section 4.2.3)	KK FSW 8	Decision II Levels. Chemical concentrations that are greater than their respective Decision I Levels will be compared to Decision II Levels. Decision II Levels are chemical screening concentrations that have been modified with site-specific parameters, such as "Tier II exposure concentrations". Please define Tier II exposure concentrations.	As stated in response to Ref. No. 34, site- and chemical-specific screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of the site-wide groundwater analytical data, as UC Berkeley and DTSC agreed during their meeting on October 27, 2009.
75	FSW p 23, Section 4.2.3 (Final FSW p 23, Section 4.2.3)	KK FSW 9	The text states that areas with concentrations less than or equal to Decision I Levels will not be further investigated. The cumulative screening risk and hazard for all detected chemicals should be calculated before no further action is recommended for a particular area.	As stated in response to Ref. No. 34, site- and chemical-specific screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of the site-wide groundwater analytical data, as UC Berkeley and DTSC agreed during their meeting on October 27, 2009.
76	FSW p 25, Section 4.3.1 (Final FSW p 22, Section 4.2.1)	KK FSW 10	Soil Data Gaps -Step 4: Define the Boundaries of the Studies. Vertical expansion of study areas will take place if surface soils from zero to two feet below ground surface (bgs) are contaminated. For risk assessment purposes, it is necessary to have soil data down to ten feet bgs. For ecological receptors, it may be necessary to have soil data below two feet. For VOCs and chemicals known to be mobile in soils, sampling at depths below two feet will be necessary.	As stated in the response to Ref. No 37, the scope of the FSW for Phase I does not include collection of soil samples and therefore does not include a discussion of the proposed methodology for collecting soil or soil gas samples.

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77	FSW p 25, Section 4.3.1	KK FSW 11	<p>Soil Data Gaps - Step 5: Develop Decision Rules.</p> <p>A) These proposed decision rules do not address the frequency of detection of specific chemicals. In general, if a chemical is detected in less than or equal to five percent of samples, that chemical may be eliminated as a chemical of concern.</p> <p>B) If a known human carcinogen (an A carcinogen) is detected in only one sample, it must be evaluated in a health risk assessment. These rules would apply to those circumstances where multi-increment sampling will not be used.</p>	These comments will be addressed in a risk assessment scoping document following completion of the data gaps sampling efforts.
78	FSW p 26, Section 4.3.1 (Final FSW p 23, Section 4.2.3)	KK FSW 12	<p>Soil Data Gaps - Step 6: Specify Performance or Acceptance Criteria. Screening Levels will be based on background concentrations, unrestricted and commercial land use California Health Hazard Screening Levels (CHHSLs), and other risk-based values. These screening levels should include ecological screening criteria.</p>	As stated in response to Ref. No. 34, site- and chemical-specific screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of the site-wide groundwater analytical data, as UC Berkeley and DTSC agreed during their meeting on October 27, 2009.
79	HSP p 6-72, Section 8.3	KK HSP 13	<p>Ambient Air Monitoring. This section summarizes the ambient air monitoring that will be performed during site investigation activities.</p> <p>A) The number of air monitoring stations and/or instruments that will usually be present should be included in this summary.</p> <p>B) The method/instruments to be used to determine upwind and downwind locations during a work day should also be described.</p> <p>C) Detection limits and fence line standards should be briefly discussed in this section.</p>	The HSP addendum for site-specific sampling plans will include relevant air monitoring requirements for individual sampling events.
80	HSP p 6-72, Section 8.4.2 (Final HSP p B-75, Section 4.8.2)	KK HSP 14	<p>Other Chemicals. Engineering controls are proposed to control emissions of metals, polychlorinated biphenyls (PCBs) and pesticides. The text states that no other chemicals have been identified at this site that may require air monitoring. Site investigatory activities in the mercury fulminate area may require air monitoring instruments for mercury vapors, and this should be so stated.</p>	The HSP was amended to include the possibility of monitoring for mercury vapors. If monitoring is deemed necessary, specific monitoring plans will be included in a HSP addendum.



Department of Toxic Substances Control

Linda S. Adams
Secretary for
Environmental Protection

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700 Heinz Avenue
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Arnold Schwarzenegger
Governor

December 1, 2009

Mr. Greg Haet
Associate Director, Environmental Protection
Office of Environment, Health & Safety
University of California, Berkeley
317 University Hall #1150
Berkeley, California 94720-1150

Dear Mr. Haet:

The Department of Toxic Substances Control (DTSC) received the Response to Comments on the Draft Field Sampling Workplan dated September 18, 2009. The purpose of the FSW is to describe the general facility-wide strategy and protocols for the field investigations that will fill the identified data gaps and allow characterization of the site. Separate site-specific field sampling plan addenda will be submitted in the future for the various investigation areas that will include background and historical information, specific data quality objectives, sampling locations, analytical methods, etc. DTSC staff has reviewed the responses and found that most comments were adequately addressed with the following exceptions. DTSC reserves final approval of the workplan until after the proposed changes has been incorporated into the revised document and DTSC has conducted its review. The following comments are number using UC Berkeley's response to comment reference number:

1 and 49: The response states that Incremental Sampling (IS) will remain in the Standard Operating Procedures (SOP) and Quality Assurance Project Plan (QAPP) with the intention that it will be used as a screening tool, to evaluate worker safety, and other site prioritization uses. It is unclear to DTSC how IS will be used as a screening tool or for other site prioritization uses. Therefore, IS should be removed from the SOP and QAPP. If at a later time, it can be demonstrated to DTSC's satisfaction that IS is a viable screening tool, the SOP and QAPP can be amended to include it.

2c: The revised FSW should include the historical aerial photographs mentioned in the response that show the possible route of discharge from the Liquid Gold Site to Western Stege Marsh.

11: DTSC assumes that the response means that degree of completeness for sample analysis will be a minimum of 95% for each matrix.

13: The response indicates that samples for VOC analysis will not be preserved using methanol. Please ensure that the QAPP indicates how samples will be collected and preserved to minimize the loss of VOCs in soil samples.

18: The original comment requested that the QAPP be revised to reflect the current state of soil gas sampling practices. The response indicated that practices no longer current or accepted were removed. DTSC assumes that the revised QAPP will include descriptions of any new methodologies and practices.

19: The intent of DTSC's comment was to have the analytical laboratory submit their SOP for review by DTSC prior to collecting samples for soil vapor. This request was made as there is no formal soil vapor certification process for analytical laboratories. Please ensure that the revised FSW includes this requirement.

34: The response provided is acceptable. However, the list of screening numbers and toxicity reference values used to set the screening numbers should be submitted to DTSC for review prior to sampling. The literature source for toxicity reference values for any Chemical of Potential Ecological Concern (COPEC) not represented by a US EPA Region IX Biological Technical Assistance Group (BTAG) value should also be provided. Please keep in mind that protection for the clapper rail will need to be evaluated at the No Observable Adverse Effect Level (NOAEL). With respect to the use of LBNL ambient concentrations values, please see response nos. 44 and 45 below.

35: Please ensure that the FSW elaborates on how home range will influence sampling strategies. For example, small home range receptors such as a shrew may forage over an area no larger than a tenth of an acre. Therefore, the FSW should explain how the size of the home range (e.g., large versus small) will influence the sampling strategy.

37: While DTSC agrees that the PCBs Aroclor-1254 and Arcolor-1260 bind to soil and are not readily leached, the FSW needs to specify that in areas where there has been grading or if there is evidence that solvents have been released, soil at deeper horizons will be analyzed for PCBs.

The statement that aldicarb, atrazine and carbaryl were not found on site does not respond to DTSC's comment. The FSW needs to identify the pesticides that will be

sampled for and why, so that DTSC can determine the potential for the chemical to leach from the soil.

44 and 45: As discussed during a meeting held between UC Berkeley and DTSC on October 27, 2009, screening values for soil and groundwater will be discussed following collection of analytical data from future sampling events. Therefore, screening values do not need to be included in the FSW; rather the process that will be used should be described.

45: The US EPA Region 9 Biological Technical Assistance Group (BTAG) Toxicity Reference Values (TRVs) are dose-based concentrations, not media-based concentrations. Therefore, they are not appropriate as screening criteria for sample concentrations. Sampling for metals should extend to the boundaries of the established ambient or background concentrations.

62: DTSC's comment concerns Data Quality Objective 7: optimize design for obtaining ground water data. DTSC recommended using real-time screening methods to help identify locations and depths for collection of grab ground water samples. Also, any piezometers should be constructed to provide ground water samples for water quality analysis in addition to water elevation data. These methods have been used successfully at the adjacent Zeneca/Former Stauffer Chemical Site. The response provided does not address these recommendations, but proposes collecting grab ground water samples to screen for piezometer construction and using data from the piezometers to determine the need to investigate deeper. DTSC does not agree with this response and real-time screening methods should be included.

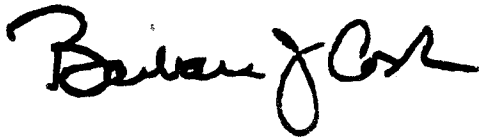
70: The response provided indicates that active soil gas sampling may be proposed if VOCs are present in soil samples exceeding screening criteria. It is unclear what screening criteria will be used. In addition, soil sampling results may be insufficient to determine whether soil gas surveys are necessary. For example, VOC detections in groundwater may also indicate that a soil gas survey is needed.

73: A general approach describing how local background concentrations will be determined needs to be included in the FSW.

Mr. Greg Haet
December 1, 2009
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If you have any questions regarding this letter, please contact Lynn Nakashima of my staff at (510) 540-3839.

Sincerely,

A handwritten signature in black ink, appearing to read 'Barbara J. Cook', with a stylized, cursive script.

Barbara J. Cook, P.E.
Acting Assistant Deputy Director
Brownfields & Environmental Restoration Program
Department of Toxic Substances Control

cc: Mr. Mark Vest
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8800 Cal Center Drive
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Final Field Sampling Workplan
University of California, Richmond Field Station Site
April 15, 2010

Draft Response to Comments
Department of Toxic Substances Control, December 1, 2009

April 15, 2010

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UC Berkeley Ref. No.	Draft FSW Page/ Sect No. (Final FSW Page/ Sect. No.)	DTSC Comment	UC Berkeley Response Revised FSW Text
1	UCB RTC 1 and 49; SOP and QAPP (Final FSW p 2, Section 1.1.2)	The response states that Incremental Sampling (IS) will remain in the Standard Operating Procedures (SOP) and Quality Assurance Project Plan (QAPP) with the intention that it will be used as a screening tool, to evaluate worker safety, and other site prioritization uses. It is unclear to DTSC how IS will be used as a screening tool or for other site prioritization uses. Therefore, IS should be removed from the SOP and QAPP. If at a later time, it can be demonstrated to DTSC's satisfaction that IS is a viable screening tool, the SOP and QAPP can be amended to include it.	All references to Multi Incremental Sampling (MIS) have been removed from the SOP and QAPP. The Final FSW states: "As FSPs for subsequent phases of work are prepared, if new sample collection methods are proposed or recommended, the QAPP will be revised or amended to include all applicable information."
2	UCB RTC 2c; FSW p 12, Section 3.1 (Attachment 1 to this RTC)	The revised FSW should include the historical aerial photographs mentioned in the response that show the possible route of discharge from the Liquid Gold Site to Western Stege Marsh.	The historical aerial photographs which demonstrate the route of discharge between the Liquid Gold Site and Western Stege Marsh are attached to this Response to Comments.
3	UCB RTC 11; QAPP p 17, Section 3.2.4 (Final QAPP p A-17, Section 3.2.4)	DTSC assumes that the response means that the degree of completeness for sample analysis will be a minimum of 95% for each matrix.	The QAPP states: "A minimum of 95 percent completeness per matrix type will be required for usable data."
4	UCB RTC 13; QAPP p 23, Section 4.1.2 (Final FSW p 22, Section 4.2.1 and Final FSW p 2, Section 1.1.2)	The response indicates that samples for VOC analysis will not be preserved using methanol. Please ensure that the QAPP indicates how samples will be collected and preserved to minimize the loss of VOCs in soil samples.	The QAPP was revised to remove all reference to methanol-preserved, discrete VOC soil samples. The FSW text was revised to state: "Investigation of soil data gaps will occur in Phases II through V. Sampling strategies, including sampling locations and potential contaminants of concern, will be addressed in upcoming FSPs." "As FSPs for subsequent phases are prepared, if new sample collection methods are recommended, the QAPP will be revised or amended to include all applicable information."
5	UCB RTC 18; QAPP p 79, Section 4.6	The original comment requested that the QAPP be revised to reflect the current state of soil gas sampling practices. The response indicated that practices no longer current or accepted were removed. DTSC assumes that the revised QAPP will include descriptions of any new methodologies and practices.	The QAPP contains current soil-gas sampling practices. The QAPP will be amended as necessary if any new soil-gas sampling methodologies are adopted by DTSC. Please see response to Ref. No. 4 regarding future updates to the QAPP.

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UC Berkeley Ref. No.	Draft FSW Page/ Sect No. (Final FSW Page/ Sect. No.)	DTSC Comment	UC Berkeley Response Revised FSW Text
6	UCB RTC 19; QAPP p 85, Table A-5 (Final QAPP p A-154, Section 7.4)	The intent of DTSC's comment was to have the analytical laboratory submit their SOP for review by DTSC prior to collecting samples for soil vapor. This request was made as there is no formal soil vapor certification process for analytical laboratories. Please ensure that the revised FSW includes the requirement.	<p>The revised QAPP states: "The following criteria will be considered when evaluating contract laboratories:</p> <ul style="list-style-type: none"> • Quality assurance and quality control documents governing laboratory operations • Initial demonstration of proficiency results for all analysts on all methods performed • Standard operating procedures for the desired analyses" <p>If soil vapor collection is proposed in a subsequent sampling phase, these criteria for laboratory selection will be followed, and the SOP from the analytical laboratory will be included in the subsequent FSP for DTSC's review and acceptance.</p>
7	UCB RTC 34; FSW, General Comment (Final FSW p 23, Section 4.2.3)	The response provided is acceptable. However, the list of screening numbers and toxicity reference values used to set the screening numbers should be submitted to DTSC for review prior to sampling. The literature source for toxicity reference values for any Chemical of Potential Ecological Concern (COPEC) not represented by a US EPA Region IX Biological Technical Assistance Group (BTAG) value should also be provided. Please keep in mind that protection for the clapper rail will need to be evaluated at the No Observance Adverse Effects Level (NOAEL). With respect to the use of LBNL ambient concentration values, please see responses nos. 44 and 45 below.	The Final FSW states: "The objectives of the phased site investigations are to identify immediate or potential risks to public health and the environment, and prioritize and implement response actions using removal actions and operable units, if appropriate, based on the relative potential risks at the site. As a first step in determining immediate or potential risk, groundwater sampling data obtained during Phase I will be evaluated to either confirm or deny the release of a hazardous substance, as defined in the DTSC Order. Site- and chemical-specific soil screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following receipt and review of groundwater analytical data, as agreed by UC Berkeley and DTSC at the meeting on October 27, 2009. For Phases II through V, screening values will be developed within each subsequent FSP in concurrence with DTSC. Screening levels will be developed so that confirmation or invalidation of a release of hazardous substance can be determined."
8	UCB RTC 35; FSW, General Comment (Final FSW p 23, Section 4.2.3)	Please ensure that the FSW elaborates on how home range will influence sampling strategies. For example, small home range receptors such as a shrew may forage over an area no larger than a tenth of an acre. Therefore, the FSW should explain how the size of the home range (e.g. large versus small) will influence the sampling strategy.	As stated in the response to Ref. No 7, the scope of the FSW for Phase I does not include the collection of soil samples and therefore does not include a discussion of ecological receptor areas.

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UC Berkeley Ref. No.	Draft FSW Page/ Sect No. (Final FSW Page/ Sect. No.)	DTSC Comment	UC Berkeley Response Revised FSW Text
9	UCB RTC 37; FSW p 15, Section 3.2 (Final FSW p 22, Section 4.2.1)	<p>While DTSC agrees that the PCBs Aroclor-1254 and Aroclor-1260 bind to soil and are not readily leached, the FSW needs to specify that in areas where there has been grading or If there is evidence that solvents have been released, soil at deeper horizons will be analyzed for PCBs.</p> <p>The statement that aldicarb, atrine and cararyl were not found on site does not respond to DTSC's comment. The FSW needs to identify the pesticides that will be sampled for and why, so that DTSC can determine the potential for the chemical to leach from the soil.</p>	<p>The Final FSW states: "Soil data gaps will be investigated through characterization of near-surface and subsurface soils throughout the RFS. Investigation of soil data gaps will occur in Phases II through V. Sampling strategies, including sampling locations and potential contaminants of concern, will be addressed in upcoming FSPs."</p> <p>Groundwater samples collected during Phase I sampling will be analyzed for PCBs and pesticides, as specified in Table 2 of the Final FSW.</p>
10	UCB RTC 44 and 45; FSW p 25, Section 4.3.1 (Final FSW p 23, Section 4.2.3)	As discussed during a meeting held between UC Berkeley and DTSC on October 27, 2009, screening values for soil and groundwater will be discussed following collection of analytical data from future sampling events. Therefore, screening values do not need to be included in the FSW; rather the process that will be used should be described.	As stated in the response to Ref. No 7, the scope of the FSW for Phase I does not include the collection of soil samples and therefore does not include a discussion of the proposed methodology for soil screening criteria.
11	UCB RTC 45; FSW p 26, Section 4.3.1 (Final FSW p 23, Section 4.2.3)	The US EPA Region 9 Biological Technical Assistance Group (BTAG) Toxicity Reference Values (TRVs) are dose-based concentrations, not media based concentrations. Therefore, they are not appropriate as screening criteria for sample concentrations. Sampling for metals should extend to the boundaries of the established ambient or background concentrations.	<p>As stated in the response to Ref. No 7, the scope of the FSW for Phase I does not include the collection of soil samples and therefore does not include a discussion of the proposed methodology for soil screening criteria.</p> <p>UC Berkeley will make efforts to ensure that detection limits on sampling occurring prior to the establishment of screening values will be low enough to extend to the boundaries of potential background concentrations. Method detection limits (MDLs) and Quantitation limits (QLs) for the groundwater sample analyses proposed for Phase I are included in the FSW in Table XX.</p>

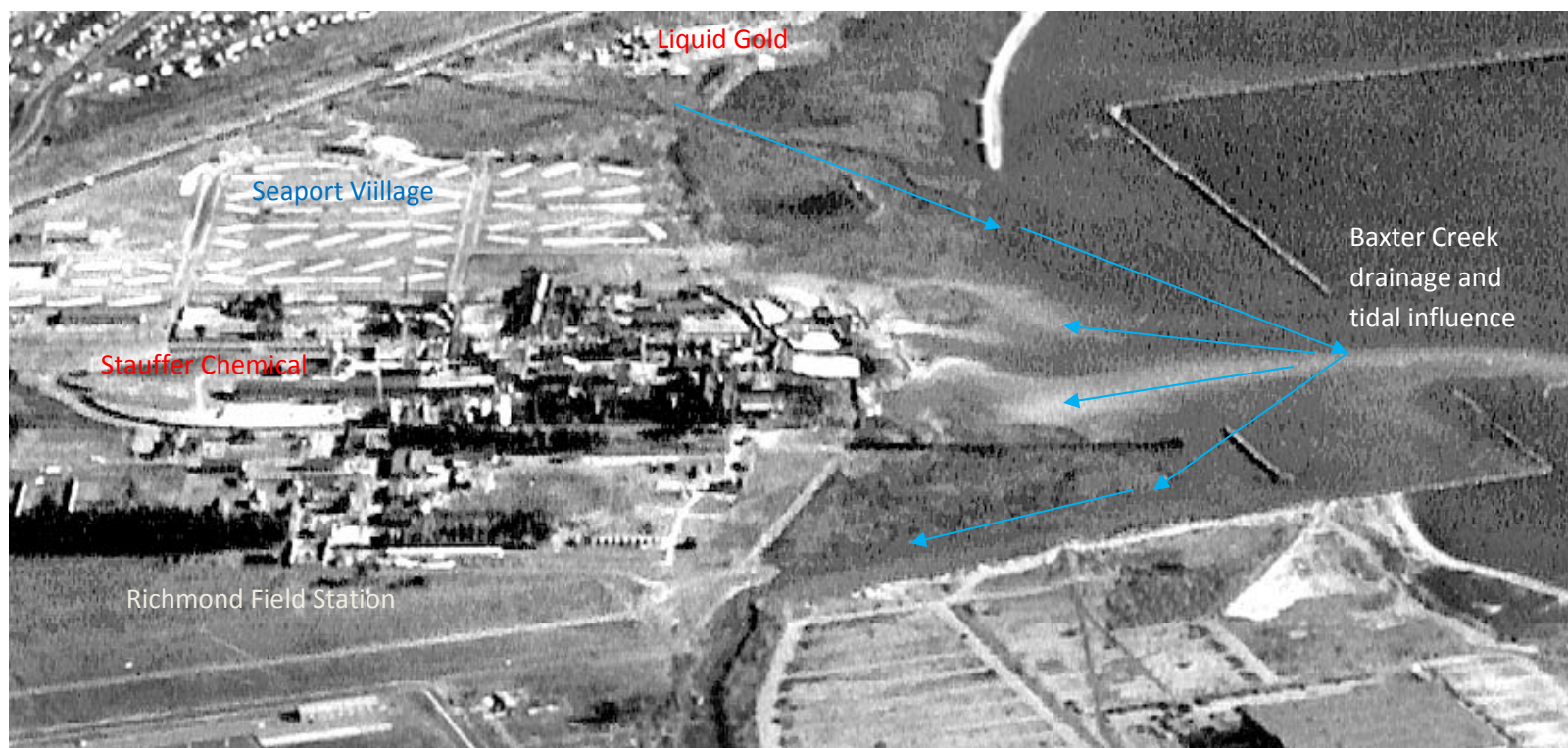
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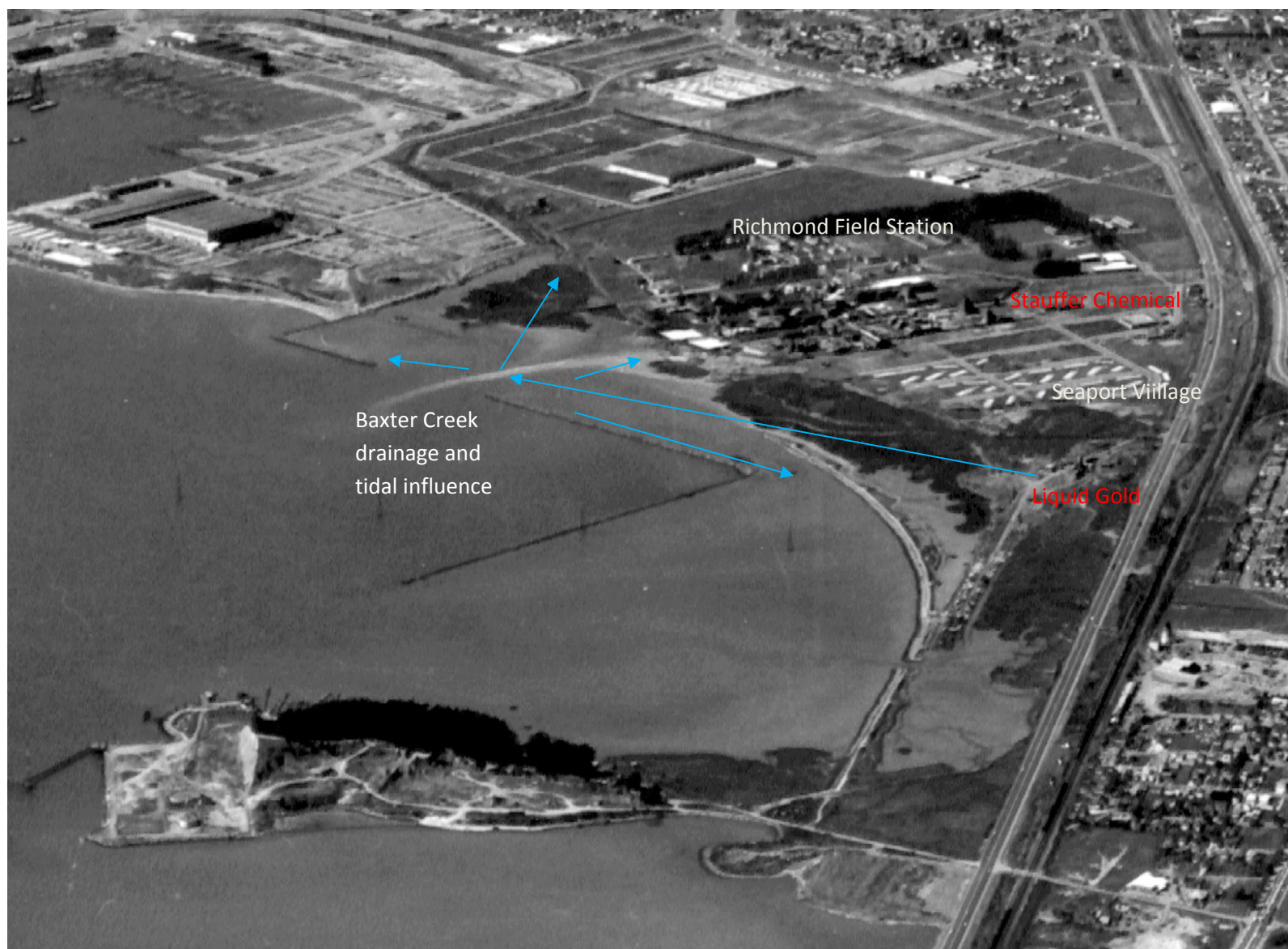
April 15, 2010

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UC Berkeley Ref. No.	Draft FSW Page/ Sect No. (Final FSW Page/ Sect. No.)	DTSC Comment	UC Berkeley Response Revised FSW Text
12	UCB RTC 62; FSW p 28, Section 4.3.2 (Final FSW p 39, Section 5.3.1)	DTSC's comment concerns Data Quality Objective 7: optimize design for obtaining ground water data. DTSC recommended using real-time screening methods to help identify locations and depths for collection of grab groundwater samples. Also, any piezometer should be constructed to provide groundwater samples for water quality analysis in addition to water elevation data. These methods have been used successfully at the adjacent Zeneca/Former Stauffer Chemical Site. The response provided does not address these recommendations, but proposes collecting grab ground water samples to screen for piezometers to determine the need to investigate deeper. DTSC does to agree with this response and real-time screening methods should be included.	<p>The Final FSW states: "All groundwater samples will be collected from completed 2-inch diameter piezometers installed using direct-push technology suitable for collecting groundwater samples. Standard information for planning and conducting field sampling for Phase I, such as such as piezometer installation, borehole logging, field equipment calibration and maintenance, sample collection methodology, sample packaging and documentation, has been outlined in the QAPP.</p> <p>Use of real-time screening methods such as a membrane interface probe (MIP) are not proposed during Phase I, as these are most effective in determining chemical delineation within known contamination, and less effective as a screening or site discovery technique. The goal of the Phase I sampling is to develop a base-line hydrogeologic model and to improve the understanding of overall site-wide groundwater quality; therefore, real-time screening methods are not proposed. Real-time screening may be considered during a subsequent sampling phase if the need for detailed and robust chemical delineation is required."</p>
13	UCB RTC 70; FSW p 19, Section 4.2 (Final FSW p 22, Section 4.2.1)	The response provided indicates that active soil gas sampling may be proposed if VOCs are present in soil samples exceeding screening criteria. It is unclear what screening criteria will be used. In addition, soil sampling results may be insufficient to determine whether soil gas surveys are necessary. For example, VOC detections in groundwater may also indicate that a soil gas survey is needed.	<p>As stated in the response to Ref. No 7, the scope of the FSW for Phase I does not include the collection of soil samples and therefore does not include a discussion of the proposed methodology for soil screening criteria.</p> <p>The Final FSW states: "FSPs for subsequent phases will address soil and soil-gas sampling to resolve data gaps outlined in the CCR, as well as any new data gaps initiated by results from the Phase I groundwater investigation. If contamination is identified in groundwater samples at levels that warrant additional work, further investigation may be proposed—including passive or active soil gas sampling or soil sampling."</p>
14	UCB RTC 73; FSW p 23, Section 4.2.3 (Final FSW p 23, Section 4.2.3)	A general approach describing how local background concentrations will be determined needs to be included in the FSW.	As stated in response to Ref. No. 7, site- and chemical-specific screening levels and proposed strategies to address background concentrations will be developed in concurrence with DTSC following the receipt and review of the site-wide groundwater analytical data, as agreed by UC Berkeley and DTSC during their meeting on October 27, 2009.



1956 aerial photo showing Richmond Field Station, Stauffer Chemical, Seaport Village, and former Liquid Gold site.



1957 aerial photo showing Richmond Field Station, Stauffer Chemical, Seaport Village, and former Liquid Gold site.

ATTACHMENT 2
GROUNDWATER LABORATORY SOPS

**USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA**

**STANDARD OPERATING PROCEDURE 315
SEMIVOLATILE ORGANIC COMPOUND ANALYSIS**

Revision 5
Effective Date: June 30, 2009

Reviewed by: _____
Richard Bauer _____ Date
Chemistry Team Leader/Technical Director

Reviewed by: _____
K. W. Hendrix, Laboratory QA Officer _____ Date

Approved by: _____
Brenda Bettencourt, Laboratory Director _____ Date

Periodic Review:

Signature	Title	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____

This SOP was prepared by ICF Consulting for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA contract no. EP-W-06-041). ESAT Document Control Number: 00404012-10854

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APPENDIX A. DEVIATIONS FROM THE REFERENCE METHOD

APPENDIX B. ANALYTES AND QUANTITATION LIMITS

APPENDIX C. QUALITY CONTROL PARAMETERS AND CRITERIA

APPENDIX D. RECOMMENDED INSTRUMENT PARAMETERS

APPENDIX E. CHEMSTATION FILE NAMING CONVENTIONS

APPENDIX F. PREVENTATIVE MAINTENANCE REQUIREMENTS

APPENDIX G. METHOD PERFORMANCE

APPENDIX H. TYPICAL DATA PACKAGE FORMAT

APPENDIX I. REVISION HISTORY

1 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the procedures used for the analysis of selected semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS) in extracts prepared from solid or liquid samples by EPA SW-846 extraction and cleanup methods appropriate to the sample matrix. This SOP is based on procedures included in EPA Method SW 846 8270D. Deviations from Method 8270D are described in Appendix A. The scope of this SOP was expanded to include the analysis of 1,4-dioxane. Analytes and quantitation limits (QLs) applicable to this analysis are listed in Appendix B.

Sample extracts are prepared using Region 9 SOP 275 *Extraction of Water Samples Using CLLE* or SOP 290 *Extraction of Soil Samples Using PFE (Pressurized Fluid Extraction-ASE)*.

The applicability of this procedure to specific project data quality objectives must be assessed on a case-by-case basis. The quality control (QC) criteria specified in this procedure do not meet compliance criteria for either drinking water or NPDES monitoring projects.

2 METHOD SUMMARY

Sample extracts are injected into a gas chromatograph (GC) with a mass spectrometer (MS) detector. Analytes are separated in a narrow bore fused silica capillary GC column in a temperature-programmed oven and detected by the MS. Each target and surrogate compound is quantitated using the average response factors from the most recent initial calibration.

Target semivolatile organic compounds of interest are identified in the sample extract by comparing the mass spectra to the mass spectra in the National Institute of Standards and Technology (NIST) library and the GC retention times of the target analytes to retention times of standards analyzed under the same conditions as samples.

3 DEFINITIONS

Atomic weight - The following terms are used to describe atomic weight: Dalton – a unit of atomic mass; atomic mass unit (amu) – one Dalton; mass to charge ratio (m/z) – a unit of ionic mass equivalent to Daltons per unit of charge.

Calibration Check Compounds (CCC) - Analytes that may show high variability if there are system leaks or reactive sites on the column. These compounds are used as indicators of deteriorating system performance.

Calibration Standard (CAL) - A solution prepared from the primary dilution standard or stock standard solution and the internal standard and surrogate analytes. The CAL solutions are used to calibrate instrument response with respect to analyte concentration.

Continuing Instrument Calibration Verification (CCV) - A standard containing the target analytes used to verify the accuracy of the analysis and monitor instrument drift.

GC/MS Tuning Solution (MS tune) - A solution of decafluorotriphenylphosphine (DFTPP), 4,4' DDT, pentachlorophenol, and benzidine used to evaluate the performance of the GC/MS system with respect to a defined set of method criteria.

Initial Calibration Standards (ICAL) - Standards used to calibrate the instrument response with respect to analyte concentration.

Internal Standard (IS) - A compound added to a sample, extract, or standard solution in a known amount and used to measure the relative responses of method analytes and surrogates that are components of the same solution.

Laboratory Control Sample (LCS) - An aliquot of reagent water, sand, or sodium sulfate to which known quantities of the method analytes are added. The LCS is treated exactly as a sample. The LCS is used to determine whether the methodology is in control and to indicate the accuracy associated with laboratory procedures. This is equivalent to a Laboratory Fortified Blank (LFB) QC sample.

Laboratory Information Management System (LIMS) - The Element Database.

Matrix Spike (MS) and Matrix Spike Duplicate (MSD) - Two aliquots of the same sample to which known quantities of the method analytes are added. The MS and MSD are treated exactly as samples. The MS and MSD are used to determine whether the sample matrix contributes bias to sample results and to measure the precision associated with laboratory procedures. These are equivalent to Laboratory Fortified Matrix (LFM) and Laboratory Fortified Matrix Duplicate (LFMD) QC samples.

Method Blank (MB) - An aliquot of reagent water, sand, or sodium sulfate that is treated exactly as a sample including exposure to all glassware, equipment, solvents, and surrogates that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the solvents, or the equipment. This is equivalent to a Laboratory Reagent Blank.

Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Primary Dilution Standard Solution (PDS) - A solution of one or more analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

Quantitation Limit Standard (QL) - The lowest level CAL solution. The QLS is used to verify analytical system response at the quantitation limit.

Sample Delivery Group (SDG) - A group of twenty samples or less from a project that is sent to the laboratory for analysis.

Second Source Calibration Verification (SCV) - Equivalent to the mid point initial calibration solution but prepared from a source different from the source of calibration standards. The SCV is used to check the accuracy of the initial calibration solutions.

Stock Standard Solution (SSS) - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials purchased from a commercial source.

Surrogate - Compounds which are extremely unlikely to be found in any sample that are added to a sample aliquot in a known amount before extraction or other processing, and measured with the same procedures used to measure other sample components. The purpose of the surrogate is to monitor method performance with each sample.

System Performance Check Compounds (SPCC) - Analytes that typically have low RRFs or are good indicators of system performance. These compounds are used as indicators of deteriorating system performance.

4 SAFETY AND HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Stock standard solutions of these compounds must be prepared in a fume hood. Routine procedures in this SOP do not require contact with concentrated solutions or neat materials. All standard preparation procedures associated with this SOP should be performed in a fume hood wearing protective clothing (lab coats) and safety glasses.

4.1.1 Dichloromethane

Dichloromethane is a suspected carcinogen. Effects of overexposure: acute inhalation or ingestion causes mild central nervous system depression. The primary toxic effect is narcosis. Other toxic effects are pulmonary edema, encephalopathy, and hemolysis. Dichloromethane irritates the eyes, skin, and respiratory tract. No systemic effects have been reported in humans, although excessive concentrations have caused cancer and liver and kidney damage in animals.

Emergency and first aid

Inhalation: immediately remove to fresh air. If not breathing, administer mouth to mouth rescue breathing. If there is no pulse, administer cardiopulmonary resuscitation (CPR), contact physician immediately.

Eye contact: rinse with copious amounts of water for at least 15 minutes. Get emergency medical assistance.

Skin contact: flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothing and shoes. Wash clothing before re use, and discard contaminated shoes. Get emergency medical assistance.

Ingestion: call local poison control center for assistance. Contact physician immediately. Never induce vomiting or give anything by mouth to a victim unconscious or having convulsions.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced,

recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-regulated Waste	Not applicable
Sample Extracts (dichloromethane with trace semivolatiles)	Hazardous Waste	See solvent MSDS

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Please refer to Region 9 SOP 275 "*Extraction of Water Samples Using CLLE*", or SOP

290 “*Extraction of Soil Samples Using PFE (Pressurized Fluid Extraction-ASE)*”.

5.2 Internal Chain-of-Custody

Sample extracts for GC/MS analysis are received from the extraction lab personnel and custody is transferred to the GC/MS laboratory staff. The GC/MS analyst acknowledges the receipt of the sample extracts by signing the appropriate sections of the completed LIMS bench sheet. Copies of tracking sheets, chain of custody records, and the original LIMS extraction bench sheet should accompany the sample extracts.

The extracts are marked with the EPA Region 9 Laboratory number, which can be checked against the tracking sheets and chain of custody record to determine the client sample identification, case number, and sample delivery group (SDG) number. Verify sample IDs and dates and times of collection against the chain-of-custody form.

5.3 Extract Storage

Store extracts in the freezer in Room 402 or 406 at $\leq -10^{\circ}\text{C}$ before and after analysis. Retain sample extracts for 90 days.

5.4 Holding Time

Extracts must be analyzed within 40 days of extraction.

6 INTERFERENCES

Method interferences can be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus. Phthalates are commonly found as laboratory contaminants. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running a method blank (MB). The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components should be avoided.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed.

Contamination of the GC system with high boiling material will cause erratic chromatographic behavior for several target analytes: pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, the nitroanilines, and benzyl alcohol.

It is important that samples and standards be contained in the same solvent, i.e., the solvent for final working standards must be the same as the final solvent used in sample

preparation. If this is not the case, chromatographic comparability of standards to samples may be affected.

Although not strictly an interference, hexachlorocyclopentadiene is subject to thermal decomposition in the GC inlet, is photoreactive, and reacts with acetone if this solvent is present in the standard mixture.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

7.1.1 GCMS System

- 7.1.1.1 Gas Chromatograph (GC): Agilent 6890, 7890, or equivalent. The GC must be capable of multilevel temperature programming and constant carrier gas flow throughout the temperature range. The GC should be equipped with an automatic sample injector, splitless injection port, and electronic pressure control (EPC).
- 7.1.1.2 GC column: 30 m, 0.25 mm ID, 0.50 μ m df. A fused silica capillary column with a bonded phase coating of 5% phenyl 95% methyl silicone such as RXI-5SILMS, DB5, DB5MS, RTX 5, HP 5, or equivalent. Any column capable of separating the target analytes and passing method QC without overloading at the concentration of the highest standard may be used. The use of a short (5 m) length of a deactivated, uncoated fused silica column (guard column) between the injection port and the analytical column, to trap nonvolatile extract residues, is optional.
- 7.1.1.3 Mass spectrometer: Agilent 5973, 5975, or equivalent, capable of scanning from 35 to 550 amu or in the SIM mode every one second or less using 70 volts (nominal) electron energy in the electron impact ionization mode. The MS must be able to produce a mass spectrum that meets acceptance criteria when 50 ng of DFTPP is injected through the GC inlet.
- 7.1.1.4 Data system: ChemStation (available from Agilent), or equivalent, able to control the GC/MS system and to acquire, store, and reduce mass spectral data. The software must be able to process any GC/MS data file by recognizing a GC peak within a retention time window, comparing the mass spectrum from the GC peak with spectral data in a database, and generate a list of tentatively identified

compounds with their retention times and scan numbers. The software must also allow integration of the ion abundance of any specific ion between specified time or scan number limits and to calculate RRFs and concentrations of analytes in samples.

7.2 Reagents

Document the receipt of all reagents in the Element database. A unique ID is assigned for each reagent. The reagent ID is reflected on all preparation and analysis batches.

Dichloromethane: High purity pesticide quality or equivalent. Recycled dichloromethane may be used if demonstrated to be suitable for use in this procedure. See Region 9 SOP 239 *Procedures for Recycling used Dichloromethane*.

7.3 Standards

Document the receipt, preparation, and open dates of all standard ampules in the Element database.

All ampulated calibration materials must be maintained in the refrigerator at $>0^{\circ}\text{C}$ to $\leq 6^{\circ}\text{C}$ and protected from light. Use the manufacturer's expiration date for ampulated standards.

Open ampules and working standards must be maintained in a freezer at $\leq -10^{\circ}\text{C}$ and protected from light. The solution is assigned an expiration date which is either 6 months from preparation or open date, or the expiration date of the stock standard used in the preparation, whichever is earlier. Analysts must allow all standard solutions to equilibrate to room temperature before use.

- 7.3.1 Internal Standard Solution (IS): A solution of acenaphthene-d10, phenanthrene-d10, chrysene-d12, 1,4 dichlorobenzene-d4, perylene-d12, and naphthalene-d8 each at 2000 ug/ml in dichloromethane. Restek 31206 or equivalent. Add 10 μL to 1 mL extract or 5 μL to 0.5 mL extract to attain an extract concentration equivalent to the continuing calibration level.
- 7.3.2 Calibration Stock Standard: A solution of target analytes and surrogates in dichloromethane at a concentration of 80 ug/mL. The solution is typically prepared from 8270 Mega Mix (Restek 31686), 3,3'-dichlorobenzidine (Restek 31835), N-Nitrosodi-n-butylamine (Supelco 48320), 1,4-dioxane (Restek 31853), base/neutral surrogates (Restek 31082), and acid surrogates (Restek 31083). Equivalent solutions may be used in lieu of any of the above mixes.

Add the following solutions to a 5 mL volumetric flask and dilute the solutions to a final volume of 5 mL with dichloromethane.

Stock Standard	Conc. (µg/mL)	Amount (µL)	Final Vol. (mL)	Final Conc. (µg/mL)
8270 Mega Mix	1000	400	5	80
3,3'-Dichlorobenzidine	2000	200	5	80
N-Nitrosodi-n-butylamine	2000	200	5	80
1,4-Dioxane	2000	200	5	80
SV B/N Surrogates	5000	80	5	80
SV Acid surrogates+	1000+	400	5	80

+ Make an intermediate 7.5x dilution from original 7500 µg/mL mixture by adding 100 µL of the acid surrogates mix to 650 µL of dichloromethane).

- 7.3.3 Calibration standards: Target and surrogate compounds are prepared at concentrations of 1, 5, 10, 20, 40, 60 and 80 µg/mL by diluting the Calibration Stock Standard solution.
- 7.3.4 Second Source Standard: A solution of target analytes listed in Appendix B and surrogates prepared from a different source (i.e. a separate supplier/manufacturer) from that used to prepare calibration standard. Second Source Standard is prepared at a concentration of 20 µg/mL. The solution may be prepared using one or a combination of the following sources, or their equivalent:
- Supelco: SVOC 8270 LCS Mix #1 (46853, 100 µg/mL), 1,4-Dioxane-d8 (2000 µg/mL, 48367), SVOC benzidines mix 2 (48467, 2000 µg/mL), N-nitrosodi-n-butylamine (48320, 2000 µg/mL), Acid surrogates (47261, 10000 µg/mL), Base/neutral surrogate Spike Mix (1) (47262, 5000 µg/mL).
- AccuStandard: BASE-NEUTRAL MIX (CLP-HC-BN-SET, 2.0 mg/mL), ACID MIX (CLP-HC-A-R, 2.0 mg/mL), COMP#2 MIX (Z-014E-R, 2.0 mg/mL), N-Nitrosodi-n-butylamine (APP-9-147-20X, 2.0 mg/mL), Diphenylamine (AS-E0263, 5.0 mg/mL), Carbazole (M-634-IS, 1.0 mg/mL), 1-Methylnaphthalene (H-001S-D-40X, 2.0 mg/mL).
- 7.3.5 GC/MS Tuning Solution (MS tune): A solution of DFTPP, 4,4' DDT, pentachlorophenol, and benzidine at 50 ng/µL each in dichloromethane. Restek 31615, 1,000µg/mL each in methylene chloride, or equivalent. The solution is prepared by diluting the 250 µL of the mix to 5 mL with dichloromethane.
- 7.3.6 Instrument Blank: A solution of 1,4-dioxane-d8 at 5 ug/mL and internal standard at 20 ug/mL. The solution is prepared by diluting 25 µL of 1,4-dioxane-d8 and 100 µL of internal standard the mix to 10 mL with dichloromethane.

7.4 Supplies

7.4.1 Syringes: 10 μ L, 25 μ L, 50 μ L, 100 μ L, 250 μ L, 500 μ L, 1 mL.

7.4.2 Helium carrier gas: Ultra-high purity, 99.999%.

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Check the mass spectrometer for leaks on a daily basis, prior to the analysis of the tuning compound. Refer to Section 8.4 and Appendix F for system maintenance requirements.

Set-up the GC/MS following operating instructions provided by the manufacturer. Use operating parameters provided in Appendix D as a starting point.

8.1.1 Mass calibration

Mass calibration of the analytical system must be performed prior to an initial calibration, whenever the source is cleaned, or whenever a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions. Use perfluorotributylamine (FC43) to perform mass calibration of the instrument.

Calibrate the Mass Axis of the MS prior to analyzing the DFTPP standard each day that samples are analyzed. Use the settings in the most recent tune file as the initial conditions; save the tune file using the naming convention in Appendix E, and generate a tune report.

Refer to Section 9.2.1 and Appendix C for acceptance criteria and corrective action requirements.

8.1.2 GC/MS System Performance Check (DFTPP analysis)

The GC/MS system must meet the mass spectral ion abundance criteria for DFTPP prior to analysis. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target compounds.

In the ChemStation data analysis module, Load a copy of the most recent ChemStation method from C:\HPCHEM\1\Methods\Initial

Inject 1 μ L of the DFTPP solution using the operating parameters provided in Appendix D.

The autofind procedure will automatically find the DFTPP peak, average three scans (the peak apex scan and the scans immediately preceding and following the apex), perform a background subtraction, and print out a hard copy of the spectrum, the chromatogram, and the table of ion abundances.

Calculate DDT breakdown and generate a tailing factor report for the pentachlorophenol and benzidine peaks.

Refer to Section 9.2.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Save the method as outlined in the "ChemStation File Naming Convention" (see Appendix E) using today's date "mmdd" in the file name under C:\HPCHEM\1\Methods\.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

Prior to analyzing an initial calibration, ensure that proper system maintenance and GC/MS tuning (auto-tune and/or manual tune) has been performed. When the instrument is ready for analysis, perform the following steps:

1. In the ChemStation data analysis module, load the current "master" initial calibration method from C:\HPCHEM\1\Methods\Initial.
2. Perform an initial calibration using calibration the recommended concentrations listed in Section 7.3.3.
3. Update the response factors in the method using the newly acquired calibration files.
4. Update the retention time in the method using the newly acquired continuing calibration level.
5. Update the qualifier ion relative responses from the CCV calibration level.
6. Save the method as outlined in the "ChemStation File Naming Convention"
7. Generate "Response Factor Report."
8. Check the calibration files listed on the "Response Factor Report" to insure that the correct files are being used.
9. Check the time and date to ensure that the correct update is used.
10. Print the raw area report for an internal standard or the target analyte for single analyte analysis. Verify that the method was updated correctly. Print analyte list from ChemStation. Verify that the average response factor is used.
11. Save a copy of this method under C:\HPCHEM\1\Methods\Initial. This method will become the "master" copy until the next ICAL is generated.
12. Save a second copy of the method under I:\RoomNumber\Instrument\Methods\Initial.

13. Analyze a SCV standard at a concentration equivalent to the CCV. Use the ChemStation custom report to calculate the SCV recoveries.
14. Manually calculate a result for one surrogate in the SCV to insure that the correct RFs are being used and write the results on the quantitation report.
15. Save a hard copy of the initial calibration files so they may be copied and included in associated packages.

The analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are not contaminated. This is accomplished through the analysis of a method blank or an instrument blank.

Refer to Section 9.2.3 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2.2 Continuing Calibration

Analyze a calibration verification standard at the beginning of each 12-hour analytical period by performing the following steps:

1. In the ChemStation data analysis module, load today's method from C:\HPCHEM\1\Methods.
2. Acquire the continuing calibration using today's method.
3. Quantitate the continuing calibration file.
4. Generate "Evaluate Continuing Calibration Report".
5. Compare the IS retention times and areas in the CCV standard to the mid-point standard of the most recent initial calibration. Adjust the electron multiplier (EM) voltage if needed (an increase of 50 volts will typically double the response). If the EM voltage is changed, reanalyze DFTPP and the CCV.
6. Manually calculate the result for one surrogate to insure that the correct RFs are being used. Record the result on the quantitation report.
7. As each run is quantitated during the day, make sure that the same date and time stamp, (e.g. "Last Update: Mon Aug 23 12:02:21 2008"), is recorded on each file header.
8. If Last Update time stamp changes, state the reason, repeat steps 4-7, and include the reports generated in the package.
9. Save a copy of the method to the LAN, when the data are backed up to the LAN the following day.

Refer to Section 9.2.4 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2.3 Quantitation Limit Verification Standard

Analyze a quantitation limit standard at the concentration of the lowest point of the initial calibration for each 12-hour analytical period.

Use the ChemStation custom report to calculate the QLS recoveries.

Refer to Section 9.2.5 and Appendix C for acceptance criteria and corrective action requirements.

8.3 Analysis

8.3.1 Sample Extract Preparation

Allow the sample extracts and internal standard solutions to reach ambient temperature before analysis.

Check that the numbers on the vials coincide with the numbers on the LIMS extraction batch to ensure that the correct sample is being analyzed.

Note: Determine if the sample has an unusual color or other physical property. If any physical signs of contamination are present, screen the samples to protect the analytical system from damage or contamination, and to determine the appropriate subsequent dilutions. Record unusual items in the LIMS "MMO" field.

Add appropriate amount of IS solutions to each field and QC sample extract to attain an extract concentration equivalent to the continuing calibration level.

8.3.2 Sample Analysis and Analytical Sequence

This section describes setting up the analytical sequence and performing the instrumental analysis using the following steps:

- Obtain a LIMS sequence number by generating an empty LIMS sequence; specify the analysis, instrument, and batch number associated with the samples to be analyzed.
- Enter sample sequence in the instrument software. Include the laboratory sample number (work order-sample number) in the "Sample" field and dilution level, if any, in the "Multiplier" field. Use the LIMS sequence number to name instrument QC as outlined in Appendix D.
- Enter the BNA method name in the "Method" field; analyze all standards and samples with this method. Name the data files according to the data file naming convention outlined in Appendix E.
- Load the samples in the autosampler according to their designated positions in the sequence file. The recommended analysis sequence is:
 1. DFTPP
 2. CCV

3. QLS
4. Samples, sample dilutions, and or QC samples as needed
5. Instrument Blanks, as needed

- Run the sequence

8.3.3 Analyte Identification and Quantitation

8.3.3.1 Analyte Identification

In order for a target compound to be identified as present in a sample both the retention time and ion ratios of the peak must match those of the standard.

The mass spectra used for qualitative identification are from the NIST library. This eliminates the presence of extraneous ions often observed when using spectra generated on the GCMS system using standard mixes that frequently include co-eluting compounds. All ions present in the standard or reference mass spectrum at a relative intensity of 10 percent of the most abundant ion must be present in the sample spectrum. The relative intensities of the ions in the sample mass spectrum must agree within 30% of the relative intensities of those ions in the standard mass spectrum. For example, an ion with an abundance of 50% in the standard spectrum can have abundance between 20% and 80% in the sample spectrum. Ions present in the sample mass spectrum at greater than 10 percent abundance but not present in the standard mass spectrum must be reviewed and accounted for by the analyst making the comparison.

If a compound cannot be verified using these criteria but in the technical judgment of the analyst is present, report the analyte and include supporting evidence in the raw data package.

Cross out (with date and initial) all ChemStation results that do not meet qualitative criteria. Review the peak to see if the compound meets reporting the requirement of a TIC. If the compound is to be reported as a TIC, the false positive peak must be deleted (QDEL) in ChemStation.

Review the chromatogram for possible false negatives and edit results as needed.

8.3.3.2 Analyte Quantitation

Quantitate the data and print out ChemStation detailed quantitation reports and chromatograms. Use the average relative response factor from the initial calibration for quantitation.

Analyte concentrations in the sample extracts as shown on the ChemStation quantitation report are calculated as follow:

$$\text{Concentration (ng/mL)} = \frac{A_x \times C_{is}}{A_{is} \times \overline{RRF}}$$

Where:

- A_x = area of the quantitation ion of the compound
- C_{is} = amount of internal standard in $\mu\text{g/L}$ (20 $\mu\text{g/L}$)
- A_{is} = area of the quantitation ion of the associated internal standard
- \overline{RRF} = analyte average relative response factor from the initial calibration

LIMS calculates the final sample concentration. To verify the LIMS reported values for water samples, calculate results for target analytes using the following equation:

$$\text{Conc. } \mu\text{g} / \text{L} = \frac{A_x \times C_{is} \times V_t \times V_i \times \text{DF}}{A_{is} \times \overline{RRF} \times V_o}$$

Where:

- A_x = area of the quantitation ion of the compound
- C_{is} = amount of internal standard in $\mu\text{g/L}$ (20 $\mu\text{g/L}$)
- V_t = volume of concentrated extract in μL
- V_i = volume of extract injected in μL
- DF = dilution factor
- A_{is} = area of the quantitation ion of the associated internal standard
- \overline{RRF} = analyte average relative response factor from the initial calibration
- V_o = volume of water extracted in mL

For soil samples, calculate results for target analytes using the following equation:

$$\text{Conc. } \mu\text{g} / \text{Kg (dry weight basis)} = \frac{A_x \times C_{is} \times V_t \times V_i \times \text{DF} \times \text{GPC}}{A_{is} \times \overline{RRF} \times W \times D}$$

Where:

- A_x = area of the quantitation ion of the compound
- C_{is} = concentration of Internal Standard in $\mu\text{g/mL}$ (normally 20 $\mu\text{g/L}$)
- V_t = volume of concentrated extract in μL
- V_i = volume of extract injected in μL
- DF = dilution factor

GPC = GPC factor, normally 1.0 if not used, 2.0 if used
 A_{IS} = area of the quantitation ion of the associated internal standard
 \overline{RRF} = analyte mean relative response factor from the initial calibration
W = weight of sample in grams
D = dry weight factor (Percent solids/100)

8.3.3.3 Manual Integration

Where the chromatography software integrates the signal inconsistently or incorrectly, follow SOP 835, *Chromatographic Integration Procedures*. All manual chromatographic integration must be initialed and dated by the analyst and approved by the supervisor, Chemistry Technical Director, Quality Assurance Officer, or designees.

8.3.4 Review of Tentatively Identified Compound

The analyst must review the library search results for the following:

- 8.3.4.1 Load the data file of the most concentrated valid analysis of the sample.
- 8.3.4.2 Examine the spectra for each peak that is not a target, surrogate or internal standard. Report those for which the response is greater than 20% of the closest internal standard and where a tentative identification can be made. If none are identified, so state.
- 8.3.4.3 Report a maximum of 10 compounds based on total area (largest).
- 8.3.4.4 Since 1,4-dioxane-d8 is present at a low concentration, it will not be used in TICs calculations or generation. 1,4-dichlorobenzene-d4 will be used for the early eluting TICs.
- 8.3.4.5 Relative intensities of the major ions in the NIST reference spectrum (ions greater than 10 percent of the most abundant ion) should be present in the sample spectrum.
- 8.3.4.6 The relative intensities of the major ions should agree within 20 percent.
- 8.3.4.7 Molecular ions present in the reference spectrum should be present in the sample spectrum.
- 8.3.4.8 Ions present in the sample spectrum but not in the reference spectrum shall be reviewed for possible background contamination or the presence of co-eluting compounds.

- 8.3.4.9 Ions present in the reference spectrum but not within the scan range of the method should not be considered when making a tentative identification.
- 8.3.4.10 If, in the technical judgment of the analyst, no valid tentative identification of the compound can be made, the compound should be reported as "Unknown". The analyst shall attempt classification of the unknown compound (i.e., unknown hydrocarbon, unknown aromatic, unknown chlorinated compound, etc.). The probable molecular weight should be included, if distinguishable.
- 8.3.4.11 Report the following:
- Class of compound instead of specific isomers unless the identity of the specific isomer is known. As an example, report dichlorobenzene instead of 1,2-dichlorobenzene. Alternatively, report 1-methylnaphthlene if the calibration standard has 2-methylnaphtalene and the TIC retention time is not that of 2-methylnaphtalene.
 - "Total" of all hydrocarbons as total hydrocarbon m/z 55 and/or total hydrocarbon m/z 57. Calculate the concentration based on ion 55 or 57 as a ratio of the quantitation ion of the closest IS. The IS closest to the center of the "hump" will be selected.
- 8.3.4.12 Exclude the following compounds from the report:
- Analytes eluting prior to the first eluting target compound.
 - TICs that were detected in the method blank.
 - Column bleed (i.e. siloxanes).
 - Common laboratory contaminants or aldol condensation products (e.g. hydroxy methyl pentanone).
 - Reagent Preservatives (e.g. amylene hydrate).
 - CO₂/fixed gases peaks.
 - Electronic noise peaks.
- 8.3.4.13 The concentrations of TICs are estimated. Use the TIC area in Equations in section 8.3.3.2 and assume the RRF is 1. Use the nearest internal standard free of interferences.

If the base peak saturates the detector, document this in the data. Do not dilute a sample extract to get the base peak of a TIC within the detector range. If a sample extract containing a saturated TIC ion was diluted to get a target compound within calibration range, use the TIC base peak area from the diluted extract to estimate the concentration of the TIC.

8.3.5 QC Review

As soon as possible after analysis (typically prior to entry into LIMS), inspect sample and QC data for compliance with QC limits in Appendix C. If no significant

problems are found, perform the following QC reviews for compliance with SOP requirements:

- Check that target analyte results are within range of the initial calibration.
- Process and review the results for the CCV, QLS, and instrument QC samples. Print a ChemStation Evaluate Continuing Calibration Report using the appropriate settings to verify that the CCV, QLS, and instrument QC results are within QC limits. See Section 9.2 for instrument QC requirements.
- Process and review the results for the MB, LCS, and MS/MSD batch QC samples and verify that the results are within QC limits. See Section 9.3 for batch QC requirements.
- Determine if surrogate recoveries for field and QC samples are within QC limits. See Section 9.4 for Sample QC requirements.
- Review all sample results to determine if any samples need to be re-analyzed at a dilution.
- Review the chromatogram for possible false negatives.
- Manually cross out all compounds that do not meet qualitative criteria and document the reason on the quantitation report. Review the peak to see if the compound meets reporting the requirement of a TIC. If the compound is to be reported as a TIC, the false positive peak must be deleted (QDEL) in ChemStation.
- If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report. All notations must be initialed and dated by the analyst.

8.3.6 Sample Dilution

- The instrument blank solution may be used to make the necessary extract dilutions. As an example if 1:10 dilution is desired, add 900 µL of the instrument blank solution to 100 µL of the sample extract.
- For 1,4-dioxne, the minimum recommended dilution is 1:20 to minimize the effect of 1,4-dioxane-d8 added as a surrogate during the extraction process. Since 1,4-dioxane-d8 is used strictly as an internal standard in this case, do not report 1,4-dioxane-d8 as a surrogate from a diluted run.

8.3.7 Data Export and LIMS Entry

- Generate epatemp.txt files for field and QC samples by also printing the report to the screen; these files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table.
- Copy sample data files from the local drive to the appropriate instrument data subdirectory on the Region 9 LAN to make them available to LIMS and to archive them.
- Create an empty upload file containing the samples analyzed in the LIMS batch or sequence. Import and merge the data files using the LIMS DataTool module. Load the resulting merged data file into the LIMS Data Entry/Review table. See LIMS manual for detailed procedure.
- Edit dilutions in DataTool or LIMS entry table as needed.
- Review results in the LIMS. Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

8.4 Maintenance

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook.

The following sections describe possible causes and corrective actions for common problems for GC and MS operations. Refer to Appendix F for routine preventative maintenance procedures and schedule.

8.4.1 GC Maintenance

Symptoms of common problems:

- Carryover
Possible causes: Analyzing a sample containing high molecular weight components or analyzing high-level and low-level samples sequentially.
Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.
- Shorter retention time.
Possible cause: column flow rate problem.
Corrective action: check flow rate and adjust as necessary.

- Longer retention time and or smaller peaks.
Possible causes: column flow rate problem, injection port leak, or column contamination.
Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.
- Loss of resolution.
Possible causes: column flow rate problem, injection port leak, or column contamination.
Corrective action: Check for leaks, replace septum, liner, and inlet seal, clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

8.4.2 MS maintenance:

Trend to be observed:

- Low m/z 502 to 69 ratio
- DFTPP ion 275 ratio is outside acceptance range
- Failing tune checks

Resolution: Clean the source.

9 QUALITY CONTROL

9.1 Demonstration of Capability

The EPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability (DOC), and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

A DOC must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880 for more details.

9.2 Instrument QC

Acceptance criteria for QC parameters are listed in Appendix C of this document.

9.2.1 Mass calibration

Review the FC43 spectrum for compliance with the criteria list in Appendix C.

If the FC43 spectrum does not meet the criteria, corrective action must be taken. The corrective action may be as simple as adjusting the voltages/retuning the MS. If retuning the MS does not produce adequate FC43 spectra, further maintenance such as cleaning the ion source may be required.

9.2.2 GC/MS System Performance Check (DFTPP analysis)

Review the DFTPP spectrum for compliance with criteria in Appendix C.

Locate the degradation products of 4,4'-DDT (4,4'-DDD and 4,4'-DDE. Calculate the breakdown of DDT using peak areas of each quantitation ion (Qion) in the following equation:

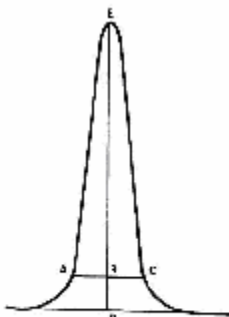
$$\% \text{ 4,4'-DDT Breakdown} = \frac{\text{Total Qion Area (DDE + DDD)}}{\text{Total Qion Area (DDE + DDD + DDT)}} \times 100$$

Where:

Qions of DDE: 246 Dalton, DDD: 235 Dalton, DDT: 235 Dalton

Benzidine and pentachlorophenol should be present at their normal responses, and should not exceed a tailing factor of 2 given by the following equation:

$$\text{TailingFactor} = \frac{BC}{AB}$$



Where the peak is defined as follows: AC is the width at 10% height; DE is the height of peak and DB is the height at 10% of DE. This equation compares the width

of the back half of the peak to the width of the front half of the peak at 10% of the height.

If the ion abundances, degradation, or tailing fail to meet the criteria, the DFTPP chromatogram should be examined for any obvious chromatographic problems (e.g., bad injection leading to poor response etc.). If the problem is related to poor chromatography, take the necessary corrective action and re-analyze the DFTPP. If the DFTPP continues to fail the ion abundance criteria, retune the mass spectrometer. It may also be necessary to clean the ion source or take other corrective action to achieve the ion abundance criteria.

If a sample is injected after the 12-hour time period has elapsed it must be re-analyzed.

9.2.3 Initial Calibration

Each GC/MS system must be calibrated whenever corrective action is performed which may change instrument response (e.g., ion source cleaning, column replacement, etc.) or if the continuing calibration acceptance criteria cannot be met.

Check the initial calibration for misidentified peaks due to retention time shifts. The most commonly misassigned pairs are benzo(a)anthracene/chrysene, phenanthrene/anthracene, and benzo(b)/benzo(k)fluoranthene.

No quantitation ion may saturate the detector.

The data system calculates the relative response factor (\overline{RRF}) for each target compound and surrogate compound using the following equation:

$$\overline{RRF} = (A_x)(C_{is}) / (A_{is})(C_x)$$

Where

- | | | |
|----------|---|---|
| A_x | = | Area of quantitation ion of compound x. The quantitation ions and internal standard assignments are listed in Appendix C. |
| A_{is} | = | Area of quantitation ion for associated internal standard |
| C_x | = | Concentration of compound x |
| C_{is} | = | Concentration of the associated internal standard |

The data system calculates the average RRF (RRF_{avg}) for all analytes and flags the analyte in the calibration summary when the average RRF is less than the minimum response factor criteria.

The data system calculates the percent relative standard deviation (%RSD) of the RRF values for each compound using the following equation.

$$\%RSD = (SD / RRF_{avg}) * 100$$

Where

$$SD = \sqrt{\frac{\sum_{i=1}^n (x_i - x_{ave})^2}{n - 1}}$$

%RSD, minimum response factors, and SCV recovery requirements are listed in Appendix C.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that the criteria are satisfied before any samples are analyzed.

If SCV criteria in Appendix C are not met, the SCV must be re-analyzed. If it fails again, prepare a fresh solution. If failure persists, take corrective action as needed, including reanalysis or re-preparation and reanalysis of the initial calibration if necessary.

9.2.4 Continuing Calibration Verification

Examine the areas of the quantitation ions of the internal standards in the calibration verification standard. If the area for any internal standard changes by more than 50% from the internal standard areas of the continuing calibration level of the most recent initial calibration, the CCV may be re-analyzed. If the failure is repeated, the analysis shall be terminated, the problem corrected, and a new calibration curve prepared.

Examine the retention times of internal standards in the calibration verification standard. If the retention time for any internal standard changes by more than 0.5 minutes compared to the continuing calibration level of the most recent initial calibration sequence, inspect the chromatographic system for malfunctions and take corrective action as needed and prepare a new calibration curve.

The data system calculates the percent deviation (%D) of the RRF values for each compound using the following equation:

$$\%D = \frac{RRF_c - RRF_{avg}}{RRF_{avg}} \times 100$$

Where:

RRF_c = Relative Response Factor of compound from CCV.
 RRF_{avg} = Average Relative Response Factor.

If the continuing calibration does not meet the %D criterion in Appendix C, the analysis shall be terminated, the problem corrected, and a new continuing calibration analyzed.

Qualify and flag results as needed in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

9.2.5 Quantitation Limit Standard

QLS must be analyzed at the beginning of the analytical run, typically just after the CCV. The QLS concentrations match the QL concentration (at the instrument). The recovery of analytes in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where

$\%R$ = percent recovery of the standard.
 M = measured concentration of the analyte, ug/L.
 T = true concentration of the analyte in the ug/L.

Generate a continuing calibration response report using the concentration option. Check that the recoveries meet the criteria specified in Appendix C.

If the QLS recovery does not meet criteria in Appendix C, rerun the QLS once to verify. If still unacceptable determine the cause and take corrective action as needed.

Qualify and flag results as needed in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

9.3 Batch QC

9.3.1 Method Blank

- Extract and analyze a method blank (MB) with each extraction batch or every

20 samples, whichever is more frequent, to demonstrate that the entire analytical system, from extraction through GC/MS analysis, is free of contamination.

- Evaluate the MB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.
- Corrective action - If the MB result exceeds QC limits, check the associated samples as follow:
 1. If the sample result is less than five times the MB result, re-analyze the MB. If the MB result still exceeds QC limits, the batch may have to be re-extracted. Consult with the Technical Director or designee.
 2. If the sample result is greater than five times the MB result or is not detected, report the sample result.
- If the surrogate recovery does not meet acceptance criteria, re-analyze the MB. If the surrogate recovery still does not meet acceptance criteria, evaluate surrogate recoveries in the LCS. If the surrogate meets criteria, flag the MB and explain the discrepancy in the LIMS MMO field. Otherwise, re-extract the batch.

9.3.2 Laboratory Control Sample

- Analyze a laboratory control sample (LCS) to demonstrate that the analytical system is in control. An LCS is extracted and analyzed once per extraction batch or every 20 samples, whichever is more frequent. The LCS is an MB spiked with matrix spiking solution.
- Calculate the percent recovery (%R) using the following equation:

$$\% R = \frac{M}{T} \times 100$$

Where

%R	=	percent recovery of the LCS.
M	=	measured concentration of the analyte, ug/L.
T	=	true concentration of the analyte in the ug/L.

- The %R must meet criteria in Appendix C. If acceptable recoveries cannot be achieved, re-analyze the LCS. If the LCS result still exceeds QC limits, re-extract the LCS and all associated samples.

9.3.3 Matrix Spike/Matrix Spike Duplicate

- Matrix spike (MS) and matrix spike duplicate (MSD) samples are extracted and analyzed with each SDG of twenty or fewer samples.

Calculate the percent recovery (%R) using the following equation:

$$\% R = [(SSR - SR)/SA] \times 100$$

Where,

SSR = Spiked sample result

SR = Unspiked sample result

SA = Spike added

- Calculate the relative percent differences (RPD) of the recoveries of each analyte in the MS and MSD using the following equation:

$$RPD = \frac{(MSC - MSDC)}{(MSC + MSDC) / 2} \times 100$$

Where,

MSC = Measured concentration of analyte in MS

MSDC = Measured concentration of analyte in MSD

- See Appendix C for QC limits.

The MS/MSD recovery limits are advisory limits only. If the limits are not met, no further action is required, as long as the LCS is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated.

- The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX			+ = PASS				- = FAIL		
CASE	1	2	3	4	5	6	7	8	
LCS - % REC	+	+	+	+	-	-	-	-	
MS/MSD -% REC	+	-	+	-	+	-	+	-	
MS/MSD - RPD	+	+	-	-	+	+	-	-	

Case 1: Extraction batch acceptable.
Case 2: Extraction batch acceptable; matrix effect confirmed.
Cases 3 & 4: Extraction batch is unsatisfactory. Investigate MS/MSD problem and document findings in the LIMS memo field.
Cases 5, 6, 7, & 8: Extraction batch rejected. If additional sample volume is available, the batch should be re-extracted.

9.4 Sample QC

9.4.1 Surrogate Recovery

Calculate the surrogate recovery in all field and QC samples immediately after analysis using the following formula:

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

Take the following steps if surrogate recovery is not within the limits:

1. Ensure that there are no calculation errors, and check the system performance.
2. Re-analyze the sample if a system performance problem or calculation error is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.

Do not reanalyze undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the LIMS MMO field.

If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis.

If the surrogate recoveries of the re-analysis are within limits, then the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. The problem must be documented in the LIMS MMO field.

- If the re-analysis does not solve the problem and additional sample volume is available, re-extract the failing samples.
- If sample re-extraction is unfeasible, or surrogate recoveries of the re-extraction are also outside the QC limits, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis

and the re-analysis by adding the "RE" suffix to the sample ID in the re-analysis. Document the problem in the LIMS MMO field.

9.4.2 Internal Standard Area:

Evaluate the internal standard areas in all field and QC samples immediately after analysis.

The internal standard areas must be within QC limits outlined in Appendix C.

1,4-Dioxane-d8 is spiked in the sample during the extraction process as a surrogate. Although the compound serves as an internal standard in calculating 1,4-dioxane concentration, it is exempt from meeting the recovery limits for internal standards since it undergoes the entire extraction process.

Take the following steps if the internal standard areas are not within the limits:

1. Check system performance.
2. Re-analyze the sample if a system performance problem is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.
3. If a system performance is identified, take corrective action and reanalyze the sample.

Do not reanalyze undiluted samples with internal standard areas outside the limits if the diluted analysis with acceptable internal standard areas is being submitted.

If the sample associated with the MS/MSD analyses does not meet internal standard area criteria, it should be re-analyzed only if the matrix spike and duplicate internal standard areas are within the limits. If the sample and spikes show the same pattern (i.e., outside limits), then the sample does not need re-analysis.

If the internal standard areas for the re-analysis are within limits, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding an "RE" suffix to the sample ID on the re-analysis. The problem must be documented in the LIMS MMO field.

9.5 Method Performance

Refer to the table in Appendix G for a summary of method performance in the Region 9 Laboratory by matrix.

Functional areas of the SOP that may be significant sources of analytical error are:

1. Addition of internal standard: The amount and concentration of internal standard

- added is critical. The nominal concentration is used in calculating target analyte concentration.
2. Samples must be stored as outlined in the SOP to minimize analyte degradation and solvent evaporation.
 3. Sample temperature: Sample extracts must be allowed to come up to room temperature prior to analysis. Failure to do so will cause heavy molecular weight analytes to precipitate thus reducing the observed concentration.
 4. Poor column condition may results in inadequate analyte separation and inaccurate integration.

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QL, MS/MSD, and LCS) are recorded in the Element database. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used in this SOP in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the Element database.

10.4 Analytical Report and Data Package

Analytical reports are produced using the Element database. The data package is produced from Element database and manual log records. Appendix H provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance.
- Subsequent instrument modifications and upgrades, including major software upgrades.
- All preventative or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840,
Notebook Documentation and Control.

10.6 SOP Read and Understood

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. The Lab QC Database is used to maintain the list of assigned analysts for each SOP. Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix I.

11 REFERENCES

Agilent 6890 Gas Chromatograph Users Manual

Agilent 7890 Gas Chromatograph Users Manual

Agilent 5973 MSD Hardware Manual

Agilent 5975 MSD Hardware Manual

Hewlett Packard/Agilent Environmental Analysis User's Guide

Hewlett Packard/Agilent EnviroQuant ChemStation User's Guide

Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry,
Revision 2.0, 1995

National Environmental Laboratory Accreditation Conference Standards, 2003

USEPA Method 525.2, Determination of Organic Compounds in Drinking Water by Liquid-Solid extraction and Capillary Column Gas Chromatography/Mass Spectrometry,
Revision 2, 1995.

USEPA Method 8000C, Determinative Chromatographic Separations, Revision 3, March 2003.

USEPA Method 8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, February 2006.

USEPA Region 9 Laboratory. *Business Plan.*

USEPA Region 9 Laboratory. *Chemical Hygiene Plan.*

USEPA Region 9 Laboratory. *Environmental Management System.*

USEPA Region 9 Laboratory SOP 125 *Disposal Procedures for Unused Aqueous Environmental Samples*

USEPA Region 9 SOP 239 *Procedures for Recycling used Dichloromethane.*

USEPA Region 9 Laboratory SOP 260, *Gel-Permeation Chromatography (GPC) Clean Up.*

USEPA Region 9 Laboratory SOP 275, *Extraction of Water Samples by Liquid-Liquid Extraction.*

USEPA Region 9 Laboratory SOP 290, *Extraction of Soil Samples Using Pressurized Fluid Extraction*

USEPA Region 9 Laboratory SOP 706, *Laboratory Waste Management Procedure.*

USEPA Region 9 Laboratory SOP 805 *Temperature Monitoring*

USEPA Region 9 Laboratory SOP 820, *Laboratory Discrepancy and Corrective Action Reporting Procedures*

USEPA Region 9 Laboratory SOP 835 *Chromatographic Integration Procedures*

USEPA Region 9 Laboratory SOP 840 *Notebook Documentation and Control*

USEPA Region 9 Laboratory SOP 880 *Demonstration of Capability*

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. SW-846 method 3500B referenced by method 8270D specifies a concentration of 200 mg/L for the acid matrix spiking solution; this SOP specifies 100 mg/L.
2. Mass spectra used for target analytes are from the NIST library. The SOP requires that all compounds be included in the calibration standards and thus comparison to spectra generated on the GCMS system where samples are analyzed is possible. However, in order to avoid extraneous peaks due to co-eluting compounds in the standard mixes, it is laboratory practice to use NIST spectra for identification purposes.
3. QC acceptance criteria for LCS, MS/MSD, and surrogates for analysis of water samples are derived from Region 9 Laboratory performance data as specified in the reference method. Insufficient data are currently available to calculate QC limits for solid analyses; default limits of 70 to 130% recovery and 20 %RSD will be used until sufficient data for solids are available.
4. Relative Retention Time (RRT) of chromatographic peak is not evaluated in this SOP as documented in the reference method. ChemStation calculates a retention time window and does not calculate RRT window. The retention time window of ± 0.2 min is more stringent than the ± 0.06 RRT units in the reference method.
5. Phenol-d5 is used as a surrogate instead of phenol-d6 as specified in the reference method.
6. 1,4-Dioxane and carbazole are included as target analytes and 1,4-dioxane-d8 is an added surrogate. 1,4-Dioxane and carbazole are not included in the reference method.
7. This procedure uses a scan range of 41-550 AMU. The reference method specifies a scan range of 35-500 AMU.
8. Chemstation software monitors the average response factor, not each calibration level as required by the method. The EPA Region 9 Laboratory analyzes a QL standard daily to verify the reporting limit.

APPENDIX B. ANALYTES AND QUANTITATION LIMITS

The following list provides quantitation limits for the semivolatile organic compound target list with associated surrogate compounds.

Compound	CAS Number	Water QL, ug/L	Soil QL, ug/kg	On Column, ng
1,4-Dioxane	123-91-1	1.0	33	1.0
Phenol	108-95-2	5.0	170	5.0
Bis (2-chloroethyl) ether	111-44-4	1.0	33	1.0
2-Chlorophenol	95-57-8	5.0	170	5.0
1,3-Dichlorobenzene	541-73-1	1.0	33	1.0
1,4-Dichlorobenzene	106-46-7	1.0	33	1.0
Benzyl alcohol	100-51-6	5.0	170	5.0
1,2-Dichlorobenzene	95-50-1	1.0	33	1.0
2-Methylphenol	95-48-7	5.0	170	5.0
Bis(2-chloro-1-methylethyl) ether	108-60-1	1.0	33	1.0
3&4-Methylphenol	106-44-5	5.0	170	5.0
N-Nitrosodipropylamine	621-64-7	1.0	33	1.0
Hexachloroethane	67-72-1	1.0	33	1.0
Nitrobenzene	98-95-3	1.0	33	1.0
Isophorone	78-59-1	1.0	33	1.0
2-Nitrophenol	88-75-5	5.0	170	5.0
2,4-Dimethylphenol	105-67-9	5.0	170	5.0
Bis(2-chloroethoxy)methane	111-91-1	1.0	33	1.0
2,4-Dichlorophenol	120-83-2	5.0	170	5.0
1,2,4-Trichlorobenzene	120-82-1	1.0	33	1.0
Naphthalene	91-20-3	1.0	33	1.0
4-Chloroaniline	106-47-8	5.0	170	5.0
Hexachlorobutadiene	87-68-3	1.0	33	1.0
4-Chloro-3-methylphenol	59-50-7	5.0	170	5.0
2-Methylnaphthalene	91-57-6	1.0	33	1.0
Hexachlorocyclopentadiene	77-47-4	5.0	170	1.0

Compound	CAS Number	Water QL, ug/L	Soil QL, ug/kg	On Column, ng
2,4,6-Trichlorophenol	88-06-2	5.0	170	5.0
2,4,5-Trichlorophenol	95-95-4	5.0	170	5.0
2-Chloronaphthalene	91-58-7	1.0	33	1.0
2-Nitroaniline	88-74-4	5.0	170	5.0
Dimethyl phthalate	131-11-3	1.0	33	1.0
Acenaphthylene	208-96-8	1.0	33	1.0
2,6-Dinitrotoluene	606-20-2	1.0	33	1.0
3-Nitroaniline	99-09-2	5.0	170	5.0
Acenaphthene	83-32-9	1.0	33	1.0
2,4-Dinitrophenol	51-28-5	5.0	170	5.0
4-Nitrophenol	100-02-7	5.0	170	5.0
Dibenzofuran	132-64-9	1.0	33	1.0
2,4-Dinitrotoluene	121-14-2	1.0	33	1.0
Diethyl phthalate	84-66-2	1.0	33	1.0
Fluorene	86-73-7	1.0	33	1.0
4-Chlorophenyl phenyl ether	7005-72-3	1.0	33	1.0
4-Nitroaniline	100-01-6	5.0	170	5.0
4,6-Dinitro-2-methyphenol	534-52-1	5.0	170	5.0
Diphenylamine	122-39-4	1.0	33	1.0
4-Bromophenyl phenyl ether	101-55-3	1.0	33	1.0
Hexachlorobenzene	118-74-1	1.0	33	1.0
Pentachlorophenol	87-86-5	5.0	170	5.0
Phenanthrene	85-01-8	1.0	33	1.0
Anthracene	120-12-7	1.0	33	1.0
Carbazole	86-74-8	1.0	33	1.0
Di-n-butyl phthalate	84-74-2	1.0	33	1.0
Fluoranthene	206-44-0	1.0	33	1.0
Pyrene	129-00-0	1.0	33	1.0
Butyl benzyl phthalate	85-68-7	1.0	33	1.0
Benzo(a)anthracene	56-55-3	1.0	33	1.0
3,3'-Dichlorobenzidine	91-94-1	1.0	33	1.0

Compound	CAS Number	Water QL, ug/L	Soil QL, ug/kg	On Column, ng
Chrysene	218-01-9	1.0	33	1.0
Bis(2-ethylhexyl)phthalate	117-81-7	1.0	33	1.0
Di-n-octyl phthalate	117-84-0	1.0	33	1.0
Benzo(b)fluoranthene	205-99-2	1.0	33	1.0
Benzo(k)fluoranthene	207-08-9	1.0	33	1.0
Benzo(a)pyrene	50-32-8	1.0	33	1.0
Indeno(1,2,3-cd)pyrene	193-39-5	1.0	33	1.0
Dibenzo(a,h)anthracene	53-70-3	1.0	33	1.0
Benzo(g,h,i)perylene	191-24-2	1.0	33	1.0
<u>Surrogates</u>				
Phenol-d5	4165-62-2			
2-Fluorophenol	367-12-4			
2,4,6-Tribromophenol	118-79-6			
Nitrobenzene-d5	4165-60-0			
2-Fluorobiphenyl	321-60-8			
Terphenyl-d14	1718-51-0			
2-Chlorophenol-d4	NA			
1, 2-Dichlorobenzene-d4	2199-69-1			
1,4-Dioxane-d8	17647-74-4			

APPENDIX C.
QUALITY CONTROL PARAMETERS AND CRITERIA

ANALYSIS	SUMMARY	Frequency																										
MS Calibration	<table><tr><th>Mass</th><th>Target % of Mass 69</th></tr><tr><td>50</td><td>0.3-5</td></tr><tr><td>69</td><td>100</td></tr><tr><td>131</td><td>20-120</td></tr><tr><td>219</td><td>20-120</td></tr><tr><td>414</td><td>0.3-10</td></tr><tr><td>502</td><td>0.3-10</td></tr></table>	Mass	Target % of Mass 69	50	0.3-5	69	100	131	20-120	219	20-120	414	0.3-10	502	0.3-10	With Every ICAL												
Mass	Target % of Mass 69																											
50	0.3-5																											
69	100																											
131	20-120																											
219	20-120																											
414	0.3-10																											
502	0.3-10																											
MS Mass Axis	Calibrate the Mass Axis of the MS prior to analyzing the DFTPP standard. Adjust the EM voltage as necessary.	Each day that samples are analyzed																										
GC/MS System Performance Check (DFTPP analysis)	<p>The ion abundance ratios must meet the following criteria.</p> <table><tr><th>Mass (m/z)</th><th>Relative Ion Abundance Criteria</th></tr><tr><td>51</td><td>30 – 60% of 198</td></tr><tr><td>68</td><td>Less than 2% of mass 69</td></tr><tr><td>70</td><td>Less than 2% of mass 69</td></tr><tr><td>127</td><td>40 –60% of 198</td></tr><tr><td>197</td><td>Less than 1% of mass 198</td></tr><tr><td>198</td><td>Base peak (100% relative abundance)</td></tr><tr><td>199</td><td>5 - 9% of mass 198</td></tr><tr><td>275</td><td>10 - 30% of 198</td></tr><tr><td>365</td><td>Greater than 1% of 198</td></tr><tr><td>441</td><td>Present but less than mass 443</td></tr><tr><td>442</td><td>Greater than 50% of mass 198</td></tr><tr><td>443</td><td>17 - 23% of mass 442</td></tr></table> <p>Benzidine and pentachlorophenol responses should be at their expected levels in the DFTPP solution and the peak-tailing factor must be less than 2.</p> <p>Breakdown of DDT is less than 20%.</p>	Mass (m/z)	Relative Ion Abundance Criteria	51	30 – 60% of 198	68	Less than 2% of mass 69	70	Less than 2% of mass 69	127	40 –60% of 198	197	Less than 1% of mass 198	198	Base peak (100% relative abundance)	199	5 - 9% of mass 198	275	10 - 30% of 198	365	Greater than 1% of 198	441	Present but less than mass 443	442	Greater than 50% of mass 198	443	17 - 23% of mass 442	Once every 12-hours
Mass (m/z)	Relative Ion Abundance Criteria																											
51	30 – 60% of 198																											
68	Less than 2% of mass 69																											
70	Less than 2% of mass 69																											
127	40 –60% of 198																											
197	Less than 1% of mass 198																											
198	Base peak (100% relative abundance)																											
199	5 - 9% of mass 198																											
275	10 - 30% of 198																											
365	Greater than 1% of 198																											
441	Present but less than mass 443																											
442	Greater than 50% of mass 198																											
443	17 - 23% of mass 442																											
Initial Calibration	<p>90% of reported analytes should meet the maximum %RSD of 20. If one or more analytes exceed the RSD limit, the initial calibration may still be acceptable if the following conditions are met:</p> <p style="padding-left: 40px;">The %RSD of the reported analytes that exceed the limit is ≤30.</p> <p style="padding-left: 40px;">The average RRF must meet the minimum response factor criteria listed in the table below.</p>	As Needed																										
Second Source Calibration	<p>Recovery for 90% of reported analytes must be within 70-130%. Data must be flagged as failing initial calibration criteria for analytes not within the acceptance limits.</p>	With Every ICAL																										

Verification		
Continuing Instrument Calibration Verification	<p>The absolute value of the %D of all reported analytes should be \leq 20%. If one or more reported analytes exceed the %D limit, the calibration verification may still be acceptable if the following conditions are met:</p> <p style="padding-left: 40px;">90% of reported analytes meet the criteria</p> <p style="padding-left: 40px;">The absolute value of the %D of the reported analytes that exceed the limit is \leq 30%.</p> <p>The CCV standard must meet the minimum response factor criteria listed in the table below.</p> <p>Internal standard retention time should be within 30 seconds from that in the mid-point standard level of the most recent initial calibration.</p> <p>EICP area for any of the internal standards should be within (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence.</p>	Once every 12-hours
Quantitation Limit Verification	The percent recovery for 90% of the reported analytes should be between 60 to 140 percent of the actual concentration.	Once every 12-hours
Method Blank (MB)	The MB is acceptable if it contains less than one-half the quantitation limit (QL) of all target compounds.	One per extraction batch
Target Analytes	<p>All ions present in the standard or reference mass spectrum at a relative intensity of 20 % of the most abundant ion should be present in the sample spectrum.</p> <p>The relative intensities of the ions in the sample mass spectrum should agree within 30% of the relative intensities of those ions in the standard mass spectrum. For example, an ion with an abundance of 50% in the standard spectrum can have abundance between 20% and 80% in the sample spectrum.</p>	NA
Internal Standards (covering reported analytes)	<p>Compare the IS retention times and areas in the CCV standard to the mid-point standard of the most recent initial calibration. The retention time for any internal standard should be within 0.5 minute and the total area of internal standard should be recovered within -50% to +100% from the mid-point standard of the most recent initial calibration.</p> <p>Compare the IS retention times and areas in the field and QC samples analyzed within the 12-hour analytical period to the associated 12-hour CCV standard. The retention time for any internal standard should be within 0.5 minute and the total area of internal standard should be recovered within -50% to +100% from the associated 12-hour CCV standard.</p> <p>1,4-Dioxane-d8 is exempt from meeting internal standard criteria.</p>	NA
LCS	90% of reported analytes should meet the acceptance criteria or the	One per

	batch may require re-extraction. Refer to the tables below for control limits.	extraction batch
MS/MSD	Refer to the tables below for control limits. Flag outliers.	One per extraction batch

Quantitation Ions, Surrogates, Internal Standards, and Minimum Response Factors

Compound	Primary Quant. Ion	Secondary Ion(s)	Int. Std	Surrogate	Min. Response Factor
1,2,4-Trichlorobenzene	180	182, 145	2	4	0.01
1,2-Dichlorobenzene	146	148, 111	1	8	0.01
1,3-Dichlorobenzene	146	148, 111	1	8	0.01
1,4-Dichlorobenzene	146	148, 111	1	1	0.01
1,4-Dioxane	64	96	7	9	0.01
2,4,5-Trichlorophenol	196	198, 97, 132, 99	3	7	0.2
2,4,6-Trichlorophenol	196	198, 200	3	7	0.2
2,4-Dichlorophenol	162	164, 98	2	7	0.2
2,4-Dimethylphenol	122	107, 121	2	1	0.2
2,4-Dinitrophenol	184	63, 154	3	3	0.01
2,4-Dinitrotoluene	165	63, 89	3	5	0.2
2,6-Dinitrotoluene	165	63, 89	3	5	0.2
2-Chloronaphthalene	162	127, 164	3	5	0.8
2-Chlorophenol	128	64, 130	1	8	0.8
2-Methylnaphthalene	142	141	2	5	0.4
2-Methylphenol	107	108, 77, 79, 90	1	1	0.7
2-Nitroaniline	65	92, 138	3	5	0.01
2-Nitrophenol	139	109, 65	2	7	0.1
3&4-Methylphenol	107	108, 77, 79, 90	1	1	0.6
3,3'-Dichlorobenzidine	252	254, 126	5	6	0.01
3-Nitroaniline	138	108, 92	3	5	0.01
4,6-Dinitro-2-methylphenol	198	51, 105	4	3	0.01
4-Bromophenyl phenyl ether	248	250, 141	4	6	0.1
4-Chloro-3-methylphenol	107	144, 142	2	7	0.2
4-Chloroaniline	127	129, 65, 92	2	4	0.01

Compound	Primary Quant. Ion	Secondary Ion(s)	Int. Std	Surrogate	Min. Response Factor
4-Chlorophenyl phenyl ether	204	206, 141	3	5	0.4
4-Nitroaniline	138	65, 108, 92, 80, 39	3	6	0.01
4-Nitrophenol	139	109, 65	3	3	0.01
Acenaphthene	154	155, 152	3	5	0.9
Acenaphthylene	152	151, 153	3	5	0.9
Anthracene	178	176, 179	4	6	0.7
Benzo(a)anthracene	228	229, 226	5	6	0.8
Benzo(a)pyrene	252	253, 125	6	6	0.7
Benzo(b)fluoranthene	252	253, 125	6	6	0.7
Benzo(g,h,i)perylene	276	138, 277	6	6	0.5
Benzo(k)fluoranthene	252	253, 125	6	6	0.7
Benzyl alcohol	108	79, 77	1	8	0.01
Bis (2-chloroethyl) ether	93	63, 95	1	8	0.7
Bis(2-chloro-1-methylethyl) ether	45	77, 121	1	4	0.01
Bis(2-chloroethoxy)methane	93	95, 123	2	4	0.3
Bis(2-ethylhexyl)phthalate	149	167, 279	5	6	0.01
Butyl benzyl phthalate	149	91, 206	5	6	0.01
Carbazole	167	166, 139	4	6	0.01
Chrysene	228	226, 229	5	6	0.7
Dibenz(a,h)anthracene	278	139, 279	6	6	0.4
Dibenzofuran	168	139	3	5	0.8
Diethyl phthalate	149	177, 150	3	5	0.01
Dimethyl phthalate	163	194, 164	3	5	0.01
Di-n-butyl phthalate	149	150, 104	4	6	0.01
Di-n-octyl phthalate	149	167, 43	6	6	0.01
Diphenylamine	169	168, 167	4	6	0.01
Fluoranthene	202	101, 203	4	6	0.6
Fluorene	166	165, 167	3	5	0.9
Hexachlorobenzene	284	142, 249	4	6	0.1
Hexachlorobutadiene	225	223, 227	2	5	0.01
Hexachlorocyclopentadiene	237	235, 272	3	5	0.05

Compound	Primary Quant. Ion	Secondary Ion(s)	Int. Std	Surrogate	Min. Response Factor
Hexachloroethane	117	201, 199	1	8	0.3
Indeno(1,2,3-cd)pyrene	276	138, 227	6	6	0.5
Isophorone	82	95, 138	2	4	0.4
Naphthalene	128	129, 127	2	5	0.7
Nitrobenzene	77	123, 65	2	4	0.2
N-Nitrosodipropylamine	70	42, 101, 130	1	4	0.5
Pentachlorophenol	266	264, 268	4	3	0.05
Phenanthrene	178	179, 176	4	6	0.7
Phenol	94	65, 66	1	1	0.8
Pyrene	202	200, 203	5	6	0.6
<u>Surrogates</u>					
1, 2-Dichlorobenzene-d4	152	115, 150	1	8	
1,4-Dioxane-d8	96	64	1	9	
2,4,6-Tribromophenol	330	332, 141	3	3	
2-Chlorophenol-d4	132	68, 134	1	7	
2-Fluorobiphenyl	172	171	3	5	
2-Fluorophenol	112	64	1	2	
Nitrobenzene-d5	82	128, 54	2	4	
Phenol-d5	99	42, 71	1	1	
Terphenyl-d14	244	122, 212	5	6	
<u>Internal Standards</u>					
1,4-Dichlorobenzene-d4	152	150, 115	1		
1,4-Dioxane-d8	96	64	7		
Acenaphthene-d10	164	162, 160	3		
Chrysene-d12	240	120, 236	5		
Naphthalene-d8	136	68	2		
Perylene-d12	264	260, 265	6		
Phenanthrene-d10	188	94, 80	4		

Water LCS and MS/MSD QC Criteria:

Water LCS and MS/MSD criteria are based on results obtained from April 2007 to March 2009. Minimum recovery criteria of 20% will be used for LCS and MS/MSD.

Analyte	LCS		Matrix Spike		RPD
	Lower	Upper	Lower	Upper	
1,2,4-Trichlorobenzene	35	110	34	110	20
1,2-Dichlorobenzene	31	110	31	110	20
1,3-Dichlorobenzene	30	110	27	110	20
1,4-Dichlorobenzene	31	110	29	110	20
1,4-Dioxane	64	144	71	131	20
1-Methylnaphthalene	45	104	47	110	20
2,3,4,6-Tetrachlorophenol	70	130	70	130	20
2,4,5-Trichlorophenol	49	112	63	123	20
2,4,6-Trichlorophenol	50	110	51	111	20
2,4-Dichlorophenol	49	110	48	110	20
2,4-Dimethylphenol	26	122	40	110	20
2,4-Dinitrophenol	20	174	69	129	20
2,4-Dinitrotoluene	55	122	63	123	20
2,6-Dinitrotoluene	57	119	62	122	20
2-Chloronaphthalene	42	110	48	110	20
2-Chlorophenol	42	110	42	110	20
2-Methylnaphthalene	41	110	44	110	20
2-Methylphenol	48	110	42	110	20
2-Nitroaniline	47	119	45	110	20
2-Nitrophenol	49	110	46	110	20
3&4-Chlorophenol	70	130	70	130	20
3&4-Methylphenol	61	114	54	114	20
3,4,5-Trichlorophenol	70	130	70	130	20
3,4-Dichlorophenol	70	130	70	130	20
3,5-Dichlorophenol	70	130	70	130	20
3-Nitroaniline	20	194	47	110	20
4,6-Dinitro-2-methylphenol	31	158	65	125	20
4-Bromophenyl phenyl ether	53	124	63	123	20
4-Chloro-3-methylphenol	49	110	51	111	20
4-Chloroaniline	50	176	50	110	20
4-Chlorophenyl phenyl ether	49	110	54	114	20
4-Nitroaniline	20	146	42	110	20
4-Nitrophenol	47	133	60	120	20
Acenaphthene	52	139	71	131	20
Acenaphthylene	42	110	43	110	20
Anthracene	56	127	58	118	20
Benzo(a)anthracene	61	126	65	125	20
Benzo(a)pyrene	41	110	43	110	20
Benzo(b)fluoranthene	51	128	64	124	20
Benzo(g,h,i)perylene	32	123	50	110	20
Benzo(k)fluoranthene	51	123	62	122	20
Benzyl alcohol	40	112	55	115	20
Bis(2-chloro-1-methylethyl) ether	26	150	61	121	20
Bis(2-chloroethoxy)methane	50	110	50	110	20

Analyte	LCS		Matrix Spike		RPD
	Lower	Upper	Lower	Upper	
Bis(2-chloroethyl)ether	42	110	48	110	20
Bis(2-ethylhexyl) phthalate	62	160	82	142	20
Butyl benzyl phthalate	59	152	81	141	20
Carbazole	20	157	59	119	20
Chrysene	62	128	65	125	20
Dibenz(a,h)anthracene	42	122	57	117	20
Dibenzofuran	46	112	54	114	20
Diethyl phthalate	50	131	65	125	20
Dimethyl phthalate	57	118	61	121	20
Di-n-butyl phthalate	55	153	74	134	20
Di-n-octyl phthalate	48	166	85	145	20
Diphenyl amine	37	110	32	110	20
Fluoranthene	55	141	69	129	20
Fluorene	52	117	60	120	20
Hexachlorobenzene	54	120	62	122	20
Hexachlorobutadiene	26	110	24	110	20
Hexachlorocyclopentadiene	20	110	20	110	20
Hexachloroethane	24	110	24	110	20
Indeno(1,2,3-cd)pyrene	41	111	51	111	20
Isophorone	40	110	45	110	20
Naphthalene	44	110	46	110	20
Nitrobenzene	49	111	58	118	20
N-Nitrosodi-n-butylamine	70	130	70	130	20
N-Nitrosodipropylamine	45	110	50	110	20
Pentachlorophenol	41	136	71	131	20
Phenanthrene	56	134	70	130	20
Phenol	42	110	42	110	20
Pyrene	55	141	70	130	20
3,3'-Dichlorobenzidine	20	167	49	110	20

Water Surrogate Recovery

Water surrogate criteria are based on sample results obtained from April 2007 to March 2009.

Water Surrogate	Lower Percent	Upper Percent
1,2-Dichlorobenzene-d4	20	123
1,4-Dioxane-d8	20	185
2,4,6-Tribromophenol	20	159
2-Chlorophenol-d4	25	120
2-Fluorobiphenyl	26	127
2-Fluorophenol	27	115
Nitrobenzene-d5	20	144
Phenol-d5	20	129
Terphenyl-d14	21	158

Soil LCS and MS/MSD QC Criteria:

Soil LCS and MS/MSD criteria are the EPA Region 9 Laboratory default limits because too few data points are available from April 2007 to March 2009 to establish historical limits. For all analytes, the LCS and MS recovery limits are 70 to 130 percent and the limit is 20 percent.

Soil Surrogate recovery

Soil surrogate criteria are based on sample results obtained from April 2007 to March 2009.

Surrogate	Lower Percent	Upper Percent
1,2-Dichlorobenzene-d4	20	110
1,4-Dioxane-d8	20	110
2,4,6-Tribromophenol	20	144
2-Chlorophenol-d4	20	111
2-Fluorobiphenyl	31	110
2-Fluorophenol	20	118
Nitrobenzene-d5	20	131
Phenol-d5	20	117
Terphenyl-d14	20	125

APPENDIX D.
RECOMMENDED INSTRUMENT PARAMETERS

BNA Method

TOPLEVEL PARAMETERS

Method Information For: C:\MSDCHEM\1\METHODS\BNL50309.M

Method Sections To Run:

() Save Copy of Method With Data
() MSTOP Pre-Run Cmd/Macro =
() Instrument Control Pre-Run Cmd/Macro =
() Data Analysis Pre-Run Cmd/Macro =
(X) Data Acquisition
(X) Data Analysis
() MSTOP Post-Run Cmd/Macro =
() Instrument Control Post-Run Cmd/Macro =
() Data Analysis Post-Run Cmd/Macro =

Method Comments:

DFTPP

END OF TOPLEVEL PARAMETERS

INSTRUMENT CONTROL PARAMETERS

=====

6890 GC METHOD

=====

OVEN

Initial temp:	35 'C (On)	Maximum temp:	330 'C
Initial time:	1.50 min	Equilibration time:	0.50 min

Ramps:

#	Rate	Final temp	Final time
1	30.00	130	0.00
2	25.00	270	0.00
3	5.00	320	2.00
4	0.0(Off)		

Post temp: 0 'C
Post time: 0.00 min
Run time: 22.27 min

FRONT INLET (SPLIT/SPLITLESS)

BACK INLET (UNKNOWN)

Mode: Pulsed Splitless

Initial temp: 280 'C (On)

Pressure: 4.06 psi (On)
Pulse pressure: 60.0 psi
Pulse time: 0.60 min
Purge flow: 20.0 mL/min
Purge time: 0.40 min
Total flow: 23.8 mL/min
Gas saver: On
Saver flow: 20.0 mL/min
Saver time: 3.00 min
Gas type: Helium

COLUMN 1

Capillary Column
Model Number: Restek 12794
RTX-625MS
Max temperature: 330 'C
Nominal length: 30.0 m
Nominal diameter: 280.00 um
Nominal film thickness: 0.50 um
Mode: constant flow
Initial flow: 1.2 mL/min
Nominal init pressure: 4.07 psi
Average velocity: 40 cm/sec
Inlet: Front Inlet
Outlet: MSD

Outlet pressure: vacuum

COLUMN 2

(not installed)

FRONT DETECTOR ()

SIGNAL 1

Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

BACK DETECTOR ()

SIGNAL 2

Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1

(No Detectors Installed)

COLUMN COMP 2

(No Detectors Installed)

THERMAL AUX 2

Use: MSD Transfer Line Heater
Description:
Initial temp: 280 'C (On)
Initial time: 0.00 min
Rate Final temp Final time
1 0.0(Off)

POST RUN

Post Time: 0.00 min

TIME TABLE

Time Specifier

Parameter & Setpoint

7673 Injector

Front Injector:

Sample Washes	0
Sample Pumps	3
Injection Volume	1.0 microliters
Syringe Size	10.0 microliters
PostInj Solvent A Washes	5
PostInj Solvent B Washes	5
Viscosity Delay	0 seconds
Plunger Speed	Fast
PreInjection Dwell	0.00 minutes
PostInjection Dwell	0.00 minutes

Back Injector:

No parameters specified

Column 1 Inventory Number :

Column 2 Inventory Number :

MS ACQUISITION PARAMETERS

General Information

Tune File : DFL50309.U

Acquisition Mode : Scan

MS Information

--

Solvent Delay : 2.30 min

EM Absolute : False

EM Offset : 0

[Scan Parameters]

Low Mass : 41.0

High Mass : 550.0

Threshold : 120

Sample # : 2 A/D Samples 4

Plot 2 low mass : 50.0

Plot 2 high mass : 550.0

[MSZones]

MS Quad : 150 C maximum 200 C

MS Source : 230 C maximum 250 C

END OF MS ACQUISITION PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

DFTPP Method

TOPLEVEL PARAMETERS

Method Information For: C:\MSDCHEM\1\METHODS\DFL50309.M

Method Sections To Run:

```
( ) Save Copy of Method With Data
( ) MSTOP                      Pre-Run Cmd/Macro  =
( ) Instrument Control         Pre-Run Cmd/Macro  =
( ) Data Analysis              Pre-Run Cmd/Macro  =
(X) Data Acquisition
(X) Data Analysis
( ) MSTOP                      Post-Run Cmd/Macro =
( ) Instrument Control         Post-Run Cmd/Macro =
( ) Data Analysis              Post-Run Cmd/Macro =
```

Method Comments:

DFTPP

END OF TOPLEVEL PARAMETERS

INSTRUMENT CONTROL PARAMETERS

===== 6890 GC METHOD =====

OVEN

```
Initial temp: 100 'C (On)           Maximum temp: 330 'C
Initial time: 0.00 min              Equilibration time: 0.50 min
Ramps:
# Rate Final temp Final time
1 30.00      310      3.00
2  0.0(Off)
Post temp: 0 'C
Post time: 0.00 min
Run time: 10.00 min
```

FRONT INLET (SPLIT/SPLITLESS)

```
Mode: Pulsed Splitless
Initial temp: 280 'C (On)
Pressure: 7.38 psi (On)
Pulse pressure: 60.0 psi
Pulse time: 0.60 min
```

BACK INLET (UNKNOWN)

USEPA Region 9 Laboratory

Semivolatile Organic Compound Analysis

Purge flow: 20.0 mL/min
Purge time: 0.40 min
Total flow: 23.8 mL/min
Gas saver: On
Saver flow: 20.0 mL/min
Saver time: 2.00 min
Gas type: Helium

COLUMN 1

Capillary Column
Model Number: Restek 12794
RTX-625MS
Max temperature: 330 'C
Nominal length: 30.0 m
Nominal diameter: 280.00 um
Nominal film thickness: 0.50 um
Mode: constant flow
Initial flow: 1.2 mL/min
Nominal init pressure: 7.39 psi
Average velocity: 41 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

COLUMN 2

(not installed)

FRONT DETECTOR ()

SIGNAL 1

Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

BACK DETECTOR ()

SIGNAL 2

Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1

(No Detectors Installed)

COLUMN COMP 2

(No Detectors Installed)

THERMAL AUX 2

Use: MSD Transfer Line Heater
Description:
Initial temp: 280 'C (On)
Initial time: 0.00 min
Rate Final temp Final time
1 0.0(Off)

POST RUN

Post Time: 0.00 min

TIME TABLE

Time Specifier

Parameter & Setpoint

7673 Injector

Front Injector:
Sample Washes

0

Sample Pumps	3
Injection Volume	1.0 microliters
Syringe Size	10.0 microliters
PostInj Solvent A Washes	3
PostInj Solvent B Washes	3
Viscosity Delay	0 seconds
Plunger Speed	Fast
PreInjection Dwell	0.00 minutes
PostInjection Dwell	0.00 minutes

Back Injector:
No parameters specified

Column 1 Inventory Number :
Column 2 Inventory Number :

MS ACQUISITION PARAMETERS

General Information

Tune File : DFL50309.U
Acquisition Mode : Scan

MS Information

--

Solvent Delay : 4.00 min

EM Absolute : False
EM Offset : 0

[Scan Parameters]

Low Mass	: 35.0	
High Mass	: 550.0	
Threshold	: 150	
Sample #	: 2	A/D Samples 4
Plot 2 low mass	: 50.0	
Plot 2 high mass	: 550.0	

[MSZones]

MS Quad	: 150 C	maximum 200 C
MS Source	: 230 C	maximum 250 C

END OF MS ACQUISITION PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

APPENDIX E. CHEMSTATION FILE NAMING CONVENTIONS

ChemStation File Naming Convention

File data, methods, and sequences on ChemStation computers and the LAN using the following naming conventions:

Directories

On the Workstation:

Data: C:\HPCHEM\1\Data\MDDY or D:\HPCHEM\1\Data\MDDYS

Methods: C:\HPCHEM\1\Methods or D:\HPCHEM\1\Methods

Sequences: C:\HPCHEM\1\Sequence or D:\HPCHEM\1\Sequence

For system controlling multiple instruments, 1 may be changed to reflect the instrument number

System running ChemStation versions C & D HPCHEM is named as MSDCHEM

On the LAN:

Data: I:\Room Number\Instrument\Year\MDDYS

Methods: I:\Room Number\Instrument\Methods

Sequences: I:\Room Number\Instrument\Sequence

Methods

MDDYITA

Sequence

MDDYS

Data Files

For GC:

MDDYICSS

For GC/MS

MDDYIQSS

Variables

A: Enter analysis, as follow:

1,4-Dioxane X

504 E

TO15 A

BNA B

BNA-L (SIM) L

Congeners C

P/P P

PCB P

RSK175 R

Soil Gas	A
TPH-G	G
TPH-D	D
VOA	V

C: Channel: A = front
B = back (if applicable)

DD: Day

I: Instrument
6890 series GCs by last number in name: e.g. 6890-1 = 1 except 5890-2 = A
All GC/MSs by last letter in name: e.g. 5973L = L

M: Month 1-9, A: October, B: November, C: December

Q: QC type

BFB	F
Blank	B
CV	C
Degradation	P
DFTPP	D
IB	Z
IC	I
LCS	L
LCV	Q
Second Source	S
MS/MSD	M

S: Sequential number 1,2 3,

T: Matrix Type (if applicable)
Water W
Solid S
Air A
Oil O
Other X

Y: Year i.e. 5 for 2005

APPENDIX F. PREVENTATIVE MAINTENANCE REQUIREMENTS

GC Maintenance

Item	Frequency	Actions/Comments
Gas purifiers (carrier gas & detector gas)	Annually	Replacement schedule is based on capacity and grade of gases. In general, replace non-indicating traps every 6-12 months or when indicating traps start to change color. Replace indicating traps when indicating material is spent.
Split vent trap	Annually	Replace.
Flow meter calibration	2 years	Manual flow meters only.
Syringes and/or syringe needles	As Needed	Replace syringe if dirt is noticeable in the syringe, if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged. Replace needle if septa wear is abnormal or the needle becomes clogged.
Inlet liner	With each ICAL	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	With each ICAL	Replace with liner or with signs of wear.
Inlet septum	Daily (when analyzing samples)	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	With each ICAL	Remove ½-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Solvent rinse	As needed	When chromatography degradation is due to column contamination. Only for bonded and cross-linked phases.
Replacement	As needed	When trimming and/or solvent rinsing no longer return chromatographic performance.
Ferrules		Replace ferrules when changing columns and inlet/detector parts.

MS Maintenance

Task	Every Week	Every 6 Months	Every Year	As Needed
Tune the MSD				✓
Check the foreline pump oil level	✓			
Check the calibration vials		✓		
Replace the foreline pump oil		✓		
Clean the ion source				✓
Check the carrier gas traps on the GC				✓
Replace worn out parts				✓
Lubricate sideplate or vent valve O-rings				✓

APPENDIX G. METHOD PERFORMANCE

Semivolatile Organic Compound Analysis Water: April 2007 to March 2009

Analyte	Number of points	Mean	StdDev	Lower Performance	Upper Performance
1,2,4-Trichlorobenzene	20	63.6	9.49	44.6	82.5
1,2-Dichlorobenzene	20	60.8	9.96	40.9	80.7
1,3-Dichlorobenzene	20	57.5	9.33	38.9	76.2
1,4-Dichlorobenzene	20	59.5	9.48	40.6	78.5
1,4-Dioxane	20	104	13.4	77.7	131
1-Methylnaphthalene	20	74.3	9.84	54.6	93.9
Bis(2-chloro-1-methylethyl) ether	20	88	20.8	46.4	130
2,3,4,6-Tetrachlorophenol	0	NA	NA	NA	NA
2,4,5-Trichlorophenol	20	80.7	10.4	59.9	102
2,4,6-Trichlorophenol	20	78.3	9.45	59.4	97.2
2,4-Dichlorophenol	20	75.2	8.75	57.7	92.7
2,4-Dimethylphenol	20	74	16.1	41.7	106
2,4-Dinitrophenol	20	92.2	27.2	37.7	147
2,4-Dinitrotoluene	20	88.5	11	66.4	111
2,6-Dinitrotoluene	20	88.1	10.3	67.4	109
2-Chloronaphthalene	20	73.9	10.7	52.6	95.2
2-Chlorophenol	20	70.6	9.4	51.8	89.4
2-Methylnaphthalene	20	71.3	10.1	51.2	91.5
2-Methylphenol	20	72.2	8.2	55.8	88.6
2-Nitroaniline	20	82.6	12	58.6	107
2-Nitrophenol	20	74.3	8.48	57.3	91.3
3&4-Chlorophenol	0	NA	NA	NA	NA
3&4-Methylphenol	20	87.9	8.83	70.2	106
3,3'-Dichlorobenzidine	20	79.8	29	21.8	138
3,4,5-Trichlorophenol	0	NA	NA	NA	NA
3,4-Dichlorophenol	0	NA	NA	NA	NA
3,5-Dichlorophenol	0	NA	NA	NA	NA
3-Nitroaniline	20	83.1	37	9.1	157
4,6-Dinitro-2-methylphenol	20	94.3	21.2	51.9	137
4-Bromophenyl phenyl ether	20	88.3	11.9	64.5	112
4-Chloro-3-methylphenol	20	78.6	9.77	59.1	98.1
4-Chloroaniline	16	113	21.1	70.9	155
4-Chlorophenyl phenyl ether	20	79.2	10.2	58.8	99.5
4-Nitroaniline	20	81.8	21.4	38.9	125
4-Nitrophenol	20	89.7	14.4	60.9	119
Acenaphthene	20	95.2	14.5	66.1	124
Acenaphthylene	20	69.8	9.31	51.1	88.4
Anthracene	20	91.1	11.9	67.4	115
Benzo(a)anthracene	20	93.3	10.8	71.7	115
Benzo(a)pyrene	20	74	11.1	51.8	96.1
Benzo(b)fluoranthene	20	89.9	12.9	64.2	116
Benzo(g,h,i)perylene	20	77	15.2	46.7	107
Benzo(k)fluoranthene	20	86.9	11.9	63.2	111

Analyte	Number of points	Mean	StdDev	Lower Performance	Upper Performance
Benzyl alcohol	20	75.8	11.9	51.9	99.7
bis(2-Chloroethoxy)methane	20	77.7	9.12	59.4	95.9
bis(2-Chloroethyl)ether	20	72.2	10.3	51.7	92.8
bis(2-Ethylhexyl) phthalate	20	111	16.2	78.6	143
Butyl benzyl phthalate	20	105	15.5	74.4	137
Carbazole	20	80.7	25.6	29.6	132
Chrysene	20	94.7	11.1	72.6	117
Dibenz(a,h)anthracene	20	82.3	13.4	55.5	109
Dibenzofuran	20	79	10.9	57.3	101
Diethyl phthalate	20	90.6	13.6	63.5	118
Dimethyl phthalate	20	87.4	10.1	67.2	108
Di-n-butyl phthalate	20	104	16.2	71.6	136
Di-n-octyl phthalate	20	107	19.7	67.7	146
Diphenyl amine	18	66.9	10	46.9	87.0
Fluoranthene	20	97.8	14.2	69.4	126
Fluorene	20	84.1	10.9	62.4	106
Hexachlorobenzene	20	87.3	11	65.3	109
Hexachlorobutadiene	20	50.4	8.26	33.9	67.0
Hexachlorocyclopentadiene	20	30.1	13	4.2	56.1
Hexachloroethane	20	51.1	9.09	32.9	69.2
Indeno(1,2,3-cd)pyrene	20	76.3	11.7	53.0	99.6
Isophorone	20	69.2	9.87	49.5	88.9
Naphthalene	20	74.9	10.3	54.3	95.5
Nitrobenzene	20	80	10.4	59.3	101
N-Nitrosodi-n-butylamine	0	NA	NA	NA	NA
N-Nitrosodipropylamine	20	75.4	10.1	55.3	95.6
Pentachlorophenol	20	88.9	15.8	57.2	121
Phenanthrene	20	94.9	13	69.0	121
Phenol	20	70.8	9.67	51.5	90.2
Pyrene	20	97.9	14.3	69.3	127

Semivolatile Organic Compound Analysis
Soil: April 2007 to March 2009

Analyte	Number of points	Mean	StdDev	Lower Performance	Upper Performance
1,2,4-Trichlorobenzene	15	65.8	11	43.8	87.9
1,2-Dichlorobenzene	15	65.2	11.9	41.4	89.1
1,3-Dichlorobenzene	15	62	12	38.1	85.9
1,4-Dichlorobenzene	15	62.8	11.7	39.5	86.1
1,4-Dioxane	12	111	23.7	64.0	159
1-Methylnaphthalene	4	71.8	3.29	65.2	78.3
Bis(2-chloro-1-methylethyl) ether	15	67.1	14.6	38.0	96.3
2,3,4,6-Tetrachlorophenol	0	NA	NA	NA	NA
2,4,5-Trichlorophenol	15	69.2	11.5	46.2	92.1
2,4,6-Trichlorophenol	15	66.1	14.9	36.3	95.9
2,4-Dichlorophenol	15	67.8	13.3	41.2	94.5

Analyte	Number of points	Mean	StdDev	Lower Performance	Upper Performance
2,4-Dimethylphenol	15	65.7	19.1	27.4	104
2,4-Dinitrophenol	14	69.5	19.7	30.1	109
2,4-Dinitrotoluene	15	79.1	14.7	49.6	109
2,6-Dinitrotoluene	15	75	13.8	47.3	103
2-Chloronaphthalene	15	67.5	12.3	42.9	92.1
2-Chlorophenol	15	68.4	13.5	41.3	95.4
2-Methylnaphthalene	15	68.7	12.7	43.4	94.1
2-Methylphenol	15	66.9	13.5	39.8	94.0
2-Nitroaniline	15	72	13.2	45.7	98.4
2-Nitrophenol	15	66.1	13.7	38.7	93.6
3&4-Chlorophenol	0	NA	NA	NA	NA
3&4-Methylphenol	15	71.7	13.4	44.9	98.5
3,3'-Dichlorobenzidine	15	70.1	21	28.1	112
3,4,5-Trichlorophenol	0	NA	NA	NA	NA
3,4-Dichlorophenol	0	NA	NA	NA	NA
3,5-Dichlorophenol	0	NA	NA	NA	NA
3-Nitroaniline	15	82	21.4	39.3	125
4,6-Dinitro-2-methylphenol	14	78.1	16.9	44.3	112
4-Bromophenyl phenyl ether	15	70.5	11.8	47.0	94.0
4-Chloro-3-methylphenol	15	71.4	13.3	44.7	98.0
4-Chloroaniline	15	65.2	40.9	0	147
4-Chlorophenyl phenyl ether	15	70.9	12.1	46.8	95.0
4-Nitroaniline	15	75.9	16.3	43.4	108
4-Nitrophenol	14	70.1	19.1	31.9	108
Acenaphthene	15	80.7	15.5	49.7	112
Acenaphthylene	15	69.2	13.3	42.7	95.7
Anthracene	15	74.8	11.9	50.9	98.6
Benzo(a)anthracene	15	79	13.7	51.5	106
Benzo(a)pyrene	14	84.2	23.9	36.3	132
Benzo(b)fluoranthene	14	84.6	24.5	35.5	134
Benzo(g,h,i)perylene	15	72.8	22.9	27.1	119
Benzo(k)fluoranthene	14	87.1	27.5	32.2	142
Benzyl alcohol	15	61.6	14.6	32.3	90.9
bis(2-Chloroethoxy)methane	15	67.7	11.7	44.3	91.1
bis(2-Chloroethyl)ether	15	63.8	16.9	30.0	97.7
bis(2-Ethylhexyl) phthalate	13	95.2	26.4	42.3	148
Butyl benzyl phthalate	14	87.7	32.8	22.1	153
Carbazole	15	75.9	15.8	44.3	107
Chrysene	15	79.3	13.5	52.4	106
Dibenz(a,h)anthracene	14	85.2	28.2	28.8	142
Dibenzofuran	15	71.1	12.5	46.2	96.0
Diethyl phthalate	15	76.8	16.4	44.0	110
Dimethyl phthalate	15	75.3	14.9	45.5	105
Di-n-butyl phthalate	15	84	26	32.0	136
Di-n-octyl phthalate	13	96.6	28.2	40.2	153
Diphenyl amine	14	79.8	16.5	46.9	113
Fluoranthene	15	76.8	12.5	51.8	102
Fluorene	15	73.3	13.2	46.9	99.8
Hexachlorobenzene	15	70.5	10.6	49.4	91.6

Analyte	Number of points	Mean	StdDev	Lower Performance	Upper Performance
Hexachlorobutadiene	15	63.5	12.6	38.4	88.7
Hexachlorocyclopentadiene	14	64.6	24.4	15.8	113
Hexachloroethane	15	62	12.2	37.7	86.4
Indeno(1,2,3-cd)pyrene	14	83.4	26.4	30.6	136
Isophorone	15	66.1	13.3	39.5	92.7
Naphthalene	15	68.2	12.1	44.0	92.4
Nitrobenzene	15	68.6	11.7	45.1	92.0
N-Nitrosodi-n-butylamine	0	NA	NA	NA	NA
N-Nitrosodipropylamine	15	65	11.4	42.2	87.8
Pentachlorophenol	14	69.9	19.1	31.7	108
Phenanthrene	15	75.8	12.7	50.5	101
Phenol	15	68	13.1	41.8	94.3
Pyrene	15	80.3	16.2	47.9	113

APPENDIX H. TYPICAL DATA PACKAGE FORMAT

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

Cover Memo (original)
Review form (cover, front only)
TDF
Modified Draft Report from Element Data System

Data Package Cover [First numbered page in the data package]

Review Forms

EPA Review Form
ESAT technical review guide
Discrepancy Reports (if applicable)
Work Order Memo (if applicable)
Daily folder review forms or checklists
Analysis matrix listing all analytical runs (for organics only)

Tracking Forms

Work Order(s)
COC(s)

Sample Preparation

Bench Sheets (and extraction logs, ASE run logs, where used)
Sample cleanup data and records (e.g. GPC logs)
Moisture data as applicable

[Analysis Method, Date] Initial Calibration Data

Sequence logs and instrument or other data as applicable, in run order and grouped by day.

[Analysis Method, Date] Data

Bench sheet(s) where not used in Sample Preparation section
Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Miscellaneous Data

Other data as applicable

Standards Records

Standards records from LIMS (and logbook pages as needed)

STANDARD OPERATING PROCEDURE: 315
Revision: 5, Effective: June 30, 2009

[illegible]

**USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA**

**STANDARD OPERATING PROCEDURE 330
ORGANOCHLORINE PESTICIDE ANALYSIS BY GAS CHROMATOGRAPHY**

Revision 4
Effective Date: February 15, 2010

Reviewed by: _____
Richard Bauer Date
Chemistry Team Leader/Technical Director

Reviewed by: _____
K. W. Hendrix, Laboratory QA Officer Date

Approved by: _____
Brenda Bettencourt, Laboratory Director Date

Periodic Review:

Signature	Title	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____

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1 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the procedures used for the analysis of certain organochlorine pesticides by gas chromatography (GC) with electron capture detectors (ECDs) in extracts prepared following USEPA Region 9 Laboratory SOP 275 for aqueous samples, SOP 290 for solid samples, and SOP 295 for wipe and waste samples. This SOP is based on procedures contained in EPA SW-846 Method 8081B, Revision 2, February 2007 and Method 8000C, Revision 3, March 2003 and is applicable to ground water, aqueous sludge, soils, sediment, wipe, and waste samples in support of Superfund, RCRA, WQM, UIC, and TSCA programs. Deviations from the reference method are described in Appendix A. The applicability of these procedures to specific project data quality objectives (DQOs) must be assessed on a case-by-case basis.

The target analytes for this procedure are listed in Appendix B. If analysis of polychlorinated biphenyls (PCBs) is required, samples should be analyzed by Region 9 SOP 335, *Polychlorinated Biphenyls (PCBs) as Aroclors by GC/ECD*, based on EPA SW-846 Method 8082A.

2 METHOD SUMMARY

This method describes the analysis of hexane extracts of environmental samples for selected organochlorine pesticides. Sample components are separated, identified, and quantitated by injecting microliter quantities of sample extracts onto a pair of high resolution fused silica capillary columns with dissimilar stationary phases in a temperature programmed GC equipped with ECDs.

Tentative identifications are obtained by comparing retention times of chromatographic peaks in the sample extract to those of organochlorine pesticide standards analyzed under the same conditions used for samples. Confirmatory information for single-response analytes is obtained by comparing their retention times and quantitative results from each column. Concentrations of the identified components are determined by comparing the response of a compound to the average response of that compound in the initial calibration. The lower of the results from the two columns is reported.

Multi-response analytes are quantitated using either selected peaks or total area response.

3 DEFINITIONS

Analytical Sample – any sample in which analytes are being determined, excluding standards, blanks, or QC reference samples.

Aroclor – an industrial trade name for commercially produced mixtures of polychlorinated biphenyl congeners.

Calibration Factor (CF) – the peak area (or height) in the standard divided by the concentration of the standard injected (in ng/mL).

Calibration Verification (CV) Standard – A solution of method analytes at the concentration of the mid level initial calibration solution prepared from the same source as the ICAL solutions. The CV standard is used to validate the initial calibration. The CV is also known as CCV.

ECD – electron capture detector.

Extraction Batch – A group twenty or fewer samples extracted together and sharing the same batch QC samples.

Initial Calibration (ICAL) Standards – Standards used to calibrate the instrument response with respect to analyte concentration.

Instrument Blank (IB) – a blank that is the same matrix as the calibration standards containing surrogates but without target analytes.

Laboratory Control Sample (LCS) – An aliquot of blank matrix to which known quantities of the method analytes are added. The LCS is analyzed like a sample, and its purpose is to determine whether the methodology is in control, and whether the Laboratory is capable of making accurate and precise measurements. The LCS is also known as a laboratory fortified blank (LFB) or blank spike (BS).

LIMS – Laboratory Information Management System. The Element database.

Matrix Spike (MS) / Matrix Spike Duplicate (MSD) – aliquots of an analytical sample to which known quantities of the method analytes are added. The MS/MSD is analyzed exactly like a sample; its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations.

Method Blank (MB) – An aliquot of blank matrix that is treated exactly as a sample. The MB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment. The MB is also known as laboratory reagent blank (LRB).

Method Detection Limit (MDL) – The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Performance Evaluation Mixture (PEM) – A solution containing 4,4'-DDT and endrin used to measure degradation of 4,4'-DDT and endrin in the GC.

Primary Dilution Standard Solution (PDS) – A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other analyte solutions.

Quantitation Limit (QL) – The concentration at which confidence in the reported value requires no qualifying remarks. A standard is analyzed at the QL to verify the previously established calibration curve.

Quantitation Limit Standard (QLS) – A standard used to check the accuracy of the analysis at the quantitation limit. The QLS is also known as the LCV.

Sample Delivery Group (SDG) – An SDG number is assigned to a set of samples, typically not to exceed 20, from the same site and of the same matrix received within a 14 day period.

Second Source Calibration Verification (SCV) – A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check the initial calibration.

Stock Standard Solution (SSS) – A concentrated standard containing the method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Surrogate (SURR) – Compounds which are extremely unlikely to be found in any sample that are added to a sample aliquot in a known amount before extraction or other processing, and measured with the same procedures used to measure other sample components. The purpose of the surrogate is to monitor method performance with each sample.

System Priming Solution – A solution of single-response analytes at or above the concentration of the highest ICAL standard. This solution is used to deactivate the GC system when it has not been used for a day or more.

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Routine procedures in this SOP do not require contact with concentrated solutions or neat materials. All standard handling and preparation should be performed in a well-vented laboratory fume hood.

Hexane liquid and vapors are extremely flammable. Keep away from ignition sources. Harmful if inhaled or swallowed. May cause damage to kidneys, nerves, and respiratory system. Irritating to skin, eyes, and mucous membranes. Toxic by ingestion and inhalation. Vapor inhalation causes irritation of nasal and respiratory passages, headache, dizziness, nausea, central nervous system depression. Chronic overexposure can cause severe nerve damage. No systemic toxicity has been reported. Emergency First Aid – Inhalation: immediately remove to fresh air. If not breathing, administer mouth-to-mouth rescue breathing. If there is no pulse, administer cardiopulmonary resuscitation (CPR). Contact physician immediately. Eye contact: Rinse with copious amounts of water for at least 15 minutes. Get emergency medical assistance. Skin contact: Flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothing and shoes. Wash clothing before re-use, and discard contaminated shoes. Get emergency medical assistance. Ingestion: Call local Poison Control Center for assistance. Contact physician immediately. Aspiration hazard - do not induce vomiting.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Many parts of the GC operate at temperatures high enough to cause serious burns. Allow heated zones to cool below 50°C before working on or around them.

Electron capture detectors contain a cell plated with ⁶³Ni, a radioactive isotope. Although beta particles in the ECD have little penetrating power, they may be

hazardous if the isotope is ingested or inhaled. Radioactive leak tests must be performed at regular intervals. Do not open the ECD cell or use solvents to clean it. Connect the ECD exhaust to a fume hood or a vent.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-regulated Waste	Not applicable
Sample extracts and diluted standards*	Hazardous waste	Toxic, Flammable, Contains PCBs. See solvent MSDS

* Expired or unusable stock solution exceeding 1 mg/L (1000 µg/L) must be segregated and disposed following procedures in EPA Region 9 Laboratory SOP 706 in compliance with RCRA and TSCA regulations.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Refer to Region 9 SOP 275 *Extraction of Water Samples Using CLLE*, SOP 290 *Extraction of Soil Samples Using PFE (Pressurized Fluid Extraction-ASE)*, or SOP 295 *Waste Dilution* for wipe and waste samples.

5.2 Internal Chain-of-Custody

Sample extracts for GC analysis are received from the extraction lab personnel and custody is transferred to the GC laboratory staff. The GC analyst acknowledges the receipt of the sample extracts by signing the appropriate sections of the completed LIMS bench sheet. Copies of tracking sheets, chain of custody records, and the original LIMS extraction bench sheet must accompany the sample extracts and be included in the data package.

Compare the EPA Region 9 Laboratory number on the extracts to the tracking sheets and chain of custody record to determine the client sample identification, case number, and sample delivery group (SDG) number. Verify sample IDs and dates and times of collection against the chain-of-custody form.

5.3 Sample Extract Storage

Store sample extracts in Room 400 at >0°C (just above freezing) to ≤6°C before and after analysis. Retain sample extracts until analysis is complete and holding time has expired.

5.4 Holding Time

Samples extracts must be analyzed within 40 days from extraction.

6 INTERFERENCES

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to anomalous peaks or elevated baselines in gas chromatograms.

Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Phthalate esters are commonly used as plasticizers and are easily extracted from plastic materials. Contact of samples, solvents, reagents, glassware, extracts, or other sample processing apparatus with plastics must be avoided.

If present, PCBs interfere significantly with target analyte identification and quantification.

High molecular weight materials in the sample extract, including some phthalates, which may contaminate the GC, can be removed by gel permeation chromatography (GPC). See Region 9 SOP 260 *Gel Permeation Chromatography (GPC) Clean-Up*.

Alumina cleanup may reduce interferences from hydrocarbons and other contaminants. Add approximately 200 mg of activated alumina to each extract vial and shake.

Contamination may occur when a sample that does not contain, or contains low concentration of pesticides is analyzed immediately after a sample containing relatively high concentrations. Samples suspected of being affected by carryover must be re-analyzed. Instrument blanks should be analyzed to ensure that carryover is not occurring. Syringes, splitless injection port liners, and inlet seals must be cleaned or replaced as required.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

Gas chromatograph with dual ECDs, dual splitless injection port(s), and electronic pressure control (EPC). (Hewlett Packard/Agilent 6890, 7890, or equivalent).

Fused silica capillary gas chromatography column – Any capillary column which provides adequate resolution, capacity, accuracy, and precision may be used. The following column pair was used for method validation:

- Column 1: RTX-CLPesticides - 30 m x 0.32 mm x 0.5 μ m (Restek cat.# 11139 or equivalent.)
- Column 2: RTX-CLPesticides2 - 30 m x 0.32 mm x 0.25 μ m (Restek cat.# 11324 or equivalent.)

Data acquisition and processing system – capable of controlling the GC and acquiring, storing, and processing GC data. The software must be able to calculate calibration factors and the concentrations of analytes in samples. Enviroquant (available from Agilent) software (or equivalent).

7.2 Reagents

All reagents must be bar-coded upon receipt and entered into the LIMS database.

Reagents may contain impurities that affect analytical data. Only materials that conform to the American Chemical Society (ACS) high purity pesticide quality or equivalent should be used. If the purity of a reagent is in question, analyze for contamination prior to use.

Alumina, activated – Chromatographic grade 80-325 mesh. Spectrum AL218-10 or equivalent.

Hexane - pesticide quality or equivalent.

7.3 Standards

All standards must be bar-coded upon receipt and entered into the LIMS database. Document the preparation of all standard dilutions in the LIMS database.

All ampulated calibration materials must be maintained in the refrigerator at $>0^{\circ}\text{C}$ (just above freezing) to $\leq 6^{\circ}\text{C}$ and protected from light. Use the manufacturer's expiration date for ampulated standards.

Opened ampules and working standards must be maintained in a freezer at $\leq -10^{\circ}\text{C}$ and protected from light. The solution is assigned an expiration date which is either 6 months from preparation or open date, or the expiration date of the stock standard used in the preparation, whichever is earlier. Analysts must allow all standard solutions to equilibrate to room temperature before use.

- Suggested Calibration Stock Standards:

Description	Vendor and Catalog #	Compounds	Concentration
Pesticide Surrogate Mix	Restek 32000	2,4,5,6-Tetrachloro-m-xylene (TCMX) Decachlorobiphenyl (DCB)	each at 200 µg/mL in acetone
Pesticide Performance Evaluation Mix	Restek 32074	TCMX, DCB, 4,4'-DDT, endrin, methoxychlor, alpha-BHC, beta-BHC, gamma-BHC (Lindane)	1 – 25 µg/mL in hexane
Organochlorine Pesticide Mix AB#2	Restek 32292	All analytes listed in Appendix B except additional compounds.	8 – 80 µg/mL in hexane/toluene
Toxaphene	Restek 32071	Toxaphene	5,000 µg/mL in isooctane
Technical Chlordane	Restek 32072	Chlordane	5,000 µg/mL in isooctane
2,4'-DDT	Restek 32200	2,4'-DDT	1,000 µg /mL in methanol
2,4'-DDD	Restek 32098	2,4'-DDD	1,000 µg /mL in methanol
2,4'-DDE	Restek 32099	2,4'-DDE	1,000 µg /mL in methanol

- Surrogate Spiking Solution – Solution of TCMX and DCB in hexane.
- Performance Evaluation Mixture – A PEM standard containing 4,4'-DDT and endrin. Prepared by diluting a stock standard such as Restek 32074.
- Matrix Fortification Solution – Prepared by diluting the same stock standard used to prepare the ICAL solutions such as Restek 32292.
- Calibration Solutions – The single-component pesticide standards are prepared in hexane at a minimum of five concentrations for each analyte, including the surrogates, from the stock standard solution and surrogate compound solution. The low point concentration corresponds to the quantitation level for each analyte. The high point concentration defines the upper end of the concentration range for which the calibration is valid. The components in the low level standard must be at or below the reported quantitation limits.
- Calibration Verification Solution (CV) – Equivalent to the concentration of the mid-point initial calibration solution. This solution should be prepared at the

same time as the other calibration levels, but at a larger volume. This solution is used to verify the initial calibration.

- Quantitation Limit Standard (QLS) – Equivalent to the concentration of the lowest level calibration standard. This solution should be prepared at the same time as the other calibration levels, but at a larger volume. The QLS is used to verify instrument response at the quantitation limit.
- System Priming Solution – Equivalent to the highest ICAL solution. It is used to deactivate the GC system when it has not been used for a day or more.
- Instrument Blank – a solution of hexane fortified with Pesticide Surrogate Mix.
- Second Source Calibration Verification Sample (SCV) – Approximately equivalent to the mid-point initial calibration solution but prepared from a source different from the source of the calibration standards. (A different lot from the same source may be used for multiple component analytes if a suitable second source is not available). The SCV is used to check the accuracy of the initial calibration solutions. See table below for suggested vendors for SCV standards.

Analyte		Suggested Vendors & Catalog Numbers	
Pesticide Mix	AccuStandard M-8081-SC	Supelco 46845-U	Ultra Scientific PPM-808C
Toxaphene	AccuStandard P-093S	Supelco 48103	Ultra Scientific PP-271-1
Chlordane	AccuStandard P-017S	Supelco 48065-U	Ultra Scientific PP-151-1
2,4'-DDT, -DDE, -DDD	AccuStandard M-8080-OP		Ultra Scientific PPM-828
PEM	AccuStandard M-8081-DS		Ultra Scientific ISM-450
TCMX, DCB	AccuStandard CLP-032R		Ultra Scientific ISM-320

7.4 Supplies

Volumetric flasks (type A): 100-mL, 50-mL, 25-mL, and 10-mL.

Microliter syringes: 10- μ L, 25- μ L, 50- μ L, 100- μ L, 250- μ L, 500- μ L, and 1-mL.

Vials with Teflon-lined screw caps: 15-mL or 12-mL and 2 mL.

Vial inserts: 5x31 mm 0.25-mL shell style (VWR catalog #66010-640, VWR catalog #66009-290, or equivalent)

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set up the instrument using operating parameters provided in Appendix D. Adjust as needed to meet method, SOP, and project requirements and good chromatographic practice.

Prior to analyzing calibration, QC, or field samples make a LIMS batch and sequence as required to obtain LIMS assigned IDs for the calibration and QC samples.

Follow the file naming conventions provided in Appendix E.

Ensure that appropriate waste containers are present and properly labeled.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

Perform an initial calibration using a minimum of five calibration standards to establish an external standard calibration using the average calibration factor for all single-component analytes. Refer to Section 9.2 and Appendix C for required frequency and QC limits.

Toxaphene and chlordane are quantitated from a single-point calibration near the mid-point of the expected linear calibration range.

While toxaphene contains a large number of compounds that will produce well resolved peaks in a chromatogram, it also contains many other components that are not chromatographically resolved. This unresolved complex mixture results in the "hump" in the chromatogram that is characteristic of this mixture. The area of the unresolved complex mixture contributes a significant portion of the area of the total response. Assign an "H" compound type indicator in ChemStation. Specify the retention time range by first entering the median retention time of the range as the analytes retention time then entering the difference between the median and the start or end point in the "Extract signals from" - and + fields. Construct the baseline of toxaphene in the standard chromatogram between the retention times of the first and last eluting toxaphene components. Use this area and the concentration of toxaphene in the standard to calculate a calibration factor. Toxaphene may also be quantitated on the basis of 4 to 6 major peaks. This approach may avoid difficulties when interferences with toxaphene peaks are present in the early portion of the chromatogram from compounds such as DDT. Follow the procedure outlined below for chlordane when toxaphene is determined using the 4 to 6 peaks approach. Whichever approach is employed, all work should be documented in LIMS.

Chlordane is a mixture of organochlorine compounds whose composition varies, but the major constituents are alpha and gamma chlordane along with other chlordane isomers, heptachlor, and nonachlor. Chlordane is quantitated using 4 to 6 selected characteristic peaks. Identify each of the 4 to 6 peaks in the data system method as belonging to a multi-component standard by assigning an "L" compound type indicator to each peak. Insert a "TOTAL" entry for the analyte after the last analyte peak. Assign the same concentration to the individual and total peaks. ChemStation will sum the areas of the individual peaks for the analyte and calculate a CF for the summed areas in the "TOTAL" entry. An ICAL based on the total area response of chlordane may be required if the chromatographic pattern in a sample does not match any standard. Follow the procedure outlined above for toxaphene when chlordane is determined using the total area approach. Whichever approach is employed, all work should be documented in LIMS.

Re-calibrate the ChemStation method using responses from the analyses of the calibration standards. Save the calibration file. Name it using the method number and date: See Appendix E for ChemStation naming conventions.

Print an initial calibration summary by choosing the Response Factors to Printer menu item from the ChemStation InitCal menu. Verify that the %RSD for each single-component analyte and surrogate meet QC criteria in Appendix C.

Generate a compound list by choosing the List Compounds menu item from the ChemStation InitCal menu; print this report and include it in the ICAL data package.

Print page 3 of the ChemStation Edit Compounds list box for one single-component analyte showing the ICAL level IDs, concentrations, and responses and include in the ICAL data package.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the failed one in the ICAL. If more than one standard fails, corrective action is required (see Section 8.4 for detailed maintenance and troubleshooting procedures).

The width of the retention time window for each (single) peak is ± 0.03 minutes. Recommended calibration levels are shown in the following table:

Recommended Calibration Levels

Analyte	Level 1 ng/mL	Level 2 ng/mL	Level 3 ng/mL	Level 4 ng/mL	Level 5 ng/mL	Level 6 ng/mL
alpha-BHC	2	5	10	20	40	80
gamma-BHC (Lindane)	2	5	10	20	40	80
beta-BHC	2	5	10	20	40	80
delta-BHC	2	5	10	20	40	80
Heptachlor	2	5	10	20	40	80
Aldrin	2	5	10	20	40	80
Heptachlor epoxide	2	5	10	20	40	80
gamma-Chlordane	2	5	10	20	40	80
alpha-Chlordane	2	5	10	20	40	80
4,4'-DDE	4	10	20	40	80	160
Endosulfan I	2	5	10	20	40	80
Dieldrin	4	10	20	40	80	160
Endrin	4	10	20	40	80	160
4,4'-DDD	4	10	20	40	80	160
Endosulfan II	4	10	20	40	80	160
4,4'-DDT	4	10	20	40	80	160
Endrin aldehyde	4	10	20	40	80	160
Methoxychlor	20	50	100	200	400	800
Endosulfan sulfate	4	10	20	40	80	160
Endrin ketone	4	10	20	40	80	160
Aroclor 1016/1260			200			
Chlordane (technical)			500			
Toxaphene			500			
2,4'-DDD	4	10	20	40	80	160
2,4'-DDE	4	10	20	40	80	160
2,4'-DDT	4	10	20	40	80	160
2,4,5,6-Tetrachloro-m- xylene	2	5	10	20	40	80
Decachlorobiphenyl	2	5	10	20	40	80

The recommended ICAL analysis sequence is:

1. System Priming Solution
2. IB
3. PEM
4. Level 1 OC Pest Calibration Standard
5. Level 2 OC Pest Calibration Standard
6. Level 3 OC Pest Calibration Standard
7. Level 4 OC Pest Calibration Standard
8. Level 5 OC Pest Calibration Standard

- 9. Level 6 OC Pest Calibration Standard
- 10. Toxaphene 500 ng/mL
- 11. Chlordane 500 ng/mL
- 12. IB
- 13. PEM
- 14. SCV

8.2.2 Second Source Calibration Verification

Analyze an SCV standard immediately after the ICAL for each analyte calibrated. The SVC is used to check the initial calibration. Verify that the results meet the %R QC criteria in Appendix C. If the SCV does not meet the acceptance criteria, take corrective action specified in Section 9.2.1.

8.2.3 Calibration Verification

The calibration verification standard is used to validate the initial calibration standard for the samples run during the associated 12-hour time period. If the instrument stops in the middle of a sequence, the calibration verification is analyzed when the condition is discovered (usually the following morning). The CV sample is typically the Level 3 calibration standard.

See Section 9.2.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2.4 Quantitation Limit Standard

The QLS is used to verify analytical system response at the quantitation limit. Analyze the Level 1 pesticide mix standard.

See Section 9.2.3 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

Allow sample extracts to reach ambient temperature before analysis.

Check that the numbers on the vials coincide with the numbers on the LIMS extraction batch to ensure that the correct sample is being analyzed.

Note if the sample has an unusual color or other physical properties. If any physical signs of contamination are present, screen the sample to protect the analytical system from damage or contamination, and to determine the

appropriate subsequent dilution. Record unusual items in the LIMS Work Order Notes field.

8.3.2 Sample Analysis and Analytical Sequence

Prepare a LIMS sequence to include instrument blanks, instrument QC (PEM, CCV, QLS), batch QC (MB, LCS, MS/MSD), and field samples. LIMS will assign identifiers for the instrument QC when the sequence is saved; batch QC identifiers will have been assigned in the LIMS bench sheet.

Prepare a sample sequence in the instrument data acquisition software. Use the LIMS identifiers for the batch and instrument QC; include the laboratory sample number (work order-sample number) in the "Sample" field and dilution level, if any in the "Multiplier" field.

Name the data files according to the data file naming convention outlined in Appendix E.

Record the analytical sequence in the instrument run log.

Load the samples in the autosampler according to their designated positions in the sequence file. The recommended analysis sequence is:

- 1) System Priming Solution
- 2) IB
- 3) PEM
- 4) QLS
- 5) OC Pest CV
- 6) Toxaphene, chlordane, QLS if required
- 7) Batch QC
- 8) Samples, sample dilutions, and instrument blanks as needed
- 9) IB
- 10) OC Pest CV
- 11) Toxaphene standard, chlordane standard, if required

8.3.3 Analyte Identification and Quantitation

Process the data using the Agilent ChemStation software data analysis module. This module identifies the method analytes in the sample chromatogram by comparing the retention time of peaks in the sample chromatogram to the retention times of peaks in calibration standards analyzed using identical conditions. Calculations use the average calibration factor from the initial calibration. Report the lower of the analyte concentrations found by the two columns.

Analyte concentrations in the sample extract as shown on the ChemStation quantitation report are calculated as:

$$ng / mL = \frac{Ax}{CF}$$

Where:

Ax = area (or height) response of the sample

CF = mean calibration factor (area/[ng/mL] = area/pg) from the initial calibration.

LIMS calculates the final sample concentration.

Analyte concentration in a liquid sample is:

$$Concentration(\mu g / L) = \frac{Ax \times Vt \times DF}{CF \times Vo \times Vi \times 1,000}$$

Where:

Ax and CF are the same as above.

Vt = Total volume of the concentrated extract in μ L.

DF = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, DF = 1.

Vi = Volume of extract injected in μ L. Normally 1 μ L.

Vo = Volume of the aqueous sample extracted in mL.

1,000 = conversion factor: pg to ng

Using the units specified for these terms will result in a concentration in ng/mL, which is equivalent to μ g/L.

Analyte concentration in a solid sample is:

$$Concentration(\mu g / kg) = \frac{Ax \times Vt \times DF \times GPC}{CF \times Vi \times Ws \times D \times 1,000}$$

Where:

Ax, Vt, DF, CF, Vi, and 1,000 are as above.

GPC = GPC factor. If no GPC is performed, GPC = 1. If GPC is performed, then GPC = 2.

D = Dry weight factor (100 - %moisture/100)

Ws = Weight of extracted sample (g).

Using the units specified for these terms will result in a concentration of ng/g, which is equivalent to µg/kg.

Review all chromatograms for correct peak identification and for correctly drawn baselines for the analytes of interest. See SOP 835, *Chromatographic Integration Procedures* for guidance in drawing baselines and required documentation.

Quantitate toxaphene by comparing the total area of the toxaphene in the sample to the total area of toxaphene in the standard. If the concentration of toxaphene in the sample is greater than 5 times the concentration of toxaphene in the standard, dilute the sample to bring the final concentration to approximately the same concentration as the standard. Construct a baseline in the sample chromatogram to be similar to the baseline in the standard chromatogram. Measure the area, and use the calibration factor to calculate the concentration in the sample.

When quantitating chlordane, the analyst must take care to evaluate the relative areas of the peaks chosen in the sample and standard chromatograms. It is highly unlikely that the peaks will match exactly, but the analyst should not employ peaks from the sample chromatogram whose relative sizes or areas appear to be disproportionally larger or smaller in the sample compared to the standard. If the concentration of chlordane in the sample is greater than 5 times the concentration of chlordane in the standard, dilute the sample to bring the final concentration to the approximate standard concentration.

8.3.4 Data and QC Review

As soon as possible after analysis, and prior to entry into LIMS inspect sample and QC data for compliance with QC limits in Appendix C. If no significant problems are found, review the following QC data for compliance with SOP requirements:

- Single-component target analyte results must be within range of the multi-point initial calibration. For target analytes using a single point calibration, consider the results to be within range if they are no greater than five times the calibration standard. If results are not within the calibration range, dilute and reanalyze.

- Review detected results to ensure that the primary and secondary columns agree. Report detected results only when positive results are detected on both columns (LIMS is set up to report the lower of two detected results). Where results exceed dual column agreement criteria (see Appendix C), qualify and report the lower result.
- Process and review results of instrument QC (PEM, CV, QLS) immediately after their analysis to verify that the results are within QC limits. If the instrument QC results are not within QC limits, stop the sequence and take corrective action before resuming the sequence. See Section 9.2 for instrument QC requirements.
- Process and review the results for the MB, LCS, and MS/MSD batch QC samples and verify that the results are within QC limits. See Section 9.3 for batch QC requirements.
- Determine if surrogate recoveries for field and QC samples are within QC limits.
- If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report. Initial and date each notation.

8.3.5 Data Export and LIMS Entry

Generate epatemp.txt files for field and QC samples by also printing the report to the screen. The Omit Target Compounds that are Missed checkbox in the ChemStation Quantitation Report Options window must be unchecked. These files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table.

Copy sample data files from the local drive to the appropriate instrument data subdirectory on the Region 9 LAN to make them available to LIMS and to archive them.

Create an empty upload table in the LIMS Data Entry/Review table then open the DataTool module. Select the instrument data files to be imported then merge the files using the appropriate cross table. Save the merged upload file in DataTool and the results in the Data Entry table.

Review results in the LIMS. Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

8.4 Maintenance

Symptoms of common problems:

- Carryover
Possible causes: Analyzing a sample containing high molecular weight components or analyzing high-level and low-level samples sequentially.
Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.
- Shorter retention time.
Possible cause: column flow rate problem.
Corrective action: check flow rate and adjust as necessary.
- Longer retention time and / or smaller peaks.
Possible causes: column flow rate problem, injection port leak, or column contamination.
Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end, thermally clean (bake out) column. If issues remain, replace the column.
- Loss of resolution.
Possible causes: column flow rate problem, injection port leak, or column contamination.
Corrective action: Check for leaks, replace septum, liner, and inlet seal, clip the column (a few inches to a foot or more) from the injector end, or thermally clean (bake out) column. If issues remain, replace the column.
- Autosampler “plunger error”
Remove syringe from autosampler and clean by drawing and expelling a 1:1 v/v hexane/acetone mixture. After withdrawing and expelling three syringe volumes, withdraw the plunger and wipe it with a Kimwipe. Repeat; continue until no residue remains on the plunger. Re-install syringe in autosampler. Replace syringe if problems continue.
- High 4,4'-DDT or endrin breakdown
Possible causes: contamination in injection port (inlet liner, inlet seal) or contamination in head of column.

Corrective action: Replace injector parts that come in contact with the sample extract (inlet liner and/or seal); clip the column (a few inches to a foot or more) from the injector end, or thermally clean (bake out) column. If issues remain, replace the column.

- High %RSD in initial calibration
Possible cause: Detector contamination from column bleed or dirty samples or incorrect makeup gas flow.
Corrective action for contaminated detector: Thermally clean (bake out) detector; see Agilent operating manual for procedure.
Corrective action for incorrect makeup gas flow: Detector linearity is affected by the makeup gas flow. Optimize the makeup gas flow by analyzing standards and calculating the %RSD of beta-BHC and methoxychlor over a range of makeup gas flows. If the %RSD for methoxychlor is higher than for beta-BHC the makeup gas flow is too high. If the %RSD for beta-BHC is higher than for methoxychlor the makeup gas flow is too low. Choose a makeup gas flow such that the %RSD for both analytes are within limits.
- Noisy baseline or abnormally high ECD output
Possible cause: contaminated detector.
Corrective action: Thermal cleaning of ECD. Follow instructions in chapter on ECD or micro-ECD detectors in Agilent Operating Manual Vol. 3 – Detectors. Replace detector if thermal cleaning does not alleviate symptoms.

Refer to Appendix F for the preventive maintenance operations and schedules.

9 QUALITY CONTROL

9.1 Demonstration of Capability

The EPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880.

9.2 Instrument QC

9.2.1 Initial Calibration

Demonstration and documentation of an acceptable initial calibration are required before any samples are analyzed. The calibration is a multi-point external standard calibration using the average calibration factor.

The GC system must be calibrated whenever corrective action which changes instrument response (e.g., detector gas adjustment, column replacement, etc.) is performed or if the calibration verification criteria cannot be met.

The data system calculates the calibration factor (CF) for each analyte and surrogate as:

$$CF = \frac{Ax}{Cx}$$

Where:

Ax = area (or height) response of the sample

Cx = Concentration of analyte (ng/mL)

The data system calculates the mean CF for all analytes and surrogates.

The data system calculates the relative standard deviation (RSD) of the calibration levels as:

$$\% RSD = \sqrt{\frac{\sum_{i=1}^n (CF_i - CF_{avg})^2}{\frac{n-1}{CF_{avg}}}} \times 100$$

Where:

CF_i = calibration factor at the specific level (i)

CF_{avg} = average calibration factor

n = number of calibration points

Verify that the ICAL meets the %RSD acceptance criteria in Appendix C.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the

cause for failure must be determined and corrected before analysis of samples can proceed.

Analyze an SCV immediately after each ICAL. If SCV criteria (see Appendix C) are not met, the SCV must be re-analyzed. If it fails again, prepare a fresh solution. Take corrective action as needed before continuing with analysis, including reanalysis or re-preparation and reanalysis of the initial calibration if necessary.

9.2.2 Calibration Verification

Analyze a calibration verification standard at the beginning of each 12-hour analytical period and at the end of the 12-hour analytical period. The 12-hour analytical period begins with the injection of the calibration verification standard and ends with the completion of analysis of the last sample that can be injected within 12 hours of the beginning of the period. Analysis of calibration verification standards, bracketed by instrument blanks, after every ten samples, is recommended. The calibration verification standard is used to validate the initial calibration for the samples run during the associated 12-hour time period. All reported samples must be bracketed by passing CCVs.

The ChemStation Environmental Data Analysis module "Evaluate Continuing Calibration Report" calculates a percent difference (%D) by comparing CF for the CV to the average CF of the ICAL:

$$\%D = \left(\frac{CF_{cv} - CF_{avg}}{CF_{avg}} \right) \times 100$$

Where:

CF_{avg} = Average CF from ICAL

CF_{cv} = CF from the CV

If CV criteria (see Appendix C) are not met, re-analyze the CV. If it fails again, prepare a fresh solution and re-analyze. Take corrective action as needed before continuing with analysis.

9.2.3 Quantitation Limit Standard

Analyze a level 1 pesticide mix standard, or of any analyte that is quantitated from the analytical sequence, each day when analyses of field or QC samples are performed. The QLS is used to verify analytical system response at the quantitation limit.

The QLS sample must meet percent recovery (%R) criteria. Calculate %R using the following equation:

$$\% R = \frac{C_s}{C_n} \times 100$$

Where:

C_s = Analyte concentration determined in the QLS

C_n = Nominal (theoretical) analyte concentration

If QLS criteria (see Appendix C) are not met, re-analyze the QLS. If it fails again, prepare a fresh solution and re-analyze. Take corrective action as needed before continuing with analysis.

9.2.4 Performance Evaluation Mixture

Analyze a PEM standard at the beginning of each 12-hour analytical period. The 12-hour analytical period begins with the injection of the calibration verification standard and ends with the completion of analysis of the last sample that can be injected within 12 hours of the beginning of the period.

The PEM sample is used to verify that the 4,4'-DDT and endrin breakdown products are within QC limits.

The PEM must meet % breakdown criteria. Calculate % breakdown using the following equations:

$$\% \text{ DDT Breakdown} = \frac{DDD + DDE \text{ areas}}{DDT + DDD + DDE \text{ areas}} \times 100$$

$$\% \text{ endrin breakdown} = \frac{\text{endrin aldehyde} + \text{endrin ketone areas}}{\text{endrin} + \text{endrin aldehyde} + \text{endrin ketone areas}} \times 100$$

If PEM criteria (see Appendix C) are not met, re-analyze the PEM. Take corrective action as needed before continuing with analysis.

9.3 Batch QC

9.3.1 Method Blank

Analyze a method blank (MB) for each extraction batch or every 20 samples, whichever is more frequent, to demonstrate that the entire analytical system - from extraction through GC analysis - is free of contamination.

See Appendix C for QC limits.

If the MB is not acceptable, the source of the contamination must be found and eliminated and the problem documented before analysis can proceed. If re-analysis does not solve the problem, the batch may have to be re-extracted.

If either surrogate recovery does not meet acceptance criteria, re-analyze the extract. If either surrogate recovery still does not meet acceptance criteria, the batch must be re-extracted. If the surrogate exceeds the upper control limit and analytes are not detected in the sample, report results without qualification and explain in the LIMS Work Order Notes field.

9.3.2 Laboratory Control Sample

Analyze an LCS for each extraction batch or every 20 samples, whichever is more frequent to demonstrate that the analytical system is in control.

The LCS must meet %R criteria. See Appendix C for QC limits.

If the LCS criteria are not met, re-analyze the LCS. If after reanalysis the %R does not meet acceptance lower criteria, re-extract the batch. If the LCS recovery exceeds the upper control limit, report non-detected analytes without qualification and explain in LIMS Work Order Notes field.

If the surrogate recovery does not meet acceptance criteria, re-analyze the extract. If the surrogate recovery still does not meet acceptance criteria, the batch may have to be re-extracted.

9.3.3 Matrix Spike/Matrix Spike Duplicate

Laboratory fortified matrix (MS) and duplicate (MSD) samples are extracted and analyzed for each extraction batch containing up to twenty samples. The MS/MSD samples demonstrate the effect of the sample matrix on method performance.

The MS/MSD must meet %R and RPD criteria. See Appendix C for QC limits. Calculate %R using the following equation:

$$\%R = \frac{C_s - C_u}{C_n} \times 100$$

Where:

C_s = Analyte concentration in spiked sample

C_u = Analyte concentration in unspiked sample

C_n = Nominal (theoretical) analyte concentration added to sample

Calculate RPD as follows:

$$RPD = \frac{|C_1 - C_2|}{\frac{(C_1 + C_2)}{2}} \times 100$$

Where:

C₁ = Analyte concentration in 1st sample aliquot.

C₂ = Analyte concentration in 2nd sample aliquot.

The MS/MSD recovery limits are advisory limits only. If the limits are not met, then no further action is required, as long as the LCS is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the analytes. A new solution should be prepared if the recoveries are not within 20% of expected.

Do not dilute MS/MSD samples to get either the spiked or non-spiked target compounds within the initial calibration range. Flag results if the concentration is over the ICAL range.

The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX				+ = PASS		! = FAIL		
CASE	1	2	3	4	5	6	7	8
LCS – % REC	+	+	+	+	!	!	!	!
MS/MSD – % REC	+	!	+	!	+	!	+	!
MS/MSD – RPD	+	+	!	!	+	+	!	!

Case 1: Extraction batch acceptable.

Case 2: Extraction batch acceptable; matrix effect confirmed.

Cases 3 & 4: Extraction batch is unsatisfactory. Investigate MS/MSD problem and document findings in the LIMS Work Order Notes field.

Cases 5, 6, 7 & 8: Extraction batch rejected. Re-extract batch.

9.4 Sample QC

Surrogate recovery

Calculate the surrogate recovery in all field and QC samples immediately after analysis. Print a ChemStation QA Check Report that includes all field and QC samples. The surrogate recoveries must be within QC limits. See Appendix C for QC limits.

Take the following steps if surrogate recovery is not within the limits:

- Check to be sure that there are no errors in the calculations or a system performance problem. If errors are found, recalculate the surrogate recovery. Examine chromatograms for interfering peaks and verify that the surrogate peaks are correctly integrated.
- If either surrogate exceeds the upper control limit and analytes are not detected in the sample, report results without qualification and explain in LIMS Work Order Notes field.
- Re-analyze the extract if a system performance problem or calculation error is not evident. If the extract needs to be diluted it may be diluted for re-analysis.
- If re-analysis of the extract does not solve the problem, the sample may have to be re-extracted.

Do not re-extract undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being reported. Document the event in the run log.

Do not re-analyze the MS or MSD samples, even if surrogate recoveries are outside the limits.

If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis. The similarity in surrogate recoveries in the sample and spike analyses must be documented in the LIMS Work Order Notes field.

If the surrogate recoveries of the re-analysis of the extract are within limits, then:

- If the re-analysis was undiluted, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses.
- If the re-analysis was diluted, the problem was a matrix effect. Report the results from the re-analysis and submit the data from both analyses.

If the re-extraction does not solve the problem, report the results from the first analysis and submit the data from both analyses.

9.5 Method Performance

Method performance is summarized in the following table based on EPA Region 9 Laboratory results obtained from September 2007 to August 2009. Data are from LCS results in water batches. Insufficient data are available to calculate statistics for solids.

Method Performance

Analyte	Number of Measurements	Mean Recovery, %	Standard Deviation (σ)	95% Confidence Interval (2σ)
4,4'-DDD	15	105	17	66-134
4,4'-DDE	15	101	19	62-138
4,4'-DDT	15	107	18	64-136
Aldrin	15	86	19	62-138
alpha-BHC	15	96	18	64-136
alpha-Chlordane	15	95	18	64-136
beta-BHC	15	93	17	66-134
Chlordane (technical)	4	83	8	84-116
delta-BHC	15	104	16	68-132
Dieldrin	15	103	17	66-134
Endosulfan I	15	89	18	64-136
Endosulfan II	15	99	18	64-136
Endosulfan sulfate	15	105	16	68-132
Endrin	15	106	13	74-126
Endrin aldehyde	15	101	20	60-140
Endrin ketone	15	112	25	50-150
gamma-BHC (Lindane)	15	100	17	66-134
gamma-Chlordane	15	100	23	54-146
Heptachlor	15	89	18	64-136
Heptachlor epoxide	15	97	17	66-134
Methoxychlor	15	104	15	70-130
Toxaphene	4	86	14	72-128

The following functional areas of the SOP may be significant sources of analytical error:

- Poor extraction efficiency due to specific analyte characteristics or other problems.
- Standard degradation.
- Chromatographic separation and peak integration.

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, SCV, CCV, QLS, PEM, MS/MSD, and LCS) are recorded in LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

Document the analytical sequence in the Element database or in the instrument Run Log. Case Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the Element database. The data package is produced from Element database and manual log records. Appendix G provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance
- Subsequent instrument modifications and upgrades, including major software upgrades
- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.6 SOP Read and Understood

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. The Lab QC Database is used to maintain the list of assigned analysts for each SOP. Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix H.

11 REFERENCES

Agilent Technologies, *EnviroQuant ChemStation Users Guide*

Agilent Technologies, *Agilent 6890 Series Gas Chromatograph Operating Manuals*

Agilent Technologies, *Agilent 7890 Series Gas Chromatograph Operating Manuals*

U.S. Environmental Protection Agency, *Method 8000C, Determinative Chromatographic Separations, Revision 3, March 2003*

U.S. Environmental Protection Agency, SW-846 Method 8081B, *Organochlorine Pesticides by Gas Chromatography*, Revision 2, February 2007

U.S. Environmental Protection Agency Region 9 *Laboratory Quality Assurance Plan*

USEPA Region 9 Laboratory. *Business Plan*.

USEPA Region 9 Laboratory. *Chemical Hygiene Plan*.

USEPA Region 9 Laboratory. *Environmental Management System*.

USEPA Region 9 Laboratory. SOP 110, *Sample Receiving and Login*

USEPA Region 9 Laboratory. SOP 125, *Disposal Procedures for Unused Aqueous Environmental Samples*

USEPA Region 9 Laboratory. SOP 260, *Gel Permeation Chromatography (GPC) Clean-Up*

USEPA Region 9 Laboratory. SOP 275, *Extraction of Water Samples by Continuous Liquid-Liquid Extraction*

USEPA Region 9 Laboratory. SOP 290, *Extraction of Soil Samples Using Pressurized Fluid Extraction*

USEPA Region 9 Laboratory. SOP 295, *Waste Dilution*

USEPA Region 9 Laboratory. SOP 706, *Laboratory Waste Management Procedures*

USEPA Region 9 Laboratory. SOP 805, *Temperature Monitoring*

USEPA Region 9 Laboratory. SOP 820, *Laboratory Discrepancy and Corrective Action Reporting Procedures*

USEPA Region 9 Laboratory. SOP 835, *Chromatographic Integration Procedures*

USEPA Region 9 Laboratory. SOP 840, *Notebook Documentation and Control*

USEPA Region 9 Laboratory. SOP 880, *Demonstration of Capability*

APPENDIX A.
DEVIATIONS FROM METHOD 8081B

1. The applicability of this SOP has been extended to cover the quantitation of 2,4-DDT, 2,4-DDD, and 2,4-DDE,.
2. The calibration factor is calculated using concentrations in ng/mL instead of mass in nanograms.
3. The system priming solution is equivalent to the highest ICAL standard, not 20 times more concentrated than the CV as specified in Method 8081B.
4. This SOP requires that the % breakdown of 4,4'-DDT and endrin must be $\leq 20\%$ instead of $\leq 15\%$ as in Method 8081B.
5. This SOP allows that 10% of all analytes may exceed the 20% RSD limit in an acceptable initial calibration provided that no analyte exceeds 30% RSD.
6. This SOP requires that the %D between the calibration verification calibration factor and the ICAL calibration factor must be $\leq \pm 30\%$. Method 8081B recommends $\pm 20\%$ as the QC limit.
7. When historical data to establish LCS or MS/MSD recovery limits are not available, the acceptance criteria are set to 65 - 135% rather than 70 - 130% as recommended in Method 8000C.
8. Retention time windows are not calculated as specified in Section 11.6 of EPA SW-846 Method 8000C; instead this SOP uses the default standard deviation of 0.01 specified in Method 8000C giving a retention time window of ± 0.03 minutes.
9. Standards are stored at $>0^{\circ}\text{C}$ (just above freezing) to $\leq 6^{\circ}\text{C}$ instead of 4°C as in the reference method.

APPENDIX B. ANALYTES AND QUANTITATION LIMITS

The following table provides the target analytes list for this SOP with the Chemical Abstracts Registry Number (CASRN) and quantitation limits (QL). QLs are based on a 1L aqueous or 30g solid sample.

Analyte	Reporting	CASRN	Water QL, µg/L	Solid QL, µg/kg
alpha-BHC	R	319-84-6	0.05	1.7
gamma-BHC (Lindane)	R	58-89-9	0.05	1.7
beta-BHC	R	319-85-7	0.05	1.7
delta-BHC	R	319-86-8	0.05	1.7
Heptachlor	R	76-44-8	0.05	1.7
Aldrin	R	309-00-2	0.05	1.7
Heptachlor epoxide	R	1024-57-3	0.05	1.7
gamma-Chlordane	R	5566-34-7	0.05	1.7
alpha-Chlordane	R	5103-71-9	0.05	1.7
4,4'-DDE	R	72-55-9	0.05	1.7
Endosulfan I	R	959-98-8	0.05	1.7
Dieldrin	R	60-57-1	0.1	3.3
Endrin	R	72-20-8	0.1	3.3
4,4'-DDD	R	72-54-8	0.1	3.3
Endosulfan II	R	33213-65-9	0.1	3.3
4,4'-DDT	R	50-29-3	0.1	3.3
Endrin aldehyde	R	7421-93-4	0.1	3.3
Methoxychlor	R	72-43-5	0.5	17
Endosulfan sulfate	R	1031-07-8	0.1	3.3
Endrin ketone	R	53494-70-5	0.1	3.3
Chlordane (technical)	A	57-74-9	5	170
Toxaphene	A	8001-35-2	5	170
2,4'-DDD	A	53-19-0	0.1	3.3
2,4'-DDE	A	3424-82-6	0.1	3.3
2,4'-DDT	A	789-02-6	0.1	3.3
2,4,5,6-Tetrachloro-m-xylene	R	877-09-8	—	—
2,2',3,3',4,4',5,5',6,6'-	R	2051-24-3	—	—
Decachlorobiphenyl				

R = Compounds typically reported.

A = Additional compounds included on a project-specific basis.

NOTE: Only the exo-epoxy isomer (isomer B) of heptachlor epoxide is used as an analytical standard.

APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

QC Measure	Criteria	Frequency
ICAL %RSD*	≤ 20%	With each ICAL
CCV %D**	≤ 30%	1/12 hour sequence
% Breakdown of 4,4'-DDT or endrin	≤ 20%	1 per 12-hour shift
Total % Breakdown	≤ 30%	1 per 12-hour shift
LCS Water %R**	65 – 135	1/extraction batch
LCS Solid %R**	65 – 135	1/extraction batch
MB	< ½ QL	1/extraction batch
QLS %R**	60-140%	1/analysis batch
Matrix Spike Water %R**	65 – 135	1/SDG of 20 or fewer samples
Matrix Spike Solid %R**	65 – 135%	1/SDG of 20 or fewer samples
Matrix Spike Duplicate Precision, RPD**	≤ 20%	1/SDG of 20 or fewer samples
Sample Retention Time Drift	±0.03 minutes	Method setup
SCV %D**	≤ 30%	With each ICAL
Surrogate %R	See Table Below	With each sample
Column Agreement, RPD	≤ 40%	All detected analytes

*Up to 10% of all analytes may exceed the %RSD QC limit of 20% in an acceptable calibration provided that no analyte exceeds 30 %RSD

** Ninety percent of compounds must meet criteria

Surrogate %Recovery Criteria (3σ)

Surrogate	Water	Solid
TCMX	20 – 125	20 – 165
DCB	20 – 155	20 – 162

Surrogate %R criteria are based on results for samples analyzed from 10/1/07 to 9/30/09.

APPENDIX D. RECOMMENDED INSTRUMENT PARAMETERS

INSTRUMENT CONTROL PARAMETERS - 6890 GC

```
=====
                        6890 GC METHOD
=====
```

OVEN

Initial temp: 50 'C (On)	Maximum temp: 310 'C
Initial time: 1.00 min	Equilibration time: 1.00 min
Ramps:	
# Rate Final temp Final time	
1 30.00 140 0.00	
2 7.00 260 0.00	
3 20.00 310 8.00	
4 0.0(Off)	
Post temp: 50 'C	
Post time: 0.00 min	
Run time: 31.64 min	

FRONT INLET (SPLIT/SPLITLESS)

Mode: Pulsed Splitless	Mode: Pulsed Splitless
Initial temp: 225 'C (On)	Initial temp: 225 'C (On)
Pressure: 8.58 psi (On)	Pressure: 8.54 psi (On)
Pulse pressure: 33.0 psi	Pulse pressure: 33.0 psi
Pulse time: 0.60 min	Pulse time: 0.60 min
Purge flow: 50.0 mL/min	Purge flow: 50.0 mL/min
Purge time: 0.55 min	Purge time: 0.55 min
Total flow: 54.6 mL/min	Total flow: 55.0 mL/min
Gas saver: On	Gas saver: On
Saver flow: 20.0 mL/min	Saver flow: 20.0 mL/min
Saver time: 1.50 min	Saver time: 1.50 min
Gas type: Helium	Gas type: Helium

BACK INLET (SPLIT/SPLITLESS)**COLUMN 1**

Capillary Column
Model Number: Restek 11139
Rtx-Clp
Max temperature: 340 'C
Nominal length: 30.0 m
Nominal diameter: 320.00 um
Nominal film thickness: 0.50 um
Mode: constant flow
Initial flow: 1.7 mL/min
Nominal init pressure: 8.58 psi
Average velocity: 30 cm/sec
Inlet: Front Inlet
Outlet: Front Detector
Outlet pressure: ambient

COLUMN 2

Capillary Column
Model Number: Restek 11324
Rtx-Clp-11
Max temperature: 330 'C
Nominal length: 30.0 m
Nominal diameter: 320.00 um
Nominal film thickness: 0.25 um
Mode: constant flow
Initial flow: 1.7 mL/min
Nominal init pressure: 8.54 psi
Average velocity: 30 cm/sec
Inlet: Back Inlet
Outlet: Back Detector
Outlet pressure: ambient

FRONT DETECTOR ()

Temperature: 310 'C (On)
Mode: Constant makeup flow
Makeup flow: 60.0 mL/min (On)

BACK DETECTOR ()

Temperature: 310 'C (On)
Mode: Constant makeup flow
Makeup flow: 60.0 mL/min (On)

Makeup Gas Type: Nitrogen	Makeup Gas Type: Nitrogen
Electrometer: On	Electrometer: On
SIGNAL 1	SIGNAL 2
Data rate: 10 Hz	Data rate: 10 Hz
Type: front detector	Type: back detector
Save Data: On	Save Data: On
Start Save Time: 8.00 min	Start Save Time: 8.00 min
Stop Save Time: 29.00 min	Stop Save Time: 29.00 min
Zero: 0.0 (Off)	Zero: 0.0 (Off)
Range: 0	Range: 0
Fast Peaks: Off	Fast Peaks: Off
Attenuation: 0	Attenuation: 0
COLUMN COMP 1	COLUMN COMP 2
Derive from front detector	Derive from back detector
	POST RUN
	Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint
------	-----------	----------------------

7673 Injector

<u>Front Injector:</u>		
Sample Washes	2	
Sample Pumps	3	
Injection Volume	1.0 microliters	
Syringe Size	10.0 microliters	
PostInj Solvent A Washes	3	
PostInj Solvent B Washes	3	
Viscosity Delay	0 seconds	
Plunger Speed	Fast	
PreInjection Dwell	0.00 minutes	
PostInjection Dwell	0.00 minutes	

<u>Back Injector:</u>		
Sample Washes	2	
Sample Pumps	3	
Injection Volume	1.0 microliters	
Syringe Size	10.0 microliters	
PostInj Solvent A Washes	3	
PostInj Solvent B Washes	3	
Viscosity Delay	0 seconds	
Plunger Speed	Fast	
PreInjection Dwell	0.00 minutes	
PostInjection Dwell	0.00 minutes	

Column 1 Inventory Number :
Column 2 Inventory Number :

END OF INSTRUMENT CONTROL PARAMETERS

APPENDIX E.

CHEMSTATION FILE NAMING CONVENTIONS

Use the following naming conventions for File data, methods, and sequences on ChemStation computers and the LAN:

Directories

On the Workstation:

Data: C:\HPCHEM\1\Data\MDDY or D:\HPCHEM\1\Data\MDDYS

Methods: C:\HPCHEM\1\Methods or D:\HPCHEM\1\Methods

Sequences: C:\HPCHEM\1\Sequence or D:\HPCHEM\1\Sequence

For system controlling multiple instruments, 1 may be changed to reflect the instrument number

System running ChemStation versions C & D HPCHEM is named as MSDCHEM

On the LAN:

Data: I:\Room Number\Instrument\Year\MDDYS

Methods: I:\Room Number\Instrument\Methods

Sequences: I:\Room Number\Instrument\Sequence

Methods

MDDYITA

Sequence

MDDYS

Data Files

For GC:

MDDYICSS

For GC/MS

MDDYIQSS

Variables

A: Enter analysis, as follow:

1,4-Dioxane	X
504	E
TO15	A
BNA	B
BNA-L (SIM)	L
Congeners	C
P/P	P
PCB	P
RSK175	R

Soil Gas	A
TPH-G	G
TPH-D	D
VOA	V

C: Channel: A = front
B = back (if applicable)

DD: Day

I: Instrument
6890 series GCs by last number in name: e.g. 6890-1 = 1 except 5890-2 = A
All GC/MSs by last letter in name: e.g. 5973L = L

M: Month 1-9, A: October, B: November, C: December

Q: QC type

BFB	F
Blank	B
CV	C
Degradation	P
DFTPP	D
IB	Z
IC	I
LCS	L
LCV	Q
Second Source	S
MS/MSD	M

S: Sequential number 1,2 3,

T: Matrix Type (if applicable)
Water W
Solid S
Air A
Oil O
Other X

Y: Year i.e. 5 for 2005

APPENDIX F.
PREVENTIVE MAINTENANCE REQUIREMENTS

Item	Frequency	Actions/Comments
Syringes	As Needed	Clean if dirt is noticeable in the syringe; replace if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged.
Inlet liner	With each ICAL	Check often. Replace when chromatography is degraded or Performance Evaluation Sample fails.
Liner O-rings	As Needed	Replace with liner.
Inlet septum	With each ICAL	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Detector adapter nut	With each ICAL	Check tightness of detector capillary column adapter nut; adapter must not be loose. Replace ferrule when adapter is still loose after you have tightened the nut.
Capillary column fittings	With each ICAL	Check tightness of capillary column ferrule nuts in detector and inlet fittings; they should be snug - do not over tighten.
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	As needed	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.). Bake out column if trimming does not restore chromatographic performance.
Column Replacement	As needed	When trimming and/or baking out no longer restores chromatographic performance.
Ferrules	As needed	Replace ferrules when changing columns and inlet/detector parts.
ECD	As needed	Thermally clean by "baking-out" when a wandering baseline, increased noise, or a change in response is present. Replace when thermal cleaning does not resolve the problem.

APPENDIX G.
TYPICAL DATA PACKAGE FORMAT

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

TDF

Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms

EPA Review Form

ESAT technical review guide

Discrepancy Reports (if applicable)

Work Order Memo (if applicable)

Daily folder review forms or checklists

Analysis matrix listing all analytical runs (for organics only)

Tracking Forms

Work Order(s)

COC(s)

Sample Preparation (for projects that require extraction or digestion)

Bench Sheets (and extraction logs, where used)

Sample cleanup data and records (e.g. GPC logs)

Moisture data as applicable

Initial Calibration Data - Arranged chronologically

Sample Data - Arranged chronologically

Miscellaneous Data

Other data as applicable (e.g. storage blanks)

Standard Records

Standards records from LIMS (and logbook pages as needed)

STANDARD OPERATING PROCEDURE: 330
Revision: 4, Effective: 02/15/2010

[illegible]

**USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA**

**STANDARD OPERATING PROCEDURE 335
POLYCHLORINATED BIPHENYLS AS AROCLORS BY GC/ECD**

Revision 2
Effective Date: March 31, 2006

Reviewed by: _____
Richard Bauer Date
Chemistry Team Leader/Technical Director

Reviewed by: _____
K. W. Hendrix, Laboratory QA Officer Date

Approved by: _____
Brenda Bettencourt, Laboratory Director Date

Periodic Review:

Signature	Title	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____

This SOP was prepared by ICF Consulting for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA contract no. 68-W-01-028). ESAT Document Control Number: 00904025-6340

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1 SCOPE AND APPLICABILITY

This standard operating procedure (SOP) describes the procedures used for the analysis of polychlorinated biphenyls (PCBs) as Aroclors by gas chromatography (GC) with electron capture detectors (ECDs) in extracts prepared from samples by USEPA Region 9 Laboratory SOP 275 for aqueous samples and SOP 290 for solid samples. This SOP is based on procedures contained in EPA SW-846 Method 8082A, Revision 1, November 2000 and is applicable to water, sludges, soils, sediments, oil, wipe samples, biological samples, and other solid matrices such as wire, sheet metal, and potting material in support of the EPA's Superfund, RCRA, WQM, UIC, and TSCA programs. The applicability of these procedures to specific project data quality objectives (DQOs) must be assessed on a case-by-case basis. This SOP applies to analyses conducted at the USEPA Region 9 Laboratory in Richmond, CA.

Refer to Appendix A for a description of deviations from the reference method and Appendix B for specific analytes and quantitation limits.

2 METHOD SUMMARY

This method describes the analysis of hexane extracts of environmental samples for selected Aroclors. The sample components are separated, identified, and quantitated by injecting microliter quantities of sample extracts onto a pair of high resolution fused silica capillary columns with dissimilar stationary phases in a temperature programmed GC equipped with electron capture detectors.

Tentative identification of an Aroclor in a sample extract is made by comparing the chromatographic pattern in the sample to the chromatographic pattern of Aroclor standards analyzed under the same conditions used for samples and by the similarity in the calculated concentrations of the characteristic peaks. Aroclor concentrations are determined by comparing the responses of from 3 to 5 major peaks, chosen to be characteristic for that Aroclor and for their capability to discriminate between the Aroclor of interest and other Aroclors, in the sample extract to those same peaks in the most similar Aroclor standard. The Aroclor concentration in the sample is calculated by the data system using the calibration factor from the initial calibration based on the sum of the areas of 3 to 5 characteristic peaks for each Aroclor. Alternatively, calibration and quantitation may be done using the total area of the peaks in an Aroclor standard and the sample; this method may be used when the Aroclor standard does not fully represent the PCBs in the sample. Tentative Aroclor identifications are confirmed using results from the second column. The lower of the results from the two columns is reported.

3 DEFINITIONS

Analytical Sample - any sample in which analytes are being determined, excluding standards, blanks, or QC reference samples.

Aroclor - an industrial trade name for commercially produced mixtures of polychlorinated biphenyl congeners.

Calibration Factor (CF) - the peak area (or height) in the standard divided by the concentration of the standard injected (in ng/mL).

Calibration Verification (CV) Standard - the mid-level 1016/1260 calibration solution or the calibration standard of the Aroclor of interest. The CV standard is used to validate the initial calibration for the samples. This is equivalent to a CCV.

Demonstration of Capability (DOC): A demonstration that the Laboratory can produce data of acceptable quality. A DOC consists of three elements:

- An approved SOP (for which each analyst is trained),
- A method detection limit study completed by the analyst, and
- A precision and accuracy study completed by the analyst.

ECD – electron capture detector.

Extraction Batch – A group of up to twenty samples or less extracted together and sharing the same batch QC samples.

Initial Calibration Standards (ICAL) – Standards used to calibrate the instrument response with respect to analyte concentration.

Instrument Blank (IB) - a blank that is the same matrix as the calibration standards containing surrogates but without the analytes.

Laboratory Control Sample (LCS) - An aliquot of blank matrix to which known quantities of the method analytes are added. The LCS is analyzed like a sample, and its purpose is to determine whether the methodology is in control, and whether the Laboratory is capable of making accurate and precise measurements. The LCS is also known as a laboratory fortified blank (LFB) or blank spike (BS).

LIMS: Laboratory Information Management System. The Element database.

Matrix Spike (MS) / Matrix Spike Duplicate (MSD) - aliquots of an analytical sample to which known quantities of the method analytes are added. The MS/MSD is analyzed exactly like a sample; its purpose is to determine whether the sample matrix contributes bias

to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations.

Method Blank (MB) - An aliquot of blank matrix that is treated exactly as a sample. The MB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment. The MB is also known as laboratory reagent blank (LRB).

Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Primary Dilution Standard Solution (PDS): A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

Quantitation Limit (QL) - The concentration at which confidence in the reported value requires no qualifying remarks. A standard is analyzed at the QL to verify the previously established calibration curve.

Quantitation Limit Standard (QLS) - A standard used to check the accuracy of the analysis at the quantitation limit.

Sample Delivery Group (SDG) - An SDG number is assigned to a set of samples not to exceed twenty (20) from the same site and of the same matrix received within a 14 day period.

Second Source Calibration Verification (SCV) - A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check the initial calibration.

Stock Standard Solution (SSS) - A concentrated standard containing the method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Surrogate (SURR): Compounds which are extremely unlikely to be found in any sample that are added to a sample aliquot in a known amount before extraction or other processing, and measured with the same procedures used to measure other sample components. The purpose of the surrogate is to monitor method performance with each sample.

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current

versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Routine procedures in this SOP do not require contact with concentrated solutions or neat materials.

Hexane liquid and vapors are extremely flammable. Keep away from ignition sources. Harmful if inhaled or swallowed. May cause damage to kidneys, nerves, and respiratory system. Irritating to skin, eyes and mucous membranes. Toxic by ingestion and inhalation. Vapor inhalation causes irritation of nasal and respiratory passages, headache, dizziness, nausea, central nervous system depression. Chronic overexposure can cause severe nerve damage. No systemic toxicity has been reported. Emergency First Aid - Inhalation: immediately remove to fresh air. If not breathing, administer mouth-to-mouth rescue breathing. If there is no pulse, administer cardiopulmonary resuscitation (CPR). Contact physician immediately. Eye contact: Rinse with copious amounts of water for at least 15 minutes. Get emergency medical assistance. Skin contact: Flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothing and shoes. Wash clothing before re-use, and discard contaminated shoes. Get emergency medical assistance. Ingestion: Call local Poison Control Center for assistance. Contact physician immediately. Aspiration hazard - do not induce vomiting.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Many parts of the GC operate at temperatures high enough to cause serious burns. Allow heated zones to cool below 50°C before working on or around them.

Electron capture detectors contain a cell plated with ^{63}Ni , a radioactive isotope. Although beta particles in the ECD have little penetrating power, they may be hazardous if the isotope is ingested or inhaled. Radioactive leak tests must be performed at regular intervals. Do not open the ECD cell or use solvents to clean it. Connect the ECD exhaust to a fume hood or a vent.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Pollution Prevention Plan* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-regulated Waste	Not applicable
Sample extracts	Hazardous waste	Toxic, Flammable, Contains PCBs. See solvent MSDS

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Refer to Region 9 SOP 275 *Extraction of Water Samples Using CLLE*, or SOP 290 *Extraction of Soil Samples Using PFE (Pressurized Fluid Extraction-ASE)*.

5.2 Internal Chain-of-Custody

Sample extracts for GC analysis are received from the extraction lab personnel and custody is transferred to the GC laboratory staff. The GC analyst acknowledges the receipt of the sample extracts by signing the appropriate sections of the completed LIMS bench sheet. Copies of tracking sheets, chain of custody records, and the original LIMS extraction bench sheet should accompany the sample extracts.

The extracts are marked with the EPA Region 9 Laboratory number, which can be checked against the tracking sheets and chain of custody record to determine the client sample identification, case number, and sample delivery group (SDG) number. Verify sample IDs and dates and times of collection against the chain-of-custody form.

5.3 Sample Storage

Store extracts in Room 400 at $>0^{\circ}\text{C}$ (just above freezing) to $\leq 6^{\circ}\text{C}$ before and after analysis. Retain sample extracts until the hold time has expired.

5.4 Holding Time

Extracts must be analyzed within 40 days of extraction.

6 INTERFERENCES

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to anomalous peaks or elevated baselines in gas chromatograms.

Interferences caused by phthalate esters can pose a major problem in PCB analysis. Phthalate esters are commonly used as plasticizers and are easily extracted from plastic materials. Contact of samples, solvents, reagents, glassware, extracts, or other sample processing apparatus with plastics must be avoided.

High-boiling materials in the sample extract, including some phthalates, which may contaminate the GC, can be removed by gel permeation chromatography (GPC). See Region 9 SOP 260 *Gel Permeation Chromatography Clean-Up*.

Elemental sulfur in sample extracts can interfere with the chromatographic determination of PCBs. Sulfur can be removed by the use of copper or tetrabutylammonium sulfate (TBA) - See EPA SW-846 Method 3660B - or by GPC.

Other chlorinated pesticides and multicomponent analytes, such as Toxaphene, Chlordane, and Strobane may interfere with the analysis of PCBs. See SW-846 Method 3620B, *Florisil Cleanup*, Method 3630C, *Silica Gel Cleanup*, and Method 3665A, *Sulfuric Acid/Permanganate Cleanup* to separate pesticides from PCBs.

Contamination may occur when a sample that does not contain, or contains low concentration of PCBs is analyzed immediately after a sample containing relatively high concentrations. Samples suspected of being affected by carryover must be re-analyzed. Instrument blanks should be analyzed to ensure that carryover is not occurring. Syringes, splitless injection port liners, and inlet seals must be cleaned carefully or replaced as needed.

Contamination of clean glassware, apparatus, and instruments and may occur from processing samples containing high levels of PCBs. Exhaustive clean up of affected items may be required to eliminate the contamination.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. Minor deviations may be made in specific apparatus and materials provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

Gas chromatograph with dual ECDs, dual splitless injection port(s), and electronic pressure control (EPC). (Hewlett Packard/Agilent 5890, 6890, or equivalent).

Fused Silica Capillary Gas Chromatography Column -- Any capillary column which provides adequate resolution, capacity, accuracy, and precision may be used. The following column pair was used for method validation:

- Column 1: RTX-CLPesticides - 30 m x 0.32 mm x 0.5 μ m (Restek cat.# 11139 or equivalent.)
- Column 2: RTX-CLPesticides2 - 30 m x 0.32 mm x 0.25 μ m (Restek cat.# 11324 or equivalent.)

Data Acquisition and Processing System -- Able to control the GC and to acquire, store, and process GC data. The software must be able to calculate calibration factors and the concentrations of analytes in samples. Chemstation (available from Agilent) software (or equivalent).

7.2 Reagents

Enter all reagents into the LIMS database.

Reagents may contain impurities that might affect analytical data. Only materials that conform to the American Chemical Society (ACS) high purity pesticide quality or equivalent should be used. If the purity of a reagent is in question, analyze for contamination prior to use.

Hexane - pesticide quality or equivalent

7.3 Standards

Document the receipt and preparation of all standards in the Element database. All standards must be barcoded upon receipt.

All ampulated calibration materials must be maintained in the refrigerator at $>0^{\circ}\text{C}$ (just above freezing) to $\leq 6^{\circ}\text{C}$ and protected from light. Use the manufacturer's expiration date for ampulated standards.

Opened ampules and working standards must be maintained in a freezer at $\leq -10^{\circ}\text{C}$ and protected from light. The solution is assigned an expiration date which is either 6 months from preparation date, or the expiration date of the stock standard used in the preparation, whichever is earlier. Analysts must allow all standard solutions to equilibrate to room temperature before use.

- Calibration Stock Standards:

Description	Suggested Vendor and Catalog #	Compounds	Concentration
Pesticide Surrogate Mix	Restek 32000	2,4,5,6-Tetrachloro-m-xylene (TCMX) Decachlorobiphenyl (DCB)	each at 200 $\mu\text{g/mL}$ in acetone
Aroclor 1016/1260	Restek 32039	Aroclor 1016 Aroclor 1260	each at 1,000 $\mu\text{g/mL}$ in hexane
Aroclor 1221	Restek 32007	Aroclor 1221	1,000 $\mu\text{g/mL}$ in hexane
Aroclor 1232	Restek 32008	Aroclor 1232	1,000 $\mu\text{g/mL}$ in hexane
Aroclor 1242	Restek 32009	Aroclor 1242	1,000 $\mu\text{g/mL}$ in hexane
Aroclor 1248	Restek 32010	Aroclor 1248	1,000 $\mu\text{g/mL}$ in hexane
Aroclor 1254	Restek 32011	Aroclor 1254	1,000 $\mu\text{g/mL}$ in hexane
Aroclor 1262	Restek 32409	Aroclor 1262	1,000 $\mu\text{g/mL}$ in hexane
Aroclor 1268	Restek 32410	Aroclor 1268	1,000 $\mu\text{g/mL}$ in hexane

- Calibration Standards: 5 levels detailed in table in Section 8.2.1. Prepare the calibration standards in hexane from the SSSs at the recommended concentrations indicated in the table.
- Calibration Verification Solution (CV), Level 3 Aroclor calibration solution.
- Quantitation Limit Standard (QLS), Level 1 Aroclor calibration solution. The QLS is used to verify instrument response at the quantitation limit.
- Second Source Calibration Verification (SCV) – Approximately equivalent to the mid-point initial calibration solution but prepared from a source different from the source of the calibration standards. The SCV is used to check the accuracy of the initial calibration solutions. Using a different lot number as a second source is acceptable. See table below for suggested vendors for SCV standards.

Aroclor		Suggested Vendors & Catalog Numbers	
1016	AccuStandard C-216S	Supelco 48097	Ultra Scientific PP-281-1
1221	AccuStandard C-221S	Supelco 48098	Ultra Scientific PP-291-1
1232	AccuStandard C-232S	Supelco 44805	Ultra Scientific PP-301-1
1242	AccuStandard C-242S	Supelco 44806	Ultra Scientific PP-311-1
1248	AccuStandard C-248S	Supelco 44807	Ultra Scientific PP-341-1
1254	AccuStandard C-254S	Supelco 44808	Ultra Scientific PP-351-1
1260	AccuStandard C-260S	Supelco 44809	Ultra Scientific PP-361-1
1262	AccuStandard C-262S	Supelco 44810	Ultra Scientific PP-372-1
1268	AccuStandard C-268S		Ultra Scientific PP-382-1

Concentrations and solvents:

AccuStandard – 35 µg/mL, isooctane

Supelco – 1,000 µg/mL, isooctane

Ultra Scientific – 100 µg/mL, hexane

- Instrument Blank – a solution of hexane fortified with Pesticide Surrogate Mix.

7.4 Supplies

Volumetric flasks (type A): 100-mL, 50-mL, 25-mL, and 10-mL.

Microliter syringes: 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1-mL.

Vials with Teflon-lined screw caps: 15-mL or 12-mL and 2 mL.

Vial inserts, 5x31 mm 0.25-mL shell style (VWR catalog #66010-640, VWR catalog #66009-290, or equivalent)

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set up the instrument using operating parameters provided in Appendix D. Adjust as needed to meet method, SOP, and project requirements and good chromatographic practice.

Prior to analyzing calibration, QC, or field samples make a LIMS batch and sequence as required to obtain LIMS assigned IDs for the calibration and QC samples.

Follow the file naming conventions provided in Appendix E.

Ensure that appropriate waste containers are present and properly labeled.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

The Aroclor 1016/1260 mix includes many of the peaks represented in the other five Aroclor mixtures. Consequently, a multi-point initial calibration with this mixture demonstrates the linearity of the detector. Mid-level standards of each of the remaining Aroclors are analyzed and used to aid the analyst in pattern recognition and to determine a single point calibration factor for these Aroclors.

Select a set of three to five peaks for each Aroclor that are characteristic for the Aroclor and capable of discriminating between Aroclors. Do not select any peaks that elute at the same retention time as DDT, DDD, or DDE. The selected peaks should have at least 25% of the area of the largest peak in the target Aroclor. In addition, the peaks chosen for Aroclors 1016 and 1260 in the 1660 mix must be unique to the corresponding Aroclor.

To calibrate using characteristic peaks, select a set of three to five peaks for each multi-component analyte that are characteristic for the analyte. The selected peaks should have at least 25% of the area of the largest peak in the analyte. Identify each of the 3 to 5 peaks in the data system method as belonging to a multi-component standard by assigning an "L" compound type indicator to each peak. Then insert a "TOTAL" entry for the analyte after the last analyte peak; assign it an "L" compound type and the same concentration as the other analyte peaks. ChemStation will sum the areas of the individual peaks for the analyte and calculate a CF for the summed areas in the "TOTAL" entry.

Perform an initial calibration for the Aroclor 1016/1260 mixture using a minimum of five calibration standards to establish an external standard calibration using the average calibration factor. Refer to Section 9.2 and Appendix C for required frequency and QC limits.

The concentration of the Level 1 Aroclor 1016/1260 mix standard is the quantitation limit for all Aroclors except for Aroclor 1221 which is at twice the QL of the other Aroclors. The remaining concentrations span the expected working range of the instrument.

Recommended Calibration Levels:

Compounds	Level 1 ng/mL	Level 2 ng/mL	Level 3 ng/mL	Level 4 ng/mL	Level 5 ng/mL
Aroclors 1016/1260	20	100	200	500	1,000
TCMX, DCB	4	20	60	100	200
Aroclor 1221			400		
TCMX, DCB			60		
All other Aroclors			200		
TCMX, DCB			60		

Re-calibrate the ChemStation method using responses from the analyses of the calibration standards. Save the calibration file. Name it using the method number and date: See Appendix E for ChemStation naming conventions.

Print an initial calibration summary by choosing the Response Factors to Print menu item from the ChemStation InitCal menu. Verify that the %RSD for Aroclors 1016, 1260 and the surrogates meet QC criteria in Appendix C.

Generate a compound list by choosing the List Compounds menu item from the ChemStation InitCal menu; print this report and include it in the ICAL data package.

Print page 3 of the ChemStation Edit Compounds list box for one analyte showing the ICAL level IDs, concentrations, and responses and include in the ICAL data package.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the failed one in the ICAL. If more than one standard fails, corrective action is required (see Section 8.4 for detailed maintenance and troubleshooting procedures).

An ICAL based on the total area response of an Aroclor may be required if the chromatographic pattern in a sample does not match any Aroclor standard. Assign an "H" compound type indicator in ChemStation. Specify the retention time range by first entering the median retention time of the range as the Aroclors retention time then entering the difference between the median and the start or end point in the "Extract signals from" - and + fields.

The width of the retention time window for each peak is ± 0.03 minutes.

8.2.2 Second Source Calibration Verification

Analyze an SCV sample after the ICAL for each Aroclor calibrated. Verify that the results meet the %R QC criteria in Appendix C. If the SCV does not meet the acceptance criteria, take corrective action specified in Section 8.4.

8.2.3 Calibration Verification

The calibration verification standard is used to validate the initial calibration standard for the samples run during the associated 12-hour time period. The CV sample is the Level 3 calibration standard.

See Section 9.2 for frequency, acceptance criteria, and corrective action requirements.

8.2.4 Quantitation Limit Standard

The QLS is used to verify analytical system response at the quantitation limit. Analyze a Level 1 standard of Aroclor 1016/1260.

See Section 9.2 for frequency, acceptance criteria, and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

Allow sample extracts to reach ambient temperature before analysis.

Check that the numbers on the vials coincide with the numbers on the LIMS extraction batch to ensure that the correct sample is being analyzed.

Note if the sample has an unusual color or other physical properties. If any physical signs of contamination are present, screen the samples to protect the analytical system from damage or contamination, and to determine the appropriate subsequent dilutions. Record unusual items in the LIMS "MMO" field.

8.3.2 Sample Analysis and Analytical Sequence

Prepare a LIMS sequence to include instrument blanks, instrument QC (CCV, QLS), batch QC (MB, LCS, MS/MSD), and field samples. LIMS will assign identifiers for the instrument QC when the sequence is saved; batch QC identifiers will have been assigned in the LIMS bench sheet.

Prepare a sample sequence in the instrument data acquisition software. Use the LIMS identifiers for the batch and instrument QC; include the laboratory sample number (work order-sample number) in the "Sample" field and dilution level, if any in the "Multiplier" field.

Name the data files according to the data file naming convention outlined in Appendix E.

Record the analytical sequence in the instrument run log.

Load the samples in the autosampler according to their designated positions in the sequence file. The recommended analysis sequence is:

1. IB
2. CCV (AR1660 or Aroclor(s) of interest)
3. QLS (AR 1660)
4. Batch QC
5. Samples, sample dilutions, and instrument blanks as needed
6. IB
7. CCV (AR1660 or Aroclor(s) of interest)

8.3.3 Analyte Identification and Quantitation

Process the data using the Agilent ChemStation software data analysis module. This module identifies the method analytes in the sample chromatogram by comparing the retention time of peaks in the sample chromatogram to the retention times of peaks in calibration standards analyzed using identical conditions. Calculations use the average calibration factor from the initial calibration. Report the lower of the "TOTAL" Aroclor concentrations found by the two columns.

Aroclor concentrations in the sample extract as shown on the ChemStation quantitation report are calculated as:

$$ng / mL = \frac{Ax}{CF}$$

Where:

Ax = area (or height) response of the sample
CF = mean calibration factor (area/[ng/mL] = area/pg) from the initial calibration.

LIMS calculates the final sample concentration.

Aroclor concentration in a liquid sample is:

$$Concentration(\mu g / L) = \frac{Ax \times Vt \times DF}{CF \times Vo \times Vi \times 1,000}$$

Where:

Ax and CF are the same as above.

Vt = Total volume of the concentrated extract in μ L.

DF = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, DF = 1.

Vi = Volume of the extract injected in μ L. Normally 1 μ L.

Vo = Volume of the aqueous sample extracted in mL.

1,000 = pg/ng

Using the units specified for these terms will result in a concentration in ng/mL, which is equivalent to μ g/L.

Aroclor concentration in a solid or oil sample is:

$$Concentration(\mu g / kg) = \frac{Ax \times Vt \times DF}{CF \times Vi \times Ws \times D \times 1,000}$$

Where:

Ax, Vt, DF, CF, Vi, and 1,000 are as above.

Ws = Weight of extracted sample (g).

D = Dry weight factor (100 - %moisture/100)

Using the units specified for these terms will result in a concentration of ng/g, which is equivalent to μ g /Kg.

Results for wipe samples are reported as μ g/wipe.

Results for wire samples are reported as μ g/100 surface area units; i.e. 100 cm², 100 in².

Aroclor amount (μ g) in a wipe or wire sample is:

$$Amount(\mu g) = \frac{A_x \times V_t \times DF}{CF \times V_i \times 1,000,000}$$

Where:

A_x , V_t , and V_i are as above.

1,000,000 = pg/ μ g

Review all chromatograms for correct peak identification and for correctly drawn baselines for the analytes of interest. See SOP 835, *Chromatographic Integration Procedures* for guidance in drawing baselines.

Aroclors are normally quantitated using area response; however, when overlapping peaks are present peak height is recommended.

An Aroclor in a sample extract is identified by comparing the chromatographic pattern of peaks in the sample to that of Aroclor standards analyzed under the same conditions as the sample by electronically overlaying the chromatograms or by visually comparing printed chromatograms and also by noting which Aroclor quantitation result shows the least variance in the calculated concentrations of the characteristic peaks. An Aroclor is quantitated using the initial calibration of the most similar Aroclor standard.

A peak that is not representative of the Aroclor in a sample may be removed from the data set by using the Q test. See the Region 9 *Laboratory Quality Assurance Plan*.

Weathering of Aroclors may alter the chromatographic pattern to the point where it may not be recognizable as a specific Aroclor. In this case, quantitate the Aroclor by comparing the total area of the PCB pattern in the sample to the total area of the most similar Aroclor standard. Note in LIMS.

Samples containing more than one Aroclor present similar problems. If the Aroclors cannot be quantitated separately, quantitate by comparing the total area of the PCB pattern in the sample to the total area of the most similar Aroclor standard. Note in LIMS.

8.3.4 QC Review

As soon as possible after analysis and prior to entry into LIMS, inspect sample and QC data for compliance with QC limits in Appendix C. If no significant problems are found, review the following QC data for compliance with SOP requirements:

- Target analyte results must be within range of initial calibration.
- Process and review results of instrument QC (CV, QLS) immediately after their analysis to verify that the results are within QC limits. If the instrument QC results are not within QC limits, stop the sequence and take corrective action before resuming the sequence. See Section 9.2 for instrument QC requirements.
- Process and review the results for the MB, LCS, and MS/MSD batch QC samples and verify that the results are within QC limits. See Section 9.3 for batch QC requirements.
- Determine if surrogate recoveries for field and QC samples are within QC limits.
- Review all sample results to determine if any samples need to be re-analyzed at a dilution.
- If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report.

8.3.5 Data Export and LIMS Entry

Generate epatemp.txt files for field and QC samples by also printing the report to the screen. The Omit Target Compounds that are Missed checkbox in the ChemStation Quantitation Report Options window must be unchecked. These files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table.

Copy sample data files from the local drive to the appropriate instrument data subdirectory on the Region 9 LAN to make them available to LIMS and to archive them.

Create an empty upload table in the LIMS Data Entry/Review table then open the DataTool module. Select the instrument data files to be imported then merge the files using the appropriate cross table. Save the merged upload file in DataTool and in the Data Entry table. See LIMS manual for detailed procedure.

Review results in the LIMS. Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

8.4 Maintenance

Symptoms of common problems:

- Carryover

Possible causes: Analyzing a sample containing high molecular weight components or analyzing high-level and low-level samples sequentially.

Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.

Possible cause: column flow rate problem.

Corrective action: check flow rate and adjust as necessary.

- Longer retention time and or smaller peaks.

Possible causes: column flow rate problem, injection port leak, or column contamination.

Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

- Loss of resolution.

Possible causes: column flow rate problem, injection port leak, or column contamination.

Corrective action: Check for leaks, replace septum, liner, and inlet seal, clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

- Autosampler “plunger error”

Remove syringe from autosampler and clean by drawing and expelling a 1:1 (v/v) Hexane/Acetone mixture. After withdrawing and expelling three syringe volumes, withdraw the plunger and wipe it with a Kimwipe. Repeat; continue until no residue remains on the plunger. Re-install syringe in autosampler. Replace syringe if problems continue.

- Noisy baseline or abnormally high ECD output

Possible cause: contaminated detector.

Corrective action: Thermal cleaning of ECD. Follow instructions in chapter on ECD or micro-ECD detectors in Agilent Operating Manual Vol 3 – Detectors. Replace detector if thermal cleaning does not alleviate symptoms.

Refer to Appendix F for the preventative maintenance operations and schedules.

9 QUALITY CONTROL

9.1 Demonstration of Capability

The EPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880 for more details.

9.2 Instrument QC

Since the reported result is the “TOTAL” Aroclor result, the QC criteria apply to the “TOTAL” Aroclor result only, not to each of the 3 to 5 characteristic peaks for each Aroclor.

9.2.1 Initial Calibration

The Aroclor 1016/1260 mix includes many of the peaks represented in the other five Aroclor mixtures. Consequently, a multi-point initial calibration with this mixture demonstrates the linearity of the detector. Mid-level standards of each of the remaining Aroclors are analyzed and used to aid the analyst in pattern recognition and to determine a single point calibration factor for these Aroclors.

Demonstration and documentation of an acceptable initial calibration are required before any samples are analyzed. The calibration for Aroclors 1016 and 1260 is a five level external standard calibration method for both Aroclors and surrogates.

The GC system must be calibrated whenever corrective action changes instrument response (e.g., detector gas adjustment, column replacement, etc.) is performed or if the calibration verification criteria cannot be met.

The data system calculates the calibration factor (CF) for each analyte and surrogate as:

$$CF = \frac{Ax}{Cx}$$

Where:

Ax = area (or height) response of the sample

Cx = Concentration of analyte (ng/mL)

The data system calculates the mean CF for all analytes and surrogates.

The data system calculates the relative standard deviation (RSD) of the calibration levels as:

$$\%RSD = \left[\frac{\sqrt{\frac{\sum_{i=1}^n (CF_i - CF_{avg})^2}{n-1}}}{CF_{avg}} \right] \times 100$$

Where:

CF_i = calibration factor at the specific level (i)

CF_{avg} = average calibration factor

n = number of calibration points

Verify that the Aroclor 1660 ICAL meets the %RSD acceptance criteria in Appendix C.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the cause for failure must be determined and corrected before analysis of samples can proceed.

Analyze an SCV of each Aroclor calibrated immediately after the ICAL. If SCV criteria (see Appendix C) are not met, the SCV must be re-analyzed. If it fails again, prepare a fresh solution. Take corrective action as needed before continuing with analysis, including reanalysis or re-preparation and reanalysis of the initial calibration if necessary.

9.2.2 Calibration Verification

Analyze a calibration verification standard at the beginning of each 12-hour analytical period and at the end of the 12-hour analytical period. The 12-hour analytical period begins with the injection of the calibration verification standard and ends with the completion of analysis of the last sample that can be injected within 12 hours of the beginning of the period. Analysis of calibration verification standards, bracketed by instrument blanks, after every ten samples is recommended. The calibration verification standard is used to validate the initial calibration for the samples run during the associated 12-hour time period.

The ChemStation Environmental Data Analysis module "Evaluate Continuing Calibration Report" calculates a percent difference (%D) by comparing CF for the CV to the average CF of the ICAL:

$$\% D = \left(\frac{CF_{cv} - CF_{avg}}{CF_{avg}} \right) \times 100$$

Where:

CF_{avg} = Average CF from ICAL

CF_{cv} = CF from the CV

If CV criteria (see Appendix C) are not met, re-analyze the CV. If it fails again, prepare a fresh solution and re-analyze. Take corrective action as needed before continuing with analysis.

9.2.3 Quantitation Limit Standard

Analyze a quantitation limit standard (QLS) of Aroclor 1660 each day when analyses of field or QC samples are performed. The QLS is used to verify analytical system response at the quantitation limit.

The QLS sample must meet percent recovery (%R) criteria. Calculate %R using the following equation:

$$\% R = \frac{C_s}{C_n} \times 100$$

Where:

C_s = Analyte concentration in sample

C_n = Nominal (theoretical) analyte concentration

If QLS criteria (see Appendix C) are not met, re-analyze the QLS. If it fails

again, prepare a fresh solution and re-analyze. Take corrective action as needed before continuing with analysis.

9.3 Batch QC

9.3.1 Method Blank

A method blank (MB) is extracted and analyzed with each extraction batch or every 20 samples, whichever is more frequent, to demonstrate that the entire analytical system - from extraction through GC analysis - is free of contamination.

See Appendix C for QC limits.

If the MB is not acceptable, the source of the contamination must be found and eliminated and the problem documented before analysis can proceed. If re-analysis does not solve the problem, the batch may have to be re-extracted. Corrective action is decided by the EPA TOPO on a case by case basis.

If the surrogate recovery does not meet acceptance criteria, re-analyze the extract. If the surrogate recovery still does not meet acceptance criteria, the batch may have to be re-extracted. Corrective action is decided by the EPA TOPO on a case by case basis.

9.3.2 Laboratory Control Sample

An LCS is extracted and analyzed once per extraction batch or every 20 samples, whichever is more frequent to demonstrate that the analytical system is in control.

The LCS must meet %R Criteria. See Appendix C for QC limits.

If the LCS criteria are not met, re-analyze the LCS. If the %R still does not meet acceptance criteria, the batch may have to be re-extracted. Corrective action is decided by the EPA TOPO on a case by case basis.

If the surrogate recovery does not meet acceptance criteria, re-analyze the extract. If the surrogate recovery still does not meet acceptance criteria, the batch may have to be re-extracted. Corrective action is decided by the EPA TOPO on a case by case basis.

9.3.3 MS/MSD

Laboratory fortified matrix (MS) and duplicate (MSD) samples are extracted

and analyzed for each extraction batch containing up to twenty samples. The MS/MSD samples demonstrate the effect of the sample matrix on method performance.

The MS/MSD must meet %R and RPD criteria. See Appendix C for QC limits.

Calculate %R using the following equation:

$$\% R = \frac{C_s - C_u}{C_n} \times 100$$

Where:

C_s = Analyte concentration in spiked sample

C_u = Analyte concentration in unspiked sample

C_n = Nominal (theoretical) analyte concentration

Calculate RPD as follows:

$$RPD = \frac{|C_1 - C_2|}{\frac{(C_1 + C_2)}{2}} \times 100$$

Where:

C₁ = Analyte concentration in 1st sample aliquot.

C₂ = Analyte concentration in 2nd sample aliquot.

The MS/MSD recovery limits are advisory limits only. If the limits are not met, then no further action is required, as long as the LCS is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the spike compounds. A new solution should be prepared if the recoveries are not within 20% of expected.

The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX				+ = PASS		- = FAIL		
CASE	1	2	3	4	5	6	7	8
LCS - % REC	+	+	+	+	-	-	-	-
MS/MSD -% REC	+	-	+	-	+	-	+	-
MS/MSD – RPD	+	+	-	-	+	+	-	-

- Case 1: Extraction batch acceptable.
Case 2: Extraction batch acceptable; matrix effect confirmed.
Cases 3 & 4: Extraction batch is unsatisfactory. Investigate MS/MSD problem and document findings in the LIMS MMO field.
Case 5: Extraction batch rejected. Batch may have to be re-extracted unless LCS problem is determined and documented.
Cases 6, 7 & 8: Extraction batch rejected. Re-extract batch.

9.4 Sample QC

Surrogate recovery

Calculate the surrogate recovery in all field and QC samples immediately after analysis using the average surrogate calibration factor from the multi-point Aroclor 1016/1260 initial calibration.

Print a ChemStation QA Check Report that includes all field and QC samples. See Appendix C for QC limits. The %R of both surrogates is calculated, but we normally only control on DCB. Do not qualify sample results due to failure of TCMX recovery.

Take the following steps if DCB surrogate recovery is not within the limits:

- Check to be sure that there are no errors in the calculations or a system performance problem. If errors are found, recalculate the surrogate recovery. Examine chromatograms for interfering peaks and verify that the surrogate peaks are correctly integrated.
- If the DCB recovery fails, but TCMX recovery is within QC limits, control on the TCMX surrogate and document this in the LIMS MMO field. Do not qualify the result. This usually occurs because of interference with DCB from the sample matrix.
- Re-analyze the extract if a system performance problem or calculation error is not evident. If the extract needs to be diluted it may be diluted for re-analysis.

- If re-analysis of the extract does not solve the problem, the sample may have to be re-extracted. Corrective action is decided by the EPA TOPO on a case by case basis.
- Document QC failure in LIMS MMO field and flag the result following Appendix M of the Region 9 QA Plan.

Do not re-extract undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being reported. Document the event in the run log.

Do not re-analyze the MS/MSD QC samples due to QC failure.

If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis. The similarity in surrogate recoveries in the sample and spike analyses must be documented in the LIMS MMO field.

If the surrogate recoveries of the re-analysis of the extract are within limits, then:

- If the re-analysis was undiluted, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses.
- If the re-analysis was diluted, the problem was a matrix effect. Report the results from the re-analysis and submit the data from both analyses.

If the re-extraction does not solve the problem, report the results from the first analysis and submit the data from both analyses.

9.5 Method Performance

Method performance is summarized in the following table based on Region 9 Laboratory results obtained from April 2004 to Oct 2005. Insufficient data are available to determine LCS recovery in oil.

Method Performance

Analyte	Matrix	QC Type	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2 σ)
AR 1016	Wipe	LCS	19	103	60.5 - 167
AR 1260	Wipe	LCS	19	107	60.6 - 177

Analyte	Matrix	QC Type	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2 σ)
AR 1016	Solid	LCS	21	94	64.9 - 123
AR 1260	Solid	LCS	21	97.6	63.5 - 132

The following functional areas of the SOP may be significant sources of analytical error:

- Poor extraction efficiency due to specific analyte characteristics or other problems.
- Standard degradation.
- Chromatographic separation and peak integration.

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QL, MS/MSD, and LCS) are recorded in the LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the Element database or in the instrument Run Log. Case Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the Element database. The data package is produced from Element database and manual log records. Appendix G provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control. Document all preventive or routine maintenance performed, as well as repairs or corrective or remedial actions in accordance with EPA

Region 9 Laboratory SOP 840, *Notebook Documentation and Control*. Also, document major changes or upgrades to instrument hardware and software in the maintenance logbook.

10.6 SOP Distribution and Acknowledgement

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. Document using the SOP Distribution and Acknowledgement List as shown in Appendix H.

11 REFERENCES

Agilent Technologies, *EnviroQuant ChemStation Users Guide*

Agilent Technologies, *Agilent 6890 Series Gas Chromatograph Operating Manual Volume 1 – General Information*

Agilent Technologies, *Agilent 6890 Series Gas Chromatograph Operating Manual Volume 2 – Inlets*

Agilent Technologies, *Agilent 6890 Series Gas Chromatograph Operating Manual Volume 3 – Detectors*

U.S. Environmental Protection Agency, *Method 8000C, Determinative Chromatographic Separations, Revision 3, March 2003*

U.S. Environmental Protection Agency, SW-846 Method 8082A, *Polychlorinated Biphenyls (PCBs) by Gas Chromatography*, Revision 1, November 2000

U.S. Environmental Protection Agency Region 9 *Laboratory Quality Assurance Plan, Revision 8, January 31, 2005*

U.S. Environmental Protection Agency Region 9 SOP 110, *Sample Receiving and Login*.

U.S. Environmental Protection Agency Region 9 SOP 125, *Disposal Procedures for Unused Aqueous Environmental Samples*

U.S. Environmental Protection Agency Region 9 SOP 260, *Gel Permeation Chromatography (GPC) Clean-Up*

U.S. Environmental Protection Agency Region 9 SOP 275, *Extraction of Water Samples by Continuous Liquid-Liquid Extraction*

U.S. Environmental Protection Agency Region 9 SOP 290, *Extraction of Soil Samples Using Pressurized Fluid Extraction*

U.S. Environmental Protection Agency Region 9 SOP 706, *Laboratory Waste Management Procedures*

U.S. Environmental Protection Agency Region 9 SOP 805, *Temperature Monitoring*

U.S. Environmental Protection Agency Region 9 SOP 820, *Laboratory Discrepancy and Corrective Action Reporting Procedures*

U.S. Environmental Protection Agency Region 9 SOP 835, *Chromatographic Integration Procedures*

U.S. Environmental Protection Agency Region 9 SOP 840, *Notebook Documentation and Control*

U.S. Environmental Protection Agency Region 9 Laboratory SOP 880, *Demonstration of Capability*

**APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD**

1. The %D between the calibration verification CF and initial calibration CF must be less than or equal to $\pm 20\%$ instead of $\pm 15\%$ as required by EPA SW-846 Method 8082A.
2. Surrogate and spiking solutions are made up in methanol instead of acetone.
3. The %D QC requirement for SCV samples is ± 30 instead of ± 20 .
4. The calibration factor is calculated using concentrations in ng/mL instead of mass in nanograms.
5. Retention time windows are not calculated as specified in Section 11.6 of EPA SW-846 Method 8000C. The default standard deviation of 0.01 minutes is used giving a retention time window of ± 0.03 minutes.
6. Aroclors are quantitated using the average calibration factor from the sum of the 3 to 5 characteristic Aroclor peaks instead of calculating the concentration of each peak and then averaging the concentrations to determine the Aroclor concentration in the sample as in the reference method.
7. TCMX surrogate recovery is evaluated if DCB recovery exceeds QC limits.
8. Standards are stored at $>0^{\circ}\text{C}$ (just above freezing) to $\leq 6^{\circ}\text{C}$ instead of 4°C as in the reference method.
9. Default QC recovery limits for matrices or analytes not otherwise listed is 65 – 135% instead of 70-130% as in the reference method.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides the target analytes list for this SOP with the Chemical Abstracts Registry Number (CASRN) and quantitation limits (QL).

Analyte	CASRN	Water QL, µg/L	Solid QL, µg/kg	Wipe QL, µg/wipe	Wire QL, µg/area *	Oil QL, µg/kg
Aroclor-1016	12674-11-2	0.2	3	0.2	0.2	200
Aroclor-1221	11104-28-2	0.4	6	0.4	0.4	400
Aroclor-1232	11141-16-5	0.2	3	0.2	0.2	200
Aroclor-1242	53469-21-9	0.2	3	0.2	0.2	200
Aroclor-1248	12672-29-6	0.2	3	0.2	0.2	200
Aroclor-1254	11097-69-1	0.2	3	0.2	0.2	200
Aroclor-1260	11096-82-5	0.2	3	0.2	0.2	200
Aroclor-1262	37324-23-5	0.2	3	0.2	0.2	200
Aroclor-1268	11100-14-4	0.2	3	0.2	0.2	200

Quantitation limits assume a 1 Liter water sample, a 30 g solid sample, a 1g oil sample, and a 10 mL final volume for wipe and wire samples. Quantitation limits have been increased for Aroclor 1221 due to the reduced number of chromatographic peaks available for measurement.

* Results for wire samples are reported as µg/100 surface area units; i.e. 100 cm², 100 in².

APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

QC Measure	Criteria	Frequency
ICAL RSD	$\leq 20\%$	With each ICAL
CCV %D	$\leq 30\%$	1/12 hour sequence
LCS %R	See Table Below	1/extraction batch or 20 samples*
MB	$< \frac{1}{2}$ QL	1/extraction batch or 20 samples*
QLS %R	60-140%	1/analysis batch
Matrix Spike %R	65-135%	1/SDG of 20 samples or less
Matrix Spike Duplicate Precision, RPD	$\leq 20\%$	1/SDG of 20 samples or less
Sample Retention Time Drift	± 0.03 minutes	Method setup
SCV %D	$\leq 30\%$	With each ICAL
DOC P&A %R	70-130%	Annually
Surrogate %R	See Table Below	With each sample

*whichever is more frequent

LCS %RECOVERY (3σ)

Analyte	Matrix	QC Limits %R
Aroclor 1016	Wipe	39 – 167
Aroclor 1260	Wipe	38 – 177
Aroclor 1016	Solid	50 – 138
Aroclor 1260	Solid	47 – 149

Insufficient data are available to establish recovery limits in oil.

Since the reported result is the “TOTAL” Aroclor result, the QC criteria apply to the “TOTAL” Aroclor result only, not to each of the 3 to 5 characteristic peaks for each Aroclor.

SURROGATE %RECOVERY (3σ)

Analyte	Matrix	QC Limits %R
DCB	Wipe	40 – 190
TCMX	Wipe	57 – 114
DCB	Solid	16 – 193
TCMX	Solid	42 – 147
DCB	Oil	80 – 130

No data are available for the recovery of TCMX in oil samples.

Default QC recovery limits for matrices or analytes not listed above is 65 – 135%.

APPENDIX D.
INSTRUMENT INFORMATION

INSTRUMENT CONTROL PARAMETERS – 6890 GC

OVEN

Initial temp: 50°C (On)

Maximum temp: 310°C

Initial time: 1.00 min

Equilibration time: 1.00 min

Ramps:

#	Rate	Final temp	Final time
1	30.00	140°C	0.00
2	7.00	260°C	0.00
3	20.00	310°C	8.00

Post temp: 50°C

Post time: 0.00 min

Run time: 31.64 min

FRONT INLET (SPLIT/SPLITLESS)

Mode: Pulsed Splitless

Initial temp: 225°C (On)

Pressure: 8.55 psi (On)

Pulse pressure: 33.0 psi

Pulse time: 0.60 min

Purge flow: 50.0 mL/min

Purge time: 0.55 min

Total flow: 54.6 mL/min

Gas saver: On

Saver flow: 20.0 mL/min

Saver time: 1.50 min

Gas type: Helium

BACK INLET (SPLIT/SPLITLESS)

Mode: Pulsed Splitless

Initial temp: 225°C (On)

Pressure: 8.53 psi (On)

Pulse pressure: 33.0 psi

Pulse time: 0.60 min

Purge flow: 50.0 mL/min

Purge time: 0.55 min

Total flow: 54.4 mL/min

Gas saver: On

Saver flow: 20.0 mL/min

Saver time: 1.50 min

Gas type: Helium

COLUMN 1

Capillary Column

Model Number: RESTEK Rtx CLP

Max temperature: 340°C

Nominal length: 30.0 m

Nominal diameter: 320.00 um

Nominal film thickness: 0.50 um

Mode: constant flow

Initial flow: 1.7 mL/min

Nominal init pressure: 8.55 psi

Average velocity: 30 cm/sec

Inlet: Front Inlet

Outlet: Front Detector

Outlet pressure: ambient

COLUMN 2

Capillary Column

Model Number: RESTEK Rtx CLP2

Max temperature: 340°C

Nominal length: 30.0 m

Nominal diameter: 320.00 um

Nominal film thickness: 0.25 um

Mode: constant flow

Initial flow: 1.7 mL/min

Nominal init pressure: 8.54 psi

Average velocity: 30 cm/sec

Inlet: Back Inlet

Outlet: Back Detector

Outlet pressure: ambient

FRONT DETECTOR

Temperature: 315°C (On)
Mode: Constant makeup flow
Makeup flow*: 60.0 mL/min (On)
Makeup Gas Type: Nitrogen
Electrometer: On

BACK DETECTOR

Temperature: 315°C (On)
Mode: Constant makeup flow
Makeup flow*: 60.0 mL/min (On)
Makeup Gas Type: Nitrogen
Electrometer: On

* Makeup flow is determined by OC Pesticides analysis; do not adjust. The makeup flow is not a critical control parameter for this analysis.

SIGNAL 1

Data rate: 10 Hz
Type: front detector
Save Data: On
Start Save Time: 8.00 min
Stop Save Time: 29.00 min
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2

Data rate: 10 Hz
Type: back detector
Save Data: On
Start Save Time: 8.00 min
Stop Save Time: 29.00 min
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

7673 INJECTOR

Front and Back Injector:

Sample Washes	2
Sample Pumps	3
Injection Volume	1.0 microliters
Syringe Size	10.0 microliters
Nanoliter Adapter	Off
PostInj Solvent A Washes	3
PostInj Solvent B Washes	3
Viscosity Delay	0 seconds
Plunger Speed	Fast
PreInjection Dwell	0.00 minutes
PostInjection Dwell	0.00 minutes

APPENDIX E.
CHEMSTATION FILE NAMING CONVENTIONS

Use the following naming conventions for File data, methods, and sequences on ChemStation computers and the LAN:

Directories

On the Workstation:

Data: C:\HPCHEM\1\Data\MDDY or D:\HPCHEM\1\Data\MDDYS

Methods: C:\HPCHEM\1\Methods or D:\HPCHEM\1\Methods

Sequences: C:\HPCHEM\1\Sequence or D:\HPCHEM\1\Sequence

For system controlling multiple instruments, 1 may be changed to reflect the instrument number

System running ChemStation versions C & D HPCHEM is named as MSDCHEM

On the LAN:

Data: I:\Room Number\Instrument\Year\MDDYS

Methods: I:\Room Number\Instrument\Methods

Sequences: I:\Room Number\Instrument\Sequence

Methods

MDDYITA

Sequence

MDDYS

Data Files

For GC:

MDDYICSS

For GC/MS

MDDYIQSS

Variables

A: Enter analysis, as follow:

1,4-Dioxane X

504 E

TO15 A

BNA B

BNA-L (SIM) L

Congeners C

P/P P

PCB P

RSK175 R

Soil Gas A

TPH-G	G
TPH-D	D
VOA	V

C: Channel: A = front
B = back (if applicable)

DD: Day

I: Instrument
6890 series GCs by last number in name: e.g. 6890-1 = 1 except 5890-2 = A
All GC/MSs by last letter in name: e.g. 5973L = L

M: Month 1-9, A: October, B: November, C: December

Q: QC type

BFB	F
Blank	B
CV	C
Degradation	P
DFTPP	D
IB	Z
IC	I
LCS	L
LCV	Q
Second Source	S
MS/MSD	M

S: Sequential number 1,2 3,

T: Matrix Type (if applicable)
Water W
Solid S
Air A
Oil O
Other X

Y: Year i.e. 5 for 2005

APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

Item	Frequency	Actions/Comments
Gas purifiers (carrier gas & detector gas)	Annually	Replacement schedule is based on capacity and grade of gases. In general, replace non-indicating traps every 6-12 months or when indicating traps start to change color. Replace indicating traps when indicating material is spent.
Syringes	As Needed	Clean if dirt is noticeable in the syringe; replace if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged.
Inlet liner	As Needed	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	As Needed	Replace with liner.
Inlet septum	With each ICAL	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Detector adapter nut	With each ICAL	Check tightness of detector capillary column adapter nut; adapter must not be loose. Replace ferrule when adapter is still loose after you have tightened the nut.
Capillary column fittings	With each ICAL	Check tightness of capillary column ferrule nuts in detector and inlet fittings; they should be snug - do not over tighten.
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	As needed	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.). Bake out column if trimming does not restore chromatographic performance.
Column Replacement	As needed	When trimming and/or baking out no longer restores chromatographic performance.
Ferrules	As needed	Replace ferrules when changing columns and inlet/detector parts.
ECD	As needed	Thermally clean by "baking-out" when a wandering baseline, increased noise, or a change in response is present. Replace when thermal cleaning does not resolve the problem.

**APPENDIX G.
TYPICAL DATA PACKAGE FORMAT**

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

TDF

Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms

Analysis matrix (for organics)

Data Package Technical Review Guide

Daily folder review forms or checklists

Other review forms as applicable

Tracking Forms

Work Order(s)

COC(s)

Sample Preparation (for projects that require extraction or digestion)

Bench Sheets (and extraction logs, where used)

Sample cleanup data and records (e.g. GPC logs)

Moisture data as applicable

[Analysis Method] Data (For each method where multiple methods in package)

Bench sheet(s) where not used in Sample Preparation section

Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Alternatively, separate calibration and sample data as:

Initial Calibration Data

Sample Data

Miscellaneous Data

Other data as applicable (e.g. storage blanks)

Standard Records

Standards records from LIMS (and logbook pages as needed)

APPENDIX H.
SOP DISTRIBUTION AND ACKNOWLEDGEMENT LIST

STANDARD OPERATING PROCEDURE: 335

Revision: 2, Effective: 03/31/06

POLYCHLORINATED BIPHENYLS BY GC/ECD

I have received, read, and understood the above referenced SOP and agree to comply with the SOP when performing the subject procedure until the effective date of future revisions.

NAME	DATE DISTRIBUTED	SIGNATURE	DATE
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
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_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

**USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA**

**STANDARD OPERATING PROCEDURE 354
VOLATILE ORGANIC COMPOUND ANALYSIS IN WATER**

Revision 9
Effective Date: November 27, 2009

Reviewed by: _____
Richard Bauer Date
Chemistry Team Leader/Technical Director

Reviewed by: _____
K. W. Hendrix, Laboratory QA Officer Date

Approved by: _____
Brenda Bettencourt, Laboratory Director Date

Periodic Review:

Signature	Title	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____

This SOP was prepared by ICF International for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA contract no. EP-W-06-041). ESAT Document Control Number: 00504022-11549.

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APPENDIX G. METHOD PERFORMANCE

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APPENDIX I. REVISION HISTORY

1 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the procedures used for the analysis of volatile organic compounds (VOCs) in water. This SOP is based on EPA Method 524.2, Revision 4.1, 1995 and EPA Method 8260B, Revision 2, December 1996. Deviations from these methods are described in Appendix A. Analytes and quantitation limits (QLs) for this analysis are listed in Appendix B.

This SOP is applicable to the analysis of surface water, ground water, and drinking water for VOCs in support of the EPA's Superfund, RCRA, WQM, UIC, and SDWA programs. The applicability of these procedures to specific project data quality objectives (DQOs) must be assessed on a case-by-case basis. The quality control (QC) criteria specified in this SOP meet compliance criteria for drinking water monitoring projects.

This SOP applies to analyses conducted at the USEPA Region 9 Laboratory in Richmond, California.

2 METHOD SUMMARY

VOCs are purged from a 25 mL water sample in a fritted sparge cell, separated in the GC column, and detected by a mass spectrometer (MS). The target VOC compounds are identified in the sample by analyzing standards under the exact same conditions employed for samples and comparing the resulting GC retention times between standards and samples and the sample mass spectra to mass spectra contained in the National Institute of Standards and Technology (NIST) Library in the MS database. Each target and surrogate compound is quantitated using the average response factor from the most recent initial calibration.

Non-target compounds are identified by comparing their mass spectra to the mass spectra contained in the National Institute of Standards and Technology (NIST) Library in the MS database. An estimated concentration for a non-target compound is calculated by comparing its total MS response to the nearest internal standard total MS response and assuming a relative response factor of 1.0.

3 DEFINITIONS

Atomic weight: The following terms are used to describe atomic weight: Dalton – Primary unit of mass in mass spectrometry equivalent to 1/12 mass of carbon-12 atom; amu - atomic mass unit equals one Dalton; (m/z) - mass to charge ratio equals ion mass (in Daltons) divided by number of unit charge for the ion.

Calibration Standard (CAL): A solution prepared from the primary dilution standard or stock. The CAL solutions are used to calibrate instrument response with respect to analyte concentration.

FC43: Perfluorotributylamine. Compound used to tune the MS.

GC/MS: Gas Chromatograph / Mass Spectrometer

GC/MS Tuning Solution (MS tune): Bromofluorobenzene (BFB) used to evaluate the performance of the GC/MS system with respect to a defined set of method criteria.

Internal Standard (IS): A compound added to a sample, extract, or standard solution in a known amount and used to measure the relative responses of method analytes and surrogates that are components of the same solution.

Laboratory Control Sample (LCS) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is analyzed like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The LCS is also known as a laboratory fortified blank (LFB) or blank spike (BS).

LIMS: Laboratory Information Management System. The Element database.

Matrix Spike (MS) - An aliquot of an analytical sample to which known quantities of the method analytes are added. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations. The MS is also known as laboratory fortified matrix (LFM).

Matrix Spike Duplicate (MSD) - A duplicate aliquot of an analytical sample to which known quantities of the method analytes are added. The MSD is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results and to determine laboratory precision. The MSD is also known as laboratory fortified matrix duplicate (LFMD).

Method Blank (MB) - An aliquot of reagent water or other blank matrix that is treated exactly as a sample. The MB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment. The MB is also known as laboratory reagent blank (LRB).

Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

NIST - National Institute of Standards and Technology

Primary Dilution Standard Solution (PDS): A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

Quantitation Limit (QL) - The concentration at which confidence in the reported value requires no qualifying remarks. A standard is analyzed at the QL to verify the previously established calibration curve.

Quantitation Limit Standard (QLS) - A standard used to check the accuracy of the analysis at the quantitation limit.

RIC - Reconstructed Ion Chromatogram

Sample Delivery Group (SDG) - A group of twenty samples or less from a project that is sent to the laboratory for analysis.

Second Source Calibration Verification (SCV) - A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check the initial calibration. The SCV is also known as quality control sample (QCS).

Stock Standard Solution (SSS) - A concentrated standard containing the method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Surrogate (SURRE) - Compounds which are extremely unlikely to be found in any sample that are added to a sample aliquot in a known amount before extraction or other processing, and measured with the same procedures used to measure other sample components. The purpose of the surrogate is to monitor method performance with each sample.

Tentatively Identified Compound (TIC) - A compound not in the target analyte list excluding surrogate compounds and internal standards identified from library spectra.

Water Sample - For the purpose of this method, a sample taken from matrices classified as drinking, surface, ground, or storm runoff water, or industrial or domestic wastewater.

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

Safety precautions must be taken when handling solutions and samples. Protective clothing including lab coats, safety glasses, and gloves must always be worn. Contact lenses must not be worn. If solutions come into contact with your eyes, flush with water continuously for 15 minutes. If solutions come in contact with your skin, wash thoroughly with soap and water. ESAT personnel should contact the Group Leader or Health and Safety and Environmental Compliance Task Manager and EPA staff should see the Team Leader or the Laboratory Safety, Health and Environmental Compliance Manager to determine if additional treatment is required.

Refer to the Material Safety Data Sheet (MSDS) located in the library and the LAN for additional information.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

No solvents are utilized in this method except the extremely small volumes of methanol needed to make calibration standards. The only other chemicals used in this method are the neat materials in preparing standards and sample preservatives. All are used in extremely small amounts and pose no threat to the environment. Refer to the *EPA Region 9 Laboratory Environmental Management System* for additional information on minimizing the laboratory's footprint on the environment.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing

the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents and solutions, to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-regulated Waste	Not applicable
Aqueous acidic VOC waste (wastewater, hydrochloric acid, trace halogenated volatile compounds)	Hazardous Waste	Corrosive
Methanol waste (methanol, halogenated volatile compounds)	Hazardous Waste	Flammable, toxic
Waste pump oil (trace halogenated volatile compounds)	Hazardous Waste	Toxic

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples should be collected in pre-cleaned 40 mL screw cap vials equipped with

Teflon faced silicone septum. Volume collected should be sufficient to allow for replicate analysis yet minimize waste disposal. Three 40-mL vials should be sufficient to meet these objectives.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form.

Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to “active out” and the location to the appropriate room number. At the end of the day, return sample containers to the “Home” locations. Update the LIMS database using the “return to home location” feature and update container disposition to “available in”. Verify that your initials are recorded whenever you update the LIMS custody information.

5.3 Preservation Verification and Storage

Drinking water compliance samples must be dechlorinated and preserved with acid to $\text{pH} < 2$ at the time of sampling. Drinking water samples that are not preserved must be resampled and preserved correctly before a valid analysis can be performed. If an unpreserved drinking water sample is received, inform the Chemistry Technical Order Manager (TOM) immediately so that the proper notifications can be made.

5.4 Storage

Samples must be stored at >0 and ≤ 6 °C. Retain samples for 60 days after the final analytical report is sent to the data user.

5.5 Holding Time

Acid preserved samples must be analyzed within 14 days from the date of sample collection; unpreserved samples must be analyzed within 7 days from the date of sample collection.

Sort samples according to date sampled, so that samples can be analyzed in order of date sampled to prevent missed holding times.

6 INTERFERENCES

Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, or solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks as described in

Section 8. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and dichloromethane) through the septum seal into the sample during storage and handling.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with methanol between analyses, rinse it with distilled water, and then dry it in an oven at 105EC. The trap and other parts of the system are also subjected to contamination; therefore, frequent bake out and purging of the entire system may be required.

Solvents and other compounds, which are target analytes must never be introduced into the laboratory where volatiles analysis is performed. Dichloromethane, acetone and other common laboratory chemicals are target analytes under this SOP and must be excluded from Room 201. Particular attention must be paid to the possibility of transport of solvent vapors on individuals. Analysts should never enter Room 201 after being in the extraction laboratories or glassware washing area.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies should meet the technical requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

- **GCMS System**

Gas Chromatograph (GC): Hewlett Packard/Agilent 6890 or 6890N, or equivalent. The GC must be capable of multilevel temperature programming and constant carrier gas flow throughout the temperature range. The GC should be equipped with an automatic sample injector, split/splitless injection port, and electronic pressure control (EPC).

Column: Hewlett Packard HP-624 25M x 0.20 mm, 1.12 micron film or equivalent. Any column capable of separating the target analytes and passing method QC without overloading at the concentration of the highest standard may be used.

Mass spectrometer: Hewlett Packard/Agilent 5973 or 5973N, or equivalent, capable of scanning from 35 to 300 amu every two second or less using 70 volts (nominal) electron energy in the electron impact ionization mode. The MS must be able to produce a mass spectrum that meets acceptance criteria when 25 ng of BFB is injected through the GC inlet.

- Data system: ChemStation (available from Agilent), or equivalent, able to control the GC/MS system and to acquire, store, and reduce mass spectral data. The software must be able to process a GC/MS data file by recognizing a GC peak within a retention time window, comparing the mass spectrum from the GC peak with spectral data in a database, and generate a list of tentatively identified compounds with their retention times and scan numbers. The software must also allow integration of the ion abundance of any specific ion between specified time or scan number limits and to calculate RRFs and concentrations of analytes in samples.
- Purge and Trap Concentrator: Tekmar 3000, Tekmar 3100, or equivalent.
- Autosampler: Varian Archon or equivalent.

Other GC/MS systems with similar configurations can be used to analyze samples following this SOP as long as the instrumentation meets the QC limits of this SOP.

7.2 Reagents

Enter all reagents except organic-free method blank water into the LIMS database.

Reagents may contain impurities that might affect analytical data. Only materials that conform to the American Chemical Society (ACS) reagent grade specifications should be used. If the purity of a reagent is in question, analyze for contamination prior to use.

- Methanol (Purge & Trap grade).
- Hydrochloric Acid, 6N HCl - Slowly add 250 mL of reagent grade concentrated HCl to 250 mL of organic-free method blank water. Prepare as needed, not to exceed annually. Also known as 1:1 or 1+1 HCl.
- Organic-free method blank water (prepared using Region 9 Laboratory SOP 205).
- Acidified organic-free method blank water – acidify with 2 drops 6N HCl per 40 mL water.

7.3 Standards

Enter all standards into the LIMS database.

Store working standards in the volatiles lab freezer at $\leq 10^{\circ}\text{C}$ and ampulated standards in the volatiles lab refrigerator at $>0^{\circ}$ to $\leq 6^{\circ}\text{C}$, separate from samples.

Stock Standards - Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials

- 4-Bromofluorobenzene Tuning Solution (BFB Solution, 50 ng/ μL)

Add 1.5 mL of purge and trap grade methanol to a clean, dry, 2 mL volumetric flask using a 5-mL syringe.

Add 20 μL of a 5000 ug/mL stock solution of 4-Bromofluorobenzene (VOA Tuning Compound solution, Restek catalog #30003 or equivalent) to the volumetric flask using a 25- μL gas tight syringe with the syringe needle beneath the surface of the methanol.

Bring the volume up to 2 mL with purge and trap grade methanol. Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).

Pour the contents of the volumetric flask into a 2-mL screw cap vial equipped with a Teflon-lined screw cap and a Mininert valve. (Do not use pipettes to transfer VOA solutions because the vacuum used to draw the solutions up into the pipettes can cause some volatile compounds to come out of solution). Label the vial "BFB Solution", date prepared, the final concentration of the BFB solution solvent used, analyst initials, and LIMS Standard ID, and expiration date.

Replace the solution after 6 months, or sooner if analysis indicates that the tuning solution has degraded. Dispose of any remaining solution in the correct waste container.

- Drinking water surrogate & IS solution (VOA IS mix, 125 ng/ μL)

Add 5 mL of purge and trap grade methanol to a clean, dry, 10-mL volumetric flask using a 5-mL syringe.

Add the stock standard solutions in the amounts indicated in the table below to the volumetric flask using a gas tight syringe with the syringe needle beneath the surface of the methanol. Rinse the syringe 5 times with methanol and a small

amount of the next stock standard to be dispensed between sampling different mixtures.

Bring the volume up to 10 mL with purge and trap grade methanol. Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).

Stock Standards	Supplier	Stock Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc.,** ng/µL
8260 IS Mix	Restek	2500	500	10	125
Dichloromethane-d2	*	2500	500	10	125
1,2-Dichlorobenzene-d4	Restek	2000	625	10	125
VOA Surrogate Spike Mix	Restek	2500	500	10	125

* Intermediate stock standard solution prepared from Aldrich neat standard.

** Internal standard concentrations are nominal values.

Pour the contents of the volumetric flask into a clean 5-mL standard reservoir vial and immediately install the standard reservoir in the appropriate standard position on the Archon autosampler.

Replace the solution after 14 days, or sooner if analysis indicates that the standard solution has degraded. Dispose of any remaining solution in the correct waste container.

- Drinking water calibration mix (DW mix, 25 ng/µL, ketones 200 ng/µL)

Add 1 mL of purge and trap grade methanol to a clean and dry 2-mL volumetric flask using a 5 mL syringe.

Add the stock standards to the volumetric flask using a gas tight syringe with the syringe needle beneath the surface of the methanol in the amounts indicated in the table below. Rinse the syringe 5 times with methanol and a small amount of the next stock standard to be dispensed between sampling different mixes.

Stock Standards	Supplier	Stock Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc., ng/µL
502.2 Cal. Mix #1	Restek	2,000	25	2	25
502.2 Cal. Mix #2*	Restek	2,000	25	2	25

Stock Standards	Supplier	Stock Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc., ng/µL
502.2 Cal. Mix #3*	Restek	2,000	25	2	25
502.2 Cal. Mix #4*	Restek	2,000	25	2	25
502.2 Cal. Mix #5*	Restek	2,000	25	2	25
502.2 Cal. Mix #6*	Restek	2,000	25	2	25
1,1,2-Trichloro-1,2,2-trifluoroethane	Restek	2,000	25	2	25
VOA Calibration Mix 1 (ketones)	Restek	5,000	80	2	200
1,2-Dibromo-3-chloropropane**	Restek	2,000	75	2	100
Carbon Disulfide	Restek	2,000	25	2	25
Custom Ether/ THF Mix	Restek	2,000	100	2	100
* Restek Mega Mix may be used in lieu of these standards	Restek	2,000	25	2	25

**1,2-Dibromo-3-chloropropane concentration includes 25 ng/µL from the 502.2 Cal Mix or the Mega Mix and 75 ng/µL from this standard.

Bring the volume up to 2 mL with purge and trap grade methanol. Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).

Transfer the contents of the volumetric flask into a 2-mL screw cap vial equipped with a Teflon-lined screw cap and a Mininert valve by gently pouring the solution out of the volumetric flask and into the vial. Label the vial indicating the contents, date prepared, the final concentration of the calibration mix, solvent used, analyst initials, LIMS Standard ID, and expiration date.

Replace the solution after 7 days, or sooner if analysis indicates that the standard solution has degraded. Dispose of any remaining solution in the correct waste container.

- Second Source Verification (SCV) Solution (DWLF solution, 25 ng/µL, ketones 200 ng/µL)

Add 1500 μL of purge and trap grade methanol to a clean, dry, 2-mL volumetric flask using a 5-mL syringe.

Add the stock standards to the volumetric flask using a gas-tight syringe with the syringe needle beneath the surface of the methanol in the amounts indicated in the table below. Rinse the syringe 5 times with methanol and a small amount of the next stock standard to be dispensed between sampling different mixes.

Bring the volume up to 2 mL with purge and trap grade methanol. Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to mix assure mixing (do not shake).

Stock Standards	Supplier	Stock Conc., $\mu\text{g/mL}$	Amount, μL	Final Volume, mL	Final Conc., $\text{ng}/\mu\text{L}$
502/524 VOC MIX	Supelco	2,000	25	2	25
VOC MIX 6	Supelco	2,000	25	2	25
<i>tert</i> -Butyl methyl ether (MTBE)	Supelco	2,000	100	2	100
1,1,2-Trichloro-1,2,2-trifluoroethane	Supelco	2,000	25	2	25
8240 Standard Mix 2	Supelco	2,000	200	2	200

Transfer the contents of the volumetric flask into a 2-mL screw cap vial equipped with a Teflon-lined screw cap and a Mininert valve by gently pouring the solution out of the volumetric flask and into the vial. Label the vial indicating the contents, date prepared, the final concentration of the LF mix, solvent used, analyst initials, LIMS Standard ID, and expiration date.

Replace the solution after 7 days, or sooner if analysis indicates that the standard solution has degraded. Dispose of any remaining solution in the correct waste container.

7.4 Supplies

- Gas-tight syringes (5- μL , 10- μL , 25- μL , 50- μL , 100- μL , 250- μL , 500- μL , 1-mL, 5-mL, 25-mL and 50 mL). All syringes utilized must be rinsed with Purge and Trap grade methanol.
- 25-mL fritted sparge vessels.
- pH paper (pH 0-14 range).
- Trap K (VOCARB 3000, or equivalent).

- 40-mL VOC vials for standards with screw-hollow cap lined with 22 mm PTFE-faced silicone septa.

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Prior to analyzing calibration, QC, or field samples make a LIMS batch containing the samples to be analyzed and an empty LIMS sequence to obtain LIMS assigned IDs for the calibration and instrument and batch QC samples.

Check the mass spectrometer for leaks on a daily basis prior to the analysis of the tuning compound using the instructions provided in Appendix D. Generate and print a leak check report.

Set up the purge and trap and auto sampler according to parameters in Appendix D.

Set-up the GC/MS following operating instructions provided by the manufacturer. Use operating parameters provided in Appendix D as a starting point.

8.1.1 GC/MS Tuning Check

At the start of the analysis day, the GC/MS system must meet the mass spectral ion abundance criteria for bromofluorobenzene (BFB). Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target and non-target compounds.

Inject 0.5 μL of a 50 ng/ μL BFB solution using the operating parameters provided in Appendix D.

Optionally, purge a 1 ng / μL BFB solution. Prepare this solution by adding 1 μL of a 50 ng / μL BFB solution to a 50-mL syringe filled with acidified method blank water and decant into a 40-mL vial as shown in Appendix D.

The autofind procedure will automatically find the BFB peak, average three scans (the peak apex scan and the scans immediately preceding and following the apex), perform a background subtraction, and print out a hard copy of the spectrum, the chromatogram, and the table of ion abundances. Follow requirements and take corrective action as described in Section 9.2.1.

8.2 Calibration and Standardization

Prepare all working calibration standards in acidified organic-free method blank water.

8.2.1 Initial Calibration

Refer to Section 8.4 for system maintenance procedures that may be required prior to analyzing an initial calibration,

Perform auto-tune or manual tune as specified in Appendix D; inject or purge BFB.

Perform an initial calibration using six calibration standards. Refer to Section 9.2.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

The recommended concentrations are listed in the following table.

Calibration Standard Amounts, Archon Autosampler, 25 mL Purge

Calibration Level	Concentration, $\mu\text{g/L}$	VOA IS Mix 125 $\mu\text{g/mL}$, μL	DW Calibration Mix 25 $\mu\text{g/mL}$, μL
1	25	1	50
2	10	1	20
3*	5	1	10
4	2	1	4
5	1	1	2
6**	0.5	1	1

* CCV, LCS, MS, MSD, except as noted below.

** QLS, except as noted below.

Since ketones, ethers, and 1,2-dibromo-3-chloropropane purge poorly from aqueous samples, the following compounds are calibrated at the indicated ranges. The QLS is analyzed at the low point for each range. CCV, LCS, MS, MSD samples are spiked at the mid-point of each range.

- | | |
|--------------------------------|------------------------|
| a. Ketones | 4-200 $\mu\text{g/L}$ |
| b. <i>tert</i> -Butanol | 10-500 $\mu\text{g/L}$ |
| c. Ethers | 2-100 $\mu\text{g/L}$ |
| d. 1,2-Dibromo-3-chloropropane | 2-100 $\mu\text{g/L}$ |

Check the initial calibration for misidentified peaks due to retention time shifts. The most commonly misassigned compounds are the 1,3- and 1,4-dichlorobenzenes.

No quantitation ion may saturate the detector.

The data system calculates the relative response factor (RRF) for each target compound and surrogate compound for all calibration standards using the following

equation. The quantitation ions and internal standard assignments are listed in Appendix C.

$$RRF = (A_x)(C_{is}) / (A_{is})(C_x)$$

Where

A_x = Area of quantitation ion of compound x
 A_{is} = Area of quantitation ion for associated internal standard
 C_x = Concentration of compound x
 C_{is} = Concentration of the associated internal standard

Check and print the calibration by performing the following steps:

1. Acquire and quantitate calibration using the method just generated in Appendix D.
2. Generate a detailed report for the continuing calibration level to verify baseline integration.
3. Run a TIC report for the continuing calibration level to verify that all chromatographic peaks are accounted for.
4. Update the response factors in the method using the newly acquired calibration files.
5. Update the retention time in the method using the newly acquired calibration verification level.
6. Update the qualifier ion ratios for each compound using the newly acquired calibration verification level.
7. To prevent confusion due to co-elution of compounds in the calibration standards, this SOP specifies the use of NIST library spectra as reference spectra; therefore, do not update the reference spectra in the method.
8. Save the method as outlined in the "ChemStation File Naming Convention"
9. Generate "Response Factor Report."
10. Check the calibration files listed on the "Response Factor Report" to insure that the correct files are being used.
11. Check the time and date to ensure that the correct update is used.
12. Print the raw area report for an internal standard or the target analyte for single analyte analysis. From the ChemStation menu, select initial calibration → edit compound → view → page 3. Verify that the method was updated correctly. Print analyte list from the ChemStation menu by selecting initial calibration → list compound. Verify that the average response factor is used.
13. Save a copy of this method under C:\HPCHEM\1\Methods\Initial. This method will become the "master" copy until the next ICAL is generated.
14. Save a second copy of the method under
I:\RoomNumber\Instrument\Methods\Initial.

15. Analyze a SCV standard at the calibration verification level to confirm the initial calibration meet QC criteria.
16. Manually calculate a result for one surrogate in the SCV to insure that the correct RFs are being used and write the results on the quantitation report.
17. Save a hard copy of the initial calibration files so they may be copied and included in associated packages.

Analyze a method or instrument blank to demonstrate that all parts of the equipment in contact with the sample and reagents are not contaminated.

Refer to Section 9.2.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2.2 Continuing Calibration Verification

Analyze a calibration verification standard at the beginning of each 12-hour analytical period by performing the following steps:

1. Acquire and quantitate calibration using the method just generated in Appendix D.
2. If necessary, update the retention time in the method using the calibration verification standard data and save the method.
3. Generate "Evaluate Continuing Calibration Report".
4. Manually calculate a result for one surrogate to ensure that the correct RFs are being used and write the results on the quantitation report.
5. As each run is quantitated during the day, make sure that the same date and time stamp of "Last Update: Mon Aug 23 12:02:21 2004" is reflected on each file header.
6. If Last Update time stamp changes, state the reason, repeat steps 3-5, and include the reports generated in the package.
7. Save a copy of the method to the LAN, when the data is backed up to the LAN the following day.

Refer to Section 9.2.3 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

Allow the sample to reach ambient temperature before analysis.

Verify that the sample identification on the vials coincides with the sample identification on the routing forms to ensure that the correct sample is being analyzed.

Check if the sample has an unusual color or other physical properties. If any physical signs of contamination are present, screen the samples to protect the analytical system from damage or contamination, and to determine the appropriate subsequent dilutions. Record unusual items in the LIMS “MMO” field.

Note: After the analysis is complete, check the pH and residual chlorine in each sample using pH 0-14 range pH paper and chlorine test strips respectively. Record the results in the injection logbook. If any samples have a pH greater than 2 or residual chlorine, make a note in the LIMS work order memo “MMO” field.

8.3.2 Analytical Sequence and Sample Analysis

This section describes preparing the analytical sequence and analyzing the samples.

Prior to analyzing calibration, QC, or field samples make a LIMS batch containing the samples to be analyzed and an empty LIMS sequence to obtain LIMS assigned IDs for the instrument and batch QC samples. Document sample dilutions by entering the initial/final volumes in the LIMS bench sheet.

Prepare all instrument and batch QC samples in acidified organic-free method blank water.

Prepare the samples to be analyzed. The following table represents the spike levels recommended for most projects:

Spike Amounts, Archon Autosampler, 25 mL Purge

Sample	VOA IS Mix 125 µg/mL, µL	DW Calibration Mix 25 µg/mL, µL
Blanks	1.0	NA
Samples	1.0	NA
BS/LCS	1.0	10.0
MS/MSD	1.0	10.0

Prepared in 50 mL volumetric and transferred to 40-mL vial.

NA = Not Applicable

Load the samples in the autosampler according to their designated positions in the sequence file. The following represents a recommended analysis sequence:

1. BFB
2. CCV
3. LCS
4. QLS
5. MB
6. Samples

7. MS/MSD, as needed
8. Sample dilutions, as needed
9. Storage Blanks and Instrument Blanks, as needed

For the Varian Archon Autosampler systems, gently place the vial in the appropriate autosampler position. See Appendix D for purge and trap parameters.

Enter sample sequence in the instrument software. Include the EPA sample number (WO-sample number) in the "Sample" field.

Name the data files according to the data file naming convention outlined in Appendix E.

8.3.2.1 Instrument Blanks

In the event that a sample is analyzed containing analytes which exceed the calibration range of the instrument, analyze an instrument blank to demonstrate that the system is free of carryover contamination. At a minimum, the analyst must evaluate the next sample to determine if carryover may have occurred.

Prepare instrument blanks in the same manner as method blanks.

The instrument blank is acceptable if it meets criteria listed in Appendix C. (Instrument blanks do not need to meet the surrogate recovery criteria).

Note: Instrument blanks may be analyzed beyond the 12 hour tune time period.

8.3.2.2 Method Blank

Prepare method blanks by filling a 40-mL screw-capped volatile vial fitted with a PTFE-faced silicone septum with acidified organic-free method blank water.

See Section 9.3.1 for frequency, acceptance criteria, and corrective action requirements.

The method blank is acceptable if it meets criteria listed in Appendix C.

8.3.2.3 Storage Blank

Every Monday morning, or the first work day of the week, fill two 40-mL screw-cap volatile vials with PTFE-faced silicone septa with acidified

organic-free method blank water and store them with the samples in the sample storage refrigerator in Room 201.

Analyze the storage blank the following Monday, or on the first workday of that week.

The storage blank is acceptable if it meets criteria listed in Appendix C.

Note: The storage blanks may be analyzed beyond the 12 hour tune time period.

8.3.3 Analyte Identification and Quantitation

8.3.3.1 Analyte Identification

In order for a target compound to be identified as present in a sample both the retention time and the mass spectra of the peak must match those of the standard.

This SOP specifies the use of NIST library spectra as reference spectra to prevent confusion due to co-elution of compounds in the calibration standards; therefore, do not update the reference spectra in the method.

All ions present in the NIST mass spectra at a relative intensity of 10 % of the most abundant ion must be present in the sample spectra.

The relative intensities of the ions must agree within 20 % between the NIST and sample spectra.

Ions present in the sample at greater than 10 % abundance but not present in the standard spectra must be reviewed and accounted for by the analyst making the comparison.

If a compound cannot be verified by these criteria but is present in the technical judgment of the analyst, the supporting evidence must be indicated on the raw data and the analyte reported.

8.3.3.2 Analyte Quantitation

Quantitate the data and print out a quantitation report and chromatogram. Use the average relative response factor from the initial calibration for quantitation.

Review the results as discussed in Section 8.3.3.1 for qualitative identification of target analytes. Cross out all reported hits that do not meet

the qualitative criteria and delete these compounds (Qdel) in ChemStation. Review all target compounds that are detected to verify they are integrated properly. Review the chromatogram for possible false negatives.

Check the sample's surrogate and internal standard recoveries with criteria in Appendix C.

8.3.3.3 Manual Integration

Where the chromatography software integrates the signal inconsistently, follow SOP 835, *Chromatographic Integration Procedures*. All manual chromatographic integration must be initialed and dated by the analyst, noted in the run log, and approved by the supervisor, Chemistry Technical Director, Quality Assurance Officer, or designees.

8.3.4 Calculations

Target analyte concentrations as shown on the ChemStation quantitation report are calculated using the following equation:

$$\text{Conc. (}\mu\text{g/L)} = \text{Ax} * \text{AMTIS} * \text{DF} / (\text{AIS} * \text{RRF})$$

Where:

Ax	= area of the quantitation ion of the compound
AMTIS	= amount of internal standard in $\mu\text{g/L}$ (5 $\mu\text{g/L}$)
DF	= dilution factor
AIS	= area of the characteristic ion of the associated internal standard
RRF	= analyte average relative response factor from the initial calibration

LIMS calculates the final analyte concentration in samples from the result in the ChemStation quantitation report and the initial and final volumes in the LIMS bench sheet.

8.3.5 Review of Tentatively Identified Compounds:

Load the data file of the most concentrated valid analysis of the sample.

Review the library search results for the following:

Check that each significant peak in the LSC Report – Integrated Chromatogram has been reported either in the ChemStation quantitation report or the LSC report.

Report those TICs for which the response is greater than 20% of the closest internal standard.

Use the nearest internal standard free of interferences for quantitation.

Report a maximum of 10 compounds based on total area (largest).

Relative intensities of the major ions in the NIST reference spectrum (ions greater than 10 % of the most abundant ion) should be present in the sample spectrum.

The relative intensities of the major ions should agree within 20 %.

Molecular ions present in the reference spectrum should be present in the sample spectrum.

Ions present in the sample spectrum but not in the reference spectrum shall be reviewed for possible background contamination or the presence of co-eluting compounds.

Ions present in the reference spectrum but not within the scan range of the method should not be considered when making a tentative identification.

If, in the technical judgment of the analyst, no valid tentative identification of the compound can be made, the compound should be reported as "Unknown"; attempt to classify the unknown compound (i.e., unknown hydrocarbon, unknown aromatic, unknown chlorinated compound, etc.).

Report the following:

- a. Class of compound instead of specific isomers unless the identity of the specific isomer is known. As an example, report dichlorobenzene instead of 1,2-dichlorobenzene. Alternatively, report 1-methylnaphthlene if the calibration standard has 2-methylnaphtalene and the TIC retention time is not that of 2-methylnaphtalene. Edit the TIC name to correct errors and remove extraneous punctuation.
- b. Total of all hydrocarbons as "Total Hydrocarbon". Determine as follows:
 - Click "Int" and make sure that "integrate a peak" option is not selected.
 - Click and hold the left mouse button and drag the cursor across the entire hydrocarbon peak range; this will generate an average spectrum of the range.
 - Determine whether m/z 55 or 57 is larger in the spectrum. Click "Int", "Ion Chromatogram" and enter the larger of the two ions (55 or 57).

- Click “Int” and select “integrate a peak” then integrate the hydrocarbon peak range.
- Click “File”, “Print Trace + spectrum”. Click “Int”, “Integration Results”, “Print”; this prints the area for the total hydrocarbon peak.
- Calculate the estimated total hydrocarbon concentration by dividing the area of the total hydrocarbon peak determined above by the area of the closest IS to the center of the total hydrocarbon peak from the quantitation report (not the LSC report) then multiplying this result by the concentration of the IS.
- Click “LSC”, “LSC for current scan”; this adds the peak to the LSC report.
- Click “LSC”, “Edit LSC Results”. Select “unknown hydrocarbon” and change name to “Total Hydrocarbon” then enter the concentration of the total hydrocarbon peak determined above.

Exclude the following compounds from the report:

- a. Analytes eluting prior to the first eluting target compound.
- b. TICs that were detected in the method blank.
- c. Column bleed (i.e. siloxanes).
- d. CO₂/fixed gases peak.
- e. Electronic noise peaks.

If the base peak saturates the detector, document this in the data. Do not dilute a sample extract to get the base peak of a TIC within the detector range. If a sample containing a saturated TIC ion was diluted to get a target compound within calibration range, use the TIC base peak area from the diluted analysis to estimate the concentration of the TIC.

8.3.6 QC Review

As soon as possible after analysis (typically prior to entry into LIMS), inspect sample and QC data for compliance with QC limits in Appendix C. If no significant problems are found, perform the following QC reviews for compliance with SOP requirements:

- Check that target analyte results are within range of the initial calibration.
- Process and review the results for the CCV and instrument QC samples. Print a ChemStation Evaluate Continuing Calibration Report using the appropriate settings to verify that the CCV and QLS results are within QC limits. See Section 9.2 for instrument QC requirements.

- Process and review the results for the MB, LCS, and MS/MSD batch QC samples and verify that the results are within QC limits. See Section 9.3 for batch QC requirements.
- Print a ChemStation QA-QC Check Report after processing all the samples.
- Examine the QA Check Report and verify that all IS areas meet QC requirements.
- Determine if surrogate recoveries for field and QC samples are within QC limits. See Section 9.4 for Sample QC requirements.
- Review all sample results to determine if any samples need to be re-analyzed at a dilution.
- Review the chromatogram for possible false negatives.
- Manually cross out all compounds that do not meet qualitative criteria and document the reason on the quantitation report. Delete the compound (Qdel) in ChemStation.
- If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report.

8.3.7 Data Export and LIMS Entry

- Generate epatemp.txt files for field and QC samples by printing the report to the screen; these files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table and to populate the empty LIMS sequence.
- Copy sample data files from the local drive to the appropriate instrument data subdirectory on the Region 9 LAN to make them available to LIMS and to archive them.
- Populate the empty LIMS sequence with the samples actually analyzed by editing the empty LIMS sequence; import the sample information using DataTool.
- Create an empty upload file containing the samples analyzed in the LIMS batch or sequence. Import and merge the data files using the LIMS DataTool module. Load the resulting merged data file into the LIMS Data Entry/Review table. See LIMS manual for detailed procedure.

- Review results in the LIMS. Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

8.4 Maintenance

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook. Routine maintenance procedures and frequency are listed in Appendix F.

8.4.1 Purge and trap maintenance

Symptom:

- Decline in chloromethane, bromoform, chloroethane, and or 1,2-dibromo-3-chloropropane responses.

Cause: purge flow rate or trap problem.

Corrective action: Check purge flow; replace trap if necessary.

- Carryover of naphthalene and/or 1,2,3-trichlorobenzene

Possible causes: Cold spot in system, especially the transfer lines between the sparge unit and the concentrator or between the concentrator and the GC or analyzing a sample containing high mole weight components or analyzing high-level and low-level samples sequentially.

Corrective action: Check temperatures of all heated zones. Adjust temperatures or replace heaters as required. Flush valve, gas lines, and sample lines with methanol or reagent water and bake out.

- Loss of sensitivity to selected analytes and increased pressure to maintain purge flow.

Possible cause: Degradation of trap.

Corrective action: Replace trap.

- Loss of all purged analytes.

Possible cause: Leak in system.

Corrective action: Leak check purge and trap system. Inspect sparge ferrules and replace them when worn or distorted.

8.4.2 GC Maintenance

Symptom

- Carryover

Possible causes: Analyzing a sample containing high mole weight components or analyzing high-level and low-level samples sequentially.

Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.

Possible cause: column flow rate problem.

Corrective action: check flow rate and adjust as necessary.

- Longer retention time and or smaller peaks.

Possible causes: column flow rate problem, injection port leak, or column contamination.

Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

- Loss of resolution.

Possible causes: column flow rate problem, injection port leak, or column contamination.

Corrective action: Check for leaks, replace septum, replace the liner, replace inlet seal, clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

8.4.3 MS maintenance:

Trend to be observed:

- Low m/z 502 to 69 ratio

- Failing tune checks

Corrective action: Clean the source.

9 QUALITY CONTROL

The following sections describe quality control measures, criteria, frequency, and corrective action. Appendix C summarizes QC measures and criteria.

9.1 Demonstration of Capability

The EPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability (DOC), and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

A DOC must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880.

9.2 Instrument QC

9.2.1 GC/MS System Performance Check (BFB analysis):

BFB must be analyzed at the beginning of each 12-hour period. The ion abundance ratios must meet the following criteria.

Mass (m/z)	Relative Ion Abundance Criteria
50	15 - 40 % of mass 95
75	30 - 60 % of mass 95
95	Base peak, 100 % relative abundance
96	5 - 9 % of mass 95
173	< 2 % of mass 174
174	>50 % of mass 95(Mass 95 must be base peak)
175	5 - 9 % of mass 174
176	> 95 but < 101 % of mass 174
177	5 - 9 % of mass 176

All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be greater than that of m/z 95.

If the ion abundances fail to meet criteria listed above the BFB chromatogram should be examined for any obvious chromatographic problems (e.g. bad injection leading to poor response etc.). If the problem is determined to be related to poor chromatography take the necessary corrective action and re-analyze the BFB. If the BFB continues to fail the ion abundance criteria retune the mass spectrometer, it may be necessary to clean the ion source, or take other corrective action to achieve the ion abundance criteria.

If a sample is injected after the 12-hour time period has elapsed it must be re-analyzed.

9.2.2 Initial Calibration

Each GC/MS system must be calibrated whenever corrective action is performed which may change instrument response (e.g., ion source cleaning, column replacement, etc.) or if the continuing calibration acceptance criteria cannot be met.

The data system calculates the percent relative standard deviation (%RSD) of the RRF values for each compound using the following equation.

$$\%RSD = (SD / RRF_{avg}) * 100$$

Where

$$SD = \sqrt{\frac{\sum_{i=1}^n (x_i - x_{ave})^2}{n - 1}}$$

The %RSD and SCV recovery requirement is listed in Appendix C. If a sample is for drinking water compliance, all regulated compounds must meet QC criteria.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that criteria are satisfied before any samples are analyzed.

Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

If the calibration does not meet the SCV criteria listed in Appendix C, the SCV may be re-analyzed. If the failure is repeated, terminate the analysis, correct the problem, and prepare a new calibration curve.

9.2.3 Continuing Calibration Verification

Examine the areas of the quantitation ions of the internal standards in the calibration verification standard. If the area for any internal standard changes by more than 50% from the internal standard areas of the continuing calibration verification level of the most recent initial calibration, re-analyze the CCV. If the failure is repeated, terminate the analysis, correct the problem, and prepare a new calibration curve.

Examine the retention time of the internal standards in the calibration verification standard. If the retention time for any internal standard changes by more than 30 seconds from the retention time in the continuing calibration level of the most recent initial calibration sequence, then inspect the chromatographic system for problems, take corrective action, and prepare a new calibration curve.

The data system calculates the percent deviation (%D) of the RF values for each compound using the following equation:

$$\%D = \frac{RRF_c - RRF_{avg}}{RRF_{avg}} \times 100$$

Where:

RRF_C: Relative Response Factor of compound c.

RRF_{avg}: Average Relative Response Factor

Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

If the continuing calibration does not meet %D criteria listed in Appendix C, the analysis shall be terminated, the problem corrected, and a new continuing calibration analyzed.

9.2.4 Quantitation Limit Standard

QLS must be analyzed at the beginning of the analytical run (typically just after the BFB and CCV). The QLS concentrations match the QL concentration (at the instrument). The recovery of analytes in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where

%R = percent recovery of the standard.

M = measured concentration of the analyte, ug/L.
 T = true concentration of the analyte in the ug/L.

Generate a QLS report and check that the recoveries meet criteria specified in Appendix C.

Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

If the QLS recovery does not meet criteria provided in Appendix C, rerun the QLS once to verify. If still unacceptable determine the cause, take corrective action.

9.3 Batch QC

9.3.1 Method Blank

Analyze at least one MB each 12-hour period or with each batch of 20 or fewer field samples, whichever is more frequent. MB values $\geq \frac{1}{2}$ QL indicate potential laboratory contamination. Use the following guidelines to determine when samples must be re-prepared and re-analyzed:

- a) If the MB analyte value $\geq \frac{1}{2}$ QL and the sample result is less than five times the MB analyte amount, all associated samples containing less than five times the MB analyte amount may have to be re-analyzed. Consult with the TOM or designee. Common laboratory contaminants (acetone, dichloromethane) are excluded; flag the results for these analytes following Appendix M of the Region 9 Quality Assurance Manual.
- b) If the MB analyte value $\geq \frac{1}{2}$ QL and the sample result is greater than five times the MB analyte concentration or is non-detected, report sample result.

9.3.2 LCS

Analyze one LCS standard each 12-hour period or once per batch of 20 field samples, whichever is more frequent. LCS recovery is calculated as:

$$\% R = \frac{C_m}{C_t} \times 100$$

Where

$\%R$ = percent recovery.
 C_m = measured analyte concentration in the LCS.
 C_t = true analyte concentration in the LCS.

Generate an LCS report and check that the recoveries meet criteria specified in Appendix C.

Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

If the LCS recovery does not meet criteria provided in Appendix C, rerun the LCS once to verify. If still unacceptable determine the cause, take corrective action, and re-analyze the LCS and associated samples.

9.3.3 Matrix Spike/Matrix Spike Duplicate

The MS and MSD are designed to provide information about the affect of sample matrix on the measurement system. One set of MS/MSD samples must be for each 20 field samples in an SDG. Do not evaluate MS/MSD recovery for any analyte whose concentration in the MS/MSD source sample is more than four times the MS/MSD spike level. Do not evaluate MS/MSD recovery for any analyte exceeding the calibration range of the instrument.

Samples identified as field blanks cannot be used for MS/MSD sample analysis.

MS/MSD recoveries are calculated as:

$$\% R = \frac{C_{ms} - C}{s} \times 100$$

Where

- $\%R$ = percent recovery.
- C_{ms} = measured concentration of analyte in the MS, corrected for sample preparation and any dilutions.
- C = measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions.
- s = expected analyte concentration in the MS, corrected for sample preparation and any dilutions.

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|C_{msd} - C_{ms}|}{(C_{msd} + C_{ms}) / 2} \times 100$$

Where

- RPD = relative percent difference.
- C_{msd} = measured concentration in the MSD, corrected for sample preparation and any dilutions.

C_{ms} = measured concentration in the MS, corrected for sample preparation and any dilutions.

If the MS/MSD analytes do not meet these criteria, examine other QC results to determine if a matrix problem exists. If laboratory performance is in control, the poor MS accuracy or precision is likely to be matrix-related.

Flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

- The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX	+ = PASS				! = FAIL			
CASE	1	2	3	4	5	6	7	8
LCS - % REC	+	+	+	+	-	-	-	-
MS/MSD -% REC	+	-	+	-	+	-	+	-
MS/MSD – RPD	+	+	-	-	+	+	-	-

Case 1: Batch acceptable.

Case 2: Batch acceptable; matrix effect confirmed.

Cases 3 & 4: Batch is unsatisfactory. Investigate MS/MSD problem and document findings in the LIMS memo field.

Cases 5, 6, 7, & 8: Batch rejected. If additional sample volume is available, the batch should be re-analyzed.

9.4 Sample QC

9.4.1 Surrogate Recovery

Check the surrogate recovery in all field and QC samples immediately after analysis.

ChemStation calculates the surrogate recovery using the following formula:

Equation 9:

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

The surrogate recovery must be within QC limits outlined in Appendix C.

Take the following steps if surrogate recovery is not within the limits:

1. Ensure that there are no calculation errors, and check the system performance.
2. Re-analyze the sample if a system performance problem or calculation error is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.

Do not reanalyze undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the run log.

Do not re-analyze the MS/MSD samples, even if surrogate recoveries are outside the limits.

If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis.

If the surrogate recoveries of the re-analysis are within limits, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding an "RE" suffix to the sample ID on the re-analysis. The problem must be documented in the LIMS MMO field.

If the re-analysis does not solve the problem, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the sample ID in the re-analysis.

9.4.2 Internal Standard Area:

Evaluate the internal standard areas in all field and QC samples immediately after analysis.

The internal standard areas must be within QC limits outlined in Appendix C.

Take the following steps if the internal standard areas are not within the limits:

1. Check the system performance.
2. Re-analyze the sample if a system performance problem is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.

Do not reanalyze undiluted samples with internal standard areas outside the limits if the diluted analysis with acceptable internal standard areas is being submitted.

Do not re-analyze the MS/MSD samples, even if internal standard areas are outside the limits.

If the sample associated with the MS/MSD analyses does not meet the internal standard areas criteria, it should be re-analyzed only if the matrix spike and duplicate internal standard areas are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis.

If the internal standard areas of the re-analysis are within limits, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding an "RE" suffix to the sample ID on the re-analysis. The problem must be documented in the LIMS MMO field.

If the re-analysis does not solve the problem, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the sample ID in the re-analysis.

9.5 Method Performance

Refer to the table in Appendix G for a summary of method performance at the 95% confidence level (2σ). Data are from the Region 9 Laboratory for water samples analyzed from July 1, 2006 to June 30, 2007.

Functional areas of the SOP that may be significant sources of analytical error are:

1. Sample handling. Loss of volatile compounds due to excessive sample handling.
2. Sample volatilization and degradation. Samples must be stored as outlined in the SOP to minimize losses.
3. Sample temperature: Samples must be allowed to come up to room temperature prior to analysis. Failure to do so will cause heavy molecular weight analytes to precipitate thus reducing the observed concentration.
4. Poor column condition may results in inadequate analyte separation and inaccurate integration.
5. Trap condition.
6. Leaks in sample transfer and GC/MS systems.

10 DOCUMENTATION

10.1 Standards

Record all standards (ICAL, CCV, QLS, MS/MSD, and LCS) in the Element database. Include a copy of each Analytical Standard Record associated with sample analysis in the data package.

10.2 Analytical sequence

Document the analytical sequence in the Element database and/or in the instrument Run Log. Record Case Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any.

Document the batch QC and field samples in a LIMS batch to obtain LIMS assigned IDs for the instrument and batch QC samples.

Document sample dilutions by entering the initial and final volumes in the LIMS bench sheet.

10.3 Analytical Report and Data Package

Analytical reports are produced using the Element database. The data package is produced from Element database and manual log records. Appendix H provides the typical format for data package deliverables.

10.4 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance.
- Subsequent instrument modifications and upgrades, including major software upgrades.
- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.5 SOP Distribution and Acknowledgement

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. The Lab QC Database is used to maintain the list of assigned analysts for each SOP. Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.6 SOP Revisions

Revisions to this SOP are summarized in Appendix I.

11 REFERENCES

Agilent Technologies EnviroQuant ChemStation User's Guide.

Agilent Technologies/HP 5973 GC/MS Users Manual.

Tekmar LSC2000 Operator's Manual.

Varian Archon Autosampler and HP 3000 Concentrator Operator's Manuals.

U.S. EPA Region 9 Laboratory, *Laboratory Quality Assurance Plan*, Latest Revision.

U.S. Environmental Protection Agency, 1995. Method 524.2, *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry*, Revision 4.1.

USEPA Method 5035A, *Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples*; Draft Revision 1, July 2002.

USEPA Method 8000C, *Determinative Chromatographic Separations*; Revision 3, March 2003.

USEPA Method 8260B, *Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry: Capillary Column Technique*; Revision 2, December 1996.

USEPA Region 9 Laboratory. *Business Plan*.

USEPA Region 9 Laboratory. *Chemical Hygiene Plan*.

USEPA Region 9 Laboratory. *Environmental Management System*.

U.S. EPA Region 9 Laboratory SOP 205, *Preparation of Organic Free Method Blank Water*.

U.S. EPA Region 9 Laboratory SOP 706, *Laboratory Waste Management Procedures*.

U.S. EPA Region 9 Laboratory SOP 820, *Laboratory Discrepancy and Corrective Action Reporting Procedures*.

U.S. EPA Region 9 Laboratory SOP 830, *Notification Procedure for Results Exceeding the Safe Drinking Water Act Maximum Contaminant Level*.

U.S. EPA Region 9 Laboratory SOP 835, *Chromatographic Integration Procedures*.

U.S. EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

U.S. EPA Region 9 Laboratory SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency*.

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. This SOP, following the Region 9 QA Plan, specifies preservation and storage temperatures of $>0^{\circ}$ to $\leq 6^{\circ}\text{C}$, while the reference method specifies $< 4^{\circ}\text{C}$.
2. The reference method specifies using m/z ion 95 as the quantitation ion for 4-Bromofluorobenzene. The Region 9 Laboratory uses m/z ion 174 for quantitation of 4-Bromofluorobenzene to avoid possible interference from a target analyte.
3. Section 11.6 of Method 524.2 describes using the spectra generated by the analytical system as reference spectra for target analyte identification. This SOP specifies the use of NIST library spectra as reference spectra to prevent confusion due to co-elution of compounds in the calibration standards.
3. This procedure uses QC limits generated from Region 9 Laboratory data. Deviations are allowed for up to 10% of these limits. This allowance is not included in the reference method.
4. Relative Retention Time (RRT) of chromatographic peak is not evaluated in this SOP as documented in method 8260B. ChemStation calculates an absolute retention time difference for sample components, not RRT difference. The retention time window of ± 0.2 min is more stringent than the ± 0.06 RRT units in the reference method.

APPENDIX B. ANALYTES AND QUANTITATION LIMITS

The following table contains target compounds and quantitation limits covered by this SOP. Routinely reported analytes are indicated; other listed compounds may be added on a project-specific basis. When required, lower quantitation limits may be reported when supported by method detection limit studies and appropriate QC and calibrations are performed. Regulated drinking water analytes are identified as shown.

Compound Name	CAS No.	QL, ug/L	Regulated	Routinely Report
Dichlorodifluoromethane	75-71-8	0.5		X
Chloromethane	74-87-3	0.5		X
Vinyl chloride	75-01-4	0.5	X	X
Bromomethane	74-83-9	0.5		X
Chloroethane	75-00-3	0.5		X
Trichlorofluoromethane	75-69-4	0.5		X
1,1-Dichloroethene	75-35-4	0.5	X	X
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	76-13-1	0.5		X
Acetone	67-64-1	4.0		X
Carbon disulfide	75-15-0	0.5		
Dichloromethane	75-09-2	0.5	X	X
<i>tert</i> -Butyl alcohol	75-65-0	10		
<i>trans</i> -1,2-Dichloroethene	156-60-5	0.5	X	X
<i>tert</i> -Butyl methyl ether (MTBE)	1634-04-4	2.0		X
1,1-Dichloroethane	75-34-3	0.5		X
Diisopropyl ether	108-20-3	2.0		
Ethyl <i>tert</i> -butyl ether	637-92-3	2.0		
2,2-Dichloropropane	594-20-7	0.5		X
<i>cis</i> -1,2-Dichloroethene	156-59-2	0.5	X	X
2-Butanone (MEK)	78-93-3	4.0		X
Bromochloromethane	74-97-5	0.5		X
Chloroform*	67-66-3	0.5	X	X
1,1,1-Trichloroethane	71-55-6	0.5	X	X
<i>tert</i> -Amyl methyl ether	994-05-8	2.0		
1,1-Dichloropropene	563-58-6	0.5		X
Benzene	71-43-2	0.5	X	X
1,2-Dichloroethane	107-06-2	0.5	X	X
Carbon tetrachloride	56-23-5	0.5	X	X
Trichloroethene	79-01-6	0.5	X	X
1,2-Dichloropropane	78-87-5	0.5	X	X
Dibromomethane	74-95-3	0.5		X
Bromodichloromethane*	75-27-4	0.5	X	X
<i>cis</i> -1,3-Dichloropropene	10061-01-5	0.5		X
4-Methyl-2-pentanone (MIBK)	108-10-1	4.0		
<i>trans</i> -1,3-Dichloropropene	10061-02-6	0.5		X
1,1,2-Trichloroethane	79-00-5	0.5	X	X
Toluene	108-88-3	0.5	X	X
2-Hexanone	591-78-6	4.0		
Tetrachloroethene	127-18-4	0.5	X	X
1,3-Dichloropropane	142-28-9	0.5		X

Compound Name	CAS No.	QL, ug/L	Regulated	Routinely Report
Chlorodibromomethane*	124-48-1	0.5	X	X
1,2-Dibromoethane (EDB)	106-93-4	0.5		X
Chlorobenzene	108-90-7	0.5	X	X
1,1,1,2-Tetrachloroethane	630-20-6	0.5		X
Ethylbenzene	100-41-4	0.5	X	X
m&p-Xylene	106-42-3	1.0	X	X
o-Xylene	95-47-6	0.5	X	X
Styrene	100-42-5	0.5	X	X
Bromoform*	75-25-2	0.5	X	X
Isopropylbenzene	98-82-8	0.5		X
Bromobenzene	108-86-1	0.5		X
1,1,2,2-Tetrachloroethane	79-34-5	0.5		X
1,2,3-Trichloropropane	96-18-4	0.5		X
Propylbenzene	103-65-1	0.5		X
2-Chlorotoluene	95-49-8	0.5		X
4-Chlorotoluene	106-43-4	0.5		X
1,3,5-Trimethylbenzene	108-67-8	0.5		X
<i>tert</i> -Butylbenzene	98-06-6	0.5		X
1,2,4-Trimethylbenzene	95-63-6	0.5		X
<i>sec</i> -Butylbenzene	135-98-8	0.5		X
1,3-Dichlorobenzene	541-73-1	0.5		X
1,4-Dichlorobenzene	106-46-7	0.5	X	X
p-Isopropyltoluene	99-87-6	0.5		X
1,2-Dichlorobenzene	95-50-1	0.5	X	X
Butylbenzene	104-51-8	0.5		X
1,2-Dibromo-3-chloropropane	96-12-8	2.0		X
1,2,4-Trichlorobenzene	120-82-1	0.5	X	X
Hexachlorobutadiene	87-68-3	0.5		X
Naphthalene	91-20-3	0.5		X
1,2,3-Trichlorobenzene	87-61-6	0.5		X
Surrogate Compounds				
1,2-Dichloroethane-d4				
Toluene-d8				
4-Bromofluorobenzene				
1,2-Dichlorobenzene-d4				
Internal Standards				
Dichloromethane-d2				
Fluorobenzene				
Chlorobenzene-d5				

* Trihalomethanes

APPENDIX C. QUALITY CONTROL MEASURES AND CRITERIA

QC Measure	Criteria
BFB	Every 12-hours
CCV %D ⁽¹⁾	≤ 30%
CCV IS, Surrogate Area	±50% of IC
CCV Retention Time Drift	±30 Sec of IC
LCS Recovery ⁽¹⁾	See Table Below
MB, SB	<½ QL
MS/MSD Recovery ⁽¹⁾	See Table Below
MS/MSD Precision (RPD) ⁽¹⁾	See Table Below
QLS Recovery ⁽¹⁾	60-140%
IC RSD ⁽¹⁾	≤ 20%
Sample IS Area	30% of CC
Sample IS Retention Time Drift	±30 sec of IC
SCV %D ⁽¹⁾	≤ 30%
DOC P&A % Recovery	80-120%
Surrogate Recovery	See Table Below

(1) Up to 10 % of the compounds may fail to meet these criteria, but if the samples are for drinking water compliance, all regulated compounds must meet all QC criteria.

Quantitation Ions, System Monitoring Compounds, and Internal Standards

Compound Name	IS Reference	SMC Reference	Primary Ion, m/z
Dichlorodifluoromethane	1	1	85
Chloromethane	1	1	50
Vinyl chloride	1	1	62
Bromomethane	1	1	94
Chloroethane	1	1	64
Trichlorofluoromethane	1	1	101
1,1-Dichloroethene	1	1	96
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	1	1	101
Acetone	1	1	43
Carbon disulfide	1	1	76
Dichloromethane	1	1	84
<i>tert</i> -Butyl alcohol	1	1	59
<i>trans</i> -1,2-Dichloroethene	1	1	96
<i>tert</i> -Butyl methyl ether (MTBE)	1	1	73
1,1-Dichloroethane	1	1	63
Diisopropyl ether	1	1	45
Ethyl <i>tert</i> -butyl ether	1	1	59
2,2-Dichloropropane	1	1	77
<i>cis</i> -1,2-Dichloroethene	1	1	96
2-Butanone (MEK)	1	1	43

Compound Name	IS Reference	SMC Reference	Primary Ion, m/z
Bromochloromethane	1	1	128
Chloroform	1	1	83
1,1,1-Trichloroethane	2	1	97
<i>Tert</i> -Amyl methyl ether	2	1	73
1,1-Dichloropropene	2	1	75
Benzene	2	2	78
1,2-Dichloroethane	2	1	62
Carbon tetrachloride	2	1	117
Trichloroethene	2	1	95
1,2-Dichloropropane	2	1	63
Dibromomethane	2	3	93
Bromodichloromethane	2	1	83
<i>cis</i> -1,3-Dichloropropene	2	1	75
4-Methyl-2-pentanone (MIBK)	3	3	43
<i>trans</i> -1,3-Dichloropropene	2	1	75
1,1,2-Trichloroethane	2	3	83
Toluene	3	2	92
2-Hexanone	3	3	43
Tetrachloroethene	3	3	166
1,3-Dichloropropane	3	3	76
Chlorodibromomethane	3	3	129
1,2-Dibromoethane (EDB)	3	3	107
Chlorobenzene	3	3	112
1,1,1,2-Tetrachloroethane	3	3	131
Ethylbenzene	3	2	91
m&p-Xylene	3	2	106
o-Xylene	3	2	106
Styrene	3	2	104
Bromoform	3	3	173
Isopropylbenzene	3	2	105
Bromobenzene	3	2	156
1,1,2,2-Tetrachloroethane	3	3	83
1,2,3-Trichloropropane	3	3	75
Propylbenzene	3	2	91
2-Chlorotoluene	3	3	91
4-Chlorotoluene	3	3	91
1,3,5-Trimethylbenzene	3	2	105
<i>tert</i> -Butylbenzene	3	2	119
1,2,4-Trimethylbenzene	3	2	105
<i>sec</i> -Butylbenzene	3	2	105
1,3-Dichlorobenzene	3	3	146
1,4-Dichlorobenzene	3	3	146
p-Isopropyltoluene	3	2	119
1,2-Dichlorobenzene	3	3	146
Butylbenzene	3	2	91
1,2-Dibromo-3-chloropropane	3	3	75
1,2,4-Trichlorobenzene	3	3	180
Hexachlorobutadiene	3	3	225
Naphthalene	3	2	128

Compound Name	IS Reference	SMC Reference	Primary Ion, m/z
1,2,3-Trichlorobenzene	3	3	180
Surrogate Compounds			
1,2-Dichloroethane-d4	2		65
Toluene-d8	3		98
4-Bromofluorobenzene	3		174
1,2-Dichlorobenzene-d4	3		152
Internal Standards			
Dichloromethane-d2	1		53
Fluorobenzene	2		96
Chlorobenzene-d5	3		117

LCS and MS/MSD QC Criteria (based on laboratory performance 7/1/06 – 6/30/07 at 99% confidence)¹

Analyte	LCS Recovery, %	MS/MSD Recovery, %	MS/MSD, RPD
Dichlorodifluoromethane	5.7-180	25-135	20
Chloromethane	47-140	47-140	20
Vinyl chloride	70-130	43-150	20
Bromomethane	50-160	38-160	20
Chloroethane	68-140	59-140	20
Trichlorofluoromethane	63-150	44-170	20
1,1-Dichloroethene	70-130	33-160	20
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	53-150	38-140	20
Acetone	32-190	46-140	20
Carbon disulfide	70-130	70-130	20
Dichloromethane	70-130	56-120	20
<i>tert</i> -Butyl alcohol	47-140	NA	20
<i>trans</i>-1,2-Dichloroethene	70-130	59-130	20
<i>tert</i> -Butyl methyl ether (MTBE)	59-150	50-140	20
1,1-Dichloroethane	70-140	47-160	20
Diisopropyl ether	90-140	NA	20
Ethyl <i>tert</i> -butyl ether	90-140	NA	20
2,2-Dichloropropane	60-150	25-150	20
<i>cis</i>-1,2-Dichloroethene	70-130	55-140	20
2-Butanone (MEK)	58-150	43-150	20
Bromochloromethane	55-150	56-140	20
Chloroform	70-130	30-170	20
1,1,1-Trichloroethane	70-130	36-150	20
<i>tert</i> -Amyl methyl ether	85-140	NA	20
1,1-Dichloropropene	75-130	50-150	20
Benzene	70-130	74-122	20
1,2-Dichloroethane	70-130	69-140	20
Carbon tetrachloride	70-130	31-160	20

1 . Except for regulated compounds, shown in bold which have acceptance limits of 70-130 per Method 524.2. If the lower value is greater than 90%, the value is set to 90%.

Analyte	LCS Recovery, %	MS/MSD Recovery, %	MS/MSD, RPD
Trichloroethene	70-130	47-160	20
1,2-Dichloropropane	70-130	30-190	20
Dibromomethane	80-120	77-120	20
Bromodichloromethane	70-130	87-130	20
<i>cis</i> -1,3-Dichloropropene	81-130	67-138	20
4-Methyl-2-pentanone (MIBK)	70-140	NA	20
<i>trans</i> -1,3-Dichloropropene	80-140	65-150	20
1,1,2-Trichloroethane	70-130	74-131	20
Toluene	70-130	68-120	20
2-Hexanone	60-150	NA	20
Tetrachloroethene	70-130	41-150	20
1,3-Dichloropropane	78-120	67-130	20
Chlorodibromomethane	70-130	62-140	20
1,2-Dibromoethane (EDB)	83-120	73-130	20
Chlorobenzene	70-130	75-120	20
1,1,1,2-Tetrachloroethane	82-130	71-130	20
Ethylbenzene	70-130	63-140	20
m&p-Xylene	70-130	67-130	20
o-Xylene	70-130	71-140	20
Styrene	70-130	20-170	20
Bromoform	70-130	43-160	20
Isopropylbenzene	83-130	61-150	20
Bromobenzene	84-120	77-120	20
1,1,2,2-Tetrachloroethane	80-120	70-130	20
1,2,3-Trichloropropane	79-130	63-140	20
Propylbenzene	83-130	59-140	20
2-Chlorotoluene	84-120	76-130	20
4-Chlorotoluene	85-120	77-130	20
1,3,5-Trimethylbenzene	84-120	68-140	20
<i>tert</i> -Butylbenzene	83-130	61-150	20
1,2,4-Trimethylbenzene	86-120	67-140	20
<i>sec</i> -Butylbenzene	81-130	54-150	20
1,3-Dichlorobenzene	83-120	77-120	20
1,4-Dichlorobenzene	70-130	76-120	20
p-Isopropyltoluene	83-130	58-150	20
1,2-Dichlorobenzene	70-130	69-130	20
Butylbenzene	83-130	57-140	20
1,2-Dibromo-3-chloropropane	64-131	54-143	20
1,2,4-Trichlorobenzene	70-130	66-130	20
Hexachlorobutadiene	76-130	46-140	20
Naphthalene	64-150	52-160	20
1,2,3-Trichlorobenzene	58-150	64-130	20

NA = Not Available, insufficient data.

Surrogate QC Criteria

Compound Name	Recovery, %
1,2-Dichloroethane-d4	76-130
Toluene-d8	83-120
4-Bromofluorobenzene	74-110
1,2-Dichlorobenzene-d4	69-120

APPENDIX D.
INSTRUMENT INFORMATION

PURGE & TRAP CONCENTRATOR/AUTOSAMPLER PARAMETERS**Purge and Trap Concentrator operating parameters**

The operating parameters for the purge & trap concentrators. These parameters may vary slightly to optimize instrument responses except Purge Time, Purge Flow, and Desorb Time cannot be altered from the method required settings.

PARAMETER	SETTING
	<u>HP/Tekmar 3000</u>
Standby temperature	38°C
Preheat temperature	N/A
Prepurge time	N/A
Sample temperature	Ambient (off)
Purge Time*	11 minutes
Dry purge	1 minute
Purge Flow*	40 mL/min
Desorb preheat temperature	245°C
Desorb Time*	4.00 minutes @ 250°C
Bake	11 minutes @ 260°C
Auto drain	On (controlled by Archon)
Bake gas bypass	Off
Valve temperature	150°C
Mount temperature	40°C
Line temperature	150°C
*Do not optimize these settings.	

Sample loading:

1. Fill a 25-mL syringe with acidified method blank water. Invert the syringe, remove any air bubbles, and bring the level to 25 mL by displacement with the plunger.
2. Spike the water with the appropriate amount of VOA IS Mix (usually 1 µL 125 µg/mL) solution. The amount used results in the analytical equivalent of 5 µg/L.
3. For standards, Blank spikes, and Matrix spike samples, spike the water with the appropriate amount of spiking solution.
4. Lay the syringe on the lab bench and spike the water with 1 µL of VOA IS Solution.
5. Attach the 25 mL syringe to the Luer lock mount on the autosampler. Open the mount valve and inject the contents of the syringe into the sparge cell and close the valve.
6. Remove the syringe from the mount.

Varian Archon Autosampler

The Archon delivers an aliquot of the water sample directly from the 40 mL sample vial into the sparge vessel on the concentrator. The Archon can be programmed to add the internal standard and surrogate into the sample during the transfer process. In water analysis mode, the settings for the Archon method are equivalent to the settings on the concentrator. The following parameters must be established on the Archon: sample volume, dilution, standard addition, purge time (same as concentrator – 11 minutes), and number of vials to be analyzed.

Sample loading:

1. Fill a 50-mL syringe with acidified method blank water.
2. Invert the syringe, remove any air bubbles, and bring 50 mL by displacement with the plunger.
3. Spike the water with the appropriate amount of VOA IS Mix (usually 1 μ L 125 μ g/mL) solution.
4. For standards, Blank spikes, and Matrix spike samples, spike the water with the appropriate amount of spiking solution.
5. Cap the end of the syringe containing the solution.
6. Rotate and invert the closed syringe to mix.
7. Let the standard solution equilibrate in the syringe for about 1 minute.
8. While the standard solution is equilibrating, label the 40-mL vial with information about the standard.
9. Gently decant the standard solution into the 40-mL vial, down the side of the vial, without any agitation. Overfill the vial to form an inverted meniscus. Cap the vial. Invert the vial to ensure that there are no air bubbles present.
10. Gently place the vial in the appropriate autosampler position.
11. The Archon autosampler will analyze a 25 mL aliquot and add 1 μ L of the 125 ng/ μ L VOA IS solution. The amount used results in the analytical equivalent of 5 μ g/L.

RECOMMENDED GC/MSD PARAMETERS**HP/Agilent 6890 GC & HP/Agilent 5973MSD**

The operating parameters for this system are listed below. Actual operating conditions may vary slightly to optimize instrument

BFB analysis

PARAMETER	SETTING
Injector temperature	200°C
Column Stability time	0.5 minutes
MS Quad	150°C
MS Source	230°C
Initial Oven Temp	110°C
Initial Oven Time	0.5 minutes
Temperature Ramp	25°C/minute for 3.6 minutes
Final Oven Temp	190°C
Final Hold Time	1.9 minutes
Inlet mode:	Split
Split vent flow:	20 mL/min
Column Flow rate	0.8/*1.2 mL/min at constant flow mode
Electron Energy	70 volts (nominal)
MS Scan range	35-260 amu

* for Restek RTX-VMS 30m x 0.25mm, 1.4 micro film column

VOA analysis

PARAMETER	SETTING
Injector temperature	200°C
Column Stability time	0.5 minutes
MS Quad	150°C
MS Source	230°C
Initial Oven Temp	35°C
Initial Oven Time	3.0 minutes
Temperature Ramp	8°C/minute to 120°C for 2 minutes; 25°C/minute to 195°C for 2.2 minutes
Final Oven Temp	200°C
Final Hold Time	2.0/* 5.0 minutes
Inlet mode:	Split
Split vent flow:	20 mL/min.
Column Flow rate	0.8/* 1.2 mL/min at constant flow mode.
Electron Energy	70 volts (nominal)
MS Scan Range	35-260 amu

* for Restek RTX-VMS 30m x 0.25mm, 1.4 micro film column

Analytical system preparation:

Leak Checking

From the ChemStation Instrument Control panel of the HP 5973 MSD select View, Tune and Vacuum control.

Select Spectrum scan. Check the nitrogen (m/z 28), water (m/z 18), to FC43 (m/z 69) ratio. Ratios for ions 28 and 18 should not exceed 20% of ion 69. Values higher than indicated above are indicative of large leaks and must be corrected.

Auto Tuning

Perform an autotune of the analytical system prior to an initial calibration, whenever the mass spectrometer is shut down, or the source is cleaned.

Perfluorotributylamine (FC43) is the compound used to perform the mass calibration of the instrument. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target and non-target compounds.

The autotune software will adjust the mass ratio, abundance, peak shape, width, isotope peak resolution, and mass assignment.

An autotune report will be generated and the parameters will be saved in ATUNE.U.

The Agilent ChemStation software requires that the FC43 spectrum meet the following criteria:

<u>Mass</u>	<u>Target % of Mass 69</u>
50	0.3-5
69	100
131	20-120
219	20-120
414	0.3-10
502	0.3-10

Preparation for an Initial Calibration

Perform an autotune of the analytical system prior to an initial calibration.

1. The system should be reset to default parameters as follow:
 - a. From the ChemStation Instrument Control panel of the HP 5973 MSD select View, Tune and Vacuum control. Select File, Reset to Default, Autotune.
 - b. If the DC polarity for the system is normally set to negative for the system, resetting the tune parameter will set it to positive. Set the parameter to negative by selecting Parameters, Manual tune, DC polarity and slide the polarity selector to negative.
2. Save the default parameters by selecting save tune, Autotune.u.
3. Autotune the system by selecting Tune, Autotune.
4. The system will generate an Autotune report.
5. Save the resulting tune file by selecting File, Save tune Value

6. The tune file name is selected as outlined in the “ChemStation File Naming Convention”.
7. Generate the tuning report by selecting File, Generate report.

Preparation for a Continuing Calibration

1. Perform a mass axis calibration of the analytical system prior to continuing calibration. By selecting calibrate, Mass axis.
2. Save the resulting tune file by selecting File, Save tune Value.
3. The tune file name is selected as outlined in the “ChemStation File Naming Convention”.
4. Generate the tuning report by selecting File, Generate report.

Manual tuning

If the system fails to meet the tuning criteria, the source may need to be cleaned or manual tuning may be required. BFB or DFTPP tuning routines may be used to correct ions ratios.

To manually tune the system, select Manual Tune from View menu in Instrument Control view and manually tune the MSD, using ATUNE.U as reference. Adjust the parameters of Ion Focus, Entrance Lens, Repeller, Entrance Lens Offset, EM voltage etc to suit your analysis needs.

Incorporate the new tune parameters and generate today's method

1. Load a copy of the last initial calibration from C:\HPCHEM\1\Methods\Initial.
2. From the ChemStation Instrument Control panel of the HP 5973 MSD click on Select MS Tune File icon, click on the name of tune file generated today.
3. Select MS/SIM Scan Parameters. If necessary, adjust the EM voltage by adding or subtracting voltage relative “REL” to today's tune voltage.
4. Save the resulting method file as outlined in the as outlined in the “ChemStation File Naming Convention” by selecting File, Save method.

Mass Calibration:

Perform mass calibration of the analytical system prior to an initial calibration, whenever the mass spectrometer is shut down, or whenever there is a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer.

APPENDIX E.
CHEMSTATION FILE NAMING CONVENTIONS

ChemStation File Naming Convention

File data, methods, and sequences on ChemStation computers and the LAN using the following naming conventions:

Directories

On the Workstation:

Data: C:\HPCHEM\1\Data\MDDY or D:\HPCHEM\1\Data\MDDYS

Methods: C:\HPCHEM\1\Methods or D:\HPCHEM\1\Methods

Sequences: C:\HPCHEM\1\Sequence or D:\HPCHEM\1\Sequence

For system controlling multiple instruments, 1 may be changed to reflect the instrument number

System running ChemStation versions C & D HPCHEM is named as MSDCHEM

On the LAN:

Data: I:\Room Number\Instrument\Year\MDDYS

Methods: I:\Room Number\Instrument\Methods

Sequences: I:\Room Number\Instrument\Sequence

Methods

MDDYITA

Sequence

MDDYS

Data Files

For GC:

MDDYICSS

For GC/MS

MDDYIQSS

Variables

A: Enter analysis, as follow:

1,4-Dioxane	X
504	E
TO15	A
BNA	B
BNA-L (SIM)	L
Congeners	C
P/P	P
PCB	P
RSK175	R

Soil Gas	A
TPH-G	G
TPH-D	D
VOA	V

C: Channel: A = front
B = back (if applicable)

DD: Day

I: Instrument
6890 series GCs by last number in name: e.g. 6890-1 = 1 except 580-2 = A
All GC/MSs by last letter in name: e.g. 5973L = L

M: Month 1-9, A: October, B: November, C: December

Q: QC type

BFB	F
Blank	B
CV	C
Degradation	P
DFTPP	D
IB	Z
IC	I
LCS	L
LCV	Q
Second Source	S
MS/MSD	M

S: Sequential number 1,2 3,

T: Matrix Type (if applicable)
Water W
Solid S
Air A
Oil O
Other X

Y: Year i.e. 5 for 2005

APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

GC Maintenance		
Item	Frequency	Actions/Comments
Split vent trap	Annually	Replace.
Syringes and/or syringe needles	As Needed	Replace syringe if dirt is noticeable in the syringe, if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged. Replace needle if septa wear is abnormal or the needle becomes clogged.
Inlet liner	With each ICAL	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	With each ICAL	Replace with liner or with signs of wear.
Inlet septum	With each ICAL	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	With each ICAL	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Column Replacement	As needed	When trimming no longer returns chromatographic performance.
Ferrules		Replace ferrules when changing columns and inlet/detector parts.
Purge/Sample Lines	Annually or as needed	Bake out and purge. Clean with organic free water if necessary.
Trap	As needed	Replace with loss of performance.

MS Maintenance				
Task	Every Week	Every 6 Months	Every Year	As Needed
Tune the MSD				✓
Check the foreline pump oil level	✓			
Check FC43 level		✓		
Replace the foreline pump oil		✓		
Clean the ion source				✓
Check the carrier gas traps on the GC				✓
Replace worn out parts				✓
Lubricate sideplate or vent valve O-rings				✓

APPENDIX G. METHOD PERFORMANCE

Volatile Organic Compound Analysis in Water 7/1/06 – 6/30/07

Analyte	Matrix	QC Type	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2 σ)
Dichlorodifluoromethane	Water	LCS	190	93.6	54.9-132
Chloromethane	Water	LCS	190	93.9	67.4-120
Vinyl chloride	Water	LCS	190	95.9	67.5-124
Bromomethane	Water	LCS	190	107	71.6-143
Chloroethane	Water	LCS	190	95.4	71.8-119
Trichlorofluoromethane	Water	LCS	190	101	70.2-133
1,1-Dichloroethene	Water	LCS	190	104	77.1-130
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	Water	LCS	190	106	74.2-137
Acetone	Water	LCS	190	101	51.3-151
Carbon disulfide	Water	LCS	102	106	70.2-141
Dichloromethane	Water	LCS	190	96.5	74.8-118
<i>tert</i> -Butyl alcohol	Water	LCS	100	103	57.2-149
<i>trans</i> -1,2-Dichloroethene	Water	LCS	190	102	77.6-127
<i>tert</i> -Butyl methyl ether (MTBE)	Water	LCS	190	96.7	70-123
1,1-Dichloroethane	Water	LCS	190	95.7	70.5-121
Diisopropyl ether	Water	LCS	100	102	80-123
Ethyl <i>tert</i> -butyl ether	Water	LCS	100	99.9	77.7-122
2,2-Dichloropropane	Water	LCS	190	107	69.9-143
<i>cis</i> -1,2-Dichloroethene	Water	LCS	190	102	77.3-128
2-Butanone (MEK)	Water	LCS	190	106	64.6-147
Bromochloromethane	Water	LCS	190	104	75.8-131
Chloroform	Water	LCS	190	99.3	74.4-124
1,1,1-Trichloroethane	Water	LCS	190	101	86.2-116
<i>tert</i> -Amyl methyl ether	Water	LCS	100	97.3	80-114
1,1-Dichloropropene	Water	LCS	190	98.9	83.4-115
Benzene	Water	LCS	190	101	90.4-111
1,2-Dichloroethane	Water	LCS	190	99.9	82-118
Carbon tetrachloride	Water	LCS	190	106	86.2-125
Trichloroethene	Water	LCS	190	100	89.1-111
1,2-Dichloropropane	Water	LCS	190	99.4	86.1-113
Dibromomethane	Water	LCS	190	103	86.3-119
Bromodichloromethane	Water	LCS	190	104	88.5-118
<i>cis</i> -1,3-Dichloropropene	Water	LCS	190	101	83.3-118
4-Methyl-2-pentanone (MIBK)	Water	LCS	102	103	82.1-124
<i>trans</i> -1,3-Dichloropropene	Water	LCS	190	105	87.2-122
1,1,2-Trichloroethane	Water	LCS	190	105	90.6-119
Toluene	Water	LCS	190	102	91.6-113
2-Hexanone	Water	LCS	102	103	74.8-131
Tetrachloroethene	Water	LCS	190	103	86.4-120
1,3-Dichloropropane	Water	LCS	190	102	88-116
Chlorodibromomethane	Water	LCS	190	111	90.2-131
1,2-Dibromoethane (EDB)	Water	LCS	190	105	90.4-120

Analyte	Matrix	QC Type	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2 σ)
Chlorobenzene	Water	LCS	190	102	91.9-112
1,1,1,2-Tetrachloroethane	Water	LCS	190	108	92.1-123
Ethylbenzene	Water	LCS	190	104	92-116
m&p-Xylene	Water	LCS	190	104	92.8-116
o-Xylene	Water	LCS	190	105	94.4-115
Styrene	Water	LCS	190	106	94-119
Bromoform	Water	LCS	190	117	83.5-151
Isopropylbenzene	Water	LCS	190	105	91.4-118
Bromobenzene	Water	LCS	190	106	91.7-120
1,1,2,2-Tetrachloroethane	Water	LCS	190	107	87.4-126
1,2,3-Trichloropropane	Water	LCS	190	104	84.8-122
Propylbenzene	Water	LCS	190	105	91.7-119
2-Chlorotoluene	Water	LCS	190	103	92.1-115
4-Chlorotoluene	Water	LCS	190	104	92.3-115
1,3,5-Trimethylbenzene	Water	LCS	190	105	92.4-118
<i>tert</i> -Butylbenzene	Water	LCS	190	105	91.1-118
1,2,4-Trimethylbenzene	Water	LCS	190	106	92.7-119
<i>sec</i> -Butylbenzene	Water	LCS	190	105	90.6-120
1,3-Dichlorobenzene	Water	LCS	190	106	92-119
1,4-Dichlorobenzene	Water	LCS	190	106	92-121
p-Isopropyltoluene	Water	LCS	190	105	91.3-119
1,2-Dichlorobenzene	Water	LCS	190	105	89.9-120
Butylbenzene	Water	LCS	190	106	90.8-122
1,2-Dibromo-3-chloropropane	Water	LCS	190	107	81.7-132
1,2,4-Trichlorobenzene	Water	LCS	190	105	83.9-127
Hexachlorobutadiene	Water	LCS	190	103	84-122
Naphthalene	Water	LCS	190	109	75.5-142
1,2,3-Trichlorobenzene	Water	LCS	190	106	79.5-133

APPENDIX H. TYPICAL DATA PACKAGE FORMAT

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms

EPA Review Form

ESAT technical review guide

Discrepancy Reports (if applicable)

Work Order Memo (if applicable)

Daily folder review forms or checklists

Analysis matrix listing all analytical runs (for organics only)

Tracking Forms

Work Order(s)

COC(s)

Sample Preparation (for projects that require extraction or digestion)

Bench Sheets (and extraction logs, where used)

Sample cleanup data and records (e.g. GPC logs)

Moisture data as applicable

[Analysis Method] Data (For each method where multiple methods in package)

Bench sheet(s) where not used in Sample Preparation section

Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Alternatively, separate calibration and sample data as:

Initial Calibration Data

Sample Data

Miscellaneous Data

Other data as applicable (e.g. conductivity for perchlorate)

Standard Records

Standards records from LIMS (and logbook pages as needed)

**APPENDIX I.
REVISION HISTORY**

**STANDARD OPERATING PROCEDURE: 354
Revision: 9, Effective: 11/27/09**

VOLATILE ORGANIC COMPOUND ANALYSIS IN WATER

Revision	Effective Date	Description
8	04/21/08	Added Method 8260B as a reference method. Added requirement that all equipment, standards, reagents, and supplies must meet technical & QC requirements of the reference method. Added requirement to prepare standards and instrument and batch QC samples in acidified organic-free water. Changed LCS %R QC Limits to 70 – 130% for regulated compounds. Added option to purge BFB. Changed RRT criteria for analyte identification from relative to absolute. Deleted requirement to re-analyze samples containing < 5 times MB amount for common laboratory contaminants. Revised Sections 8.2.1 and 8.2.2 and Appendix D to clarify and reflect current practice.
9	11/27/09	1. Revised Appendix D to require adherence to instrument operating conditions specified in the reference method. 2. Minor changes throughout to update SOP to current requirements of SOP 850 for format.

**USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA**

**STANDARD OPERATING PROCEDURE 375
LOW LEVEL SEMIVOLATILE ORGANICS ANALYSIS**

Revision 3
Effective Date: April 13, 2009

Reviewed by: _____
Richard Bauer Date
Chemistry Team Leader/Technical Director

Reviewed by: _____
K. W. Hendrix, Laboratory QA Officer Date

Approved by: _____
Brenda Bettencourt, Laboratory Director Date

Periodic Review:

Signature	Title	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____

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APPENDIX A. DEVIATIONS FROM THE REFERENCE METHOD

APPENDIX B. ANALYTES AND QUANTITATION LIMITS

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APPENDIX E. CHEMSTATION FILE NAMING CONVENTIONS

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APPENDIX G. METHOD PERFORMANCE

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APPENDIX I. REVISION HISTORY

1 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the procedures used for the low level analysis of selected semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS) with selected ion monitoring (SIM) in extracts prepared from solid or liquid samples by EPA SW-846 extraction and cleanup methods appropriate to the sample matrix. This SOP is based on procedures contained in EPA Method SW 846 8270D. Deviations from Method 8270 are described in Appendix A. Analytes and Quantitation Limits (QLs) for this analysis are listed in Appendix B.

Sample extracts are prepared using EPA Region 9 Lab SOP 290 *Extraction of Soil Samples Using Pressurized Fluid* or SOP 265 *Extraction of Low Level Phenols and Polycyclic Aromatic Hydrocarbons from Water*. In some instances, samples extracted using the procedures in EPA Region 9 Lab SOP 275 *Extraction of Water Samples by Continuous Liquid-Liquid Extraction* may be analyzed by this procedure. In this event, the surrogate concentrations will exceed the calibration range and will not be reported.

The applicability of this procedure to specific project data quality objectives must be assessed on a case-by-case basis. The quality control (QC) criteria specified in this procedure do not meet compliance criteria for either drinking water or NPDES monitoring projects. This SOP applies to analyses conducted at the USEPA Region 9 Laboratory in Richmond, CA.

2 METHOD SUMMARY

Sample extracts are injected into a gas chromatograph (GC) with a mass spectrometer (MS) detector. Analytes are separated in a narrow bore fused silica capillary GC column in a temperature-controlled oven and detected by the MS in SIM mode. Each target and surrogate analyte is quantitated using the average response factors from the most recent initial calibration.

Target analytes of interest are identified in the sample extract by comparing the selected characteristic ion(s) and GC retention time of the analyte to the characteristic ion(s) and retention time of standards analyzed under the same conditions.

3 DEFINITIONS

Atomic weight - The following terms are used to describe atomic weight: Dalton – a unit of atomic mass; atomic mass unit (amu) – one Dalton; mass to charge ratio (m/z) – a unit of ionic mass equivalent to Daltons per unit of charge.

Calibration Standard (CAL) - A solution prepared from the primary dilution standard or stock standard solution and the internal standard and surrogate analytes. The CAL solutions are used to calibrate instrument response with respect to analyte concentration.

Continuing Instrument Calibration Verification (CCV) - A standard containing the analytes of interest, which is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout the analysis sequence (after every ten samples and at the end of the analytical run). The CCV meets the requirement of the instrument performance check sample specified in the reference method.

GC/MS Tuning Solution (MS tune) - A solution of decafluorotriphenylphosphine (DFTPP), 4,4' DDT, pentachlorophenol, and benzidine used to evaluate the performance of the GC/MS system with respect to a defined set of method criteria.

Initial Calibration Standards (ICAL) - Standards used to calibrate the instrument response with respect to analyte concentration.

Internal Standard (IS) - A compound added to a sample, extract, or standard solution in a known amount and used to measure the relative responses of method analytes and surrogates that are components of the same solution.

Laboratory Control Sample (LCS) - An aliquot of reagent water, sand, or sodium sulfate to which known quantities of the method analytes are added. The LCS is treated exactly as a sample. The LCS is used to determine whether the methodology is in control and to indicate the accuracy associated with laboratory procedures. This is equivalent to a Laboratory Fortified Blank (LFB) QC sample.

Laboratory Information Management System (LIMS) - The Element Database.

Matrix Spike (MS) and Matrix Spike Duplicate (MSD) - Two aliquots of the same sample to which known quantities of the method analytes are added. The MS and MSD are treated exactly as samples. The MS and MSD are used to determine whether the sample matrix contributes bias to sample results and to measure the precision associated with laboratory procedures. These are equivalent to Laboratory Fortified Matrix (LFM) and Laboratory Fortified Matrix Duplicate (LFMD) QC samples.

Method Blank (MB) - An aliquot of reagent water, sand, or sodium sulfate that is treated exactly as a sample including exposure to all glassware, equipment, solvents, and surrogates that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the solvents, or the equipment. This is equivalent to a Laboratory Reagent Blank.

Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

PAH – polynuclear aromatic hydrocarbons.

Primary Dilution Standard Solution (PDS) - A solution of one or more analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

Second Source Calibration Verification (SCV) - Equivalent to the mid point initial calibration solution but prepared from a source different from the source of calibration standards. The SCV is used to check the accuracy of the initial calibration solutions.

Quantitation Limit Standard (QL) - The lowest level CAL solution. The QLS is used to verify analytical system response at the quantitation limit.

Sample Delivery Group (SDG) - A group of twenty samples or less from a project that is sent to the laboratory for analysis.

Stock Standard Solution (SSS) - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials purchased from a commercial source.

Surrogate - Compounds which are extremely unlikely to be found in any sample that are added to a sample aliquot in a known amount before extraction or other processing, and measured with the same procedures used to measure other sample components. The purpose of the surrogate is to monitor method performance with each sample.

4 SAFETY AND HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

Dichloromethane is a suspected carcinogen. Effects of overexposure: acute inhalation or ingestion causes mild central nervous system depression. The primary toxic effect is narcosis. Other toxic effects are pulmonary edema, encephalopathy, and hemolysis. Dichloromethane irritates the eyes, skin, and respiratory tract. No systemic effects have been reported in humans, although excessive concentrations have caused cancer and liver and kidney damage in animals.

Emergency and first aid:

- Inhalation: immediately remove to fresh air. If not breathing, administer mouth to mouth rescue breathing. If there is no pulse, administer cardiopulmonary resuscitation (CPR), contact physician immediately.
- Eye contact: rinse with copious amounts of water for at least 15 minutes. Get emergency medical assistance.
- Skin contact: flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothing and shoes. Wash clothing before re use, and discard contaminated shoes. Get emergency medical assistance.
- Ingestion: call local poison control center for assistance. Contact physician immediately. Never induce vomiting or give anything by mouth to a victim unconscious or having convulsions.

Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Stock standard solutions of these compounds must be prepared in a fume hood. Routine procedures in this SOP do not require contact with concentrated solutions or neat materials. All standard preparation procedures associated with this SOP should be performed in a fume hood wearing protective clothing (lab coats) and safety glasses.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory*

Environmental Management System provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, does not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-regulated Waste	Not applicable
Sample Extracts	Hazardous Waste	See solvent MSDS

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Please refer to EPA Region 9 Lab SOP 290 *Extraction of Soil Samples Using Pressurized Fluid* or SOP 265 *Extraction of Low Level Phenols and Polycyclic Aromatic Hydrocarbons from Water*.

5.2 Internal Chain-of-Custody

Sample extracts for GC/MS analysis are received from the extraction lab personnel and custody is transferred to the GC/MS laboratory staff. The GC/MS analyst acknowledges the receipt of the sample extracts by signing the appropriate sections of the completed LIMS bench sheet. Copies of tracking sheets, chain of custody records, and the original LIMS extraction bench sheet should accompany the sample extracts.

The extracts are marked with the EPA Region 9 Laboratory number, which can be checked against the tracking sheets and chain of custody record to determine the client sample identification, case number, and sample delivery group (SDG) number. Verify sample IDs and dates and times of collection against the chain-of-custody form.

Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to “active out” and the location to the appropriate room number. At the end of the day, return sample container to the “Home” locations. Update the LIMS database using the “return to home location” feature and update container disposition to “available in”. Verify that your initials are recorded whenever you update the LIMS custody information.

5.3 Sample Storage

Store extracts in the freezer in Room 402 or 406 at $\leq -10^{\circ}\text{C}$ before and after analysis. Retain samples extracts until holding time has expired.

5.4 Holding Time

Extracts must be analyzed within 40 days of extraction.

6 INTERFERENCES

Method interferences can be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus. Phthalates are commonly found as laboratory contaminants. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running a method blank (MB). The use of non-

polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components should be avoided.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed.

It is important that samples and standards be contained in the same solvent, i.e., the solvent for final working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to samples may be affected.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

7.1.1 GCMS System

7.1.1.1 Gas Chromatograph (GC): Agilent 6890, 6890N, 7890A, or equivalent. The GC must be capable of multilevel temperature programming and constant carrier gas flow throughout the temperature range. The GC should be equipped with an automatic sample injector, splitless injection port, and electronic pressure control (EPC).

7.1.1.2 GC column: 30 m, 0.25 mm ID, 0.5 μ m DF. A fused silica capillary column with a bonded phase coating of 5% diphenyl 95% methyl silicone such as DB5, DB5MS, RTX 5, RXI-5Sil MS, HP 5, or equivalent. Any column capable of separating the target analytes and passing method QC without overloading at the concentration of the highest standard may be used.

7.1.1.3 Mass spectrometer: Agilent 5973, 5973N, 5975, or equivalent, capable of continuous scanning and selective ion monitoring from 35 to 500 amu every one second or less using 70 volts (nominal) electron energy in the electron impact ionization mode. The MS must be able to produce a mass spectrum that meets acceptance criteria when 50 ng of DFTPP is injected through the GC inlet.

7.1.1.4 Data system: ChemStation (available from Agilent), or equivalent, able to control the GC/MS system and to acquire, store, and reduce mass spectral data. The software must be able to process any GC/MS data file by

recognizing a GC peak within a retention time window, comparing the mass spectrum from the GC peak with spectral data in a database. The software must also allow integration of the ion abundance of any specific ion between specified time or scan number limits and to calculate RRFs and concentrations of analytes in samples.

7.2 Reagents

Document the receipt of all reagents in the LIMS. A unique ID is assigned for each reagent. The reagent ID is reflected on all preparation and analysis batches.

Dichloromethane: High purity pesticide quality or equivalent. Recycled dichloromethane may be used if demonstrated to be suitable for use in this procedure.

7.3 Standards

Prepare standard solutions to include the project specific analytes of interest over the required concentration range. Document the receipt, preparation, and ampule open dates of all standards in the LIMS.

Store all ampulated calibration materials in the refrigerator at $>0^{\circ}\text{C}$ to $\leq 6^{\circ}\text{C}$ protected from light. Use the manufacturer's expiration date for ampulated standards.

Store open stock ampules and working standards in a freezer at $\leq -10^{\circ}\text{C}$ protected from light. The solution is assigned an expiration date which is either 6 months from preparation date, or the expiration date of the stock standard used in the preparation, whichever is earlier. Allow all standard solutions to equilibrate to room temperature before use.

- 7.3.1 Internal Standard Solution (IS): A solution of acenaphthene-d10, phenanthrene-d10, chrysene-d12, 1,4 dichlorobenzene-d4, perylene-d12, and naphthalene-d8 each in dichloromethane. Prepare by diluting purchased solutions to attain an extract concentration equivalent to the continuing calibration verification level. Restek 31206 or equivalent.
- 7.3.2 Surrogate solution: A solution of 2-fluorobiphenyl, nitrobenzene-d5, p-terphenyl-d14, and 1,2-dichlorobenzene-d4 (base/neutral surrogates); 2-fluorophenol, phenol-d5, 2,4,6-tribromophenol, and 2-chlorophenol-d4 (acid surrogates). Base/neutral surrogates - Restek 31072 or equivalent; acid surrogates - Restek 31003 or equivalent.
- 7.3.3 Calibration Stock Standard: A solution of project-specific target analytes in dichloromethane. Restek 8270 Mega Mix (Restek 31686), 8270 Calibration Mix #5 (Restek 31622), or equivalent.

- 7.3.4 Calibration standards: A solution of target analytes listed in Appendix B prepared by diluting the calibration stock standard and mixing it with the appropriate amount of IS solution to attain the project specific concentration range.

The suggested target analyte concentrations are listed in the following table:

Analysis Type	Calibration Levels (ng/L)					
	1 (QLS)	2	3 (CCV)	4	5	6
PAH	50	100	500	1,000	5,000	8,000
Phenols	1,000	2,000	5,000	10,000	15,000	20,000

- 7.3.5 Second Source Standard: A solution of target analytes listed in Appendix B and surrogates prepared from a source different from the calibration standard.
- 7.3.6 GC/MS Tuning Solution (MS tune). A solution of DFTPP, 4,4' DDT, pentachlorophenol, and benzidine at 50 ng/μL each in dichloromethane. ULTRA Scientific, GCM150, or equivalent.

7.4 Supplies

- 7.4.1 Syringes: 10 μL, 25 μL, 50 μL, 100 μL, 250 μL, 500 μL, 1 mL.
- 7.4.2 Helium carrier gas: Ultra-high purity, 99.999%.

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Check the mass spectrometer for leaks on a daily basis, prior to the analysis of the tuning compound. Refer to Section 8.4 and Appendix F for system maintenance requirements.

Set-up the GC/MS following operating instructions provided by the manufacturer. Use the method provided in Appendix D as a starting point.

8.1.1 Mass axis calibration

Calibrate the Mass Axis of the MS prior to analyzing the DFTPP standard each day that samples are analyzed. Use the settings in the most recent tune file as the initial conditions; save the tune file using the naming convention in Appendix E and generate a tune report.

Since DFTPP is analyzed in the full scan mode, the most recent BNA method will be used for the analysis of DFTPP. Select the most recent BNA method and associate the tune file with this method; name the method using the naming convention in Appendix E and save it. Use this method for all subsequent DFTPP analyses.

Select the most recent low level SIM method (phenols or PAH, depending upon the procedure used) and associate the tune file with this method; name the method using the naming convention in Appendix E and save it. Use this method for all subsequent SIM analyses.

Refer to Section 9.2.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.1.2 GC/MS tuning

The GC/MS system must meet the mass spectral ion abundance criteria for DFTPP prior to analysis. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target compounds.

Inject 1 µL of the DFTPP solution using the BNA method provided in Appendix D.

Quantitate the DFTPP solution data and generate a DFTPP report using the Autofind DFTPP to printer menu item from the Tuner → Evaluate DFTPP menu.

The autofind procedure will automatically find the DFTPP peak, average three scans (the peak apex scan and the scans immediately preceding and following the apex), perform a background subtraction and print out a hard copy of the spectrum, the chromatogram, and the table of ion abundances.

Generate a tailing factor report for the pentachlorophenol and benzidine peaks.

Refer to Section 9.2.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

Prior to analyzing an initial calibration, ensure that proper system maintenance and GC/MS tuning (auto-tune and/or manual tune) has been performed.

Since retention times may drift due to column maintenance or condition, it is necessary to verify the retention times for all compounds. To verify retention times, analyze a high calibration level standard (i.e. level 6) in the full scan mode using the BNA method used for DFTPP analysis prior to analyzing the initial calibration. Adjust SIM groups' retention time windows accordingly.

When the instrument is ready for analysis, perform the following steps:

1. In the ChemStation data analysis module, load the SIM method created in Section 8.1.1.
2. Perform an initial calibration using the initial calibration standards. The recommended concentrations are listed in Section 7.3.4.
3. Update the response factors in the method using the newly acquired calibration files.
4. Update the retention time and ion ratios in the method using the newly acquired continuing calibration verification level.
5. Save the method as outlined in the "ChemStation File Naming Convention". Refer to Appendix E.
6. Generate "Response Factor Report."
7. Check the calibration files listed on the "Response Factor Report" to insure that the correct files are being used.
8. Check the time and date to ensure that the correct update is used.
9. Print the raw area report (ChemStation ICAL page 3) for an internal standard or the target analyte for single analyte analysis. Verify that the method was updated correctly.
10. Print analyte list from ChemStation. Verify that the average response factor is used.
11. Save a copy of this method under C:\HPCHEM\1\Methods\Initial. This method will become the "master" copy until the next ICAL is generated.
12. Save a second copy of the method under I:\RoomNumber\Instrument\Methods\Initial.
13. Analyze a SCV standard at calibration level 3. Generate the "evaluate file as continuing calibration" and review the report for SCV recoveries. See Appendix C for criteria. Make sure that the same date and time stamp (example: "Last Update: Mon Aug 23 12:02:21 2004") is reflected on each file header.
14. Manually calculate a result for one surrogate in the SCV to insure that the correct RFs are being used and write the results on the quantitation report.

15. Save a hard copy of the initial calibration files so they may be copied and included in associated packages.

Refer to Section 9.2.3 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2.2 Continuing Calibration Verification

Analyze a calibration verification standard at the beginning of each analytical sequence by performing the following steps:

1. In the ChemStation data analysis module, load today's method from C:\HPCHEM\1\Methods
2. Acquire the continuing calibration using today's method.
3. Quantitate the continuing calibration verification file.
4. Generate "Evaluate Continuing Calibration Report".
5. Manually calculate a result for one surrogate to insure that the correct RFs are being used and write the results on the quantitation report.
6. As each run is quantitated during the day, make sure that the same date and time stamp (example: "Last Update: Mon Aug 23 12:02:21 2004") is reflected on each file header.
7. If Last Update time stamp changes, state the reason, repeat steps 4-6, and include the reports generated in the package.

Save a copy of the method to the LAN, when the data is backed up to the LAN the following day.

Refer to Section 9.2.4 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2.3 Quantitation Limit Verification Standard

Analyze a quantitation limit standard at the concentration of the lowest point of the initial calibration for each analytical sequence.

Refer to Section 9.2.5 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

Allow the sample extracts to reach ambient temperature before analysis.

Check that the numbers on the vials coincide with the numbers on the LIMS extraction batch to ensure that the correct sample is being analyzed.

Note if the sample has an unusual color or other physical properties. If any physical signs of contamination are present, screen the samples to protect the analytical system from damage or contamination, and to determine the appropriate subsequent dilutions. Record unusual items in the LIMS "MMO" field.

Add appropriate amount of IS solutions to each field and QC sample extract to attain an IS extract concentration equivalent to the continuing calibration verification level.

8.3.2 Sample Analysis and Analytical Sequence

Obtain a LIMS sequence number by generating an empty LIMS sequence; specify the analysis, instrument, and batch number associated with the samples to be analyzed.

Enter sample sequence in the instrument software. Include the laboratory sample number (work order-sample number) in the "Sample" field and dilution level, if any in the "Multiplier" field. Use the LIMS sequence number to name instrument QC as outlined in Appendix D.

Enter the BNA method name in the "Method" field; analyze the DFTPP sample with this method.

Enter the daily instrument SIM method name in the "Method" field; analyze all standards and samples with this method.

Name the data files according to the data file naming convention outlined in Appendix E.

Load the samples in the autosampler according to their designated positions in the sequence file. The recommended analysis sequence is:

1. DFTPP
2. CCV
3. QLS
4. Samples, sample dilutions, and or QC samples as needed
5. Instrument Blanks, as needed

- ✓ Run the sequence.
- ✓ Document the sequence in the instrument run log.

8.3.3 Analyte Identification and Quantitation

8.3.3.1 Analyte Identification

In order for a target compound to be identified as present in a sample both the retention time and the characteristic ions of the peak must match those of the standard.

If a compound cannot be verified using these criteria but in the technical judgment of the analyst is present, report the analyte and include supporting evidence in the raw data package.

Cross out all reported hits that do not meet qualitative criteria and document the reason on the quantitation report.

Review the chromatogram for possible false negatives and edit results as needed.

8.3.3.2 Analyte Quantitation

Quantitate the data and print out ChemStation detailed quantitation reports and chromatograms. Use the average relative response factor from the initial calibration for quantitation.

Analyte concentrations in the sample extracts as shown on the ChemStation quantitation report are calculated as follow:

LIMS calculates final analyte concentrations in samples. To verify the LIMS reported values for water samples, calculate results for target analytes using the following equation:

$$\text{Conc. } (\mu\text{g/L}) = A_x * \text{AMTIS} * \text{DF} / (\text{AIS} * \text{RRF}_{\text{avg}})$$

Where:

- A_x = area of the characteristic ion of the compound
- AMTIS = amount of internal standard in $\mu\text{g/L}$ (500 $\mu\text{g/L}$)
- DF = dilution factor
- AIS = area of the characteristic ion of the associated internal standard
- RRF_{avg} = analyte average relative response factor from the initial calibration

For soil samples, calculate results for target analytes

$$\text{Conc. } \mu\text{g / Kg (dry weight basis)} = \frac{A_x \times C_{\text{is}} \times V_t \times V_i \times \text{DF} \times \text{GPC}}{A_{\text{is}} \times \text{RRF} \times W \times D}$$

Where:

A_X	= area of the quantitation ion of the compound
C_{IS}	= concentration of Internal Standard in $\mu\text{g/L}$ (500 $\mu\text{g/L}$)
D	= dry weight factor (Percent solids/100)
W	= weight of sample in grams
A_{IS}	= area of the characteristic ion of the associated internal standard
RRF	= analyte mean relative response factor from the initial calibration
V_t	= volume of concentrated extract in μL
DF	= dilution factor
GPC	= GPC factor, normally 1.0 if not used, 2.0 if used
V_i	= volume of extract injected in μL

8.3.3.3 Manual Integration

Where the chromatography software integrates the signal inconsistently, follow SOP 835, *Chromatographic Integration Procedures*. All manual chromatographic integration must be initialed and dated by the analyst, noted in the run log, and approved by the supervisor, Chemistry Technical Director, Quality Assurance Officer, or designees.

8.3.4 QC Review

- Process and review the results for the CCV and QLS instrument QC samples. Print a ChemStation Evaluate Continuing Calibration Report using the appropriate settings to verify that the CCV and QLS QC sample results are within QC limits. See Section 9.2 for instrument QC requirements and Appendix C for acceptance criteria.
- Process and review the results for the MB, LCS, and MS/MSD batch QC samples and verify that the results are within QC limits. See Section 9.3 for Batch QC requirements.
- Determine if surrogate recoveries for field and QC samples are within QC limits. See Section 9.4 for Sample QC requirements.
- Review all sample results to determine if any samples need to be re-analyzed at a dilution.
- If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report.

- Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

8.3.5 Data Export and LIMS Entry

- Generate epatemp.txt files for field and QC samples by printing the report to the screen; these files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table.
- Copy sample data files from the local drive to the appropriate instrument data subdirectory on the Region 9 LAN to make them available to LIMS and to archive them.
- Populate the empty LIMS sequence file by editing the sequence using Data Tool to import the sequence information.
- Create an empty upload file containing the samples analyzed in the LIMS batch or sequence. Import and merge the data files using the LIMS DataTool module. Load the resulting merged data file into the LIMS Data Entry/Review table.
- Edit dilutions in DataTool or LIMS entry table as needed.
- Review results in the LIMS. Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

8.4 Maintenance

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook.

The following sections describe possible causes and corrective actions for common problems for GC and MS operations. Refer to Appendix F for routine preventative maintenance procedures and schedule.

8.4.1 GC Maintenance

Symptoms of common problems:

- Carryover
Possible causes: Analyzing a sample containing high molecular weight components or analyzing high-level and low-level samples sequentially.

Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.
Possible cause: column flow rate problem.
Corrective action: check flow rate and adjust as necessary.
- Longer retention time and or smaller peaks.
Possible causes: column flow rate problem, injection port leak, or column contamination.
Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.
- Loss of resolution.
Possible causes: column flow rate problem, injection port leak, or column contamination.
Corrective action: Check for leaks, replace septum, liner, and inlet seal, clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

8.4.2 MS maintenance:

Trend to be observed:

- Low m/z 502 to 69 ratio
- DFTPP ion 275 ratio is outside acceptance range
- Failing tune checks

Resolution: Clean the source.

9 QUALITY CONTROL

9.1 Demonstration of Capability

The EPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

A demonstration of capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880 for more details.

9.2 Instrument QC

9.2.1 Mass calibration

Review the FC43 spectrum for compliance with the criteria list in Appendix C.

If the FC43 spectrum does not meet the criteria, corrective action must be taken. The corrective action may be as simple as adjusting the voltages/retuning the MS. If retuning the MS does not produce adequate FC43 spectra, further maintenance such as cleaning the ion source may be required.

9.2.2 GC/MS Tune

Review the DFTPP spectrum for compliance with the criteria list in Appendix C.

Locate the degradation products of 4,4'-DDT (4,4'-DDD and 4,4'-DDE. Calculate the breakdown of DDT using peak areas of each quantitation ion (Qion) in the following equation:

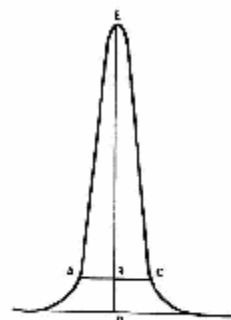
$$\% \text{ 4,4'-DDT Breakdown} = \frac{\text{Total Qion Area (DDE + DDD)}}{\text{Total Qion Area (DDE + DDD + DDT)}} \times 100$$

where:

Qions of DDE: 246 Dalton, DDD: 235 Dalton, DDT: 235 Dalton

Benzidine and pentachlorophenol should be present at their normal responses. The tailing factor is calculated by the following equation:

$$\text{TailingFactor} = \frac{BC}{AB}$$



Where the peak is defined as follows: AC is the width at 10% height; DE is the height of peak and DB is the height at 10% of DE. This equation compares the width of the back half of the peak to the width of the front half of the peak at 10% of the height.

Refer to Appendix C for frequency, acceptance criteria, and corrective action requirements.

If the ion abundances, degradation, or tailing fail to meet the criteria, the DFTPP chromatogram should be examined for any obvious chromatographic problems (e.g., bad injection leading to poor response etc.). If the problem is related to poor chromatography, take the necessary corrective action and re-analyze the DFTPP. If the DFTPP continues to fail the ion abundance criteria, retune the mass spectrometer. It may also be necessary to clean the ion source or take other corrective action to achieve the ion abundance criteria.

If a sample is injected after the analytical time period has elapsed it must be re-analyzed.

9.2.3 Initial Calibration

Each GC/MS system must be calibrated whenever corrective action is performed which may change instrument response (e.g., ion source cleaning, column replacement, etc.) or if the continuing calibration acceptance criteria cannot be met.

Check the initial calibration for misidentified peaks due to retention time shifts. The most commonly misassigned pairs are benzo(a)anthracene/chrysene and benzo(b)/benzo(k)fluoranthene

No quantitation ion may saturate the detector.

The data system calculates the relative response factor (RRF) for each target compound and surrogate compound using the following equation:

$$RRF = (A_x)(C_{is}) / (A_{is})(C_x)$$

Where

- A_x = Area of quantitation ion of compound x. The recommended quantitation ions and internal standard assignments are listed in Appendix B.
- A_{is} = Area of quantitation ion for associated internal standard
- C_x = Concentration of compound x
- C_{is} = Concentration of the associated internal standard

The data system calculates the average RRF (RRF_{avg}) for all analytes.

The data system calculates the percent relative standard deviation (%RSD) of the RRF values for each compound using the following equation.

$$\%RSD = (SD / RRF_{avg}) * 100$$

Where

$$SD = \sqrt{\frac{\sum_{i=1}^n (x_i - x_{ave})^2}{n - 1}}$$

The %RSD and SCV recovery requirements are listed in Appendix C.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that the criteria are satisfied before any samples are analyzed.

If SCV criteria (see Appendix C) are not met, the SCV must be re-analyzed. If it fails again, prepare a fresh solution. If failure persists, take corrective action as needed, including reanalysis or re-preparation and reanalysis of the initial calibration if necessary.

9.2.4 Continuing Calibration Verification

Examine the areas of the quantitation ions of the internal standards in the calibration verification standard.

Refer to Appendix C for frequency, acceptance criteria, and corrective action requirements.

If the area for any internal standard does not meet the criteria, the CCV may be re-analyzed. If the failure is repeated, the analysis shall be terminated, the problem corrected, and a new calibration curve prepared.

Examine the retention times of internal standards in the calibration verification standard. If the retention time for any internal standard does not meet the criteria, inspect the chromatographic system for malfunctions and take corrective action as needed and prepare a new calibration curve.

The data system calculates the percent difference (%D) of the RRF values for each compound using the following equation:

$$\%D = \frac{RRF_c - RRF_{avg}}{RRF_{avg}} \times 100$$

Where:

RRF_c = Relative Response Factor of compound c.
 RRF_{avg} = Average Relative Response Factor.

If the continuing calibration does not meet %D criterion listed in Appendix C, the analysis shall be terminated, the problem corrected, and a new continuing calibration analyzed.

Qualify and flag results as needed in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

9.2.5 Quantitation Limit Standard

QLS must be analyzed at the beginning of the analytical run, typically just after the CCV. The QLS concentrations match the QL concentration (at the instrument). The recovery of analytes in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where

$\%R$ = percent recovery of the standard.
 M = measured concentration of the analyte, ug/L.
 T = true concentration of the analyte in the ug/L.

Generate a continuing calibration response report using the concentration option. Check that the recoveries meet the criteria specified in Appendix C.

If the QLS recovery does not meet criteria provided in Appendix C, rerun the QLS once to verify. If still unacceptable determine the cause, take corrective action.

Qualify and flag results as needed in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

9.3 Batch QC

9.3.1 Method Blank

- Extract and analyze a method blank (MB) to demonstrate that the entire analytical system - from extraction through GC/MS analysis - is free of contamination.
- Evaluate the MB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.
- If the surrogate recovery does not meet acceptance criteria, re-analyze the MB. If the surrogate recovery still does not meet acceptance criteria, the batch may require re-extraction – see group leader or Technical Director for instructions
- Corrective action - If the MB result exceeds QC limits, check the associated samples as follow:
 1. If the sample result is greater than five times the MB result or is not detected, report the sample result.
 2. If the sample result is less than five times the MB result, re-analyze the MB. If the MB result still exceeds QC limits, it may be necessary to re-extract the MB and all associated samples or raise the quantitation limit to the amount found in the MB for each affected analyte. Consult with the group leader and Technical Director before proceeding.

9.3.2 Laboratory Control Sample

- Analyze a laboratory control sample (LCS) to demonstrate that the analytical system is in control. The LCS is an MB spiked with matrix spiking solution.
- Calculate the percent recovery (%R) using the following equation:

$$\% R = [MR/SA] \times 100$$

Where,

MR = Measured result

SA = Spike added

- The %R must be within the QC limits in Appendix C. If acceptable recoveries cannot be achieved, re-analyze the LCS. If the LCS result still exceeds QC limits, re-extract the LCS and all associated samples.

9.3.3 Matrix Spike/Matrix Spike Duplicate

- Matrix spike (MS) and matrix spike duplicate (MSD) samples are extracted and analyzed for each batch of twenty or fewer samples extracted as a group.
- Calculate the recovery of each analyte.

$$\% R = [(SSR - SR)/SA] \times 100$$

Where,

SSR = Spiked sample result

SR = Unspiked sample result

SA = Spike added

- Calculate the relative percent differences (RPD) of the recoveries of each analyte in the MS and MSD using the following equation:

$$RPD = \frac{(MSC - MSDC)}{(MSC + MSDC) / 2} \times 100$$

Where,

MSC = Measured concentration of analyte in MS

MSDC = Measured concentration of analyte in MSD

- See Appendix C for QC limits.

The MS/MSD recovery limits are advisory limits only. If the limits are not met, then no further action is required, as long as the LCS is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the spike compounds. A new solution should be prepared if the recoveries are not within 20% of expected.

- The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX + = PASS - = FAIL								
CASE	1	2	3	4	5	6	7	8
LCS - % REC	+	+	+	+	-	-	-	-
MS/MSD -% REC	+	-	+	-	+	-	+	-
MS/MSD – RPD	+	+	-	-	+	+	-	-

Case 1: Extraction batch acceptable.

Case 2: Extraction batch acceptable; matrix effect confirmed.

Cases 3 & 4: Extraction batch is unsatisfactory. Investigate MS/MSD problem and document findings in the LIMS memo field.

Cases 5, 6, 7, & 8: Extraction batch rejected. If additional sample volume is available, the batch should be re-extracted.

9.4 Sample QC

9.4.1 Surrogate Recovery

- Calculate the surrogate recovery in all field and QC samples immediately after analysis using the following formula:

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

- Take the following steps if surrogate recovery is not within the limits listed in Appendix C:
 - Ensure that there are no calculation errors, and check the system performance.
 - Re-analyze the sample if a system performance problem or calculation error is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.
- Do not reanalyze undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the run log.
- Do not re-analyze the MS/MSD samples, even if surrogate recoveries are outside the limits.
- If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate

surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis.

- If the surrogate recoveries of the re-analysis are within limits, then the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. The problem must be documented in the LIMS MMO field.
- If the re-analysis does not solve the problem and additional sample volume is available, the failing samples should be re-extracted.
- If sample re-extraction is unfeasible, or surrogate recoveries of the re-extraction are also outside the QC limits, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the sample ID in the re-analysis. The problem must be documented in the LIMS MMO field.

9.4.2 Internal Standard Area:

- Evaluate the internal standard areas in all field and QC samples immediately after analysis.
- The internal standard areas must be within QC limits outlined in Appendix C.
- Take the following steps if the internal standard areas are not within the limits:
 1. Check the system performance.
 2. Re-analyze the sample if a system performance problem is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.
- Do not reanalyze undiluted samples with internal standard areas outside the limits if the diluted analysis with acceptable internal standard areas is being submitted.
- Do not re-analyze the MS/MSD samples, even if internal standard areas are outside the limits.
- If the sample associated with the MS/MSD analyses does not meet the internal standard areas criteria, it should be re-analyzed only if the matrix spike and duplicate internal standard areas are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis.
- If the internal standard areas of the re-analysis are within limits, then, the problem was within the laboratory's control. Report the results from the re-

analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding an "RE" suffix to the sample ID on the re-analysis. The problem must be documented in the LIMS MMO field.

9.5 Method Performance

Refer to the table in Appendix G for a summary of method performance in the Region 9 Laboratory by matrix from January 1, 2007 to January 14, 2009.

Functional areas of the SOP that may be significant sources of analytical error are:

1. Addition of internal standard: The amount and concentration of internal standard added is critical. The nominal concentration is used in calculating target analyte concentration.
2. Samples must be stored as outlined in the SOP to minimize analyte degradation and solvent evaporation.
3. Sample temperature: Sample extracts must be allowed to come up to room temperature prior to analysis. Failure to do so will cause heavy molecular weight analytes to precipitate thus reducing the observed concentration.
4. Poor column condition may results in inadequate analyte separation and inaccurate integration.

10 DOCUMENTATION

10.1 Standards

Record all standards (ICAL, ICV/CCV, QL, MS/MSD, and LCS) in the LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the Element database or in the instrument Run Log. Case Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the Element database. The data package is produced from Element database and manual log records. Appendix H provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance
- Subsequent instrument modifications and upgrades, including major software upgrades.
- All preventative or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.6 SOP Read and Understood

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. The Laboratory QC Database is used to maintain the list of assigned analysts for each SOP. Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Laboratory QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix I.

11 REFERENCES

Agilent 6890 Gas Chromatograph Users Manual

Agilent 7890 Gas Chromatograph Users Manual

Environmental Laboratory Accreditation Conference Standards, July 12, 2002.

Agilent 5973 MSD Hardware Manual

Agilent 5975 MSD Hardware Manual

Hewlett Packard/Agilent Environmental Analysis User's Guide

Hewlett Packard/Agilent EnviroQuant ChemStation User's Guide

Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry,
Revision 2.0, 1995

National Environmental Laboratory Accreditation Conference, 2002. National

USEPA Method 525.2, Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography / Mass Spectrometry, Revision 2.0, 1995.

USEPA Method 3500C, Organic Extraction and Sample Preparation, Revision 3, February 2007.

USEPA Method 8000B, Determinative Chromatographic Separations, Revision 2, December 1996.

USEPA Method 8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, February 2007.

USEPA Region 9 Laboratory. *Business Plan*.

USEPA Region 9 Laboratory. *Chemical Hygiene Plan*.

USEPA Region 9 Laboratory. *Environmental Management System*.

USEPA Region 9 Laboratory SOP 125 *Disposal Procedures for Unused Aqueous Environmental Samples*

USEPA Region 9 Laboratory SOP 260, *Gel-Permeation Chromatography (GPC) Clean Up*.

USEPA Region 9 Laboratory SOP 265, *Extraction of Low Level Phenols and Polycyclic Aromatic Hydrocarbons from Water*.

USEPA Region 9 Laboratory SOP 275, *Extraction of Water Samples by Continuous Liquid-Liquid Extraction*.

USEPA Region 9 Laboratory SOP 290, *Extraction of Soil Samples Using Pressurized Fluid*

USEPA Region 9 Laboratory SOP 706, *Laboratory Waste Management Procedure*.

USEPA Region 9 Laboratory SOP 805 *Refrigerator Temperature Monitoring*

USEPA Region 9 Laboratory SOP 820, *Laboratory Discrepancy and Corrective Action Reporting Procedures.*

USEPA Region 9 Laboratory SOP 835 *Chromatographic Integration Procedures*

USEPA Region 9 Laboratory SOP 840 *Notebook Documentation and Control*

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. SW-846 method 3500C referenced by method 8270D specifies a concentration of 200 mg/L for the acid matrix spiking solution; this SOP specifies 150 mg/L.
2. The reference method has criteria for calibration check compounds (CCCs). Currently CCCs are not analyzed under this SOP.
3. Relative Retention Time (RRT) of chromatographic peak is not evaluated in this SOP as documented in the reference method. ChemStation calculates a retention time window and does not calculate RRT window. The retention time window of ± 0.2 min in this procedure is more stringent than the ± 0.06 RRT units in the reference method.

APPENDIX B. ANALYTES AND QUANTITATION LIMITS

The following is the target compounds list for semivolatile organics that have been detected using this SOP, as well as the internal standards and surrogates. Include are the CAS number, primary and secondary ion quantitation ions, associated internal standard and surrogate, and quantitation limits. The parameters below are recommended starting points and may be modified to meet method and project requirements. All parameters are documented in the ChemStation method.

Low Level PAH (polynuclear aromatic hydrocarbons):

Compound	CAS Number	Primary Quant Ion	Secondary Ion(s)	Int. Std	Surrogate	Water ng/L	Soil ug/kg	On Col. pg
Naphthalene	91-20-3	128	102	1	1	50	2.5	50
2-Methylnaphthalene	91-57-6	142	141	1	1	50	2.5	50
1-Methylnaphthalene	90-12-0	142	141	1	1	50	2.5	50
Acenaphthylene	208-96-8	152	151, 153	2	1	50	2.5	50
Acenaphthene	83-32-9	153	152, 154	2	1	50	2.5	50
Fluorene	86-73-7	166	165	2	1	50	2.5	50
Phenanthrene	85-01-8	178	179, 152	3	2	50	2.5	50
Anthracene	120-12-7	178	179, 152	3	2	50	2.5	50
Fluoranthene	206-44-0	202	101	3	2	50	2.5	50
Pyrene	129-00-0	202	101, 100	4	2	50	2.5	50
Benzo(a)anthracene	56-55-3	228	229, 114	4	2	50	2.5	50
Chrysene	218-01-9	228	114, 229	4	2	50	2.5	50
Benzo(b)fluoranthene	205-99-2	252	253, 126	5	2	50	2.5	50
Benzo(k)fluoranthene	207-08-9	252	253, 126	5	2	50	2.5	50
Benzo(a)pyrene	50-32-8	252	253, 126	5	2	50	2.5	50
Indeno(1,2,3-cd)pyrene	193-39-5	276	138	5	2	50	2.5	50
Dibenzo(a,h)anthracene	53-70-3	278	139, 279	5	2	50	2.5	50
Benzo(g,h,i)perylene	191-24-2	276	138, 277	5	2	50	2.5	50

Surrogates (as utilized)

2-Fluorobiphenyl	321-60-8	172	171	2	1
Terphenyl-d14	1718-51-0	244	122	4	2

Internal Standards

Compound	CAS Number	Primary Quant Ion	Secondary Ion(s)	Int. Std	Surrogate	Water ng/L	Soil ug/kg	On Col. pg
Naphthalene-d8	1146-65-2	136	108	1				
Acenaphthene-d10	15067-26-2	164	162, 160	2				
Phenanthrene-d10	1517-22-2	188	160	3				
Chrysene-d12	1719-03-5	240	120, 236	4				
Perylene-d12	1520-96-3	264	132, 265	5				

Low Level Phenols

Compound	CAS Number	Primary Quant Ion	Secondary Ion(s)	Int. Std	Surrogate	Water ug/L	Soil ug/kg	On Col. pg
Phenol	108-95-2	94.05	66	1	1	1	33	1000
2-Chlorophenol	95-57-8	128	64	1	1	1	33	1000
2-Methylphenol	95-48-7	107	108	1	1	1	33	1000
3&4-Methylphenol	106-44-5	107	108	1	1	2	67	2000
2,4-Dimethylphenol	105-67-9	122	107	2	1	1	33	1000
2,4-Dichlorophenol	120-83-2	161.95	164	2	1	1	33	1000
3&4-Chlorophenol		65	130	2	1	1	33	1000
2,4,6-Trichlorophenol	88-06-2	196	198	3	2	1	33	1000
2,4,5-Trichlorophenol	95-95-4	196	198	3	2	1	33	1000
3,5-Dichlorophenol	591-35-5	162	164, 99	3	1	1	33	1000
3,4-Dichlorophenol	95-77-2	162	164, 99	3	1	1	33	1000
2,3,4,6-Tetrachlorophenol	58-90-2	232	230	3	2	1	33	1000
3,4,5-Trichlorophenol	609-19-8	196	198, 200	3	2	1	33	1000
Pentachlorophenol	87-86-5	266	264, 268	4	2	1	33	1000
<u>Surrogates (as utilized)</u>								
Phenol-d5		99	71					
2-Chlorophenol-d4	93951-73-6	132.05	68	1	1			
2,4,6-Tribromophenol	118-79-6	330	332, 141	3	2			
<u>Internal Standards</u>								
1,4-Dichlorobenzene-d4	3855-82-1	152	150	1				
Naphthalene-d8	1146-65-2	136.1	68	2				
Acenaphthene-d10	15067-26-2	164	162, 160	3				
Phenanthrene-d10	1517-22-2	188	94, 80	4				

APPENDIX C.
QUALITY CONTROL PARAMETERS AND CRITERIA

ANALYSIS	SUMMARY	FREQUENCY																										
MS Tune (FC 43)	<table><tr><th>Mass</th><th>Target % of Mass 69</th></tr><tr><td>50</td><td>0.3-5</td></tr><tr><td>69</td><td>100</td></tr><tr><td>131</td><td>20-120</td></tr><tr><td>219</td><td>20-120</td></tr><tr><td>414</td><td>0.3-10</td></tr><tr><td>502</td><td>0.3-10</td></tr></table>	Mass	Target % of Mass 69	50	0.3-5	69	100	131	20-120	219	20-120	414	0.3-10	502	0.3-10	With every ICAL												
Mass	Target % of Mass 69																											
50	0.3-5																											
69	100																											
131	20-120																											
219	20-120																											
414	0.3-10																											
502	0.3-10																											
GC/MS System Performance Check (DFTPP analysis)	<p>The ion abundance ratios must meet the following criteria.</p> <table><tr><th>Mass (m/z)</th><th>Relative Ion Abundance Criteria</th></tr><tr><td>51</td><td>30 – 60% of 198</td></tr><tr><td>68</td><td>Less than 2% of mass 69</td></tr><tr><td>70</td><td>Less than 2% of mass 69</td></tr><tr><td>127</td><td>40 –60% of 198</td></tr><tr><td>197</td><td>Less than 1% of mass 198</td></tr><tr><td>198</td><td>Base peak (100% relative abundance)</td></tr><tr><td>199</td><td>5 - 9% of mass 198</td></tr><tr><td>275</td><td>10 - 30% of 198</td></tr><tr><td>365</td><td>Greater than 1% of 198</td></tr><tr><td>441</td><td>Present but less than mass 443</td></tr><tr><td>442</td><td>Greater than 50% of mass 198</td></tr><tr><td>443</td><td>17 - 23% of mass 442</td></tr></table> <p>Benzidine and pentachlorophenol responses should be at their expected levels in the DFTPP solution and the peak-tailing factor should be less than 2. Breakdown criteria for DDT is less than 20%.</p>	Mass (m/z)	Relative Ion Abundance Criteria	51	30 – 60% of 198	68	Less than 2% of mass 69	70	Less than 2% of mass 69	127	40 –60% of 198	197	Less than 1% of mass 198	198	Base peak (100% relative abundance)	199	5 - 9% of mass 198	275	10 - 30% of 198	365	Greater than 1% of 198	441	Present but less than mass 443	442	Greater than 50% of mass 198	443	17 - 23% of mass 442	At the start of 12-hour analytical sequence
Mass (m/z)	Relative Ion Abundance Criteria																											
51	30 – 60% of 198																											
68	Less than 2% of mass 69																											
70	Less than 2% of mass 69																											
127	40 –60% of 198																											
197	Less than 1% of mass 198																											
198	Base peak (100% relative abundance)																											
199	5 - 9% of mass 198																											
275	10 - 30% of 198																											
365	Greater than 1% of 198																											
441	Present but less than mass 443																											
442	Greater than 50% of mass 198																											
443	17 - 23% of mass 442																											
Initial Calibration	<p>90% of reported analytes should meet the maximum %RSD of 20. If one or more analytes exceed the RSD limit, the initial calibration may still be acceptable if the following conditions are met:</p> <p>The %RSD of the reported analytes that exceed the limit is ≤ 30</p> <p>The mean of the %RSD values for all reported analytes is less than or equal to 20%.</p>	As needed																										
Second Source Calibration Verification	RRF for reported analytes must be within 30% of the mean RRF in the initial calibration.	Once with every ICAL																										
Instrument	All reported analytes should meet a maximum %D of 20	At the start of																										

ANALYSIS	SUMMARY	FREQUENCY
Calibration Verification	<p>and minimum RRF of 0.010. If one or more reported analytes exceed maximum %D limit, the calibration verification may still be acceptable if the following conditions are met:</p> <p>90% of reported analytes meet a maximum %D of 20</p> <p>The %D of the reported analytes that exceed the limit is ≤ 30</p> <p>The mean of the %D values for all reported analytes is less than or equal to 20.</p> <p>Internal standard retention time should be within 30 seconds from that in the mid-point standard level of the most recent initial calibration.</p> <p>EICP area for any of the internal standards should be within (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence.</p>	12-hour analytical sequence
Quantitation Limit Verification	The percent recovery for 90% of the reported analytes should be between 60 to 140 percent of the actual concentration.	At the start of 12-hour analytical sequence
Method Blank (MB)/Instrument Blank	The MB is acceptable if it contains less than one-half the quantitation limit (QL) of all target compounds.	One per extraction batch or every 20 samples whichever is more frequent
Target Analytes	<p>All ions present in the standard or reference mass spectrum at a relative intensity of 20 % of the most abundant ion should be present in the sample spectrum.</p> <p>The relative intensities of the ions in the sample mass spectrum should agree within 30% of the relative intensities of those ions in the standard mass spectrum.</p> <p>For example, an ion with an abundance of 50% in the standard spectrum can have abundance between 20% and 80% in the sample spectrum.</p>	
Internal Standards (covering reported analytes)	<p>Compare the IS retention times in field and QC samples analyzed within the 12-hour analytical period of the initial calibration to the IS retention times in the CCV standard. The total area of internal standard should be recovered within -50% to +100% of the corresponding internal standard from the preceding 12-hour calibration standard.</p> <p>The retention time for any internal standard should be</p>	

ANALYSIS	SUMMARY	FREQUENCY
	within 0.5 minute from the mid-point standard of the most recent initial calibration.	
Laboratory control sample analysis (LCS)	Refer to the table below for recovery limits – based on laboratory data when sufficient points are available.	One per batch or every 20 samples, whichever is more frequent.
Matrix Spike/ Matrix Spike Duplicate MS/MSD	Refer to the table below for recovery limits – based on laboratory data when available. Insufficient data for soil at this time.	One per batch or every 20 samples, whichever is more frequent

Matrix Spikes MS/MSD, LCS, and Surrogates**Low Level Polynuclear Aromatic Hydrocarbons**

Analyte	Matrix	LCS Recovery		Matrix Spike		RPD
		Lower	Upper	Lower	Upper	
1-Methylnaphthalene	Water	22	110	20	156	20
2-Methylnaphthalene	Water	21	110	20	145	20
Acenaphthene	Water	32	110	20	143	45
Acenaphthylene	Water	32	110	30	130	25
Anthracene	Water	35	117	36	133	18
Benzo(a)anthracene	Water	43	140	50	132	19
Benzo(a)pyrene	Water	40	129	36	119	23
Benzo(b)fluoranthene	Water	43	131	42	111	23
Benzo(g,h,i)perylene	Water	48	119	25	111	29
Benzo(k)fluoranthene	Water	40	130	29	121	23
Chrysene	Water	48	115	44	116	19
Dibenz(a,h)anthracene	Water	39	133	22	125	29
Fluoranthene	Water	34	129	40	132	18
Fluorene	Water	32	112	28	140	23
Indeno(1,2,3-cd)pyrene	Water	40	131	20	129	33
Naphthalene	Water	21	110	20	166	35
Phenanthrene	Water	39	112	37	130	34
Pyrene	Water	56	111	42	129	23

<i>Surrogate</i>						
2-Fluorobiphenyl	Water	33	112			
Terphenyl-d14	Water	38	129			

Low Level Phenols

Analyte	Matrix	LCS Recovery		Matrix Spike		RPD
		Lower	Upper	Lower	Upper	
2,3,4,6-Tetrachlorophenol	Water	30	130	49	110	20
2,4,5-Trichlorophenol	Water	41	125	47	110	20
2,4,6-Trichlorophenol	Water	47	114	42	110	20
2,4-Dichlorophenol	Water	45	117	42	110	20
2,4-Dimethylphenol	Water	34	110	20	110	20
2-Chlorophenol	Water	50	114	58	118	20
2-Methylphenol	Water	38	119	20	110	20
3&4-Chlorophenol	Water	39	124	40	110	20
3&4-Methylphenol	Water	46	118	20	110	20
3,4,5-Trichlorophenol	Water	25	131	59	119	20
3,4-Dichlorophenol	Water	48	129	56	116	20
3,5-Dichlorophenol	Water	18	161	48	110	20
Pentachlorophenol	Water	20	121	58	118	20
Phenol	Water	41	124	41	110	20

<i>Surrogate</i>						
2,4,6-Tribromophenol	Water	20	168			
2-Chlorophenol-d4	Water	47	131			

Low Level Polynuclear Aromatic Hydrocarbons

		LCS Recovery		Matrix Spike		RPD
Analyte	Matrix	Lower	Upper	Lower	Upper	
1-Methylnaphthalene	Soil	27	110	31	110	20
2-Methylnaphthalene	Soil	28	110	34	110	20
Acenaphthene	Soil	33	110	33	110	20
Acenaphthylene	Soil	28	110	21	110	20
Anthracene	Soil	36	110	30	110	20
Benzo(a)anthracene	Soil	54	114	38	110	20
Benzo(a)pyrene	Soil	45	110	35	110	20
Benzo(b)fluoranthene	Soil	47	110	37	110	20
Benzo(g,h,i)perylene	Soil	25	110	19	110	20
Benzo(k)fluoranthene	Soil	49	110	35	110	20
Chrysene	Soil	49	110	35	110	20
Dibenz(a,h)anthracene	Soil	40	110	32	110	20
Fluoranthene	Soil	46	110	42	110	20
Fluorene	Soil	37	110	50	110	20
Indeno(1,2,3-cd)pyrene	Soil	37	110	35	110	20
Naphthalene	Soil	32	110	23	110	20
Phenanthrene	Soil	38	110	34	110	20
Pyrene	Soil	47	110	33	110	20

Surrogate

2-Fluorobiphenyl	Soil	15	110			
Terphenyl-d14	Soil	15	147			

Low Level Phenols

		LCS Recovery		Matrix Spike		RPD
Analyte	Matrix	Lower	Upper	Lower	Upper	
2,3,4,6-Tetrachlorophenol	Soil	70	130	70	130	20
2,4,5-Trichlorophenol	Soil	70	130	70	130	20
2,4,6-Trichlorophenol	Soil	70	130	70	130	20
2,4-Dichlorophenol	Soil	70	130	70	130	20
2,4-Dimethylphenol	Soil	70	130	70	130	20
2-Chlorophenol	Soil	70	130	70	130	20
2-Methylphenol	Soil	70	130	70	130	20
3&4-Chlorophenol	Soil	70	130	70	130	20
3&4-Methylphenol	Soil	70	130	70	130	20
3,4,5-Trichlorophenol	Soil	70	130	70	130	20
3,4-Dichlorophenol	Soil	70	130	70	130	20
3,5-Dichlorophenol	Soil	70	130	70	130	20
Pentachlorophenol	Soil	70	130	70	130	20
Phenol	Soil	70	130	70	130	20

<i>Surrogate</i>						
2,4,6-Tribromophenol	Soil	70	130			
2-Chlorophenol-d4	Soil	70	130			

APPENDIX D.
RECOMMENDED INSTRUMENT PARAMETERS

A. DFTPP Method

INSTRUMENT CONTROL PARAMETERS

=====

6890 GC METHOD

=====

OVEN

Initial temp: 40 'C (On) Maximum temp: 350 'C
Initial time: 2.00 min Equilibration time: 0.50 min
Ramps:
 # Rate Final temp Final time
 1 15.00 330 6.00
 2 0.0(Off)
Post temp: 0 'C
Post time: 0.00 min
Run time: 27.33 min

FRONT INLET (SPLIT/SPLITLESS)**BACK INLET (UNKNOWN)**

Mode: Pulsed Splitless
Initial temp: 280 'C (On)
Pressure: 7.12 psi (On)
Pulse pressure: 30.0 psi
Pulse time: 0.50 min
Purge flow: 40.0 mL/min
Purge time: 0.40 min
Total flow: 43.6 mL/min
Gas saver: On
Saver flow: 20.0 mL/min
Saver time: 2.00 min
Gas type: Helium

COLUMN 1**COLUMN 2**

Capillary Column (not installed)
Model Number: Agilent 122-5536
DB-5ms, 0.25mm * 30m * 0.5um
Max temperature: 350 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.50 um
Mode: constant flow
Initial flow: 1.0 mL/min
Nominal init pressure: 7.12 psi
Average velocity: 36 cm/sec
Inlet: Front Inlet
Outlet: MSD

Outlet pressure: vacuum

FRONT DETECTOR ()

BACK DETECTOR ()

SIGNAL 1

Data rate: 20 Hz

Type: test plot

Save Data: Off

Zero: 0.0 (Off)

Range: 0

Fast Peaks: Off

Attenuation: 0

SIGNAL 2

Data rate: 20 Hz

Type: test plot

Save Data: Off

Zero: 0.0 (Off)

Range: 0

Fast Peaks: Off

Attenuation: 0

COLUMN COMP 1

(No Detectors Installed)

COLUMN COMP 2

(No Detectors Installed)

THERMAL AUX 2

Use: MSD Transfer Line Heater

Description:

Initial temp: 280 'C (On)

Initial time: 0.00 min

#	Rate	Final temp	Final time
---	------	------------	------------

1	0.0(Off)		
---	----------	--	--

POST RUN

Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint
------	-----------	----------------------

7673 Injector

Front Injector:

Sample Washes	0
---------------	---

Sample Pumps	3
--------------	---

Injection Volume	1.0 microliters
------------------	-----------------

Syringe Size	10.0 microliters
--------------	------------------

Nanoliter Adapter	Off
-------------------	-----

PostInj Solvent A Washes	3
--------------------------	---

PostInj Solvent B Washes	3
--------------------------	---

Viscosity Delay	0 seconds
-----------------	-----------

Plunger Speed	Fast
---------------	------

PreInjection Dwell	0.00 minutes
--------------------	--------------

PostInjection Dwell	0.00 minutes
---------------------	--------------

Back Injector:

No parameters specified

Column 1 Inventory Number : DB-5

Column 2 Inventory Number :

MS ACQUISITION PARAMETERS

General Information

Tune File : DF12028.U

Acquisition Mode : Scan

MS Information

--

Solvent Delay : 3.20 min

EM Absolute : False

EM Offset : 353

Resulting EM Voltage : 1552.9

[Scan Parameters]

Low Mass : 41.0

High Mass : 550.0

Threshold : 120

Sample # : 2 A/D Samples 4

Plot 2 low mass : 50.0

Plot 2 high mass : 550.0

[MSZones]

MS Quad : 180 C maximum 200 C

MS Source : 230 C maximum 250 C

END OF MS ACQUISITION PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

B. PAH Method

INSTRUMENT CONTROL PARAMETERS

=====

6890 GC METHOD

=====

OVEN

Initial temp: 40 'C (On) Maximum temp: 350 'C
Initial time: 2.00 min Equilibration time: 0.50 min
Ramps:
 # Rate Final temp Final time
 1 15.00 330 6.00
 2 0.0(Off)
Post temp: 0 'C
Post time: 0.00 min
Run time: 27.33 min

FRONT INLET (SPLIT/SPLITLESS)

BACK INLET (UNKNOWN)

Mode: Pulsed Splitless
Initial temp: 280 'C (On)
Pressure: 7.11 psi (On)
Pulse pressure: 30.0 psi
Pulse time: 0.50 min
Purge flow: 20.0 mL/min
Purge time: 0.40 min
Total flow: 23.5 mL/min
Gas saver: On
Saver flow: 20.0 mL/min
Saver time: 2.00 min
Gas type: Helium

COLUMN 1

COLUMN 2

Capillary Column (not installed)
Model Number: Agilent 122-5536
DB-5ms, 0.25mm * 30m * 0.5um
Max temperature: 350 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.50 um
Mode: constant flow
Initial flow: 1.0 mL/min
Nominal init pressure: 7.11 psi
Average velocity: 36 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

FRONT DETECTOR (NO DET)

BACK DETECTOR (NO DET)

SIGNAL 1

Data rate: 20 Hz

Type: test plot

Save Data: Off

Zero: 0.0 (Off)

Range: 0

Fast Peaks: Off

Attenuation: 0

SIGNAL 2

Data rate: 20 Hz

Type: test plot

Save Data: Off

Zero: 0.0 (Off)

Range: 0

Fast Peaks: Off

Attenuation: 0

COLUMN COMP 1

(No Detectors Installed)

COLUMN COMP 2

(No Detectors Installed)

THERMAL AUX 2

Use: MSD Transfer Line Heater

Description:

Initial temp: 280 'C (On)

Initial time: 30.00 min

Rate Final temp Final time

1 0.0(Off)

POST RUN

Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint
------	-----------	----------------------

7673 Injector

Front Injector:

Sample Washes	0
Sample Pumps	3
Injection Volume	1.0 microliters
Syringe Size	10.0 microliters
Nanoliter Adapter	Off
PostInj Solvent A Washes	3
PostInj Solvent B Washes	3
Viscosity Delay	0 seconds
Plunger Speed	Fast
PreInjection Dwell	0.00 minutes
PostInjection Dwell	0.00 minutes

Back Injector:

No parameters specified

Column 1 Inventory Number : DB-5

Column 2 Inventory Number :

MS ACQUISITION PARAMETERS

General Information

Tune File : DF03209.U

Acquisition Mode : SIM

MS Information

--

Solvent Delay : 9.90 min

EM Absolute : False

EM Offset : -35

Resulting EM Voltage : 1400.0

[Sim Parameters]

GROUP 1

Group ID : 21

Resolution : High

Plot 1 Ion : 136.0

Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(102.0, 25) (108.0, 25) (128.0, 25)
(136.0, 25) (141.0, 25) (142.0, 25)
(171.0, 25) (172.0, 25)

GROUP 2

Group ID : 43

Resolution : High

Group Start Time : 12.76

Plot 1 Ion : 151.0

Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(151.0, 25) (152.0, 25) (153.0, 25)
(154.0, 25) (160.0, 25) (162.0, 25)
(164.0, 25)

GROUP 3

Group ID : 52

Resolution : High

Group Start Time : 13.81

Plot 1 Ion : 166.0

Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(152.0, 25) (160.0, 25) (165.0, 25)
(166.0, 25) (178.0, 25) (179.0, 25)
(188.0, 25)

GROUP 4

Group ID : 66

Resolution : High

Group Start Time : 16.86

Plot 1 Ion : 101.0

Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)

(100.0, 25) (101.0, 25) (122.0, 25)

(202.0, 25) (244.0, 25)

GROUP 5

Group ID : 71

Resolution : High

Group Start Time : 19.29

Plot 1 Ion : 240.0

Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)

(114.0, 25) (120.0, 25) (228.0, 25)

(229.0, 25) (236.0, 25) (240.0, 25)

GROUP 6

Group ID : 77

Resolution : High

Group Start Time : 21.03

Plot 1 Ion : 264.0

Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)

(126.0, 25) (132.0, 25) (252.0, 25)

(253.0, 25) (264.0, 25) (265.0, 25)

GROUP 7

Group ID : 80

Resolution : High

Group Start Time : 23.50

Plot 1 Ion : 278.0

Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)

(138.0, 25) (139.0, 25) (276.0, 25)

(277.0, 25) (278.0, 25) (279.0, 25)

[MSZones]

MS Quad : 180 C maximum 200 C

MS Source : 250 C maximum 250 C

END OF MS ACQUISITION PARAMETERS

TUNE PARAMETERS

EMISSION : 34.610

ENERGY : 69.922

REPELLER : 24.427

IONFOCUS : 88.259

ENTRANCE_LE : 0.000

EMVOLTS : 1435.294

AMUGAIN : 2161.000

AMUOFFSET : 126.000

FILAMENT : 1.000
DCPOLARITY : 0.000
ENTLENSOFFS : 19.576@ 50 16.063@ 69 15.059@131 14.055@219 12.549@414
13.051@502
MASSGAIN : 236.213
MASSOFFSET : -13.089

END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

TUNE PARAMETERS

EMISSION : 34.610
ENERGY : 69.922
REPELLER : 24.427
IONFOCUS : 88.259
ENTRANCE_LE : 0.000
EMVOLTS : 1435.294
AMUGAIN : 2161.000
AMUOFFSET : 126.000
FILAMENT : 1.000
DCPOLARITY : 0.000
ENTLENSOFFS : 19.576@ 50 16.063@ 69 15.059@131 14.055@219 12.549@414
13.051@502
MASSGAIN : 236.213
MASSOFFSET : -13.089

END OF TUNE PARAMETERS

C. Phenol MethodTOPLEVEL PARAMETERS

Method Information For: D:\MSDCHEM\1\2009\METHODS\3249LO.M

Method Sections To Run:

- () Save Copy of Method With Data
- () Pre-Run Cmd/Macro =
- (X) Data Acquisition
- () Data Analysis
- () Post-Run Cmd/Macro =

Method Comments:

Low Level Phenol SIM METHOD

END OF TOPLEVEL PARAMETERS
-----INSTRUMENT CONTROL PARAMETERS

Sample Inlet: GC
Injection Source: GC ALS
Mass Spectrometer: Enabled

=====

6890 GC METHOD

=====

OVEN

Initial temp: 40 'C (On) Maximum temp: 350 'C
Initial time: 2.00 min Equilibration time: 0.50 min
Ramps:
 # Rate Final temp Final time
 1 15.00 330 6.00
 2 0.0(Off)
Post temp: 0 'C
Post time: 0.00 min
Run time: 27.33 min

FRONT INLET (UNKNOWN)

BACK INLET ()

Mode: Pulsed Splitless
Initial temp: 280 'C (On)
Pressure: 7.11 psi (On)
Pulse pressure: 30.0 psi
Pulse time: 0.50 min
Purge flow: 40.0 mL/min

Purge time: 0.40 min
Total flow: 43.8 mL/min
Gas saver: On
Saver flow: 20.0 mL/min
Saver time: 2.00 min
Gas type: Helium

COLUMN 1

Capillary Column
Model Number: Restek 13638
Rxi-5Sil MS
Max temperature: 350 °C
Nominal length: 30.0 m
Nominal diameter: 250.00 µm
Nominal film thickness: 0.50 µm
Mode: constant flow
Initial flow: 1.0 mL/min
Nominal init pressure: 7.11 psi
Average velocity: 36 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

COLUMN 2

(not installed)

FRONT DETECTOR (NO DET)

SIGNAL 1

Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

BACK DETECTOR (NO DET)

SIGNAL 2

Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1

(No Detectors Installed)

COLUMN COMP 2

(No Detectors Installed)

THERMAL AUX 2

Use: MSD Transfer Line Heater
Description:
Initial temp: 280 °C (On)
Initial time: 0.00 min
Rate Final temp Final time
1 0.0(Off)

POST RUN

Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint
------	-----------	----------------------

7673 Injector

Front Injector:

Sample Washes 0
Sample Pumps 3
Injection Volume 1.0 microliters
Syringe Size 10.0 microliters
PostInj Solvent A Washes 3
PostInj Solvent B Washes 3
Viscosity Delay 0 seconds
Plunger Speed Fast
PreInjection Dwell 0.00 minutes
PostInjection Dwell 0.00 minutes

Back Injector:

No parameters specified

MS ACQUISITION PARAMETERS

General Information

Tune File : DFL3249.U
Acquisition Mode : SIM

MS Information

--

Solvent Delay : 6.00 min

EM Absolute : False
EM Offset : 200
Resulting EM Voltage : 2482.4

[Sim Parameters]

GROUP 1

Group ID : 1
Resolution : High
Plot 1 Ion : 64.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(64.0, 100) (66.0, 100) (71.0, 100)
(94.0, 100) (99.0, 100) (112.1, 100)

GROUP 2

Group ID : 2
Resolution : High
Group Start Time : 8.07
Plot 1 Ion : 132.1
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(64.0, 100) (68.0, 100) (107.1, 100)
(108.0, 100) (128.0, 100) (132.1, 100)
(150.0, 100) (152.0, 100)

GROUP 3

Group ID : 3
Resolution : High
Group Start Time : 9.51
Plot 1 Ion : 136.1
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(65.0, 100) (68.0, 100) (107.0, 100)
(122.1, 100) (130.0, 100) (136.1, 100)
(161.9, 100) (164.0, 100)

GROUP 4

Group ID : 4
Resolution : High
Group Start Time : 11.34
Plot 1 Ion : 162.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(99.0, 100) (160.0, 100) (161.9, 100)
(162.0, 100) (164.0, 100) (164.2, 100)
(195.9, 100) (198.0, 100)

GROUP 5

Group ID : 5
Resolution : High
Group Start Time : 13.48
Plot 1 Ion : 332.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(141.0, 100) (195.9, 100) (198.0, 100)
(200.0, 100) (230.0, 100) (231.9, 100)
(329.8, 100) (332.0, 100)

GROUP 6

Group ID : 6
Resolution : High
Group Start Time : 15.14
Plot 1 Ion : 188.2
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(80.0, 100) (94.0, 100) (188.2, 100)
(264.0, 100) (265.9, 100) (268.0, 100)

[MSZones]

MS Quad : 180 C maximum 200 C
MS Source : 250 C maximum 250 C

END OF MS ACQUISITION PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

APPENDIX E.
CHEMSTATION FILE NAMING CONVENTIONS

ChemStation File Naming Convention

File data, methods, and sequences on ChemStation computers and the LAN using the following naming conventions:

Directories

On the Workstation:

Data: C:\HPCHEM\1\Data\MDDY or D:\HPCHEM\1\Data\MDDYS

Methods: C:\HPCHEM\1\Methods or D:\HPCHEM\1\Methods

Sequences: C:\HPCHEM\1\Sequence or D:\HPCHEM\1\Sequence

For system controlling multiple instruments, 1 may be changed to reflect the instrument number

System running ChemStation versions C & D HPCHEM is named as MSDCHEM

On the LAN:

Data: I:\Room Number\Instrument\Year\MDDYS

Methods: I:\Room Number\Instrument\Methods

Sequences: I:\Room Number\Instrument\Sequence

Methods

MDDYITA

Sequence

MDDYS

Data Files

For GC:

MDDYICSS

For GC/MS

MDDYIQSS

Variables

A: Enter analysis, as follow:

1,4-Dioxane X

504 E

TO15 A

BNA B

Phenols (SIM) L

PAH (SIM) H

Congeners C

P/P P

PCB P

RSK175	R
Soil Gas	A
TPH-G	G
TPH-D	D
VOA	V

C: Channel: A = front
B = back (if applicable)

DD: Day

I: Instrument
6890 series GCs by last number in name: e.g. 6890-1 = 1 except 580-2 = A
All GC/MSs by last letter in name: e.g. 5973L = L

M: Month 1-9, A: October, B: November, C: December

Q: QC type

BFB	F
Blank	B
CV	C
Degradation	P
DFTPP	D
IB	Z
IC	I
LCS	L
LCV	Q
Second Source	S
MS/MSD	M

S: Sequential number 1,2 3,

T: Matrix Type (if applicable)
Water W
Solid S
Air A
Oil O
Other X

Y: Year i.e. 5 for 2005

APPENDIX F. PREVENTATIVE MAINTENANCE REQUIREMENTS

GC Maintenance

Item	Frequency	Actions/Comments
Gas purifiers (carrier gas & detector gas)	Annually	Replacement schedule is based on capacity and grade of gases. In general, replace non-indicating traps every 6-12 months or when indicating traps start to change color. Replace indicating traps when indicating material is spent.
Split vent trap	Annually	Replace.
Flowmeter calibration	2 years	Manual flowmeters only.
Syringes and/or syringe needles	As Needed	Replace syringe if dirt is noticeable in the syringe, if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged. Replace needle if septa wear is abnormal or the needle becomes clogged.
Inlet liner	With each ICAL	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	With each ICAL	Replace with liner or with signs of wear.
Inlet septum	Daily (when analyzing samples)	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	With each ICAL	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Solvent rinse	As needed	When chromatography degradation is due to column contamination. Only for bonded and cross-linked phases.
Replacement	As needed	When trimming and/or solvent rinsing no longer return chromatographic performance.
Ferrules		Replace ferrules when changing columns and inlet/detector parts.

MS Maintenance**Maintenance schedule**

Task	Every week	Every 6 months	Every year	As needed
Tune the MSD				✓
Check the foreline pump oil level	✓			
Check the calibration vials ¹		✓		
Replace the foreline pump oil ¹		✓		
Clean the ion source				✓
Check the carrier gas traps ² on the GC				✓
Replace the worn out parts				✓
Lubricate sideplate or vent valve O-rings ²				✓

1 Every 3 months for CI MSDs using ammonia reagent gas.

2 Vacuum seals other than the side plate O-ring and vent valve O-ring do not need to be lubricated. Lubricating other seals can interfere with their correct function.

**APPENDIX G.
METHOD PERFORMANCE**

Low level Polynuclear Aromatic Hydrocarbons

Analyte	Matrix	Number of Measurements	Mean % Recovery	StdDev	95% Confidence Interval (2σ)	
1-Methylnaphthalene	Water	39	58.6	12.2	34.2	83
2-Methylnaphthalene	Water	39	58.7	12.6	33.5	83.9
Acenaphthene	Water	42	65	11	43	87
Acenaphthylene	Water	42	67.2	11.6	44	90.4
Anthracene	Water	42	75.8	13.7	48.4	103.2
Benzo(a)anthracene	Water	42	91.3	16.1	59.1	123.5
Benzo(a)pyrene	Water	42	84.8	14.8	55.2	114.4
Benzo(b)fluoranthene	Water	42	86.7	14.7	57.3	116.1
Benzo(g,h,i)perylene	Water	42	83.2	11.9	59.4	107
Benzo(k)fluoranthene	Water	42	84.8	15.1	54.6	115
Chrysene	Water	42	81.6	11.1	59.4	103.8
Dibenz(a,h)anthracene	Water	42	85.8	15.6	54.6	117
Fluoranthene	Water	42	81.3	15.8	49.7	112.9
Fluorene	Water	42	71.7	13.3	45.1	98.3
Indeno(1,2,3-cd)pyrene	Water	42	85.8	15.2	55.4	116.2
Naphthalene	Water	42	65.4	14.9	65.6	95.2
Phenanthrene	Water	42	75.1	12.2	50.7	99.5
Pyrene	Water	42	83.5	9.1	65.3	101.7

Low Level Phenols

Analyte	Matrix	Number of Measurements	Mean % Recovery	StdDev	95% Confidence Interval (2σ)	
2,3,4,6-Tetrachlorophenol	Water	27	79.8	16.6	46.5	113
2,4,5-Trichlorophenol	Water	30	82.9	13.9	55.2	111
2,4,6-Trichlorophenol	Water	30	80.1	11.2	57.7	102
2,4-Dichlorophenol	Water	30	81.3	12.1	57.1	105
2,4-Dimethylphenol	Water	27	64.6	10.2	44.1	85.1
2-Chlorophenol	Water	31	81.8	10.8	60.3	103
2-Methylphenol	Water	31	78.6	13.4	51.7	106

Low Level Phenols

Analyte	Matrix	Number of Measurements	Mean % Recovery	StdDev	95% Confidence Interval (2σ)	
3&4-Chlorophenol	Water	34	81.4	14	53.3	110
3&4-Methylphenol	Water	31	81.9	12	57.9	106
3,4,5-Trichlorophenol	Water	30	78.2	17.7	42.7	114
3,4-Dichlorophenol	Water	30	88.6	13.5	61.6	116
3,5-Dichlorophenol	Water	31	89.4	23.8	41.8	137
Pentachlorophenol	Water	26	67.4	17.9	31.6	103
Phenol	Water	31	82.5	14	54.5	110

Low level Polynuclear Aromatic Hydrocarbons

Analyte	Matrix	Number of Measurements	Mean % Recovery	StdDev	95% Confidence Interval (2σ)	
1-Methylnaphthalene	Soil	6	56.5	17.6	21.2	91.8
2-Methylnaphthalene	Soil	6	58.1	20.8	16.5	99.6
Acenaphthene	Soil	12	62.5	15.6	31.2	93.8
Acenaphthylene	Soil	12	57.6	15.6	26.4	88.8
Anthracene	Soil	12	65.7	13.5	38.6	92.8
Benzo(a)anthracene	Soil	12	83.6	13.6	56.4	111
Benzo(a)pyrene	Soil	12	74.6	10.7	53.1	96
Benzo(b)fluoranthene	Soil	12	76.9	9.61	57.6	96.1
Benzo(g,h,i)perylene	Soil	12	55	51.1	24.7	85.3
Benzo(k)fluoranthene	Soil	12	78.8	9.92	58.9	98.6
Chrysene	Soil	12	78.7	12	54.8	103
Dibenz(a,h)anthracene	Soil	12	70.3	14.6	41.1	99.6
Fluoranthene	Soil	12	75.7	12	51.8	99.7
Fluorene	Soil	12	67.2	16.4	34.4	100
Indeno(1,2,3-cd)pyrene	Soil	12	67.1	11.7	43.7	90.5
Naphthalene	Soil	12	62.4	19.6	23.2	102
Phenanthrene	Soil	12	68.1	13.3	41.6	94.6
Pyrene	Soil	12	76.7	12.8	51.2	102

APPENDIX H. TYPICAL DATA PACKAGE FORMAT

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

Cover Memo (original)
Review form (cover, front only)
TDF
Modified Draft Report from Element Data System

Data Package Cover [First numbered page in the data package]

Review Forms

EPA Review Form
ESAT technical review guide
Discrepancy Reports (if applicable)
Work Order Memo (if applicable)
Daily folder review forms or checklists
Analysis matrix listing all analytical runs

Tracking Forms

Work Order(s)
COC(s)

Sample Preparation

Bench Sheets (and extraction logs, ASE run logs, where used)
Sample cleanup data and records (e.g. GPC logs)
Moisture data as applicable

[Analysis Method, Date] Initial Calibration Data

Sequence logs and instrument or other data as applicable, in run order and grouped by day.

[Analysis Method, Date] Data

Bench sheet(s) where not used in Sample Preparation section
Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Miscellaneous Data

Other data as applicable

Standards Records

Standards records from LIMS (and logbook pages as needed)

STANDARD OPERATING PROCEDURE: 375
Revision: 3, Effective: 4/13/09

[illegible]

**USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA**

**STANDARD OPERATING PROCEDURE 380
PURGEABLE HYDROCARBONS BY GC FID**

Revision 7
Effective Date: 03/01/2010

Reviewed by: _____
Richard Bauer
Chemistry Team Leader/Technical Director

_____ Date

Reviewed by: _____
K. W. Hendrix, Laboratory QA Officer

_____ Date

Approved by: _____
Brenda Bettencourt, Laboratory Director

_____ Date

Periodic Review:

Signature	Title	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____

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APPENDIX A. DEVIATIONS FROM THE REFERENCE METHOD
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APPENDIX H. REVISION HISTORY

1 SCOPE AND APPLICABILITY

This method describes the procedures used to determine total petroleum hydrocarbons as gasoline (TPH-g) in water and solid matrices.

This SOP is based on procedures from EPA SW 846: Method 5030C Revision 3, May 2003; Method 5035A Draft Revision 1, July 2002; and Method 8015C Revision 3, February 2007. Deviations from reference methods are described in Appendix A.

Analytes and quantitation limits are provided by matrix in Appendix B.

2 METHOD SUMMARY

An inert gas is bubbled through a portion of an aqueous sample (or methanol extract from solid samples). Volatile organic compounds are vaporized and swept through a sorbent column where they are adsorbed. The sorbent column is heated and back flushed with inert gas to desorb the components onto a gas chromatographic column. A temperature program is used in the gas chromatograph to separate the organic compounds followed by detection using a flame ionization detector (FID).

TPH as gasoline is quantitated by determining the retention times of 2-methylpentane and 1,2,4-trimethylbenzene and using these markers to establish the retention time range of the gasoline. The area sum response of the sample over this retention time range is compared to the area sum response of gasoline standards analyzed under the same conditions as the sample. If required, probable identification of gasoline in samples is done by comparing the chromatographic pattern generated by analysis of the sample to the chromatographic pattern of gasoline analyzed under the same conditions as the standard. The identification of TPH as gasoline may be complicated by environmental processes such as evaporation, biodegradation, or the presence of more than one fuel type.

3 DEFINITIONS

Analytical Sample - Any sample in which analytes are being determined, excluding standards, blanks, or QC reference samples.

Continuing Instrument Calibration Verification (CCV) – A standard containing the analytes of interest, which is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout the analysis sequence.

FID - Flame Ionization Detector.

Initial Calibration Standards (ICAL) – Standards used to calibrate the instrument response

with respect to analyte concentration.

Instrument Blank (IB) - A blank that is the same matrix as the calibration standards, but without the analytes.

Laboratory Control Sample (LCS) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is analyzed like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The LCS is also known as a laboratory fortified blank (LFB) or blank spike (BS).

LIMS - Laboratory Information Management System. The Element database.

Matrix Spike (MS) - An aliquot of an analytical sample to which known quantities of the method analytes are added. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations. The MS is also known as laboratory fortified matrix (LFM).

Matrix Spike Duplicate (MSD) - A duplicate aliquot of an analytical sample to which known quantities of the method analytes are added. The MSD is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results and to determine laboratory precision. The MSD is also known as laboratory fortified matrix duplicate (LFMD).

Method Blank (MB) - An aliquot of reagent water or other blank matrix that is treated exactly as a sample. The MB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment. The MB is also known as laboratory reagent blank (LRB).

Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

PID - Photo Ionization Detector.

Quantitation Limit (QL) - The concentration at which confidence in the reported value requires no qualifying remarks.

Quantitation Limit Standard (QLS or LCV) - A standard used to check the accuracy of the analysis at the quantitation limit. Equivalent to the lowest level calibration standard.

RT - retention time.

Sample Delivery Group (SDG) - A group of twenty samples or less from a project that is sent to the laboratory for analysis.

Second Source Calibration Verification (SCV) - A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check the initial calibration. The SCV is also known as quality control sample (QCS).

Solid Sample - For the purpose of this method, a sample taken from matrices classified as soil, solid, sludge, or sediment.

Stock Standard Solution (SSS) - A concentrated standard containing the method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Storage Blank (SB) - An aliquot of reagent water stored with samples in the sample storage refrigerator. The storage blank indicates whether contamination may have occurred during sample storage.

Surrogate Analyte (SA or SURR) - An analyte which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in a known amount before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

TPH - Total Petroleum Hydrocarbon.

Water Sample - For the purpose of this method, a sample taken from matrices classified as drinking, surface, groundwater, storm runoff water, or industrial or domestic wastewater.

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation must be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and

exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

Safety precautions must be taken when handling solutions and samples. Protective clothing including laboratory coats, safety glasses, and gloves must always be worn. Contact lenses must not be worn. If solutions come into contact with your eyes, flush with water continuously for 15 minutes. If solutions come in contact with your skin, wash thoroughly with soap and water. ESAT personnel should contact the Group Leader or Health and Safety and Environmental Compliance Task Manager and EPA staff should see the Team Leader or the Laboratory Safety, Health and Environmental Compliance Manager to determine if additional treatment is required. Refer to the Material Safety Data Sheets located in the library and the LAN for additional information.

4.1.1 Methanol

Methanol is the primary solvent used for the preparation of standards and for soil sample extraction in these procedures. Methanol is harmful if inhaled and may be fatal or cause blindness if ingested. Symptoms of overexposure via inhalation are drowsiness and intoxication, headache, visual disturbances leading to blindness, coughing, and shortness of breath, collapse, and death at high concentrations. Skin contact may result in absorption producing toxic effects. Repeated skin contact may cause burning, itching, redness, blisters or dermatitis. Eye contact can cause burning, watering, redness and swelling. High vapor concentration will result in similar symptoms in the eyes. Medical attention must be sought whenever symptoms of inhalation or ingestion are observed as many effects are delayed due to the slow rate of metabolism.

Methanol is classified as a flammable solvent and must be handled accordingly. Use methanol in a laboratory fume hood with appropriate personal protective equipment (laboratory coat, nitrile gloves and safety glasses). Store methanol in a flammable storage cabinet away from oxidizers and sources of ignition.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Many parts of the GC and autosampler operate at temperatures high enough to cause serious burns. Allow heated zones to cool below 50°C before working on or around them.

Flame ionization detectors use hydrogen gas as fuel. If hydrogen flow is on and no column is connected to the detector inlet fitting, hydrogen gas can flow into the oven and create an explosion hazard. Detector fittings must either be capped or have a column connected at all times.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure produces the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-regulated Waste	Not applicable
Sample extracts, methanol portion	Hazardous Waste	Flammable
Regulated solid sample waste (spent samples, glass vials, etc.)	Hazardous Waste	Toxic

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Aqueous samples should be collected in 40-mL VOA vials and preserved with HCl to pH <2.

Soil samples should be collected using one of the following methods:

1. Collect sample in 5g EnCore™ samplers and cool to 4 ± 2 °C (or freeze to $< -7^{\circ}\text{C}$ and $\geq -20^{\circ}\text{C}$) for no more than 48 hours, then preserve upon laboratory receipt.
2. Extrude the sample into a tared 40 mL VOA vial, cap immediately and cool to 4 ± 2 °C (or freeze to < -7 °C and ≥ -20 °C) for no more than 48 hours then preserve upon laboratory receipt.
3. Extrude the sample into a tared 40 mL VOA vial containing methanol for medium level analysis and cool to 4 ± 2 °C.

Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, and minimize waste disposal. Three VOA vials of water or three 5 g aliquots of solid sample should be sufficient to meet these objectives. Note that a separate 10 g aliquot of solid material should be provided for moisture determination.

5.2 Internal Chain-of-Custody

The sample custodian delivers water samples to a sample refrigerator in Room 201 or other area where the samples will be analyzed. The sample custodian delivers solid samples to a sample freezer in Room 201 or other area where the samples will be analyzed.

Verify sample IDs and dates of collection against the chain-of-custody form.

- 5.3 Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to “active out” and the location the appropriate room number. When finished with the samples, return sample containers and excess aliquots to the designated sample locations. Update the LIMS database to change the container disposition to “available in” and use the “return to home location” designation to update sample location.

5.4 Preservation Verification

Water samples must be analyzed within 7 days of sampling; preserved water samples must be analyzed within 14 days of sampling.

Solid samples must be extracted within 48 hours of sampling following Section 8.3.2. Sample extracts must be analyzed within 14 days.

5.5 Sample Storage

Store water samples in a refrigerator maintained at $> 0^{\circ}\text{C}$ to 6°C .

Store solid samples and sample extracts as outlined in section 5.1.

6 INTERFERENCES

Chromatographic interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to anomalous peaks or elevated baselines in chromatograms, or by carryover when low concentration extracts are analyzed after high concentration extracts.

Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and dichloromethane) through the septum seal into the sample during storage and handling.

6.1 Carryover

Contamination by carryover can occur whenever high level and low level samples are analyzed in sequence. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses.

For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging vessel with a detergent solution between analyses, rinse it with distilled water, then methanol. Dry in an oven at 105°C . In addition, purge an aliquot of methanol through the affected port. Analyze reagent water blank to show that the port is not contaminated before analyzing further samples. The trap and other parts of the system

are also subjected to contamination; therefore, frequent bakeout and purging of the entire system may be required.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

- Analytical balance - capable of measuring differences of 0.01 g.
- Gas chromatograph equipped with a FID detector (or PID/FID in series) and a splitless injection port (Hewlett Packard 5890 Series II gas chromatograph, Agilent AG6890 gas chromatograph, or equivalent).
- Data Acquisition and Processing System - able to control the GC and to acquire, store, and process gas chromatographic data. The software must be able to calculate calibration factors and the concentrations of analytes in samples. Agilent Technologies EnviroQuant ChemStation software and data acquisition computers (or equivalent).
- Fused Silica Capillary Gas Chromatography Column - 75m x 0.53mm x 3µm RTX-624 wide bore capillary column (Restek part # 10974 or equivalent). Any capillary column that provides adequate resolution, capacity, accuracy, and precision, may be used. The column is interfaced to the purge and trap device (OI Analytical, Tekmar 3100, or equivalent).
- Purge and trap concentrator. (OI 4560, Tekmar 3000 purge and trap concentrator, or equivalent.)
- Autosampler: OI DPM-16, Varian Archon, or equivalent.
- Tenax trap (OI #7) or VOCARB 3000 type K, – alternate traps may be used provided that the adsorption and desorption characteristics obtained achieve equivalent or better method sensitivity and precision.

7.2 Reagents

Record purchased reagents, such as methanol, in the Region 9 laboratory information management system (LIMS).

- Methanol, Burdick and Jackson purge and trap grade (232-1) or equivalent.
- Reagent Water: All references to water in this method refer to water in which method analytes or other interferences are at less than one-half the QL of the analytes of interest. The Region 9 Laboratory organic-free deionized water is further cleaned by bubbling contaminant-free inert gas through the water.
- Reagent Sand - Sand, sea washed (VWR Cat. #VW3358-3 or equivalent). Bake at 400°C for at least 1 hour before use. Store in a closed container.

7.3 Standards

All standards must be entered into the Region 9 LIMS.

Store unopened ampulated stock standard solutions, and all working standard solutions in glass bottles or vials with Teflon lined screw caps, at ≤ -10 °C. Protect all standards from light. Fresh standards should be prepared every six months, or sooner if comparison with check-standards indicates a problem. The standard solution must be checked frequently for stability. Replace all working standard solutions after six months or sooner if QC results indicate a problem.

Opened ampules of standards must be discarded six months after opening or earlier if evidence of degradation is observed. LIMS expiration dates must be revised when ampules are opened if the remaining time on the vendor expiration date exceeds six months. The vendor expiration date should be recorded in the comment portion of the standard record.

The following solution concentrations are recommended only; other concentrations can be used.

CAUTION: Allow all standard solutions to equilibrate to room temperature before use.

- Gasoline Stock Standard: Restek #30205 (XHc Unleaded Gasoline Composite Standard at 50,000 µg/mL) or equivalent.
- Gasoline Primary Dilution Standards (PDS): Prepare a solution by diluting the Gasoline Stock Standard to concentration of 100 µg/mL in P&T methanol (20 µL to 10 mL) when using the OI autosampler, and 1,000 µg/mL in P&T methanol (200 µL to 10 mL) when using the Archon autosampler, or equivalent.
- SCV Stock Standard: Supelco # 47519-U (Gasoline at 20,000 µg/mL) or equivalent.

- SCV Primary Dilution Standards (SCVPDS): Prepare a solution by diluting the SCV Stock Standard to concentration 100 µg/mL in P&T methanol (50 uL to 10 mL)), or equivalent, when using the OI autosampler.
- Window Defining Standard (WDS): AccuStandard Custom Mix S-10760-2.5X or equivalent. This solution contains 2-methylpentane and 1,2,4-trimethylbenzene at 5,000 µg/mL in methanol.
- WDS Primary Dilution Standards (WDSPDS): Prepare by diluting the WDS standard to 100 µg/mL in P&T methanol (200 uL to 10 mL), or equivalent.
- Surrogate Spike: Restek #30068, solution of α,α,α -trifluorotoluene in methanol at 2,500 µg/mL, or equivalent.
- Water Surrogate Spike: Prepare a solution by diluting the Surrogate Spike Solution Stock Standard to concentration of 125 µg/mL in P&T methanol (500 uL to 10 mL), or equivalent, when using the OI autosampler, and 625 µg/mL in P&T methanol (500 uL to 2 mL), or equivalent, when using the Archon autosampler.
- Soil Matrix Spike/LCS Solution: the soil matrix spike/LCS solution is Gasoline Stock Standard at 50,000 µg/mL.
- Water Matrix Spike/LCS Solution: the water matrix spike/LCS solution is Gasoline PDS Standard at 100µg/mL.
- Calibration Verification (CCV) - Equivalent to the mid-point initial calibration solution: 500 µg/L.
- Quantitation Limit Standard (QLS) - Equivalent to the lowest level calibration standard: 50 µg/L.
- Second Source Verification (SCV) - Equivalent to the mid-point initial calibration solution, 500 µg/L but prepared from a source different from the source of calibration standards (use SCV Primary Dilution Standards (SCVPDS) to make this standard).
- Site specific hydrocarbon standards may also be supplied by the project manger for use in the laboratory.

7.3.1 Calibration Solutions

The following calibration solution concentrations are typical concentrations only; other concentrations may be used. Use of gastight syringes is required for sample and standard preparation.

When using the OI autosampler:

- Prepare the calibration standards by adding the following solutions to 5 mL of water in a gastight syringe prior to injecting the resulting solution into the OI sparge tube.

QC Type	Solution	Conc. µg/mL	Volume Used, µL	Final Volume, mL	Final Conc., µg/L
WDS	WDSPDS	100	25	5	500
	Surrogate Spike	125	5	5	125
ICAL 1 QLS	PDS Solution	100	2.5	5	50
	Surrogate Spike	125	5	5	125
ICAL 2	PDS Solution	100	5	5	100
	Surrogate Spike	125	5	5	125
ICAL 3/CCV/LCS	PDS Solution	100	25	5	500
	Surrogate Spike	125	5	5	125
ICAL 4	PDS Solution	100	50	5	1,000
	Surrogate Spike	125	5	5	125
ICAL 5	PDS Solution	100	100	5	2,000
	Surrogate Spike	125	5	5	125
SCV	SCV PDS	100	25	5	500
	Surrogate Spike	125	5	5	125

When using the Archon autosampler:

- Prepare the calibration standards by adding the following solutions to 50 mL of water in a syringe to make standards at recommended concentrations prior to mixing and transferring the resulting solution to a 40 ml VOA vial and loading the vial onto the Archon autosampler.

QC Type	Solution	Conc. $\mu\text{g/mL}$	Volume Used, μL	Final Volume, mL	Final Conc., $\mu\text{g/L}$
WDS	WDSPDS	100	25	5	500
ICAL 1 QLS	PDS Solution	100	2.5	5	50
ICAL 2	PDS Solution	100	5	5	100
ICAL 3/CCV/LCS	PDS Solution	100	25	5	
ICAL 4	PDS Solution	100	50	5	1,000
ICAL 5	PDS Solution	100	100	5	2,000
SCV	SCV PDS	100	25	5	500

The Archon autosampler introduces 1 μL of the Surrogate Spike Solution to each sample at 625 $\mu\text{g/mL}$ in P&T methanol for a final concentration of 125 $\mu\text{g/L}$.

7.4 Supplies

- pH paper (pH 0-14 range).
- Sand, white quartz - Aldrich Cat # 27,473-9, or equivalent.
- Gas-tight syringes (5- μL , 10- μL , 25- μL , 50- μL , 100- μL , 250- μL , 500- μL , 1-mL, 5-mL, 25-mL, and 50-mL).
- Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers.
- Sparge Tubes - 18 mm x 150 mm Disposable Culture Tubes, VWR no. 60825-673 or equivalent.
- Stainless steel spatulas

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Note: If the instrument is equipped with a functioning PID, the detector should be calibrated for the surrogate. The information provided by the more selective detector can be used to verify that the purge and trap device is working properly even in the presence of significant hydrocarbons. However, the surrogate should always be reported from the FID; the PID calibration is not required for method control (i.e. do not stop analysis or rerun samples for PID failure).

Set up instruments using operating parameters provided in Appendix D. Adjust as needed to meet method and SOP requirements and chromatographic practice. Use a sparge volume of 5 mL.

Enter data into ChemStation using file naming conventions provided in Appendix E.

Bake the trap (when using the OI concentrator, ensure an empty sparge tube is mounted on the autosampler at the selected position) and the GC oven for at least 14 minutes each day before samples are analyzed.

Prior to analyzing calibration, QC, or field samples make a LIMS batch and sequence as required to obtain LIMS assigned IDs for the calibration and QC samples.

8.2 Calibration and Standardization

The calibration standards preparation is detailed in Section 7.3.1

Set up the purge and trap concentrator for water analysis ensuring that the sparge needles reach to within 5 mm of the bottom of the sparge cells. The same calibration is used for the analysis of both water and soil methanol extracts.

8.2.1 Initial Calibration

Perform an initial calibration using the WDS standard and a minimum of five calibration standards to establish an external standard linear calibration using the average calibration factor. Refer to Section 9.3.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Check that compound type in ChemStation is set to H. This setting sums the area between the start and end of the analyte range. The chromatogram from the WDS standard will be used to set the start and stop integration times in ChemStation.

Analyze each of the standards and instrument blanks as described in Section 8.3.1. An example initial calibration sequence appears below:

Sample Name		Sample Name	
1	IB	6	1,000 µg/L gasoline
2	500 µg/L WDS standard	7	2,000 µg/L gasoline
3	50 µg/L gasoline (QLS)	8	IB
4	100 µg/L gasoline	9	500 µg/L gasoline SCV
5	500 µg/L gasoline (CCV)		

Spike the water with the appropriate amount of primary dilution standard for the specific calibration solution being analyzed. See Section 7.3.1 for details.

Inspect the WDS standard and update start and stop integration times in the method to correspond to the 2-methylpentane and 1,2,4-trimethylbenzene peaks in the WDS standard. Quantitate each calibration standard and samples using this retention time range.

Update each level of the ChemStation ICAL method. All target analyte and surrogate responses in the ICAL method should be replaced with the new responses.

Print a ChemStation Response Factor Report. See Appendix C for QC limits.

Print page 3 of the ChemStation ICAL for gasoline to show that the method was updated correctly.

Print the ChemStation initial calibration compound list report to verify that the average calibration factor is used.

Save the method as outlined in Appendix E (ChemStation File Naming Conventions).

Analyze a SCV standard immediately after each initial calibration. See Section 9.3.1 of this SOP for frequency and Appendix C for QC limits.

If the initial calibration, the SCV, and the IB meet all criteria specified in Appendix C, the remainder of the 12-hour analytical period may be used for the analysis of field and QC samples.

As needed, analyze other hydrocarbons such as Turpentine, Stoddard Solvent, Mineral Spirits, Naphtha, and Lacquer Thinner at 500 µg/L with each ICAL. These standards are used for identification purpose only. Use stock solution such as AccuStandard # HS-004S-40X, HS-005S-40X, HS-002S-40X, HS-003S-40X, and HS-001S-40X or equivalent.

8.3 Sample Analysis

Check that the LIMS ID and client sample ID on the vials coincide with the numbers on the LIMS Work Order to ensure that the correct sample is being analyzed.

If the sample has an unusual color, or other physical characteristic such as more than one phase, the presence of a precipitate, unusual viscosity, or physical signs of contamination a screening analysis is required to protect the analytical system from damage or contamination and to determine the appropriate subsequent dilution. If an initial screening is necessary, analyze the sample at a 1:50 dilution, unless the group

leader or Technical Director specifies otherwise. Document observed anomalies in the LIMS MMO field.

Note in the LIMS MMO field in the work order window if there is headspace present in the sealed sample vial. If the bubble exceeds 6 mm in diameter, data qualification may be required.

8.3.1 Water Sample Preparation

- Allow the samples to reach ambient room temperature before analysis.
- Break the chain of custody seal on the vial with a scalpel or other appropriate implement, and note if the seal is missing or compromised in any way.
- Fill a 5-mL syringe with the sample. Invert the syringe, remove any air bubbles, and bring the level to 5-mL by displacement with the plunger. Place any excess sample displaced from the syringe in the aqueous waste containers.
- Prepare MS, MSD, and LCS samples by spiking with the analytes of interest. Add 25 µL of the 100 µg/mL gasoline water matrix spike/LCS solution to the matrix spike sample to prepare an MS/MSD or to reagent water to prepare an LCS.
- If using OI autosampler, spike the water with 5 µL of the 125µg/mL surrogate solution. Attach the syringe to the Luer lock mount on the purge and trap concentrator. Open the mount valve, inject the contents of the syringe into the sparge cell, and close the valve. Remove the syringe from the mount. Rinse the syringe with DI water after each sample.
- If using the Archon autosampler, load the samples in the Archon autosampler. The autosampler will add surrogate.
- Check the pH of the sample using pH 0-14 range pH paper. Record the pH in the injection logbook. Note any samples that have a pH greater than 2 in the LIMS MMO field in the work order window.

8.3.2 Soil Sample Preparation

This section contains procedures for the extraction and analysis of soil samples collected as bulk samples in glass jars or other containers (see Section 5.1 for documentation requirements when bulk samples are received), in EnCore™ sampler devices, or pre-weighed vials preserved in the field with methanol.

The typical sample weight is 5 g (nominal).

The percent moisture is determined from a separate aliquot as described in EPA Region 9 Laboratory SOP 460, *Percent Moisture Determination*.

To prevent the loss of certain volatile organics the sample must not be allowed to reach room temperature. The following steps must be taken as rapidly as possible to prevent loss of volatile components. Have the LIMS benchsheet prepared and all vials, standards, etc. ready prior to beginning the next steps.

1. Remove the sample from the refrigerator immediately prior to extraction or analysis. Samples should be extracted as soon as possible after receipt and within 48 hours of collection even if analysis will not to be performed immediately.
2. Break the chain of custody seal on the container with a scalpel or other appropriate implement, again making note in the logbook if the seal is missing or compromised in any way. Observe the sample closely for evidence of contamination. If the sample appears to contain hydrocarbons (an oily appearance or sheen) the sample must be analyzed at a dilution to prevent damage to the analytical system.
3. To extract bulk samples, use a stainless steel spatula. Immediately transfer approximately 5 g into a 20-mL tared vial. Record the weight of soil added to the container to the nearest 0.01 g in the LIMS bench sheet. If possible, all samples within a sample delivery group should be extracted at the same time along with the MB preparation.
4. To extract samples collected with the EnCore™ sampling device, transfer the contents of the EnCore™ sampler into a 20-mL tared vial. Record the weight of soil added to the container to the nearest 0.01 g in the LIMS bench sheet.
5. Quickly add 10.0 mL of purge and trap grade methanol and 25 µL of the 2,500 µg/mL soil surrogate stock solution to the vial. Spike MS/MSD samples with 5 µL of the Gasoline Stock Standard containing 50,000 µg/mL of gasoline. Cap the vial and vortex for 30 seconds. These steps must be done rapidly in order to prevent the loss of volatile organics from the sample.
6. Prepare a soil LCS by spiking 5 g of reagent sand in a 20-mL vial with 5 µL of the Gasoline Stock Standard containing 50,000 µg/mL of gasoline. Add 10.0 mL of purge and trap grade methanol and 25 µL of the 2,500 µg/mL soil surrogate spike solution to the vial. Cap the vial and vortex for 30 seconds.
7. Prepare a soil MB using 5 g of reagent sand in a 20-mL vial. Add 10.0 mL of purge and trap grade methanol and 25 µL of the 2,500 µg/mL soil surrogate spike solution to the vial. Cap the vial and vortex for 30 seconds.

8. Transfer approximately 1 mL of each extract to a GC vial for storage in the laboratory freezer at $\leq -10^{\circ}\text{C}$. Extracts must be analyzed within 14 days from sample collection. Use this extract for the analysis and any subsequent dilutions that may be necessary.
9. Weigh samples collected in pre-weighed containers preserved in the field with methanol to the same level of precision as the weight recorded on the chain-of-custody or vial (0.1 g or 0.01 g). Enter the vial and methanol weight (the pre-weight) from the chain-of-custody or vial in the LIMS bench sheet and calculate the sample weight by subtraction. Quickly add soil surrogate spike solution to the vial at the rate of 2.5 μL per mL of methanol.
10. If using OI autosampler, analyze 100 μL of the extract in 4.9 mL of reagent water according to the instructions for 5-mL water analysis in Section 8.3.1.
11. If using Archon autosampler, analyze 1mL of the extract to 49 mL of reagent water in a syringe. Mix and transfer the resulting solution to a 40 ml VOA vial and loading the vial onto the Archon autosampler. **MAKE SURE TO USE A SOIL METHOD WHICH DOES NOT ADD ADDITIONAL SURROGATE.**

8.3.3 Analytical Sequence and Sample Analysis

Set up a ChemStation data acquisition sequence from the LIMS sequence using the GC operating parameters in Appendix D. Include the client sample ID and the laboratory sample ID in the sample description field. Additional header information shall include the dilution factor, instrument ID, and the analyst's initials. Enter this sequence in the instrument run log, if used.

For water analysis:

1. The method defaults are 5 mL sample, 5 mL final volume, and dilution factor 1. These values produce correct reporting limits but are only a starting point for data entry.
2. Batch samples as usual and leave the initial and final values in the batch as 5 mL and 5 mL respectively.
3. In the bench sheet, the sample the initial and final volumes default to 5 mL.
4. Edit the bench sheet initial volume for samples and QC to reflect the actual volumes used.
5. When setting up the ChemStation sample sequence, enter 1 as the dilution factor in the multiplier field

For Soil analysis:

1. The method defaults are 5 g sample, 5 mL final volume, and dilution factor 100. These values produce correct reporting limits but are only a starting point for data entry.
2. Batch samples as usual and leave the initial and final values in the batch as 5 g and 5 mL, respectively. (Note that the 5 mL volume represents the purge volume not the methanol extract volume.
3. In the bench sheet, the sample weight defaults to 5 g. Edit the initial weight to the actual weight used as needed.
4. Edit the bench sheet final volumes for samples and QC from 5 mL to the actual of methanol used to extract the samples (which is usually 10 mL).
5. When setting up the ChemStation sample sequence, enter 50 as the dilution factor in the multiplier field. (Do not apply the multiplier field to sample or surrogate results in ChemStation; LIMS does this later). The dilution factor, $D = \text{syringe volume} / \text{methanol extract volume in the syringe}$. This is typically $50 \text{ mL} / 1 \text{ mL} = 50$. If a greater dilution is required, calculate the dilution factor based on the volume of methanol used, e.g. for 100 μL , D is $50 \text{ mL} / 0.1 \text{ mL} = 500$.

See Section 9.4 for batch quality control (QC) frequency and corrective action requirements. It is highly recommended that the MB, LCS, and MS/MSD be analyzed as early as possible in the analysis of a batch.

If the initial calibration, the SCV, and the IB meet all criteria specified in Appendix C, the remainder of the 12-hour analytical period may be used for the analysis of field and QC samples.

Example Field Sample Analysis Sequence:

Sample Name		Sample Name	
1	IB	6	MS (as needed)
2	500 $\mu\text{g/L}$ gasoline CCV	7	MSD (as needed)
3	50 $\mu\text{g/L}$ gasoline QLS	8-18	Field samples (as needed)
4	MB	19	IB
5	LCS	20	500 $\mu\text{g/L}$ gasoline CCV

Enter the first and last sample positions in the concentrator and, with the ChemStation software in data acquisition mode, press the start button on the concentrator to begin purging the first sample. The purge and trap concentrator parameters are found in Appendix D.

When possible or if there are indications that the sample may foam, observe the initial purging. If the sample does foam, it can be analyzed as long as the foam does not enter the sparge vessel neck and enter the transfer line leading to the trap.

If it appears that the sample will foam excessively, discontinue the purging by pressing the [2nd], [on], and [enter] keys. Drain the sparge cell; rinse it with methanol, then reagent water. Place the sample waste and rinsate in the aqueous waste container. Bake out the trap and the GC for 25 minutes before analyzing additional samples. Analyze reagent water blank to show that the sampler is free from contamination before analyzing sample.

Analyze the sample at a 1:10 dilution, or other appropriate dilution to prevent foaming even though the detection limits are elevated. Document any sample foaming in the run log and the LIMS WO MMO field.

8.3.4 Analyte Identification and Quantitation

Update the center of the retention time window for the surrogate by using the absolute retention times from the calibration verification standard at the beginning of the analytical shift. Establish the ChemStation window as ± 0.06 minutes (peaks that drift more than 0.03 minutes will be flagged "f" by the data system as possible false positive).

All surrogates in the field and QC samples must fall within the ± 0.03 minute retention time window or the analyst must reject the analysis or review and accept the data with a written comment such as "retention time shift due to high concentration of interfering hydrocarbon".

If the retention time does not fall within the retention time window and no source of drift is identified, then take corrective action to restore the system. If repairs to the system are required then a new initial calibration must be performed.

Review the sample chromatograms for appropriate qualification. Several situations are routinely encountered:

- The chromatographic pattern resembles the standards; proceed with quantitation and reporting.
- The chromatogram differs markedly from the standard; visually compare the sample chromatogram to available hydrocarbons analyzed with the initial calibration. Software tools such as overlaying various standard chromatograms on the sample chromatogram should be employed when helpful or to support the qualification. Use the WO Memo field and/or appropriate qualifier flags (F1, J) to report the data. A comment such as "hydrocarbon pattern does not resemble available standards" with a list of those hydrocarbon mixtures may be appropriate.

- The majority of the area is due to a single-component and not a hydrocarbon mixture; consult the group leader and/or technical director to determine if the peak should be excluded from the quantitation. Use the WO Memo field and appropriate qualifier flags (F1, J) to report the data.
- The client has requested qualitative review against various standards; refer to the TDF and project notes to determine the project specific analysis and reporting procedures. This may include calibrating with a source supplied by the client, review against numerous standard chromatograms, or other procedures. Always document this process in the WO Memo field and in the data package and report as necessary

Quantitate the sample data using the ChemStation software using the appropriate initial calibration mean CFs. Quantitate methanolic extracts of soil samples with the same initial calibration used to quantitate water samples. If applicable, indicate degree of similarity of sample chromatogram to the gasoline standard. Print out quantitation reports and chromatograms for each field and QC sample.

LIMS calculates final analyte concentrations in samples. To verify the LIMS reported values for water samples, calculate results for target analytes using the following equation:

8.3.4.1 Water Calculations

Calculate target analyte concentrations in aqueous samples using Equation 1.

Equation 1:

$$\text{Concentration (ug / L)} = \frac{A_x \times DF}{RF}$$

Where:

A_x = area response for analyte x

DF = dilution factor

RF = mean response factor from the initial calibration
(area/concentration)

8.3.4.2 Soil Calculations

Calculate target analyte concentrations in soil samples using Equation 2.

Equation 2:

$$\text{Concentration (mg / Kg dry weight basis)} = \frac{A_x \times V_t \times DF \times V_p \times 1,000}{RF \times W \times D \times V_i \times 1,000}$$

Where:

A_x = area response for analyte x
D = dry weight factor (Percent solids/100)
W = weight of sample in grams
RF = mean response factor from the initial calibration
(area/concentration)
 V_t = total volume of extract in mL (see note)
DF = dilution factor (volume of water divided by volume of
extract (nominally 5 mL / 0.1 mL or 50)
 V_i = volume of extract injected in μ L
 V_p = volume of extract purged in mL (i.e. 5 mL)
1,000 (in numerator) 1000 μ L = 1 mL
1,000 (in denominator) 1000 mL = 1 L

Yields concentration units of μ g/g = mg/Kg

Note: V_t is equal to the volume of methanol (see benchsheet) plus the volume of water from the solid calculated as (1-%solid) * W. See EPA Region 9 Lab SOP 460 for percent solids determination.

8.3.5 Manual Integration

Review the baseline drawn by the data system integrator to verify that it accurately reflects the area response of the sample components. If in the judgment of the analyst, it does not, then correct the integration using the ChemStation QEDIT software module. Document manual integrations, if any, following the procedure described in USEPA Region 9 Laboratory SOP 835, *Chromatographic Integration Procedures*.

8.3.6 QC Review

As soon as possible after analysis (typically prior to entry into LIMS), inspect sample and QC data for compliance with QC limits in Appendix C. If no significant problems are found, review the following QC data for compliance with SOP requirements:

- Target analyte results must be within range of initial calibration.
- Process and review the results for the IB, CCV, and QLS instrument QC samples. Print a ChemStation Evaluate Continuing Calibration Report using the appropriate settings to verify that the CCV and QLS QC sample results are within QC limits. See Section 9.3 for instrument QC requirements.
- Process and review the results for the MB, LCS, and MS/MSD batch QC samples and verify that the results are within QC limits. See Section 9.4 for batch QC requirements.

- Check that surrogate compound retention times are within the window specified in Section 9.5.1 and Appendix C. Determine if surrogate recoveries for field and QC samples are within QC limits. See Section 9.5 for sample QC requirements.
- Review all sample results to determine if any samples need to be re-analyzed at a dilution. If any of the target compounds in soil extract or water samples exceed the initial calibration range of the instrument, dilute by using a smaller aliquot of the water sample or soil extract combined with reagent water to a total volume of 5 mL.
- If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report.

8.3.7 Data Export and LIMS Entry

Export data from the instrument into text files. Import into the LIMS using DataTool.

1. Copy data files from the local drive to the appropriate instrument data subdirectory on the Region 9 LAN to make them available to LIMS and for archiving.
2. Populate the empty LIMS sequence with the samples actually analyzed by editing the empty LIMS sequence; import the sample information using Data Tool.
3. After making an empty upload file containing the samples analyzed in the LIMS batch or sequence, import and merge the data files using the LIMS Data Tool module. Load the resulting merged data file into the LIMS Data Entry/Review table.

Review final results in the LIMS. Report all results to two significant figures. Report detected results to one-half the QL. Flag values between one-half the QL and the QL as estimated (J).

- Generate epatemp.txt files for field and QC samples by also printing the report to the screen; these files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table.
- In order to take the dilution that occurs during soil sample preparation into account, the dilution factor for undiluted soil samples in the LIMS Data Entry/Review table must be 50. Any actual sample dilutions must be

multiplied by 50 to obtain the effective sample dilution to be entered in LIMS. Edit dilutions in DataTool or LIMS entry table as needed.

- Review results in the LIMS. Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

8.4 Maintenance

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook. Preventative maintenance procedures are listed in Appendix F.

The following sections describe possible causes and corrective actions for common problems. Refer to Appendix F for routine preventative maintenance procedures and schedule.

8.4.1 Purge and trap maintenance

Symptom:

- Carryover
Possible causes: Cold spot in system, especially the transfer lines between the sparge unit and the concentrator or between the concentrator and the GC or analyzing a sample containing high mole weight components or analyzing high-level and low-level samples sequentially.
Corrective action: Check temperatures of all heated zones. Adjust temperatures or replace heaters as required. Flush valve, gas lines, and sample lines with methanol or reagent water and bake out.
- Loss of sensitivity to selected analytes and increased pressure to maintain purge flow.
Possible cause: Degradation of trap.
Corrective action: Replace trap.
- Loss of all purged analytes.
Possible cause: Leak in system.
Corrective action: Leak check purge and trap system. Inspect sparge ferrules and replace them when worn or distorted.

8.4.2 GC Maintenance

Symptom:

- Carryover
Possible causes: Analyzing a sample containing high mole weight components or analyzing high-level and low-level samples sequentially.
Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.
- Shorter retention time.
Possible cause: column flow rate problem.
Corrective action: check flow rate and adjust as necessary.
- Longer retention time and or smaller peaks.
Possible causes: column flow rate problem, injection port leak, or column contamination.
Corrective action: as necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.
- Loss of resolution.
Possible causes: column flow rate problem, injection port leak, or column contamination.
Corrective action: check for leaks, replace septum, replace the liner, replace inlet seal, and clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

9 QUALITY CONTROL

9.1 Retention Time Windows

- Establish retention time windows for the surrogate whenever a new GC column is installed or a new DOC is required on each chromatographic column and instrument.
- Before establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the sample matrix to be analyzed.
- Make three injections of the CCV level calibration standard over the course of at least a 72 hour period. Serial injections or injections over a period of less than 72 hours may result in retention time windows that are too narrow.

- Record the retention time to three decimal places (e.g., 9.007) from three injections.
- Calculate the mean and standard deviation of the three absolute retention times. If the standard deviation of the retention times for a target compound is less than 0.01 minutes then use a default standard deviation of 0.01 minutes.
- The width of the retention time window is defined as ± 3 times the standard deviation of the mean retention time. If the default standard deviation is employed, the width of the window will be ± 0.03 minutes. Set the ChemStation window to ± 6 times the standard deviation so the software will identify peaks within the wider window and flag those which exceed the retention time window with the “F” flag (the flag is added to peaks outside one half the window) to prevent false negatives.
- For samples run during the same shift as an initial calibration, use the retention time of each analyte and surrogate in the mid-point standard of the initial calibration as the center of the retention time window.
- The first successful CCV of each daily sequence is used to establish the retention time around which the windows are calculated for that sequence. Update the retention time for each analyte in the ChemStation method. Updating the retention time windows will cause the “Last Update time” stamp to change. Save the method using today’s date and utilize this method in quantitating today’s runs. Print ICAL summary from the ICAL method and today’s method to establish that the response factors did not change.
- Document the RT window calculations in a spreadsheet and store them in the laboratory where the samples are analyzed. Provide a copy to the Laboratory QAO.

9.2 Demonstration of Capability

The EPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency* for more details.

9.3 Instrument QC

9.3.1 Initial Calibration

Demonstration and documentation of an acceptable initial calibration are required before any samples are analyzed

The GC system must be calibrated whenever corrective action that changes instrument response (e.g., detector gas adjustment, column replacement, etc.) is performed or if the calibration verification criteria cannot be met.

- The data system calculates the calibration factor (CF) using Equation 3.

Equation 3

$$CF = (A_x) / (C_x)$$

Where

A_x = Area of analyte x, or area sum response of gasoline

C_x = Concentration of the standard injected (µg/L)

- The data system calculates the percent relative standard deviation (%RSD) of the CF values for each analyte using Equation 4.

Equation 4

$$\%RSD = (SD / CF_{avg}) \times 100$$

Where SD is the sample standard deviation and is calculated as:

$$SD = \sqrt{\frac{\sum_{i=1}^n (CF_i - CF_{avg})^2}{n - 1}}$$

Where:

CF_{avg} = Mean calibration factor from the initial calibration.

CF_i = Calibration factor for a calibration level.

- Print a ChemStation Response Factor Report. Verify that the %RSD of the target analytes and the surrogate are within QC limits immediately after the initial calibration is finished. See Appendix C for QC limits.

- If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the failed one in the ICAL. If more than one standard fails, corrective action is required.
- Analyze an SCV sample immediately after each initial calibration. Calculate the calibration factor (CF) for the target analytes and the surrogate compound using Equation 3.
- Calculate the percent difference (%D) between the SCV CF and the initial calibration average CF for the target analytes and the surrogate using Equation 5.

Equation 5:

$$\% D = \frac{CF_c - CF_{avg}}{CF_{avg}} \times 100$$

Where:

CF_c = SCV or CCV CF

CF_{avg} = ICAL mean CF

- See Appendix C for QC limits. If the SCV sample fails it may be repeated once. If the second SCV fails, the cause for failure must be determined and corrected before analysis of samples can proceed.

Note: Fuel standards from different sources may contain different compound mixes and therefore may not be reliable for verifying calibration standards.

9.3.2 Continuing Calibration Verification

- Analyze a CCV standard at the beginning of each 12-hour analytical period and at the end of the 12-hour analytical period. The 12-hour analytical period begins with the injection of the CCV standard and ends with the injection of the last sample that can be injected within 12 hours of the beginning of the period.
- Calculate the calibration factor (CF) for the target analytes and the surrogate compound using Equation 3.
- Calculate the percent difference (%D) between the calibration verification CF and the initial calibration average CF for the target analytes and the surrogate using Equation 5.
- The %D must be within QC limits. See Appendix C for QC. If an analyte fails this criterion a second calibration verification may be analyzed.

Repeated failure requires that corrective action be taken to restore the system before any additional samples are analyzed. All affected samples must be re-analyzed.

If repairs to the system are required then a new initial calibration must be performed. The analyst should observe trends in the data such as declining response, erratic response, etc., which may signal the need for instrument maintenance.

- Acceptable sample analyses must be bracketed by the analyses of calibration verification standards that meet QC limits.

9.3.3 Quantitation Limit Standard

- Analyze a quantitation limit standard (QLS) each day when analyses of field or QC samples are performed. The QLS is used to verify analytical system response at the quantitation limit.
- Calculate the concentration of the target analytes using Equation 1.
- Calculate the percent of true value (TV) for the target analytes using Equation 6.

Equation 6:

$$\% \text{ True Value} = (\text{Cd} / \text{Tv}) \times 100$$

Where:

Cd = Concentration determined by analysis

Tv = True value of standard

- If the % TV is not within the QC limits in Appendix C, analyze a second QLS sample. Repeated failure requires that the cause be determined and corrected before analysis of samples can begin. If repairs to the system are required then a new initial calibration must be performed.

9.3.4 Instrument Blank

- At a minimum, one acceptable IB is required for each 12-hour analysis period.
- Evaluate the IB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

- If the IB results are not within QC limits, analyze a second IB. If the second IB also fails but the system is significantly cleaner, another IB may be analyzed; if not, take corrective action.
- Corrective action - If the IB is not acceptable the source of the contamination must be found and eliminated and the problem documented before analysis can proceed.
- Surrogate recovery is not evaluated for IB QC samples.

9.4 Batch QC

9.4.1 Method Blank

- Extract and analyze a method blank (MB) with each extraction batch or every 20 samples, whichever is more frequent, to demonstrate that the entire analytical system – from extraction through GC analysis – is free of contamination.
- For aqueous samples a MB is identical to an IB. For soil sample analysis it is necessary to prepare an extracted MB.
- If the surrogate recovery does not meet acceptance criteria, re-analyze the MB. If the surrogate recovery still does not meet acceptance criteria, the batch may have to be re-extracted
- Evaluate the MB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.
- Corrective action – if the MB result exceeds QC limits and the sample result is less than five times the MB analyte result, re-analyze the MB. If the MB result still exceeds QC limits then the MB and all associated samples must be re-prepared and re-analyzed. If the MB result exceeds QC limits and the sample result is \geq five times the MB result or is not detected then report the sample result.

9.4.2 Laboratory Control Sample

- Analyze a laboratory control sample (LCS) to demonstrate that the analytical system is in control. An LCS is extracted and analyzed once per extraction batch or every 20 samples, whichever is more frequent. The LCS is an MB spiked with matrix spiking solution.
- Calculate the percent recovery (%R) using Equation 7.

Equation 7:

$$\% \text{ Rec} = (\text{LCS}/\text{SA}) \times 100$$

Where,

LCS = LCS result

SA = Spike added

- The %R must be within the QC limits in Appendix C. If acceptable accuracy cannot be achieved, the problem must be located and corrected prior to reporting any sample data and before additional samples are analyzed.

9.4.3 Matrix Spike/Matrix Spike Duplicate

- Matrix spike (MS) and matrix spike duplicate (MSD) samples are extracted and analyzed for each batch of twenty or fewer samples extracted as a group. Matrix QC samples are usually designated in the field. In the event that a sample was not designated as the matrix spike sample and adequate sample volume exists, the analyst will choose one representative sample from the SDG for QC analysis. Do not choose any obvious field blanks as the QC sample.
- Calculate the recovery of each analyte using Equation 8.

Equation 8:

$$\% \text{ Rec} = ((\text{SSR} - \text{SR})/\text{SA}) \times 100$$

Where,

SSR = Spiked sample result

SR = Unspiked sample result

SA = Spike added

- Calculate the relative percent differences (RPD) of the recoveries of each analyte in the MS and MSD using Equation 9.

Equation 9:

$$\text{RPD} = \frac{(\text{MSC} - \text{MSDC})}{(\text{MSC} + \text{MSDC}) / 2} \times 100$$

Where,

MSC = Measured concentration of analyte in MS

MSDC = Measured concentration of analyte in MSD

- See Appendix C for QC limits.

The MS/MSD recovery limits are advisory limits only. If the limits are not met, then no further action is required, as long as the LCS is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the spike compounds. A new solution should be prepared if the recoveries are not within 20% of expected.

9.4.4 Storage Blank

- Every Monday morning, or the first workday of the week, fill three 40-mL screw-cap volatile vials with PTFE-faced silicone septum with reagent water, acidify to $\text{pH} \leq 2$, and store them with the samples, in the sample storage refrigerator.
- Analyze storage blank (SB) once every week while samples are being stored waiting for analysis. The storage blank indicates whether contamination may have occurred during sample storage.
- If samples have been stored in the refrigerator during the previous week, analyze the storage blank the following Monday, or on the first work day of that week. If samples have not been stored in the refrigerator during the previous week, discard the blanks and place new storage blanks in the refrigerator.
- Evaluate the SB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.
- If the SB does not meet QC criteria all affected data must be qualified.

9.5 Sample QC

9.5.1 Surrogate Recovery

- Calculate the surrogate recovery in all field and QC samples immediately after analysis using the following formula:

Equation 10:

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

- The surrogate recovery must be within QC limits. See Appendix C for QC limits.
- Take the following steps if surrogate recovery is not within the limits:
 1. If the system is equipped with a functioning PID, the second detector can be used to provide further information. If sample matrix is the source of the error, as demonstrated by acceptable surrogate recovery on the PID, document the issue in the WO MMO field and on the chromatogram, and continue. If not, proceed with troubleshooting.
 2. Ensure that there are no calculation errors, and check the system performance.
 3. Re-analyze the extract if a system performance problem or calculation error is not evident. The extract may be diluted for re-analysis if examination of the chromatogram so indicates.
 4. If re-analysis of the extract does not solve the problem, the sample may have to be re-extracted. Corrective action is decided by the EPA Chemistry Technical Director on a case-by-case basis.
- Do not re-extract undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the run log.
- Do not re-analyze the MS/MSD samples, even if surrogate recoveries are outside the limits.
- If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the matrix interference is confirmed and the sample does not need re-analysis.
- If the surrogate recoveries of the re-analysis of the extract are within limits, then:
 1. If the re-analysis was undiluted, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Mark the first chromatogram as "Not Reported, see re-analysis."

2. If the re-analysis was diluted, the problem was a matrix effect. Report the results from the re-analysis and submit the data from both analyses and discuss the result in the LIMS WO MMO filed. Mark the first chromatogram as "Not Reported, see re-analysis."
3. If the surrogate recoveries of the re-extraction are within limits, then the problem was within the laboratory's control. Report the results from the re-extraction, mark the first chromatogram as "Not Reported, see re-analysis."
4. If the re-extraction does not solve the problem, report the results from the first analysis and submit the data from both analyses.

9.6 Method Performance

Region 9 Laboratory performance for this procedure from February 23, 2009 to February 24, 2010 is summarized in the following table.

Method Performance

Analyte	Matrix	QC Type	Number of Measurements	Mean Recovery, %	STD, % (σ)	95% Confidence Interval (2σ)
TPH as Gasoline	Water	LCS	30	94.4	6.48	81.5 - 107
TPH as Gasoline	Solid	LCS	43	95.8	13.3	69.3 - 122

The following functional areas of the SOP may be significant sources of analytical error:

- Poor purge efficiency due to specific analyte characteristics or other problems.
- Standard degradation
- Volatile compound losses in spike solutions and standards.

10 DOCUMENTATION

10.1 Standards

Record the preparation of all standards in the Element database. Include a copy of each Analytical Standard Record associated with sample analysis in the data package.

10.2 Analytical sequence

The analytical sequence is documented in the Element database in the instrument Run

Log. Case Number, SDG number, date of analysis, QC solution IDs, analyst initials, laboratory sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.3 Analytical Report and Data Package

Analytical reports are produced using the Element database. The data package is produced from Element database and manual log records. Appendix G provides the typical format for data package deliverables.

10.4 Maintenance Logbook

Maintain a maintenance logbook for each instrument. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control. Document all preventive or routine maintenance performed, as well as repairs or corrective or remedial actions in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.5 SOP Read and Understood

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. The Lab QC Database is used to maintain the list of assigned analysts for each SOP. Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.6 SOP Revisions

Revisions to this SOP are summarized in Appendix H.

11 REFERENCES

Agilent Technologies EnviroQuant ChemStation User's Guide

HP 5890 Gas Chromatograph Users Manual

Agilent AG6890 Gas Chromatograph Users Manual

OI 4560 and DPM16 Operator's Manuals.

U.S. Environmental Protection Agency, *Method 5030C, Purge-and-Trap for Aqueous Samples*, Revision 3, May 2003.

- U.S. Environmental Protection Agency, *Method 5035A, Closed-system Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples*, Draft Revision 1, July 2002.
- U.S. Environmental Protection Agency, *Method 8000C, Determinative Chromatographic Separations*, Revision 3, March 2003.
- U.S. Environmental Protection Agency, *Method 8015C, Nonhalogenated Organics Using GC/FID*, Revision 3, February 2007.
- U.S. Environmental Protection Agency Region 9 *Laboratory Quality Assurance Plan*, Revision 10, November 5, 2007.
- U.S. Environmental Protection Agency Region 9 SOP 110, *Sample Receiving and Login*.
- U.S. Environmental Protection Agency Region 9 SOP 125, *Disposal Procedures for Unused Aqueous Environmental Samples*
- U.S. Environmental Protection Agency Region 9 SOP 460, *Percent Solids Determination*
- U.S. Environmental Protection Agency Region 9 SOP 706, *Laboratory Waste Management Procedures*
- U.S. Environmental Protection Agency Region 9 SOP 805, *Refrigerator Temperature Monitoring*
- U.S. Environmental Protection Agency Region 9 SOP 820, *Laboratory Discrepancy and Corrective Action Reporting Procedures*
- U.S. Environmental Protection Agency Region 9 SOP 835, *Chromatographic Integration Procedures*
- U.S. Environmental Protection Agency Region 9 SOP 840, *Notebook Documentation and Control*
- U.S. Environmental Protection Agency Region 9 Laboratory SOP 880, *Demonstration of Capability*

**APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD**

1. The CF is area/concentration unit ($\mu\text{g/L}$) not area/mass (ng) as in the reference method. The formulas for determining sample analyte concentrations have been modified to reflect this change.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

Analyte	QL, on column, µg/L	QL, 5g Solid, mg/kg	QL, 5 mL Water, µg/L
TPH as gasoline	50	5.0	50

**APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA**

QC Measurement	Frequency	Criteria
Initial Calibration (ICAL) RSD	Instrument setup, after maintenance, and when CCV fails criteria	≤ 20
Second Source Verification (SCV) %D	After each ICAL	± 30
Calibration Verification (CCV) %D	Beginning of each daily sequence, every 12 hours, end of sequence	± 20
Quantitation Limit Standard (QLS)	After first CCV of sequence, and after 40 samples.	$\pm 40\%$ of TV
Blanks :		$< \frac{1}{2}$ QL
MB	Each batch of 20 or fewer samples	
IB	After each CCV	
SB	Once per week	
Laboratory Control Sample (LCS) %R	Each batch of 20 or fewer samples	Water: 75 - 114 Soil: 56 - 136
MS/MSD %R	Each SDG of 20 or fewer samples	Water: 71 - 114 Soil: 72-108
MS/MSD RPD	Each SDG of 20 or fewer samples	Water: 11 Soil: 20
Surrogate Recovery of QC and field samples (except IB) %R	Every samples	Water: 76 - 121 Soil: 75 - 119
Retention Time Windows	Each CCV	± 3 SD of RT Study*

*ChemStation window is ± 6 SD of RT Study (SD is usually 0.01 min) and peaks are flagged at the more restrictive window.

APPENDIX D.
RECOMMENDED INSTRUMENT PARAMETERS

OI 4560 Concentrator

Recommended operating settings for the OI 4560 purge & trap concentrator that is interfaced with the HP 5890 Series II GC and the DPM-16 autosampler is as follows.

<u>PARAMETER</u>	<u>SETTING</u>
Purge temperature	20°C
Sample temperature	ambient
Purge Time	11 minutes
Dry purge	2.3 minutes
Purge Flow	35 - 40 mL/min
Desorb	2.00 minutes @ 180°C
Bake	14 minutes @ 190°C
Valve temperature	100°C
Mount temperature	40°C
Line temperature	100°C
DPM16 transfer line	100°C
DPM Valve temperature	100°C
Water Management	ON
Purge Temperature	100°C
Desorb Temperature	20°C
Bake Temperature	240°C

HP 5890 Series II OR AG6890 Gas Chromatograph

<u>PARAMETER</u>	<u>SETTING</u>
Injector temperature	225°C
Column Equilibration time	0.5 minutes
Initial Oven Temp	35°C
Initial Oven Time	3.0 minutes
Temperature Ramp	10°C/minute
Final Oven Temp	250°C
Final Hold Time	0 minutes
Column Flow rate	~ 8 mL/min
Detector B (PID) Temp	280°C
Signal 1 (A)	FID
Signal 2 (B)	PID (If Present)
Column Flow	Constant (If applicable)
Split flow	20 mL (If applicable)
Split Ratio	2 (If applicable)

Recommended Purge and Trap Concentrator operating parameters**Tekmar 3000 Concentrator**

The recommended operating method for the Tekmar 3000 A purge & trap concentrator which is interfaced with the AG6890 GC and Varian Archon Autosampler is as follows.

PARAMETER	SETTING
Standby temperature	32°C
Preheat temperature	N/A
Prepurge time	N/A
Sample temperature	Ambient for medium-level/40°C for low-level
Purge Time	11 min
Dry purge	0.6 min
Purge Flow	35 - 40 mL/min
Desorb preheat temperature	245 °C
Desorb	2 min @ 250 °C
Bake	10 min @ 260 °C
Auto drain	On
Bake gas bypass	Off
Valve temperature	140 °C
Mount temperature	40 °C
Line temperature	140 °C
Bottom of trap temperature	NA

Varian Archon Autosampler

The recommended operating method for the Archon autosampler which is interfaced with the Tekmar 3000 and the HP5973 GC/MS is as follows.

PARAMETER	SETTING
Valve temperature	100 °C
Line temperature	110 °C

APPENDIX E. CHEMSTATION FILE NAMING CONVENTIONS

ChemStation File Naming Convention

File data, methods, and sequences on ChemStation computers and the LAN using the following naming conventions:

Directories

On the Workstation:

Data: C:\HPCHEM\1\Data\MDDY or D:\HPCHEM\1\Data\MDDYS

Methods: C:\HPCHEM\1\Methods or D:\HPCHEM\1\Methods

Sequences: C:\HPCHEM\1\Sequence or D:\HPCHEM\1\Sequence

For system controlling multiple instruments, 1 may be changed to reflect the instrument number

System running ChemStation versions C & D HPCHEM is named as MSDCHEM

On the LAN:

Data: I:\Room Number\Instrument\Year\MDDYS

Methods: I:\Room Number\Instrument\Methods

Sequences: I:\Room Number\Instrument\Sequence

Methods

MDDYITA

Sequence

MDDYS

Data Files

For GC:

MDDYICSS

For GC/MS

MDDYIQSS

Variables

A: Enter analysis, as follow:

1,4-Dioxane	X
504	E
TO15	A
BNA	B
BNA-L (SIM)	L
Congeners	C
P/P	P
PCB	P
RSK175	R

Soil Gas	A
TPH-G	G
TPH-D	D
VOA	V

C: Channel: A = front
B = back (if applicable)

DD: Day

I: Instrument
6890 series GCs by last number in name: e.g. 6890-1 = 1 except 580-2 = A
All GC/MSs by last letter in name: e.g. 5973L = L

M: Month 1-9, A: October, B: November, C: December

Q: QC type

BFB	F
Blank	B
CV	C
Degradation	P
DFTPP	D
IB	Z
IC	I
LCS	L
LCV	Q
Second Source	S
MS/MSD	M

S: Sequential number 1,2 3,

T: Matrix Type (if applicable)
Water W
Solid S
Air A
Oil O
Other X

Y: Year i.e. 5 for 2005

**APPENDIX F.
PREVENTIVE MAINTENANCE REQUIREMENTS**

Item	Frequency	Actions/Comments
Flowmeter calibration	2 years	Manual flowmeters only.
Syringes and/or syringe needles	As Needed	Replace syringe if dirt is noticeable in the syringe, if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged. Replace needle if septa wear is abnormal or the needle becomes clogged.
Inlet liner	As Needed	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	As Needed	Replace with liner or with signs of wear.
Inlet septum	As Needed	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	As Needed	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Solvent rinse	As needed	When chromatography degradation is due to column contamination. Only for bonded and cross-linked phases.
Replacement	As needed	When trimming and/or solvent rinsing no longer return chromatographic performance.
Ferrules		Replace ferrules when changing columns and inlet/detector parts.
FID Jets & Collector	As needed	Clean when deposits are present. Replace when they become scratched, bent, or damaged, or when having difficulty lighting FID or keeping flame lit.
Purge/Sample Lines	Annually or as needed	Bake out and purge. Clean with organic free water if necessary.
Trap	As needed	Replace when loss of performance.

Item	Frequency	Actions/Comments
PID	Annually or as needed	Clean window

APPENDIX G. TYPICAL DATA PACKAGE FORMAT

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms

EPA Review Form

ESAT technical review guide

Discrepancy Reports (if applicable)

Work Order Memo (if applicable)

Daily folder review forms or checklists

Analysis matrix listing all analytical runs

Tracking Forms

Work Order(s)

COC(s)

Sample Preparation (for projects that require extraction or digestion)

Bench Sheets (and extraction logs, where used)

Sample cleanup data and records (e.g., GPC logs)

Moisture data as applicable

[Analysis Method] Data (For each method where multiple methods in package)

Bench sheet(s), where not used in the Sample Preparation section

Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Alternatively, separate calibration and sample data as:

Initial Calibration Data

Sample Data

Miscellaneous Data

Other data as applicable (e.g., conductivity for perchlorate)

Standard Records

Standards records from LIMS (and logbook pages as needed)

STANDARD OPERATING PROCEDURE: 380
Revision: 6, Effective: 03/01/2010

[illegible]

**USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA**

STANDARD OPERATING PROCEDURE 385

EXTRACTABLE PETROLEUM HYDROCARBONS BY GC/FID

Revision 3

Effective Date: March 28, 2005

Reviewed by: _____
Richard Bauer
Chemistry Team Leader/Technical Director

_____ Date

Reviewed by: _____
K. W. Hendrix, Laboratory QA Officer

_____ Date

Approved by: _____
Brenda Bettencourt, Laboratory Director

_____ Date

Periodic Review:

Signature	Title	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____

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APPENDIX A. DEVIATIONS FROM THE REFERENCE METHOD 8015B

APPENDIX B. ANALYTES AND QUANTITATION LIMITS

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APPENDIX F. PREVENTIVE MAINTENANCE REQUIREMENTS

APPENDIX G. TYPICAL DATA PACKAGE FORMAT

APPENDIX H. INTEGRATION EXAMPLES

APPENDIX I. SOP DISTRIBUTION AND ACKNOWLEDGEMENT LIST

1 PURPOSE AND APPLICABILITY

This method describes the procedures used to analyze dichloromethane extracts for total petroleum hydrocarbons (TPH). Gas chromatography (GC) with a flame ionization detector (FID) is used for the quantitative and qualitative determination of hydrocarbons. Water samples are prepared using SOP 275 *Extraction of Water Samples by Continuous Liquid-Liquid Extraction*. Solid samples are prepared using SOP 290 *Extraction of Soil Samples Using Pressurized Fluid Extraction*.

This method is applicable to the determination of TPH as diesel and TPH as motor oil and in extracts prepared from solid or liquid samples. The method may also be used to determine kerosene (jet fuel) in these matrices. This SOP is based on procedures contained in EPA SW-846 method 8015B, Revision 2, December 1996. Deviations from the reference method are described in Appendix A.

Quantitation limits are provided in Appendix B by matrix and analyte.

2 SUMMARY

Sample extracts, which have been fortified with surrogate analytes, are injected into a GC with FID. Sample components are separated in a fused-silica capillary GC column during temperature programming and detected by the FID.

The fuel of interest is quantitated by comparing its area sum response over the retention time range which it elutes to the area sum response of a fuel standard analyzed under the same conditions as the sample. Probable identification of fuels in samples is done by comparing the chromatographic pattern generated by analysis of the sample to the chromatographic pattern of fuels analyzed under the same conditions as the standard. The identification of specific fuel types may be complicated by environmental processes such as evaporation, biodegradation, or the presence of more than one fuel type.

3 DEFINITIONS

FID - Flame Ionization Detector.

Laboratory Control Sample (LCS) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine if the methodology is in control, and if the laboratory is capable of making accurate and precise measurements. The LCS is also known as a blank spike (BS).

LIMS - Laboratory Information Management System. The Element database.

Matrix Spike (MS) and Matrix Spike Duplicate (MSD) - Two aliquots of the same environmental sample to which known quantities of the method analytes are added in the laboratory. The MS and MSD are treated exactly like a sample, and their purpose is to determine whether the sample matrix contributes bias to the analytical results and to indicate the precision associated with laboratory procedures. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations.

Method Blank (MB) - An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, internal standards, and surrogates that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

Method Detection Limit (MDL) - The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte.

Second Source Verification (SCV) - A solution of method analytes of known concentrations which are used to prepare mid level standard(s). The SCV solution is obtained from a source different from the source of calibration standards. It is used to check the accuracy of the initial calibration solutions.

Quantitation Limit (QL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The QL is the concentration of the lowest non-zero standard in the calibration curve. Sample QLs are highly matrix-dependent.

Quantitation Limit Standard (QLS) - The lowest level CAL solution. The QLS is used to verify analytical system response at the quantitation limit.

Surrogate Analyte (SA) - A pure analyte which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in a known amount before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

Stock Standard Solution (SSS) - A concentrated solution containing one or more method analytes purchased from a reputable commercial source.

Total Petroleum Hydrocarbons (TPH).

4 HEALTH & SAFETY

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation must be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

4.1.1 Dichloromethane

Dichloromethane is a suspected carcinogen. Effects of overexposure: acute inhalation or ingestion causes mild central nervous system depression. The primary toxic effect is narcosis. Other toxic effects are pulmonary edema, encephalopathy, and hemolysis. Dichloromethane irritates the eyes, skin, and respiratory tract. No systemic effects have been reported in humans, although excessive concentrations have caused cancer and liver and kidney damage in animals. Emergency and first aid - Inhalation: immediately remove to fresh air. If not breathing, administer mouth-to-mouth rescue breathing. If there is no pulse, administer cardiopulmonary resuscitation (CPR). Contact physician immediately. Eye contact: flush with water continuously for 15 minutes. Get emergency medical assistance. Skin contact: flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothes and shoes. Get emergency medical assistance. Ingestion: call local poison control center for assistance. Contact physician immediately. Never induce vomiting or give anything by mouth to a victim unconscious or having convulsions.

4.1.2 Acetone

Acetone liquid and vapors are highly flammable. Avoid heat, sparks, open flame, open containers, and poor ventilation. Effects of overexposure: Acetone is a mild eye and mucous membrane irritant, primary skin irritant, and central nervous system depressant. Acute exposure irritates the eyes and upper respiratory tract. Direct skin contact produces dermatitis, characterized by dryness and erythema through defatting of skin. High concentrations produce narcosis and hypoglycemia. Emergency first aid - Inhalation: immediately

remove to fresh air. If not breathing, administer mouth-to-mouth rescue breathing. If there is no pulse, administer CPR. Contact physician immediately. Eye contact: flush with water continuously for 15 minutes. Get emergency medical assistance. Skin contact: flush thoroughly for at least 15 minutes. Wash affected skin with soap and water. Remove contaminated clothes and shoes. Wash clothing before re-use, and discard contaminated shoes. Get emergency medical assistance. Ingestion: call local poison control center for assistance. Contact physician immediately. Never induce vomiting or give anything by mouth to a victim unconscious or having convulsions.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Flame ionization detectors use hydrogen gas as fuel. If hydrogen flow is on and no column is connected to the detector inlet fitting, hydrogen gas can flow into the oven and create an explosion hazard. Detector fittings must either be capped or have a column connected at all times.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Pollution Prevention Plan* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever

possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or their designees.

This procedure produces the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-regulated Waste	Not applicable
Sample Extracts	Hazardous Waste	See solvent, diesel fuel and motor oil MSDs

5 SAMPLE HANDLING AND PRESERVATION

5.1 Internal Chain-of-Custody

- Sample extracts for GC analysis are received from the extraction lab personnel and custody transferred to the GC laboratory staff by signing the appropriate sections in the extraction logbook. Copies of tracking sheets, chain-of-custody records, extraction logbook pages, and moisture determination records should accompany the sample extracts.
- The extracts are marked with Region 9 Laboratory numbers and checked against the tracking sheets and chain-of-custody record to determine the client sample number, case number, and Sample Delivery Group (SDG) number.

5.2 Sample Extract Storage

- Store sample extracts in the refrigerator in Room 400 maintained at > 0°C to 6°C

prior to analysis. Sample extracts must be analyzed within 40 days of extraction. Maintain a refrigerator temperature log daily. Report deviations following U.S. Environmental Protection Agency Region 9 SOP 805, *Refrigerator Temperature Monitoring*.

- Following analysis and reporting, the extracts must be stored under refrigeration for an additional 60 days before segregating for disposal. The sample results and preparation information are used to determine proper disposal.

6 INTERFERENCES

Chromatographic interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to anomalous peaks or elevated baselines in chromatograms, or by carryover when low concentration extracts are analyzed after high concentration extracts.

6.1 Extract contaminants

- Phthalate esters are commonly used as plasticizers and are easily extracted from plastic materials. Avoid contacting samples, solvents, reagents, glassware, extracts, or other sample processing apparatus with plastic materials.

6.2 Carryover

- Interfering contamination may occur when a sample containing low analyte concentrations is analyzed immediately after a sample containing relatively high analyte concentrations. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed. After analysis of a sample containing high analyte concentrations, a laboratory instrument blank should be analyzed to ensure that accurate values are obtained for the next sample.
- Interfering contamination may occur when a sample containing oil range hydrocarbons, especially with carbon numbers exceeding C₄₀, is analyzed. After analysis of a sample containing oil range hydrocarbons, a laboratory instrument blank should be analyzed to ensure that accurate values are obtained for the next sample. The column may need to be heated to an elevated temperature, not exceeding the column limit, until the baseline returns to previous levels. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis.

Minor deviations may be made in specific apparatus and materials provided that they are documented and equivalency is maintained.

7.1 Instrumentation

- Gas chromatograph with FID detector and splitless injection port (Agilent 6890, or equivalent).
- Fused Silica Capillary Gas Chromatography Column -- Any capillary column with a phase ratio (β) of about 265 that provides adequate resolution and capacity may be used. The column used for method validation was 15M x 0.32 mm x 0.1 μ m Rtx-1.
- Data Acquisition and Processing System -- Able to control the GC and to acquire, store, and process gas chromatographic data. The software must be able to calculate calibration factors and the concentrations of analytes in samples. Agilent Technologies EnviroQuant ChemStation software and data acquisition computers (or equivalent).

7.2 Reagents

- Acetone - capillary GC/GC-MS solvent grade.
Caution: Acetone liquid and vapors are highly flammable. See Section 4.1.1 for precautions.
- Dichloromethane - recycled or capillary GC/GC-MS solvent grade.

Caution: Dichloromethane is a suspected carcinogen. See Section 4.1.2 for precautions.

7.3 Standards

All standards must be entered into the Region 9 laboratory information management system (LIMS).

- Surrogate Spiking Solution - Solution of n-hexacosane ($n\text{-C}_{26}\text{H}_{54}$) in dichloromethane:acetone 2:1 v/v at 2,500 μ g/mL. Prepare from neat n-hexacosane by weighing 125 mg n-hexacosane into a 50 mL volumetric flask, dissolving it in 33 mL of dichloromethane (may require sonication or warming) and diluting to volume with acetone.

- Instrument Blank - Solution of n-hexacosane in dichloromethane at 50 µg/mL. Prepare from the surrogate spiking solution by diluting 1 mL to 50 mL in dichloromethane.
- Stock Standard Solutions - Individual solutions of analytes purchased from commercial suppliers, such as Restek #31258 (XHc Diesel Fuel #2 Composite Standard), or equivalent, or Restek #31256 (XHc Kerosene Composite standard), or equivalent, or Restek #31464 (Motor Oil Composite Standard), or equivalent, or a homologous n-alkane series covering the carbon number range of interest. These solutions are diluted with dichloromethane to make the calibration solutions.

Note: Whenever possible, the instrument should be calibrated using a sample of the fuel or oil that is contaminating the site. The calibration standard should be selected prior to the start of the project in conjunction with the client. A different calibration standard may be required if the fuel type in the sample does not match the calibration standard.

- TPH Matrix Spiking Solution - A solution of the fuel of interest at a concentration of 2,500 µg/mL in acetone. This solution is valid for six months from the date of preparation, or until ongoing QC indicates a problem exists, whichever is sooner.
- Calibration Verification Solution - Equivalent to the mid-point initial calibration solution.
- Quantitation Limit Standard (QLS) - Equivalent to the lowest level calibration standard. The QLS is used to verify instrument response at the quantitation limit.
- Second Source Verification (SCV) - Equivalent to the mid-point initial calibration solution but prepared from a source different from the source of calibration standards. The SCV is used to check the accuracy of the initial calibration solutions.

7.3.1 Calibration Solutions

Prepare TPH-diesel and TPH-motor oil calibration solutions at five concentrations in dichloromethane from stock standard solutions at concentrations of 50,000 µg/mL and surrogate spiking solutions at concentrations of 2,500 µg/mL as shown in the tables below. All solutions are valid for six months from the date of preparation, or until ongoing QC indicates a problem. A standard can also be prepared from a homologous n-alkane series covering the expected carbon number range.

TPH-Diesel Solution	Volume Used, μL	Final Volume, mL	Final Concentration, μg/mL
Stock Standard	10	10	50
Surrogate Spike	40	10	10
Stock Standard	30	10	150
Surrogate Spike	100	10	25
Stock Standard	100	10	500
Surrogate Spike	200	10	50
Stock Standard	250	10	1,250
Surrogate Spike	300	10	75
Stock Standard	800	10	4,000
Surrogate Spike	400	10	100
TPH-Motor Oil Solution	Volume Used, μL	Final Volume, μL	Final Concentration, μg/mL
Stock Standard	40	10	200
Surrogate Spike	200	10	50
Stock Standard	80	10	400
Surrogate Spike	200	10	50
Stock Standard	200	10	1,000
Surrogate Spike	200	10	50
Stock Standard	800	10	4,000
Surrogate Spike	200	10	50
Stock Standard	2000	10	10,000
Surrogate Spike	200	10	50

As an alternative to purchasing commercially available calibration solutions, standards may be prepared from neat fuels or oils as follows: Determine the density of the hydrocarbon fuel mixture by filling a tared 10 mL volumetric flask to volume with neat fuel at room temperature; record the weight in grams to the nearest 0.1mg. Divide the net weight by 10 to obtain the density in g/mL. Use the experimentally determined density in the following calculations.

Prepare a 4,000 mg/L (nominal) range standard by injecting 5 μ L of neat standard per mL of dichloromethane. The actual concentration, in mg/L, will be

5,000 times the density of the neat standard in g/mL. For example, injecting 250 μ L of kerosene into about 49 mL of solvent in a 50 mL volumetric flask, then adding additional solvent to volume, would result in a 3,910 mg/L standard assuming a density of 0.782 g/mL for kerosene.

If the neat standard, such as motor oil, is too viscous to measure with a micro liter syringe, weigh out about 200 mg (0.2 g) using an analytical balance and dilute to 50 mL with dichloromethane.

Prepare the other calibration solutions by serially diluting the 4,000 mg/L standard.

7.3.2 Storage of Standard Solutions

Store the unopened ampulated stock standard solutions at $> 0^{\circ}\text{C}$ to 6°C . Store all other working standard solutions in glass bottles or vials with Teflon lined screw caps at $\leq -10^{\circ}\text{C}$ and protect all standards from light. Fresh standards should be prepared every six months, or sooner if comparison with check-standards indicates a problem. The standard solution must be checked frequently for stability. Replace all working standard solutions after six months, or sooner if comparison with SCV samples indicates a problem. CAUTION: Analysts must allow all standard solutions to equilibrate to room temperature before use. Hexacosane has poor solubility at low temperatures. Solutions containing hexacosane must be sonicated before use.

7.4 Supplies

- Volumetric flasks, type A, 100-mL, 50-mL, 25-mL, and 10-mL.
- Microliter syringes (10- μ L, 25- μ L, 50- μ L, 100- μ L, 250- μ L, 500- μ L, and 1-mL).

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set up the instrument operating parameters provided in Appendix D. Adjust as needed to meet method and SOP requirements and chromatographic practice.

Enter data into ChemStation using file naming conventions provided in Appendix E.

Perform a blank column compensation run if necessary after the GC system stabilizes to establish the column bleed background which will be subtracted from all subsequent GC runs. Whenever conditions change or the system becomes contaminated it may be necessary to repeat this step to ensure a flat baseline for reliable integration.

Prior to analyzing calibration, QC, or field samples make a LIMS batch and sequence as required to obtain LIMS assigned IDs for the calibration and QC samples.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

Perform an initial calibration using a minimum of five calibration standards to establish an external standard linear calibration using the average calibration factor. See Section 9.2.1 of this SOP for required frequency and QC limits. Prepare calibration solutions according to Section 7.3.1.

Analyze each of the initial calibration standards and an instrument blank as described in Section 8.3.2. Using the chromatography software, calculate the average calibration factors and %RSD. See 8.3.3 for integration procedures.

8.2.2 Retention Time Windows

Calculate retention time windows when a new GC column is installed or when a new DOC is required for the surrogate on each chromatographic column and instrument. Before establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the sample matrix to be analyzed. See Section 9.2 for retention time window criteria.

- Record the retention time to three decimal places (e.g., 9.007) for the surrogate from three injections over the course of a 72 hour period. Serial injections or injections over a period of less than 72 hours may result in retention time windows that are too tight.
- Calculate the mean and standard deviation of the three absolute retention times for the surrogate using Equation 4. If the standard deviation of the retention times for a target compound is less than 0.01 minutes then use a default standard deviation of 0.01 minutes.
- The width of the retention time window for the surrogate is defined as ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period. If the default standard deviation is employed, the width of the window will be ± 0.03 minutes.

8.2.3 Secondary Calibration Verification

- Analyze a SCV standard immediately after each initial calibration. See Section 9.2.3 of this SOP for frequency and QC limits.

Note: Fuel standards from different sources may contain different compound mixes and therefore may not be reliable for verifying calibration standards.

8.2.4 Calibration Verification

Analyze a calibration verification standard in every 12-hour analytical time period prior to an instrument blank analysis. The calibration verification standard is used to validate the initial calibration standard for the samples run during the associated 12-hour time period. The calibration verification standard concentrations are 500 µg/mL for TPH-diesel and 1,000 µg/mL for TPH-motor oil. See Section 9.2.4 for calibration verification requirements and Appendix C for QC limits.

8.2.5 Quantitation Limit Standard

- Analyze a quantitation limit standard (QLS) each day when analyses of field or QC samples are performed. The QLS is used to verify analytical system response at the quantitation limit. The QLS is 50 µg/mL for TPH-diesel and 200 µg/mL for TPH-motor oil. See Section 9.2.5 for QLS requirements and Appendix C for QC limits.
- If the initial calibration, the SCV, and the IB meet all the criteria specified in Appendix C, the remainder of the 12-hour analytical period may be used for the analysis of field and QC samples using the average CF from the initial calibration to quantitate the data.

8.3 Sample Analysis

8.3.1 Sample Preparation

Samples can be analyzed only after the initial calibration or calibration verification, QLS, MB, and IB meet all of the appropriate criteria specified in Appendix C.

Generate a LIMS batch and sequence as required prior to analyzing QC or field samples to obtain LIMS assigned IDs for the calibration and QC samples.

8.3.2 Analytical Sequence and Analysis

Set up a data acquisition sequence from the LIMS sequence using the GC operating parameters in Appendix D. Identify samples by laboratory sample ID.

Additional header information shall include the dilution factor, instrument ID, and the analyst's initials. Enter this sequence in the instrument run log, if used.

Include all QC sample extracts. See Section 9.3 for batch QC frequency and corrective action requirements. It is highly recommended that the MB, LCS, and MS/MSD extracts be analyzed as early as possible in the analysis of a batch.

8.3.3 Analyte Identification and Quantitation

After completion of analysis, review the chromatogram to identify the fuel in the sample. Compare the chromatographic pattern generated by analysis of the sample to the chromatographic pattern of fuels analyzed under the same conditions as the sample by visually comparing the printed chromatograms or by electronically overlaying the chromatograms, if needed. The fuel and oil ranges contain large number of chemical components which overlap. Use the following table in reporting the fuel and oil ranges:

Report	Chromatogram indicates the presence of:			
	TPH-Diesel Only	TPH-Motor Oil Only	Both	Other components
TPH-Diesel	Quantitate against the TPH-diesel standard and report.	Quantitate the overlap area against the TPH-diesel standard and report the value as "non-detect"*	Manually drop a vertical line from the valley separating the components and report both components.	Quantitate, flag as estimated, and indicate findings in the narrative.
TPH-Motor Oil	Quantitate the overlap area against the oil standard and report the value as "non-detect"*	Quantitate against the oil standard and report.	Manually drop a vertical line from the valley separating the components and report both components.	Quantitate, flag as estimated, and indicate findings in the narrative.

* If the sample concentration is greater than the QL, raise the QL to the value found. If the sample concentration is less than the QL, report as non-detect at the QL.

Review the baseline drawn by the data system integrator to verify that it accurately reflects the area response of the fuel in the sample. If in the judgment of the analyst, it does not then draw a manual baseline from the point where the baseline starts to deviate from the trend to a second inflection point in the chromatogram, or to the end of the chromatogram if there is no second inflection point. See Appendix G for examples. Document any manual integrations following the procedure described in U.S. Environmental

Protection Agency Region 9 SOP 835, *Chromatographic Integration Procedures.*

If only TPH-diesel is present, integrate the retention time over which it elutes and report it. Quantitate the overlap area against the TPH-motor oil standard and report this value as non detected (U). If only TPH-motor oil is present, quantitate and report in like manner, reporting the TPH-motor oil value as calculated and the TPH-diesel overlap as non detected (U).

If both TPH-diesel and TPH-motor oil range components are present manually drop a vertical line from the valley or inflection point separating the two components. Use this retention time as the end RT for TPH-diesel and the beginning RT for TPH-motor oil and quantitate and report both components. If there is no valley or inflection point separating the two components, determine the RT for separating the ranges by overlaying the chromatograms for the TPH-diesel and TPH-motor oil CV standards.

Quantitate the chromatogram using the appropriate initial calibration mean CFs for the identified fuel. If applicable, indicate degree of similarity of sample chromatogram to the fuel to which it is being compared. Print out quantitation reports and chromatograms for each field and QC sample.

- Water calculations

Calculate results for target analytes using Equation 1:

Equation 1:

$$\text{Conc. ug / L} = \frac{A_x \times V_t \times DF}{CF \times V_o}$$

Where:

A_x = area sum response of the sample
 DF = dilution factor
 CF = mean calibration factor from the initial calibration
 V_o = volume of water extracted in Liters
 V_t = volume of concentrated extract in mL

- Soil calculations

Calculate results for target analytes using Equation 2:

Equation 2:

$$\text{Conc. mg/kg (dry weight basis)} = \frac{A_x \times V_t \times DF}{CF \times W \times D}$$

Where:

A_x = area sum response of the sample
 D = dry weight factor (Percent solids/100)
 W = weight of sample in grams
 CF = mean calibration factor from the initial calibration
 V_t = volume of concentrated extract in mL
 DF = dilution factor

Yields concentration units of $\mu\text{g/g} = \text{mg/kg}$

- Check surrogate recovery for each sample with criteria in Appendix C.
- Dilute and inject a new aliquot of the extract if the on-column concentration of the fuel of interest in any sample exceeds the initial calibration range. Use the following criteria in performing dilutions:
 1. Use the results of the original analysis to determine the approximate dilution factor required to get the fuel of interest within the initial calibration range.
 2. Do not dilute MS/MSD samples to get either the spiked or non- spiked target compounds within the initial calibration range. If the sample from which the spike aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis, and note the problem in the report narrative.
 3. In the case of extremely contaminated samples several dilutions may be required.
 4. Distinguish between the undiluted and diluted analysis by adding a "RE[X]" suffix to the laboratory sample ID on the diluted analysis, where X is a sequential number that identifies the reanalysis.
 5. Demonstrate that there is no carryover to subsequent analyses after a sample is analyzed that contains compounds at a level exceeding the initial calibration range of the system. This can be done by analyzing an instrument blank.

Review the results for the sample analyzed immediately after a contaminated sample for all compounds that were in the contaminated

sample that exceeded the limits above. The sample should not contain a concentration above the QL for the target compound that exceeded the limits in the contaminated sample.

6. The most common cause of carryover is hydrocarbon in the oil/asphalt range. This may require cleaning the injection port and baking out the column.

8.3.4 QC Review

As soon as possible after analysis (typically prior to entry into LIMS), inspect sample and QC data for compliance with QC limits in Appendix C. If no significant problems are found, review the following QC data for compliance with SOP requirements:

- Target analyte results must be within range of initial calibration.
- Process and review results of instrument QC (CV, QLS) immediately after their analysis to verify that the results are within QC limits. If the instrument QC results are not within QC limits, stop the sequence and take corrective action before resuming the sequence. See Section 9.2 for instrument QC requirements.
- Process and review the results for the MB, LCS, and MS/MSD batch QC samples and verify that the results are within QC limits. See Section 9.3 for batch QC requirements.
- Check that surrogate compound retention times are within the window specified in Section 9.4. Determine if surrogate recoveries for field and QC samples are within QC limits.
- Review all sample results to determine if any samples need to be re-analyzed at a dilution.
- If a run is rejected for any reason, mark the raw data “Not Used” in large print and document the reason on the quantitation report.

8.3.5 Data Export and LIMS Entry

- Generate epatemp.txt files for field and QC samples by also printing the report to the screen; these files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table.
- Copy sample data files from the local drive to the appropriate instrument

data subdirectory on the Region 9 LAN to make them available to LIMS and to archive them.

- Create an empty upload file containing the samples analyzed in the LIMS batch or sequence. Import and merge the data files using the LIMS DataTool module. Load the resulting merged data file into the LIMS Data Entry/Review table. See LIMS manual for detailed procedure.
- Edit dilutions in DataTool or LIMS entry table as needed.
- Review results in the LIMS. Qualify and flag results in the LIMS Data Entry/Review table following Appendix M of the Region 9 Quality Assurance Manual.

8.3.6 Instrument Maintenance

The following are suggested remedial actions that may improve method performance; re-calibration may be necessary after most of these actions:

- Check and adjust GC operating conditions and temperature programming parameters.
- Clean or replace the splitless injector liner with a new, silanized liner.
- Break off a short portion of the GC column from the end near the injector, or replace the column. Breaking off a portion of the column will somewhat shorten the analyte retention times.
- Prepare fresh calibration solutions and repeat the initial calibration.
- Replace any components in the GC that permit analytes to come in contact with hot metal surfaces.

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook. Preventative maintenance procedures are listed in Appendix E.

The following sections describe possible causes and corrective actions for common problems. Refer to Appendix E for routine preventative maintenance procedures and schedule.

Symptom

- Carryover
Possible causes: Analyzing a sample containing high mole weight components or analyzing high-level and low-level samples sequentially.
Corrective action: As necessary, replace inlet liner, clean inlet, bake out

inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.
Possible cause: column flow rate problem.
Corrective action: check flow rate and adjust as necessary.
- Longer retention time and or smaller peaks.
Possible causes: column flow rate problem, injection port leak, or column contamination.
Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.
- Loss of resolution.
Possible causes: column flow rate problem, injection port leak, or column contamination.
Corrective action: Check for leaks, replace septum, replace the liner, replace inlet seal, and clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

9 QUALITY CONTROL

9.1 Demonstration of Capability

The EPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of the QC Criteria is provided in Appendix C.

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in U.S. Environmental Protection Agency Region 9 Laboratory SOP 880 *Demonstration of Laboratory Capability and Analyst Proficiency* for more details.

9.2 Instrument QC

9.2.1 Initial Calibration

Demonstration and documentation of an acceptable initial calibration are

required before any samples are analyzed. The calibration is a five level external standard calibration method.

The GC system must be calibrated whenever corrective action changes instrument response (e.g., detector gas adjustment, column replacement, etc.) is performed or if the calibration verification criteria cannot be met.

- Analyze the initial calibration standards according to Section 8.2.1.
- Obtain area sums for each fuel mixture or homologous n-alkane series over the retention time range during which at least 90% of the material elutes.
- Draw a manual baseline if the baseline drawn by the data system integrator does not accurately reflect the total area response, including the unresolved area that lies below the individual peaks, of the fuel. Draw a manual baseline from the point where the baseline starts to deviate from the trend to a second inflection point in the chromatogram, or to the end of the chromatogram if there is no second inflection point. Manual integrations must conform to U.S. Environmental Protection Agency Region 9 SOP 835, *Chromatographic Integration Procedures*. See Appendix G for example chromatograms.
- The data system calculates the calibration factor (CF) for the target fuel or n-alkane mixture from its area sum response and for the surrogate for all five calibration standards using Equation 3.

Equation 3

$$CF = (A_x) / (C_x)$$

Where

A_x = Area of compound x

C_x = Concentration of the standard injected (μg/mL)

- Calculate the average CF for all analytes.
- Calculate the percent relative standard deviation (%RSD) of the CF values for each compound using Equation 4.

Equation 4

$$\%RSD = (SD / CF_{avg}) \times 100$$

Where SD is calculated as:

$$SD = \sqrt{\frac{\sum_{i=1}^n (CF_i - CF_{ave})^2}{n-1}}$$

- Verify that the %RSD of both the target fuel(s) and surrogate are within QC limits immediately after the initial calibration is finished. See Appendix C for QC limits.
- If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the failed one in the ICAL. If more than one standard fails, corrective action is required.

9.2.2 Retention time windows

Retention time windows must be established when a new GC column is installed or when a new DOC is required.

- All surrogates in the field and QC samples must fall within the established retention time windows.
- If the surrogate retention time does not fall within the retention time window, evaluate the chromatogram and take corrective action to restore the system if necessary. If repairs to the system are required then a new initial calibration must be performed.

9.2.3 SCV Analysis

Analyze an SCV sample immediately after each initial calibration. See Appendix C for QC limits. If the SCV sample fails it may be repeated once. If the second SCV fails, the cause for failure must be determined and corrected before analysis of samples can proceed.

Note: Fuel standards from different sources may contain different compound mixes and therefore may not be reliable for verifying calibration standards.

9.2.4 Calibration Verification

- Analyze a calibration verification standard at the beginning of each 12-hour analytical period and at the end of the 12-hour analytical period. The 12-hour analytical period begins with the injection of the calibration

verification standard and ends with the completion of analysis of the last sample that can be injected within 12 hours of the beginning of the period. Analysis of calibration verification standards, bracketed by instrument blanks, after every ten samples is recommended. The calibration verification standard is used to validate the initial calibration for the samples run during the associated 12-hour time period.

- Analyze the calibration verification standard according to Section 8.2.4.
- Calculate the calibration factor (CF) for the target fuel from its area sum response and for the surrogate compound using Equation 3.
- Calculate the percent difference (%D) between the calibration verification CF and the initial calibration average CF for the target fuel and the surrogate using Equation 5.

Equation 5.

$$\%D = \frac{CF_c - CF_{avg}}{CF_{avg}} \times 100$$

Where:

CF_c = calibration verification CF

CF_{avg} = initial calibration average CF

- The %D must be within QC limits. See Appendix C for QC. If an analyte fails this criterion a second calibration verification may be analyzed. Repeated failure requires that corrective action be taken to restore the system before any additional samples are analyzed. All affected samples must be re-analyzed.

If repairs to the system are required then a new initial calibration must be performed. The analyst should observe trends in the data such as declining response, erratic response, etc., which may signal the need for instrument maintenance.

- Acceptable sample analyses must be bracketed by the analyses of calibration verification standards that meet QC limits.

9.2.5 Quantitation Limit Standard (QLS)

- Analyze a quantitation limit standard (QLS) each day when analyses of field or QC samples are performed. The QLS is used to verify analytical system response at the quantitation limit. The QLS is analyzed at 50 µg/mL of

TPH-diesel and 200 µg/mL for TPH-motor oil.

- Analyze a standard of the fuel of interest at the concentration of the lowest initial calibration level according to Section 8.2.1 of this SOP.
- Calculate the concentration of the target fuel.
- Calculate the percent of true value for the target fuel using Equation 6.

Equation 6:

$$\% \text{ True Value} = (\text{Cd} / \text{Tv}) \times 100$$

Where:

Cd = Concentration determined by analysis

Tv = True value of standard

- If the %D is not within the QC limits in Appendix C, a second QLS sample may be analyzed. Repeated failure requires that the cause be determined and corrected before analysis of samples can begin. If repairs to the system are required then a new initial calibration must be performed.

9.2.6 Instrument Blank (IB)

- Analyze an instrument blank after the initial calibration or calibration verification is performed and before samples are analyzed. The instrument blank chromatogram and quantitation report must be checked to insure it is within QC limits in Appendix C. It is also important to monitor the chromatographic baseline to insure there are no humps or disruptions which could be integrated as peak area when sample constituents elute on top of them. Surrogate recovery is not evaluated for IB samples. If the instrument blank meets these requirements sample analysis may proceed.

9.3 Batch QC

9.3.1 Method Blank

- A method blank (MB) is extracted and analyzed with each extraction batch or every 20 samples, whichever is more frequent, to demonstrate that the entire analytical system - from extraction through GC analysis - is free of contamination.
- Analyze the MB according to Section 8.
- Evaluate the MB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.
- Corrective action - If the MB is not acceptable, the source of the contamination must be found and eliminated and the problem documented before analysis can proceed. If re-analysis does not solve the problem, the

batch may have to be re-extracted. Corrective action is decided by the EPA TOPO on a case by case basis.

- If the surrogate recovery does not meet acceptance criteria, re-analyze the extract. If the surrogate recovery still does not meet acceptance criteria, the batch may have to be re-extracted. Corrective action is decided by the EPA TOPO on a case by case basis.

9.3.2 Laboratory Control Sample

- Analyze a laboratory control sample (LCS) to demonstrate that the analytical system is in control. A LCS is extracted and analyzed once per extraction batch or every 20 samples, whichever is more frequent. The LCS is an MB spiked with laboratory fortified matrix solution.
- Analyze a LCS containing the target fuel at a concentration of 2,500 µg/L for water or 50 mg/kg for soil according to Section 8 of this SOP.
- Calculate the percent recovery (%R) using Equation 7.
- The %R must be within the QC limits in Appendix C. If acceptable accuracy cannot be achieved, the problem must be located and corrected prior to reporting any sample data and before additional samples are analyzed.

9.3.3 Matrix Spike/Matrix Spike Duplicate

- Laboratory fortified matrix (MS) and duplicate (MSD) samples are extracted and analyzed for each SDG, which typically contain twenty or fewer samples. Matrix QC samples are usually designated in the field. In the event that a sample was not designated as the laboratory fortified matrix spike sample and adequate sample volume exists, the analyst will choose one representative sample from the SDG for QC analysis. The analyst shall not designate any obvious field blanks as the QC sample.
- Analyze the MS/MSD extracts according to Section 8 of this SOP as soon as possible following the analysis of the sample designated as the laboratory fortified matrix sample.
- Calculate the recovery of each compound using Equation 7.

Equation 7:

$$\% \text{ Rec} = ((\text{SSR} - \text{SR})/\text{SA}) \times 100$$

Where,

SSR = Spiked sample result

SR = Sample result

SA = Spike added

- Calculate the relative percent differences (RPD) of the recoveries of each

compound in the MS and MSD using Equation 8.

Equation 8:

$$RPD = \frac{(MSC - MSDC)}{(MSC + MSDC) / 2} \times 100$$

Where,

MSC = Measured concentration of analyte in MS

MSDC = Measured concentration of analyte in MSD

- See Appendix C for QC limits.

The MS/MSD recovery limits are advisory limits only. If the limits are not met, then no further action is required, as long as the LCS is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the spike compounds. A new solution should be prepared if the recoveries are not within 20% of expected.

- The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX+ = PASS - = FAIL								
CASE	1	2	3	4	5	6	7	8
BS - % REC	+	+	+	+	-	-	-	-
MS/MSD -% REC	+	-	+	-	+	-	+	-
MS/LMSD - RPD	+	+	-	-	+	+	-	-

Case 1: Extraction batch acceptable.

Case 2: Extraction batch acceptable; matrix effect confirmed.

Cases 3 & 4: Extraction batch is unsatisfactory. Investigate MS/MSD problem and document findings in report narrative.

Case 5: Extraction batch rejected. Batch may have to be re-extracted unless LCS problem is determined and documented.

Cases 6, 7 & 8: Extraction batch rejected. Re-extract batch.

9.4 Sample QC

9.4.1 Surrogate Recovery

- Calculate the surrogate recovery in all field and QC samples immediately after analysis using the following formula:

Equation 9:

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

- The surrogate recovery must be within QC limits. See Appendix C for QC limits.
- Take the following steps if surrogate recovery is not within the limits:
 1. Ensure that there are no calculation errors, and check the system performance.
 2. Re-analyze the extract if a system performance problem or calculation error is not evident. The extract may be diluted for re-analysis if examination of the chromatogram so indicates.
 3. If re-analysis of the extract does not solve the problem, the sample may have to be re-extracted. Corrective action is decided by the EPA TOPO on a case by case basis.
- Do not re-extract undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the run log.
- Do not re-analyze the MS or MSD samples, even if surrogate recoveries are outside the limits.
- If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis. The similarity in surrogates recoveries in the sample and spike analyses must be discussed in the report narrative
- If the surrogate recoveries of the re-analysis of the extract are within limits, then:
 1. If the re-analysis was undiluted, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding a "RE[X]" suffix to the laboratory sample ID on the re-analysis. The problem must be documented in the report narrative.

2. If the re-analysis was diluted, the problem was a matrix effect. Report the results from the re-analysis and submit the data from both analyses and discuss the result in the report narrative. Distinguish between the undiluted and diluted analysis by adding a "RE[X]" suffix to the laboratory sample ID on the diluted analysis. The problem must be documented in the report narrative.
 3. If the surrogate recoveries of the re-extraction are within limits, then the problem was within the laboratory's control. Report the results from the re-extraction. Distinguish between the original analysis and the re-analysis by adding the "RE[X]" suffix to the laboratory sample ID in the re-analysis. The problem must be documented in the report narrative.
- If the re-extraction does not solve the problem, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE[X]" suffix to the laboratory sample ID in the re-analysis. The problem must be documented in the report narrative.

9.5 Method Performance

Region 9 Laboratory performance for this procedure from January 1, 2003 to February 28, 2005 is summarized in the following table.

Method Performance

Analyte	Matrix	QC Type	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2 σ)
TPH-d	water	LCS	46	89.8	70.7-109
TPH-d	solid	LCS	29	87.9	73.9-102
TPH-mo	water	LCS	Insufficient data	-	-
TPH-mo	solid	LCS	Insufficient data	-	-

The following functional areas of the SOP may be significant sources of analytical error:

- Poor extraction efficiency due to specific analyte characteristics or other problems.
- Standard degradation.
- Chromatographic separation and peak integration.

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QL, MS/MSD, and LCS) are recorded in the Element database. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Analytical sequence

Document the analytical sequence in the Element database and the instrument Run Log.

Record the instrument ID and the LIMS calibration ID for each sequence. Record the Lab number, analysis, container, position, LIMS standard ID, LIMS IS ID as applicable for each field and QC sample in the Element analysis sequence.

Record the Case and SDG number and other run log header information as applicable. Record the data file name, date and time of analysis, analyst initials, laboratory sample IDs, client sample IDs, dilution factors and comments, if any for each field and QC sample in the run log.

10.3 Analytical Report and Data Package

Analytical reports are produced using the Element database. The data package is produced from Element database and manual log records. Appendix F provides the typical format for data package deliverables.

10.4 Maintenance Logbook

Maintain a maintenance logbook for each instrument. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control. Document all preventive or routine maintenance performed, as well as repairs or corrective or remedial actions in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.5 SOP Distribution and Acknowledgement

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. Document using the SOP Distribution and Acknowledgement List as shown in Appendix H.

11 REFERENCES

Agilent Technologies 6890 Gas Chromatograph Users Manual

Agilent Technologies EnviroQuant ChemStation User's Guide

U.S. Environmental Protection Agency, *Method 8000B, Determinative Chromatographic Separations, Revision 2, December, 1996.*

U.S. Environmental Protection Agency, *Method 8015B, Nonhalogenated Organics Using GC/FID, Revision 2, Dec. 1996.*

U.S. Environmental Protection Agency Region 9 SOP 125, *Disposal Procedures for Unused Aqueous Environmental Samples.*

U.S. Environmental Protection Agency Region 9 SOP 275, *Extraction of Water Samples by Continuous Liquid-Liquid Extraction.*

U.S. Environmental Protection Agency Region 9 SOP 290, *Extraction of Soil Samples Using Pressurized Fluid Extraction.*

U.S. Environmental Protection Agency Region 9 SOP 706, *Laboratory Waste Management Procedures.*

U.S. Environmental Protection Agency Region 9 SOP 805, *Refrigerator Temperature Monitoring.*

U.S. Environmental Protection Agency Region 9 SOP 835, *Chromatographic Integration Procedures.*

U.S. Environmental Protection Agency Region 9 SOP 840, *Notebook Documentation and Control.*

U.S. Environmental Protection Agency Region 9 Laboratory SOP 880, *Demonstration of Capability.*

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD 8015B

1. The reference method reports petroleum hydrocarbons as diesel range organics (DRO) while this SOP reports TPH as diesel. In the SOP, the retention time range for TPH-diesel is established from diesel fuel standards, not the retention time of C₁₀ and C₂₈ alkanes as specified in the reference method. In addition, the SOP extends the chromatographic range of the method to include TPH as motor oil as an analyte.
2. The CF is area/concentration unit (µg/mL) not area/mass (ng) as in the reference method. The formulas for determining sample analyte concentrations have been modified to reflect this change.
3. Control limits for surrogate, LCS, and MS/MSD recoveries are specified in the SOP, not from evaluation of laboratory data.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

Hydrocarbon Fuel	QL, on column, µg/mL	QL, Solid, mg/kg (30g sample)	QL, Water, µg/L (1 L sample)
Diesel	50	5	250
Oil range	200	20	1,000

APPENDIX C.
CONTROL MEASURES AND CRITERIA

QC MEASURE	CRITERIA
Initial Calibration (ICAL)	RSD < 20
Second Source Verification (SCV)	Analyze after ICAL. CF within 30% of mean ICAL CF
Calibration Verification (CCV)	Analyze before QC or field samples and every 12hrs, or more frequently, thereafter. Results: %D \leq \pm 15
Quantitation Limit Standard (QLS)	Analyze each day that field or QC samples are analyzed. Result: \pm 40% of true value
Method Blank (MB)	Extracted once per extraction batch or every 20 samples, whichever is more frequent. Results must be < 1/2 QL of target analytes.
Instrument Blank (IB)	< 1/2 QL of target analytes
Laboratory Control Sample (LCS) fortified with Diesel	Extracted once per extraction batch or every 20 samples, whichever is more frequent. Result: %R between 70 – 130
MS/MSD fortified with Diesel	Extracted once per SDG or every 20 samples, whichever is more frequent. Result: %R between 70 - 130 and RPD \leq 25
Surrogate Recovery of QC and field samples (except IB)	%R between 70 - 130

APPENDIX D. RECOMMENDED INSTRUMENT OPERATING PARAMETERS

Instrument: Agilent 6890

Chromatographic column: 15m x 0.32mm ID, 0.1µm film (Restek Rtx-1)

OVEN

Maximum temperature: 350°C
 Equilibration time: 0.50 min.
 Initial temperature: 50°C
 Initial time: 2.00 min.

Ramp:
 Rate 1: 15.00°C/min
 Final temperature 1: 325
 Final time 1: 14.00 min.

INLET

Mode: Pulsed splitless
 Temperature: 320°C
 Pressure: 3.00 psig
 Pulse pressure: 10.0 psig
 Pulse time: 0.30 min
 Purge flow: 60 mL/min.
 Purge time: 0.30 min.
 Gas saver: On
 Gas saver flow: 20.0 mL/min
 Gas saver time: 2.00 min.
 Carrier gas: Helium

COLUMN

Mode: Ramped pressure
 Initial pressure: 3.00 psig
 Initial time: 2.00 min.
 Rate 1: 0.61 psig/min.
 Final pressure 1: 20.00 psig
 Final time 1: 0.13 min.
 Rate 2: 20.00 psig/min.
 Final pressure 2: 30.00 psig
 Final time 2: 5.00 min.
 Nominal initial flow: 1.1 mL/min.
 Average velocity: 21 cm/sec

DETECTOR (FID)

Temperature: 350°C
 Hydrogen flow: 40 mL/min.
 Air flow: 440 mL/min.
 Mode: Constant makeup
 flow
 Makeup flow: 49.0 mL/min
 Makeup gas: Nitrogen

SIGNAL

Signal: Signal - Col Comp
 Data rate: 50 Hz
 Start save time: 1.80 min.
 Stop save time: 30.00 min.
 Column Comp: On

INJECTOR (7673)

Sample washes: 1
 Sample pumps: 3
 Injection volume: 2.0 microliters
 Syringe size: 10 microliters
 PostInj Solvent A washes: 3
 PostInj Solvent B washes: 3
 Viscosity delay: 0 seconds
 Plunger speed: Fast
 Pre Injection dwell: 0.00 min.
 Post Injection dwell: 0.00 min.

APPENDIX E.
CHEMSTATION FILE NAMING CONVENTIONS

ChemStation File Naming Convention

File data, methods, and sequences on ChemStation computers and the LAN using the following naming conventions:

Directories

On the Workstation:

Data: C:\HPCHEM\1\Data\MDDY or D:\HPCHEM\1\Data\MDDYS

Methods: C:\HPCHEM\1\Methods or D:\HPCHEM\1\Methods

Sequences: C:\HPCHEM\1\Sequence or D:\HPCHEM\1\Sequence

For system controlling multiple instruments, 1 may be changed to reflect the instrument number

System running ChemStation versions C & D HPCHEM is named as MSDCHEM

On the LAN:

Data: I:\Room Number\Instrument\Year\MDDYS

Methods: I:\Room Number\Instrument\Methods

Sequences: I:\Room Number\Instrument\Sequence

Methods

MDDYITA

Sequence

MDDYS

Data Files

For GC:

MDDYICSS

For GC/MS

MDDYIQSS

Variables

A: Enter analysis, as follow:

1,4-Dioxane X

504 E

TO15 A

BNA B

BNA-L (SIM) L

Congeners C

P/P P

PCB	P
RSK175	R
Soil Gas	A
TPH-G	G
TPH-D	D
VOA	V

C: Channel: A = front
B = back (if applicable)

DD: Day

I: Instrument
6890 series GCs by last number in name: e.g. 6890-1 = 1 except 580-2 = A
All GC/MSs by last letter in name: e.g. 5973L = L

M: Month 1-9, A: October, B: November, C: December

Q: QC type

BFB	F
Blank	B
CV	C
Degradation	P
DFTPP	D
IB	Z
IC	I
LCS	L
LCV	Q
Second Source	S
MS/MSD	M

S: Sequential number 1,2 3,

T: Matrix Type (if applicable)
Water W
Solid S
Air A
Oil O
Other X

Y: Year i.e. 5 for 2005

APPENDIX F.
PREVENTIVE MAINTENANCE REQUIREMENTS

Item	Frequency	Actions/Comments
Gas purifiers (carrier gas & detector gas)	Annually	Replacement schedule is based on capacity and grade of gases. In general, replace non-indicating traps every 6-12 months or when indicating traps start to change color. Replace indicating traps when indicating material is spent.
Split vent trap	Annually	Replace.
Flowmeter calibration	2 years	Manual flowmeters only.
Syringes and/or syringe needles	As Needed	Replace syringe if dirt is noticeable in the syringe, if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged. Replace needle if septa wear is abnormal or the needle becomes clogged.
Inlet liner	With each ICAL	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	With each ICAL	Replace with liner or with signs of wear.
Inlet septum	Daily (when analyzing samples)	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	With each ICAL	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Solvent rinse	As needed	When chromatography degradation is due to column contamination. Only for bonded and cross-linked phases.
Replacement	As needed	When trimming and/or solvent rinsing no longer return chromatographic performance.
Ferrules		Replace ferrules when changing columns and inlet/detector parts.
FID Jets & Collector	As needed	Clean when deposits are present. Replace when they become scratched, bent, or damaged, or when having difficulty lighting FID or keeping flame lit.

**APPENDIX G.
TYPICAL DATA PACKAGE FORMAT**

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms

Daily folder review forms or checklists
Other review forms as applicable

Tracking Forms

Work Order(s)
COC(s)

Sample Preparation (for projects that require extraction or digestion)

Bench Sheets (and extraction logs, where used)
Sample cleanup data and records (e.g., GPC logs)
Moisture data as applicable
Analysis matrix (for organics)

[Analysis Method] Data (For each method where multiple methods in package)

Bench sheet(s) where not used in Sample Preparation section
Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Alternatively, separate calibration and sample data as:

Initial Calibration Data
Sample Data

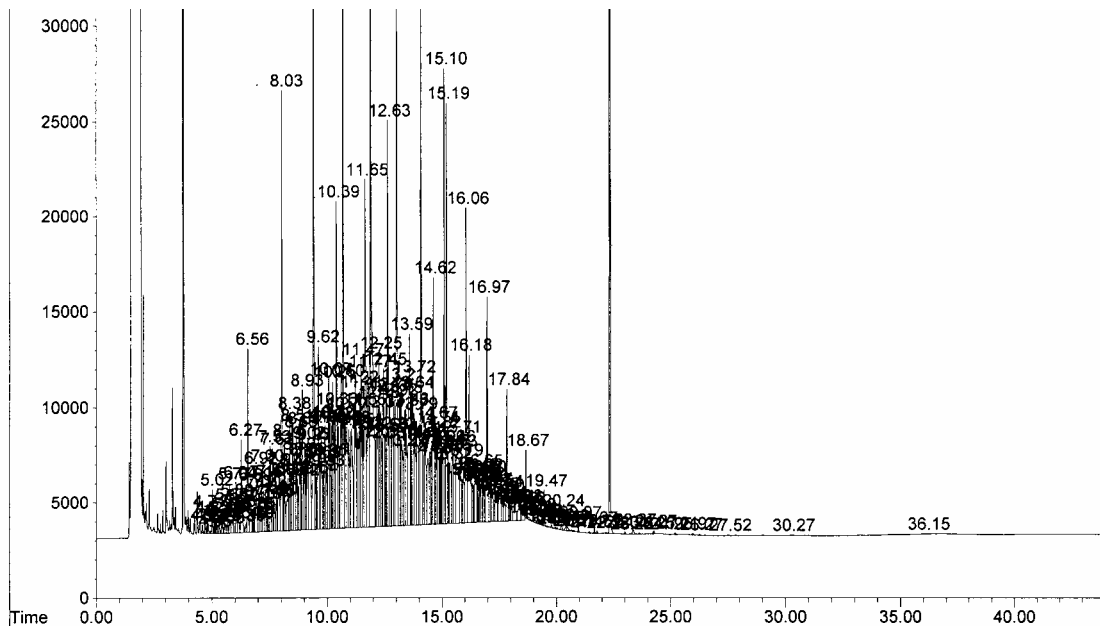
Miscellaneous Data

Other data as applicable (e.g., conductivity for perchlorate)

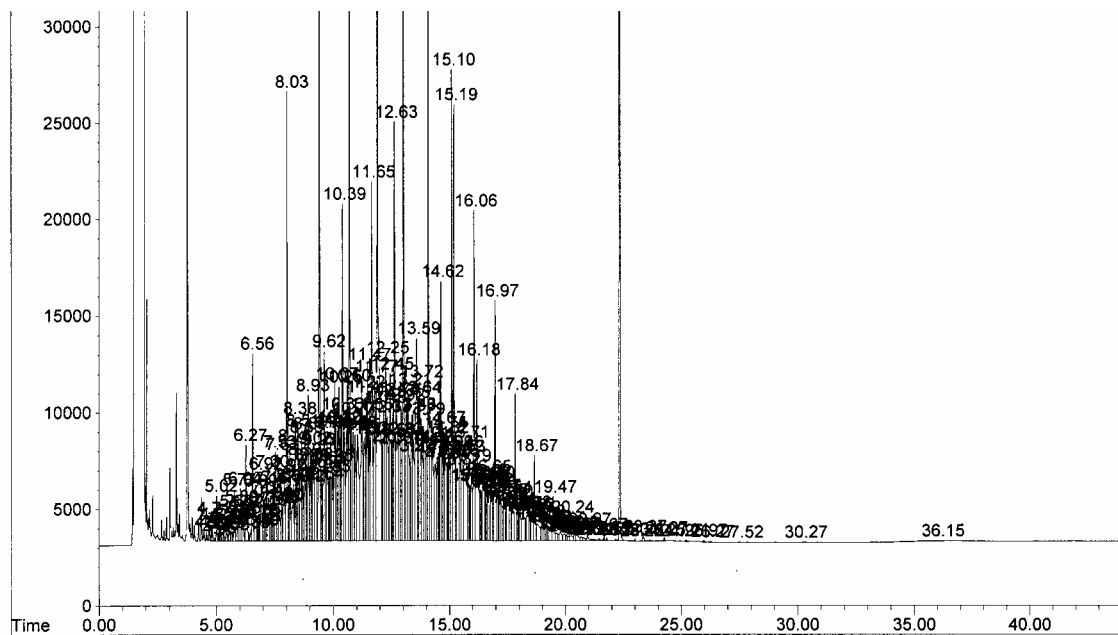
Standard Records

Standards records from LIMS (and logbook pages as needed)

APPENDIX H. INTEGRATION EXAMPLES



INCORRECT BASELINE INTEGRATION



CORRECT BASELINE INTEGRATION

APPENDIX I.
SOP DISTRIBUTION AND ACKNOWLEDGEMENT LIST

STANDARD OPERATING PROCEDURE: 385

Revision: 5, Effective: 3/28/05

Extractable Petroleum Hydrocarbons by GC/FID

I have received, read, and understood the above referenced SOP and agree to comply with the SOP when performing the subject procedure until the effective date of future revisions.

NAME	DATE DISTRIBUTED	SIGNATURE	DATE
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
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_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

**USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA**

**STANDARD OPERATING PROCEDURE 461
ANALYSIS OF TOTAL DISSOLVED SOLIDS**

Revision #6
Effective Date: August 15, 2007

Reviewed by: _____
Peter Husby
Biology Team Leader/Technical Director
Date

Reviewed by: _____
K. W. Hendrix, Laboratory QA Officer
Date

Approved by: _____
Brenda Bettencourt, Laboratory Director
Date

Periodic Review:

Signature	Title	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____

STANDARD OPERATING PROCEDURE 461

ANALYSIS OF TOTAL DISSOLVED SOLIDS

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APPENDIX A. DEVIATIONS FROM THE REFERENCE METHOD

APPENDIX B. ANALYTES AND QUANTITATION LIMITS

APPENDIX C. QUALITY CONTROL MEASURES AND CRITERIA

APPENDIX D. INSTRUMENT INFORMATION

APPENDIX E. SOP DISTRIBUTION AND ACKNOWLEDGEMENT LIST

APPENDIX F. TYPICAL DATA PACKAGE FORMAT

1 PURPOSE AND APPLICABILITY

This method is applicable for drinking, ground, surface, and saline waters, domestic and industrial wastes. This SOP is based on Standard Methods 20th Edition, Method #2540C, Total Dissolved Solids Dried at 180°C.

The range of the determination is from 20 to 20,000 mg/L. The quantitation limit is 20 mg/L total dissolved solids (TDS).

Refer to Appendix A for a description of deviations from the reference method. Refer to Appendix B for specific analytes and quantitation limits.

2 SUMMARY

A well-mixed sample aliquot is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C. If total suspended solids are also being determined, the filtrate from that method may be used to determine total dissolved solids.

3 DEFINITIONS

Analytical Sample - Any sample in which TDS is being determined, excluding method blanks or QC reference samples.

Conductivity Standard - A commercially purchased potassium chloride solution used to calibrate a conductivity meter. Sample conductivity is used to select a sample volume for analysis.

Field Duplicates (FD) - Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection and storage as well as with laboratory procedures.

Laboratory Control Sample (LCS) - A solution containing a known TDS concentration. The LCS may be prepared internally or obtained from a commercial source. It is used to check laboratory performance.

Laboratory Duplicate (LD) - An aliquot of sample prepared and analyzed separately with identical procedures. Analysis of the sample and LD indicates precision associated with the laboratory procedures, but not with sample collection, preservation or storage procedures.

Laboratory Reagent Blank (LRB) - An aliquot of reagent water that is treated exactly as a sample.

The LRB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment.

Method Detection Limit (MDL) - The minimum TDS in an environmental sample that can be measured and reported with 99% confidence that the TDS concentration is greater than zero.

Quantitation Limit (QL) - The concentration at which confidence in the reported value requires no qualifying remarks. A standard is run at the QL to verify acceptable data quality.

Quantitation Limit Standard (QLS) - A standard prepared internally that is run at the QL to verify acceptable data quality.

Sample Delivery Group (SDG) is a group of twenty samples or less from a case that is sent to the laboratory for analysis

Total Dissolved Solids (TDS) - The residue from an aqueous sample, which is passed through a glass fiber filter and dried to constant weight at 180°C. TDS is often referred to as filterable residue.

Total Suspended Solids (TSS) - TSS is defined as the solids incapable of passing through a glass fiber filter and dried to constant weight at 103-105°C. TSS is often referred to as non-filterable residue.

Water Sample - For the purpose of this method, a sample taken from matrices classified as drinking, surface, ground, or storm runoff water; or industrial or domestic wastewater.

4 HEALTH & SAFETY

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Reagents

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation must be performed in a well-ventilated area or, if appropriate, a laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to

them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Since samples are of an unknown nature, the drying of the samples should be done in an oven that is ventilated outside of the laboratory space, to prevent possible noxious fumes.

All sample dish transfers to and from the oven should be performed using tongs or heat-resistant gloves.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Pollution Prevention Plan* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from

hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM).

This procedure produces the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-regulated Waste	Not applicable
Water sample aliquots from determination of sample conductivity.	Regulated Waste	Unknown

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples may be collected in plastic or glass

5.2 Internal Chain-of-Custody

Samples are received at the Region 9 Laboratory by EPA staff in Room 503. Sample IDs and dates of collection are verified against the chain-of-custody form.

5.3 Preservation Verification

NA

5.4 Sample Storage

Samples must be stored at 0 – 6 °C

5.5 Holding Time

Samples must be analyzed within 7 days from the date of collection.

6 INTERFERENCES

6.1 TDS residue from highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation, and rapid weighing.

6.2 Samples containing high concentrations of bicarbonate will require careful and possible prolonged drying at 180°C to ensure that all the bicarbonate is converted to carbonate.

6.3 The sample size for samples containing high TDS must be selected such that the total residue does not exceed 200 mg. Too much residue in the evaporating dish will interfere with evaporation of water during the drying step. A crust may form on the residue, which can trap sample moisture, and lead to long drying times and incomplete drying.

7 APPARATUS AND MATERIALS

7.1 Instruments and Equipment

Analytical balance, capable of weighing to 0.1 mg.

ASTM Class 1 weights.

Conductivity meter.

Desiccator.

Evaporating dishes, porcelain, 150-mL volume

Filter holder or membrane filter funnel.

Graduated cylinder, 100-mL.

Ovens, 1 capable of maintaining $104 \pm 1^\circ\text{C}$, and 1 capable of maintaining $180 \pm 2^\circ\text{C}$

Plastic or Teflon spray bottle.

Suction flask, 250- to 500-mL capacity.

Vacuum pump or in-house vacuum source.

Volumetric Class "A" Pipettes, 5.0- to 10.0-mL.

Volumetric flasks, 1000-mL.

7.2 Reagents

Reagents may contain impurities, which might affect analytical data. Only reagent grade chemicals should be used. If the purity of a reagent is in question, analyze for contamination.

7.2.1 Conductivity standard - A commercially purchased potassium chloride solution with known conductivity (1000 or 1413 uS/cm) is used for conductivity measurement. Alternatively, prepare 0.01 M potassium chloride (KCl) by dissolving 0.7456 grams of anhydrous KCl in 1000 mL of reagent water. At 25°C this standard should have a conductivity of 1413 uS/cm.

7.2.2 Reagent water - All references to water in this method refer to ASTM Type II grade water.

7.3 Standards

Record the use or preparation of standards in the LIMS and label each standard with a

unique LIMS generated identification number. Maintain the original Certificate-of- Analysis for each purchased standard in a binder in the laboratory.

7.3.1 Laboratory Control Sample (LCS) - One TDS LCS solution is required per batch of 20 or fewer samples. The LCS solution may be obtained from a commercial vendor such as E.R.A. or Inorganic Ventures.

7.3.2 Quantitation Limit Standard (QLS) - One TDS QLS solution is required per batch of 20 or fewer samples. The QL standard must be prepared by diluting an aliquot of LCS solution so that the concentration will be approximately 20 mg/L TDS. The solution should be prepared fresh every three months.

7.4 Supplies

Glass fiber filter discs, without organic binder, Reeve Angel type 934-AH, Whatman Catalog No. 1827-047, or equivalent.

8 ANALYTICAL PROCEDURES

- 8.1 Calibration and Standardization - The analyst is advised to follow the recommended operating conditions provided by the manufacturer. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions satisfy the analytical requirements, and to maintain quality control data verifying instrument performance.
- 8.2 Balance Calibration Verification - On a daily basis, prior to use for TDS measurements, check the analytical balance with ASTM Class 1 weights of 100 mg, 500 mg, 1 g, 10 g and 100 g. The acceptable tolerances for those weights are taken from the NIST Handbook 44. For the weights used they are ± 1 mg, 3 mg, 4 mg 15 mg and 70 mg respectively. The results of the balance verification must be recorded in the balance logbook.
- 8.3 Conductivity Meter Verification - On a daily basis, prior to measuring sample conductivity, check the calibration of the conductivity meter by pouring out a portion of the commercially purchased potassium chloride solution (or 0.01 M KCl solution) into a container. Insert the conductivity probe into the KCl solution, stir it gently to loosen any air bubbles and allow it to sit for 15 seconds. Make sure that the meter is in the automatic temperature control (ATC) mode. The control limits are $\pm 5\%$ (taken from SOP 545, Determination of Specific Conductance). If the control limits are exceeded, check the solution and/or meter and re-calibrate. Record the results in the conductivity meter logbook.
- 8.4 Drying Oven Verification (104 °C temperature) - Set the oven temperature to 104 °C. Prior to use and before removing samples, check the oven temperature. Each temperature measurement and the measurement time must be recorded in the oven temperature logbook. The measurement of oven temperature can be done manually or by remote control (e.g., with

a temperature data logger). The oven temperature must be monitored to ensure that it is within the limits of 103-105 °C. If the oven is not able to maintain a constant temperature, it cannot be used in the TDS analysis. If the temperature drifts excessively during an analysis, the samples must be re-dried when the oven is brought back into control.

- 8.5 Drying Oven Verification (180 °C temperature) - Set the oven temperature to 180 °C. Prior to use and before removing samples, check the oven temperature. Each temperature measurement and the measurement time must be recorded in the oven temperature logbook. The measurement of oven temperature can be done manually or by remote control (e.g., with a temperature data logger). The oven temperature must be monitored to ensure that it is within the limits of $180 \pm 2^{\circ}\text{C}$. If the oven is not able to maintain a constant temperature, it cannot be used in the TDS analysis. If the temperature drifts excessively during an analysis, the samples must be re-dried when the oven is brought back into control.

8.6 Equipment Preparation

- 8.6.1 Preparation of evaporating dishes - Scrub dishes with a brush and tap water. Rinse with reagent water. Heat the clean dishes for one hour at 180°C. Cool in a desiccator to room temperature. Weigh each dish immediately before use to the nearest 0.1 mg and record the weight.
- 8.6.2 Determination of volume of sample to be filtered - Shake the sample and pour out an aliquot of the sample into a container. Insert the conductivity probe into the solution, stir it gently to loosen any air bubbles and allow it to sit for 15 seconds. Make sure that the meter is in the automatic temperature control (ATC) mode. Record the sample conductivity. From the following table determine the correct volume to filter for TDS determination. Failure to check sample conductivity beforehand may cause technical holding times to be exceeded if samples are reanalyzed because of high TDS.

Sample Conductivity (uS/cm)	Volume to filter (mL)
0 - 3000	100
3000 - 6000	50
6000 - 12000	25

- 8.6.3 Preparation of glass fiber filter - Connect suction hose from filtration flask to in-house vacuum or vacuum pump. Place a filter on the filter assembly. Apply vacuum and wash filter with three successive 20 mL volumes of reagent water. Continue to apply vacuum until all traces of water are removed. Discard the washings and rinse the filter flask with reagent water.

8.7 Sample Analysis

- 8.7.1 Sample filtration - Shake the sample vigorously and rapidly transfer the appropriate volume to the pre-washed filter apparatus using a 100-mL graduated cylinder. Record the volume used on the bench sheet/logbook. Apply vacuum and filter the sample. Rinse the graduated cylinder with three successive 10 mL portions of reagent water and continue to apply vacuum for about three minutes to remove as much water as possible.
- 8.7.2 Sample evaporation and weighing - Transfer the filtrate to a pre-weighed evaporating dish and evaporate in the oven at 103-105 °C to dryness. Dry the evaporated sample for at least one hour at 180 ± 2 °C. Cool in a desiccator to room temperature and weigh. Record the weight. Repeat the drying, cooling and weighing cycle until the weights from two consecutive cycles differ by less than 4% or 0.5 mg, whichever is less. Use the smallest weight from the final two cycles for calculation purposes.
- 8.7.3 A typical sample analytical sequence is listed in the following table:

Seq.	Desc.	Seq.	Desc.	Seq.	Desc.
1	LRB	11	S7	21	S16
2	QL	12	S8	22	S17
3	LCS (SRM)	13	S9	23	S18
4	S1	14	S10	24	S19
5	S1 – LD	15	S11	25	S20
6	S2	16	S11 -LD		
7	S3	17	S12		
8	S4	18	S13		
9	S5	19	S14		
10	S6	20	S15		

8.8 Data Reduction and Reporting

- 8.8.1 Calculate TDS as follows:

$$TDS = \frac{(A - B)}{C} \times 1000$$

Where

TDS	=	Total Dissolved Solids in mg/L.
A	=	weight of residue + evaporating dish, mg.
B	=	tare weight of evaporating dish, mg.
C	=	sample volume, mL.

If the sample residue exceeds 200 mg (A-B), the sample must be re-analyzed using a smaller sample aliquot.

8.8.2 Sample results are reported in the concentration unit of mg/L. All results should be reported using no more than two significant figures; however, no values of less significance than the QL may be reported (values near the QL will be reported with only one significant figure). Report down to $\frac{1}{2}$ the QL. Values between $\frac{1}{2}$ the QL and the QL will be flagged as estimated (J flag). For rounding results, adhere to the following rules:

- a) If the number following those to be retained is less than 5, round down;
- b) If the number following those to be retained is greater than 5, round up; or
- c) If the number following the last digit to be retained is equal to 5, round down if the digit is even, or round up if the digit is odd.

9 QUALITY CONTROL

- 9.1 EPA Region 9 Laboratory operates a formal quality control (QC) program. As it relates to this SOP, the QC program consists of a demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks, QCS samples and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.
- 9.2 Demonstration of Capability (DOC) - Prior to use in routine analysis, a DOC must be performed following the procedures noted in Region 9 SOP #880.
- 9.3 Routine Analytical Quality Control - The various routine QC samples analyzed during each analytical run are specified in this section.

- 9.3.1 LRB - The laboratory must analyze at least one LRB daily with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the QL indicate laboratory contamination. The LRB must be re-prepared along with the affected samples, and re-analyzed.
- 9.3.2 LCS Analysis - The TDS in the LCS sample must be measured daily or once per batch of 20 samples or fewer samples, whichever is more frequent. The recoveries must be within 85-115% or the samples in the batch must be reanalyzed.

$$\% R = \frac{TDS_m}{TDS} \times 100$$

Where

%R = percent recovery.
TDS_m = measured TDS in the QCS.
TDS_t = expected TDS in the QCS.

- 9.3.3 QL - The accuracy of the batch at the quantitation limit shall be verified by the analysis of a QL standard. The QL must be analyzed at the beginning of each analytical batch. The QL standard has a true value of 20 mg/L. The recovery of the TDS in the QL is calculated as follows:

$$\% R = \frac{M}{T} \times 100$$

Where

%R = percent recovery of the standard.
M = calculated concentration of the QL, mg/L.
T = true concentration of the QL, mg/L.

If the QL recovery exceeds the limits of 70-130%, the analysis shall be terminated. The cause of the poor recovery must be determined and the problem corrected. All affected samples must be reanalyzed.

- 9.3.4 LD - Sample homogeneity can affect the quality and interpretation of the data. LD results can be used to assess sample homogeneity.

One LD must be prepared for every 10 routine samples of the same matrix in a sample batch. Homogenize the routine sample selected as the LD, obtain a representative aliquot, and proceed with sample preparation and analysis, treating the LD sample as a routine sample.

Calculate the relative percent difference using the following equation:

$$RPD = \frac{|C_{ld} - C|}{(C_{ld} + C) / 2} \times 100$$

Where

RPD = relative percent difference.

C_{ld} = measured TDS in the LD.

C = measured TDS in the routine sample.

The relative percent difference (RPD) must be $\leq 5\%$. If the control limits are exceeded, flag the associated sample result in the spreadsheet.

9.4 Method Performance

A number of factors can affect the results of a TDS analysis. The most important sources of uncertainty include: the measurement of crucible weights; the temperature of drying; timing of desiccation, drying and weighing; the measurement of sample volumes; the representativeness of the subsample; and the quality of the blank/rinse water. The quality of each of these potential sources of uncertainty is controlled by various measures in the SOP.

Method performance is assessed using an LRB, LCS, QLS sample that are processed with each batch. The criteria for these samples is < 10 mg/L, 85-115% R, and 70-130% R respectively. At the Region 9 Laboratory, the mean percent recovery and standard deviation of the LCS and QLS samples run during the period Aug. 1, 2006 to Jul. 31, 2007 are summarized in the Method Performance Table below. In addition, the RPD of duplicate analyses must be $\leq 5\%$.

Method Performance

Analyte	Matrix	QC Type	Number of Measurements	Mean Recovery, %	95% C.I. (2s) (as %)
TDS	Water	QLS (20 mg/L)	44	102	14.8
TDS	Water	LCS (~2000 mg/L)	44	97.7	4.10
TDS	Water	Duplicate RPD	21	RPD Mean 1.45	4.58

10 DOCUMENTATION

- 10.1 Each reagent and standard that is used or prepared for the analysis is entered in the LIMS. A label is created for each standard and the unique identification number is used to track the standard and its use.
- 10.2 The TDS Reporting Bench-sheet must be filled out for each sample batch that is analyzed. Entries are made for the case number, SDG number, date of analysis, QC solution ID, analyst initials, initial and final oven temperatures, lab sample IDs, client sample IDs, crucible number, sample volume in mL, weight of crucible + residue in grams, tare weight of the crucible in grams, weight of the residue in grams, total dissolved solids in mg/L, conductivity check in uS/cm and comments, if any. The logbook is maintained in Room 300. Copies of the appropriate page(s) are included in the data package.
- 10.3 A LIMS Data Report is created for each SDG. The contents of the report and data package are outlined in Attachment D.
- 10.4 Analytical Balance Calibration Logbook - An entry is made for each weight (100 mg, 500 mg, 1 g, 10 g and 100 g). The logbook is maintained in Room 300. Copies of the appropriate page(s) are included in the data package.
- 10.5 Temperature Logbooks – A record of the temperature is made each time materials are placed in or removed from the oven. The record should include: Date, Time, Set Temperature, Acceptable Temperature Range, Actual Temperature, Oven ID# and Analyst Initials. The logbook is maintained in Room 300. Copies of the appropriate page(s) is (are) included in the data package. The accuracy of the digital reading on the oven is verified annually by the QA Officer.
- 10.6 SOP Distribution and Acknowledgment
Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. Document the process using the SOP Distribution and Acknowledgement List as shown in Appendix E.

11 REFERENCES

American Public Health Association, 1998, *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, Method 2540-C Total Dissolved Solids Dried at 180°C, 1998.

U.S. Environmental Protection Agency, 1983, *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, EPA Method 160.1, Revised March, 1983.

Region 9 SOP 840, Notebook Documentation and Control.

Region 9 SOP 880, Demonstration of Laboratory Capability and Analyst Proficiency.

Region 9 SOP 545, Determination of Specific Conductance.

Region 9 SOP 850, Preparation of Standard Operating Procedures

**APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD**

The use of a Quantitation Limit Standard and a Lab Control Standard and the criteria for their acceptability are not found in the method.

The method calls for the use of a sample volume that will yield a total weight of residue between 2.5 and 200 mg. This SOP standardizes the sample volume at 100 mL and has a quantitation limit of 20 mg/L. As a result the acceptable total weight of residue range for this SOP is 2.0 to 200 mg.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides the target analytes list for this SOP with the CAS number and quantitation limits.

<u>Analyte</u>	<u>Chemical Abstracts Registry Number (CASRN)</u>	<u>Water Quantitation Limit, mg/L</u>	<u>Soil Quantitation Limit, µg/kg</u>
Total Dissolved Solids (TDS)	NA	20	NA

APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

<u>Standard Name</u>	<u>QC Limit</u>
QLS (20 mg/L)	70 – 130 %R
LCS (mid level)	85 – 115 %R
Duplicate RPD	$\leq 5\%$
Blank	< 10 mg/L (1/2 QL)
Evaporation Temperature	$104 \pm 1^{\circ}\text{C}$
Drying Temperature	$180 \pm 2^{\circ}\text{C}$
Replicate consecutive weighing	$\leq 0.0005 \text{ g}$ or 4% whichever is less
Conductivity Standard	95 – 105 %R
Balance calibration tolerances	100 mg $\pm 1 \text{ mg}$ 500 mg $\pm 3 \text{ mg}$ 1 g $\pm 4 \text{ mg}$ 10 g $\pm 15 \text{ mg}$ 100 g $\pm 70 \text{ mg}$

**APPENDIX D.
INSTRUMENT INFORMATION**

NA

**APPENDIX E.
SOP DISTRIBUTION AND ACKNOWLEDGEMENT LIST**

STANDARD OPERATING PROCEDURE: 461

Revision: 6, Effective: 8/15/07

Total Dissolved Solids

I have received, read, and understood the above referenced SOP and agree to comply with the SOP when performing the subject procedure until the effective date of future revisions.

NAME	DATE DISTRIBUTED	SIGNATURE	DATE
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
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_____	_____	_____	_____
_____	_____	_____	_____

**APPENDIX F.
TYPICAL DATA PACKAGE FORMAT**

Data package contents, in order.

LIMS cover memo or cover letter.

Final LIMS report.

Copy of the TDS raw data sheets.

Copy of QLS (CCV) Standard printout from LIMS

Copy of LCS (SRM) Standard printout from LIMS

Copy of the relevant pages from both incubator temperature logbooks.

Copy of the relevant pages from balance calibration logbook.

Copy of the work order.

Copy of the chain-of-custody form.

STANDARD OPERATING PROCEDURE: 461
Revision: 6, Effective: 08/15/07

[illegible]

**USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA**

**STANDARD OPERATING PROCEDURE 505
DETERMINATION OF TRACE ELEMENTS IN WATER BY ICP-AES**

Revision 7
Effective Date: September 17, 2009

Reviewed by: _____
Richard Bauer Date
Chemistry Team Leader/Technical Director

Reviewed by: _____
K. W. Hendrix, Laboratory QA Officer Date

Approved by: _____
Brenda Bettencourt, Laboratory Director Date

Periodic Review:

Signature	Title	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____

This SOP was prepared by ICF International for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA contract no. EP-W-06-041). ESAT Document Control Number: 00404035-11240

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1 SCOPE AND APPLICABILITY

This SOP provides procedures for the determination of dissolved and total recoverable elements by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) in environmental samples for use in the USEPA Region 9 Laboratory, Richmond, CA. These procedures are applicable to water samples only. This SOP is based on EPA Method 200.7, Rev. 4.4, *Determination of Trace Elements in Waters and Wastes by ICP-AES*, May 1994. Deviations from the reference method are described in Appendix A. Analytes and quantitation limits (QLs) are listed in Appendix B.

Water samples with turbidity > 1 NTU or where silver and/or total recoverable analytes are requested must be digested following Region 9 Laboratory SOP 403 prior to analysis. Other water samples may be analyzed directly after proper filtration and/or acid-preservation.

2 METHOD SUMMARY

An aqueous sample is nebulized and the resulting aerosol is introduced to the inductively coupled plasma torch of the ICP-AES instrument where element-specific emission spectra are produced. These spectra are dispersed by a grating and their intensities are monitored at specific wavelengths by a photomultiplier tube. The resulting intensities are proportional to the concentration of the trace elements and are processed by a computer system.

Water samples for total recoverable analytes, silver analysis, or having turbidity > 1 NTU are acid digested prior to analysis. However, dissolved elements are analyzed by “direct analysis” after filtration and acid preservation of aqueous samples. Drinking water samples are also analyzed by “direct analysis” without acid digestion if the samples have been properly acid-preserved and have turbidity of < 1 NTU.

3 DEFINITIONS

Analytical Sample - Any sample introduced into the ICP-AES instrument, excluding calibration standards, blanks, or QC reference samples.

Calibration Blank (CB) - A blank that is the same matrix as the calibration standards, but without the analytes. The calibration blank is also a zero standard used to calibrate the ICP-AES instrument.

Continuing Instrument Calibration Verification (CCV) - The CCV standard is the same solution as the ICV standard and is used to verify the accuracy of the analysis and monitor

instrument drift. It is analyzed periodically throughout the analysis sequence (after every ten samples and at end of the analytical run). The CCV is also known as the continuing instrument performance check (IPC) standard.

Dissolved Analyte - The concentration of analyte in an aqueous sample that is filtered through a 0.45- μ m membrane filter assembly prior to sample acidification.

Initial Calibration Standard (ICAL) - A solution prepared from the dilution of stock standard solutions. The ICAL solutions are used to calibrate the instrument response with respect to analyte concentration.

Initial Instrument Calibration Verification (ICV) - A standard containing the analytes of interest that is used to verify the accuracy of the analysis. It is analyzed immediately after calibration. The ICV is also known as the initial instrument performance check (IPC) standard.

Laboratory Control Sample (LCS) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is analyzed exactly like a sample and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements. The LCS is also known as a laboratory fortified blank (LFB) or blank spike (BS).

Laboratory Information Management System (LIMS) - The Element Database.

Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear.

Matrix Spike (MS) - An aliquot of an analytical sample to which known quantities of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations. The MS is also known as the laboratory fortified matrix (LFM) sample.

Matrix Spike Duplicate (MSD) - A duplicate aliquot of an analytical sample to which known quantities of the method analytes are added in the laboratory. The MSD is analyzed exactly like a sample and its purpose is to determine whether the sample matrix contributes bias to the analytical results and to determine laboratory precision. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MSD corrected for background concentrations. The MSD is also known the laboratory fortified matrix duplicate (LFMD) sample.

Method Blank (MB) - An aliquot of reagent water or other blank matrix that is treated exactly as a sample. The MB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment. The MB is also known as a laboratory reagent blank (LRB).

Method Detection Limit (MDL) - The minimum concentration of an analyte in an environmental sample that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Optical Alignment Solution - A solution of manganese used to align the optical paths of the ICP-AES instrument.

Quantitation Limit (QL) - The concentration at which confidence in the reported value requires no qualifying remarks. A standard is run at the QL to verify acceptable data quality.

Quantitation Limit Standard (QLS) - A standard used to check the accuracy of the analysis at the quantitation limit.

Sample Delivery Group (SDG) - A group of twenty samples or less from a project that is sent to the laboratory for analysis.

Second Source Calibration Verification (SCV) - A solution of method analytes of known concentration that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check instrument or laboratory performance with externally prepared test materials. The SCV is also known as a quality control standard (QCS). For this SOP, SCV is also the ICV.

Spectral Interference Check (SIC) Solution - A solution of selected method analytes of higher concentration which is used to evaluate the procedural routine for correcting known inter-element spectral interferences with respect to a defined set of method criteria.

Stock Standard Solution (SSS) - A concentrated standard containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Total Recoverable Analyte Concentration - The concentration of an analyte in an unfiltered aqueous sample after preparation by acid digestion.

Water Sample - For the purpose of this method, a sample taken from matrices classified as drinking, surface, ground, or storm runoff water, or industrial or domestic wastewater.

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

Areas of high, lethal voltages exist within the instrument. Never touch parts of the instrument that are not intended for access by the instrument operator. Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-regulated Waste	Not applicable
ICP-AES instrument liquid waste (nitric acid, hydrochloric acid, trace metals)	Hazardous Waste	Corrosive, Toxic

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples should be collected in pre-cleaned polyethylene containers. Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, and minimize waste disposal. A 500 mL sample volume should be sufficient to meet these objectives.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form.

Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to “active out” and the location to the appropriate room number. At the end of the day, return sample containers to the “Home” locations. Update the LIMS database using the “return to home location” feature and update container disposition to “available in”. Verify that your initials are recorded whenever you update the LIMS custody information.

5.3 Preservation Verification

1. Drinking Water Samples - Samples are preserved by acidifying with dilute nitric acid to pH < 2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient). Preservation may be done at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, samples may be shipped to the laboratory within two weeks of collection and preserved upon receipt in the laboratory. Following acidification, the sample is mixed and held for sixteen hours and then verified to be pH < 2 just prior to withdrawing an aliquot for turbidity measurement.
2. Dissolved Analyte Samples - The samples must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. Glass or plastic filtering apparatus are recommended to avoid contamination. The laboratory must perform filtration immediately if the step was not performed in the field. Acidify the filtrate with dilute (1:1) nitric acid immediately following filtration to pH < 2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient).
3. Aqueous Total Recoverable Analyte Samples - Samples are preserved by acidifying with dilute nitric acid to pH < 2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient). Preservation may be done at the time of collection.

However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, samples may be shipped to the laboratory within two weeks of collection and preserved upon receipt in the laboratory. Following acidification, the sample is mixed and held for sixteen hours and then verified to be $\text{pH} < 2$ just prior to withdrawing an aliquot for digestion. If the pH of the sample is > 2 , more acid must be added and the sample held for sixteen hours until verified to be $\text{pH} < 2$.

5.4 Sample Storage

Samples must be stored at > 0 and ≤ 6 °C. Retain samples for 60 days after the final analytical report is sent to the data user.

5.5 Holding Time

Samples must be analyzed within six months from collection.

6 INTERFERENCES

1. Spectral Interferences

Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or the unresolved overlap of molecular band spectra.

Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurement(s) adjacent to the analyte wavelength peak. The location(s) used for the routine measurements must be free of off-line spectral interferences (inter-element or molecular) or adequately corrected to reflect the same change in background intensity that occurs at the wavelength peak.

Spectral overlaps can be compensated for by equations that correct for the inter-element contributions, which involve measuring the interfering elements. When present and uncorrected, these interferences will produce false-positive or false negative results and be reported as analyte concentrations.

When inter-element corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions. Inter-element corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating plus the entrance and exit slit widths, and by the order of dispersion. Inter-element corrections will also vary depending upon the choice of

background correction points. Selecting a point where an interfering emission line may appear should be avoided when practical. Inter-element corrections that constitute a major portion of an emission signal may not yield accurate data. It should not be forgotten that some samples contain uncommon elements that could contribute spectral interferences.

The interference effects must be evaluated for each individual instrument. Intensities will vary not only with the optical resolution but also with the operating conditions (such as power, viewing height, and argon flow). The Region 9 Laboratory has determined and documented for each wavelength the effect from the known interferences given in Table 1 of Appendix D, and utilizes a computer routine for their automatic correction on all analysis. To determine the appropriate location for the off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line inter-element spectral interference or a computer routine must be used for their automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the user must determine and document both the on-line and off-line spectral interference effect from all method analytes and provide for their automatic correction on all analyses. Tests to determine the spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 50 mg/L to 100 mg/L single element solutions are sufficient, however, for analytes such as iron that may be found at high concentration a more appropriate test would be to use a concentration near the upper LDR limit.

When inter-element corrections are **not** used, the ongoing SIC solutions (Section 7.3.8) must be analyzed to verify the absence of inter-element spectral interference. When the interference accounts for 10% or more of the analyte concentration, another approved test procedure must be used to complete the analysis. Users should be aware that, depending upon the instrumental resolution, alternate wavelengths with adequate sensitivity and freedom from interference might not be available for all matrices. In these circumstances, the analyte must be determined using another approved test procedure.

2. Physical Interferences

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples that contain high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by such means as high solids nebulizer, diluting the sample, and using a peristaltic pump. Another problem that can occur is salt buildup at the tip of the nebulizer, which affects the aerosol rate and causes

instrument drift. This problem can be controlled by a high solids nebulizer, wetting the argon prior to nebulization, using a tip washer, or diluting the sample.

3. Chemical Interferences

Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. Normally, these effects are not significant with the ICP-AES technique. If observed, they can be minimized by careful selection of operating conditions (such as incident power and observation height), by buffering the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependant on matrix type and the specific analyte element.

4. Memory Interferences

Memory interferences are related to sample transport and result when there is carryover from one sample to the next. Sample carryover can result from sample deposition on the uptake tubing to the nebulizer, and from incomplete rinsing of the sample solution from the plasma torch and the spray chamber between samples. These memory effects are dependent upon both the analyte being measured and sample matrix and are minimized through the use of extended rinse times.

5. Chemical Contamination

When determining boron in aqueous samples, only plastic, PTFE, or quartz labware should be used from time of collection to completion of analysis. When possible, borosilicate glass should be avoided to prevent contamination of boron.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives and isolated from other laboratory glassware. Refer to Region 9 Laboratory SOP 130, *Glassware Cleaning Procedures*, for specific instructions.

7.1 Instruments and Equipment

- Perkin Elmer Optima 5300 DV Inductively Coupled Plasma - Optical Emission Spectrometer

- Perkin Elmer AS-93plus Auto-sampler

7.2 Reagents

Reagents may contain impurities that might affect analytical data. Only materials that conform to the American Chemical Society (ACS) specifications should be used. If the purity of a reagent is in question, analyze for contamination prior to use.

Record all reagent preparations in the LIMS.

- Reagent Water - All references to reagent water in this SOP refer to laboratory deionized water as described in EPA Region 9 Laboratory SOP 825.
- Hydrochloric Acid (HCl), concentrated, trace metals grade or better (e.g. Baker Instra-Analyzed)
- Nitric Acid (HNO₃), concentrated, trace metals grade or better (e.g. Baker Instra-Analyzed)
- Argon gas supply, high-purity grade, 99.99%

7.2.1 Hydrochloric Acid, dilute (1:1) - Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

7.2.2 Nitric Acid, dilute (1:1) - Add 500 mL concentrated HNO₃ to 400 mL reagent water and dilute to 1L.

7.3 Standards

Record all standard and standard preparations in the LIMS.

7.3.1 Stock Standards

Stock standard solutions are available from a commercial supplier such as Spex or Inorganic Ventures. Individual (1,000 mg/L) and multi-element solutions containing elements listed in Appendix B are typically used.

7.3.2 Initial Calibration Standards

Prepare initial calibration standard solutions to contain final concentrations listed in Table 2 of Appendix D. Prepare each calibration solution using an appropriate amount of the calibration stock standard (Section 7.3.1) and dilute to 200 mL with 2% nitric acid / 2% hydrochloric acid solution.

7.3.3 ICV/CCV/SCV Standard

The ICV standard and CCV standard are identical and only differentiated by their place within the analytical sequence. It is obtained from an outside source different from the initial calibration stock standards. The ICV standard also serves as the SCV. This standard is available from Spex and consists of solution LPC Standard 1, P/N LPC-1-500 (containing Al, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Sb, Se, SiO₂, Sn, Ag, Na, Sr, Tl, V, and Zn). Titanium and cerium are added from separate 1,000 mg/L individual stock standards. Prepare the ICV/CCV/SCV standard by adding 50 mL of the LPC Standard 1 and 1 mL each of the Ti and Ce 1,000 mg/L stock standards, dilute to 500 mL with 2% nitric acid / 2% hydrochloric acid solution. ICV standard for Lithium is prepared from a separate individual standard and run in a separate method. The ICV/CCV concentrations are listed in Table 3 of Appendix D. Similar mixes from other vendors can be substituted as needed.

7.3.4 CB

Dilute concentrated nitric acid and hydrochloric acid with reagent water to obtain a 2% nitric acid / 2% hydrochloric acid solution.

7.3.5 MB

Prepare the MB using reagent water plus all of the reagents used in processing the samples. The MB is taken through the entire preparation and analytical sequence.

7.3.6 LCS and MS/MSD

Use commercially available spiking solutions (e.g. Inorganic Ventures Laboratory Fortifying Stock Solutions WW-LFS-1 containing Al, As, Ba, Be, B, Cd, Ca, Ce, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Ni, K, Se, Ag, Na, Sr, Tl, V, and Zn and WW-LFS-2 containing Sb, Mo, SiO₂, Sn, and Ti). Prepare the LCS by spiking 0.5 mL each of the two spiking solutions into 50 mL reagent water and adding the appropriate acids. Prepare the MS and MSD by spiking 0.5 mL each of the two spiking solutions into 50 mL of the designated MS and MSD samples and adding the appropriate acids. The final concentrations for the LCS and MS/MSD are listed in Table 3 of Appendix D.

7.3.7 SCV

The SCV must be obtained from an outside source different from the standard

stock solutions and prepared in the same acid mixture as the calibration standards. The ICV standard also serves as the SCV for this procedure.

7.3.8 Spectral Interference Check (IEC/SIC) Solutions

When inter-element corrections are applied, spectral interference check (SIC) solutions containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors are needed. The SIC solutions used are 300 mg/L Ca, 200 mg/L Mg, 200 mg/L Al, 300 mg/L Fe, 50 mg/L Ba, 50 mg/L Cd, 50 mg/L Be, 50 mg/L Ce, 50 mg/L Co, 50 mg/L Cr, 50 mg/L Cu, 50 mg/L Mn, 50 mg/L Mo, 50 mg/L Ni, 50 mg/L Ti, and 50 mg/L V. Prepare SIC solutions by diluting 1,000 µg/mL single element stock solutions in 2% nitric acid / 2% hydrochloric acid solution.

7.3.9 QLS

Prepare the QLS as needed from multi-element stock solutions (Section 7.3.1) in 2% nitric acid / 2% hydrochloric acid solution. The QLS are listed in Appendix B.

7.3.10 Optical Alignment Solution

A solution of 1 mg/L manganese is needed to align the optical paths of the instrument. The solution is made by diluting 1.0 mL of 1,000 µg/mL manganese stock standard to 1,000 mL with 2% nitric acid / 2% hydrochloric acid solution.

7.3.11 Rinse Blank

Dilute concentrated nitric acid and hydrochloric acid with reagent water to obtain a 2% nitric acid / 2% hydrochloric acid solution.

7.4 Supplies

- Automatic pipettes capable of delivering volumes of 10 to 1,000 µL
- Class A volumetric flasks, graduated cylinders, and funnels (glass and/or metal-free plastic)
- Class A volumetric pipettes
- Metal-free disposable tips
- Narrow-mouth storage bottles with screw closure, 125-mL to 1-L capacities
- Syringe with 0.45 µm disk filters
- Wash Bottle with screw closure, 1,000 mL capacity

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set-up the ICP-AES following operating instructions provided by the manufacturer and discussed below. Use operating parameters provided in Appendix E as a starting point.

Ensure that all appropriate waste containers are properly connected and labeled.

Check the condition of the pump tubing for wear. Replace as needed. Tighten the pump tubing on the pump. Check torch for salt build up. Ignite the plasma and allow to stabilize for at least 30 minutes. During instrument warm up, observe the nebulizer and spray chamber for proper nebulization.

8.1.1 Method File Setup

Select the appropriate master method file and save it to correspond to the current date (e.g., 2009_year/month/day). Enter the results data set file name to also correspond to the current date (e.g., 10908311, indicating ICP instrument number (1), present date (year/month/day), and analytical run number (1)) in the automated analysis control window. Save all changes.

Set up the sample information editor table with the desired sample run. Last old sample information editor files may be written over and resaved. Print the run list from the automated analysis control window. Place the standards and samples in the racks as indicated by the run list and enter into the Run Log.

8.1.2 Alignment of the Optical Paths

Align the axial and radial optical paths of the instrument using the 1 mg/L Mn solution. Aspirate the alignment solution and run the alignment routine as per the manufacturer's procedure, using manganese. Alignment is performed when the sample introduction apparatus is adjusted, such as a new torch, injector tip, or after manipulation of the spray chamber.

8.2 Calibration

8.2.1 Initial Calibration

A calibration blank (Section 7.3.4) and a calibration standard (Section 7.3.2) are used for calibration. The calibration standards are given in Table 2 of Appendix D. The calibration is automatically saved in the result data set file as they are run.

Perform an initial calibration for every analytical batch. Refer to Section 9.2.4 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Analyze the ICV/SCV, CB, QLS, IEC (measurement), and SIC (verification) according to Section 8.3.2 immediately after analyzing the initial calibration standards. If QC criteria are not met, take corrective action as described in Section 9.2.4 and Appendix C.

8.2.2 Continuing Calibration

Prepare the CCV and CB as described in Sections 7.3.3 and 7.3.4. Refer to Section 9.2.5 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

Digest samples with turbidity > 1 NTU and/or where silver is requested following Region 9 Laboratory SOP 403 prior to analysis.

Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices, and even fortified blanks if determined as a dissolved analyte or by "direct analysis" where the sample has not been processed using the total recoverable mixed acid digestion. For this reason, samples are digested prior to the determination of silver. The total recoverable sample digestion procedure is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, a smaller volume of a well mixed sample aliquot must be digested until the analysis solution contains < 0.1 mg/L silver.

8.3.1.1 Aqueous Samples, Total Recoverable Analytes

For the determination of total recoverable analytes in water, digest samples following Region 9 Laboratory SOP 403 prior to analysis.

The digestion procedures used in SOP 403 will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and

unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

The total recoverable sample digestion procedure is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed sample aliquots must be prepared until the analysis solution contains < 0.1mg/L silver.

8.3.1.2 Aqueous Samples, Dissolved Analytes

For the determination of dissolved analytes in ground and surface waters, add a 30 mL aliquot of the filtered, acid preserved sample into a 50-mL polypropylene tube. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis.

The LCS and MS/MSD are prepared by spiking 0.3 mL each of the two spiking solutions (Section 7.3.6) into 30 mL of the designated LCS, MS, and MSD samples. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The final concentrations for the LCS and MS/MSD are listed in Table 3 of Appendix D.

NOTE: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be digested using the procedure in Region 9 Laboratory SOP 403 prior to analysis.

8.3.1.3 Drinking Water Samples, Total Recoverable Analytes, Direct Analysis

Drinking water samples with turbidity < 1 NTU must be acidified and analyzed directly without digestion. Add a 30 mL aliquot of the unfiltered, acid-preserved sample into a 50-mL polypropylene tube. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis.

The LCS and MS/MSD are prepared by spiking 0.3 mL each of the two spiking solutions (Section 7.3.6) into 30 mL of the designated LCS, MS and MSD samples. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The final concentrations for the LCS and MS/MSD are listed in Table 3 of Appendix D.

NOTE: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be digested using the procedure in Region 9 Laboratory SOP 403 prior to analysis.

8.3.2 Sample Analysis and Analytical Sequence

This section describes setting up the analytical sequence and performing the instrumental analysis. Record the analytical sequence in the instrument run log or the LIMS sequence page, if available.

After calibration, the auto-sampler continues with the samples and QC. Load SIC solutions according to the requested analyte list. An example of a typical loading list for an analytical run sequence is listed in the table below.

Seq.	Description	Seq.	Description	Seq.	Description	Seq.	Description
1	ICV/SCV	15	Mo IEC	29	Ti SIC	43	S7
2	CB	16	Ni IEC	30	V SIC	44	S8
3	QLS	17	Ti IEC	31	MB	45	S9
4	Ca IEC	18	V IEC	32	LCS	46	S10
5	Mg IEC	19	Al SIC	33	S1	47	S11
6	Ba IEC	20	Cr SIC	34	S1-MS	48	S11-MS
7	Al IEC	21	Co SIC	35	S1-MSD	49	CCV
8	Cr IEC	22	Cu SIC	36	S2	50	CB
9	Co IEC	23	Fe SIC	37	CCV	51	QLS
10	Cu IEC	24	Mn SIC	38	CB	52	S11-MSD
11	Fe IEC	25	CCV	39	S3	53	S12
12	Mn IEC	26	CB	40	S4	54	S13
13	CCV	27	Mo SIC	41	S5	55	CCV
14	CB	28	Ni SIC	42	S6	56	CB

NOTE: Be, Ce, and Cd SIC solution should be analyzed if samples contain these elements at a significant enough concentration to interference on the analyte of interest (i.e. 1 mg/L).

Review results for QC compliance and off-scale results. Identify samples that must be re-analyzed. Samples having analytes at concentrations higher than 90% of the linear dynamic range must be diluted into range and re-analyzed. Refer to Appendix G for guidance on what elements may be reported from this analysis.

8.3.3 Analyte Quantitation

After set-up and calibration, the software report results for the analyzed solution in the units of mg/L without inter-elemental correction. The data are then reprocessed to include inter-elemental correction.

Procedure to reprocess data:

1. Open the result data set in the Inter-Element Correction Model Builder (IEC Model Builder) set-up page. Assign the analytes limits of correction in the set limits page, generally $\frac{1}{2}$ each of the corresponding QL.
2. Select the IEC samples (IEC measurement solutions) to form the data set in the calculate factor page. Assign each solution the correct interfering elements and factors are automatically calculated.
3. Save the IEC Model Builder as 200.7IECmonth/day/year/A or B, where A corresponds to the first IEC Model Builder and B for the second of that day.
4. Update the daily method from the summarize factors page of the IEC Model Builder and save as the same method name with R at the end of name to indicate that it is a reprocessed method file.
5. Print the method and summarize factor table and include with the data package.
6. Open the data reprocessing window and reprocess the result data set. Print and save in a reprocessed result data set file with the same file name as the original data set with an R at the end to indicate that it is a reprocessed data.
7. The reprocessed data includes the calibrations and IEC corrected data for all samples analyzed.

8.3.3.1 Aqueous Samples - Data for aqueous samples should be reported in units of $\mu\text{g/L}$ using the following calculation:

$$C = M \times \frac{1000 \mu\text{g}}{\text{mg}} \times D$$

Where

C = final reported concentration, in $\mu\text{g/L}$

M = measured concentration reported by instrument, in mg/L

D = Sample analysis dilution factor, to account for any dilution performed after sample preparation. For samples analyzed by direct analysis, include the factor introduced by the addition of 1:1 nitric acid.

8.3.3.2 Hardness by Calculation

Hardness is determined by calculation if samples are known to contain high concentrations of heavy metals and cannot be analyzed by titration or when requested by a client. The calculation is based on calcium and magnesium results by EPA Method 200.7.

Hardness is calculated using the following equation:

$$\text{Hardness, mg/L CaCO}_3 = \text{Ca, mg/L (2.497)} + \text{Mg, mg/L (4.118)}$$

8.3.4 QC Review

- Review the results of instrument QC (ICV/SCV, CCV, CB, QLS, and SIC) immediately after their analysis to verify that the results are within QC limits. See Section 9.2 for corrective action requirements and Appendix C for QC limits.
- Review the results of batch QC (MB, LCS, MS/MSD) immediately after their analysis to verify that the results are within QC limits. See Section 9.3 for corrective action requirements and Appendix C for QC limits.

8.3.5 Data Export and LIMS Entry

- Export data from the instrument into text files. In LIMS, create an empty upload file containing the samples analyzed in the LIMS batch or sequence. Import and merge text files using DataTool. Load the resulting merged data file into the LIMS Data Entry/Review table. Review final results in the LIMS.

- Report all results to two significant figures. Report detected results to one-half the QL. Flag values between one-half the QL and the QL as estimated (J).
- Archive data files to the appropriate instrument data subdirectory on the Region 9 LAN.

8.4 Maintenance

Perform the following maintenance:

- Inspect pump tubing for wear daily, replace if necessary.
- Inspect spray chamber for good nebulization.
- Inspect torch if starting is difficult or if unusual carry over is observed during analysis. Remove and clean as necessary.
- Clean and lubricate auto-sampler as needed.

Refer to Appendix F for preventative maintenance procedures and schedules.

9 QUALITY CONTROL

9.1 Demonstration of Capability

The EPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880 for more details.

9.2 Instrument QC

9.2.1 Linear Dynamic Range

The upper limit of the LDR must be established for each element used in quantifying results. Analyze a series of standards with concentrations spanning the range from the QL to the LDR standard concentration. The upper concentration factor can be adjusted by the analyst to account for detector characteristics or dissolved solids limitations/restrictions. From the analysis

determine the maximum concentration for which the measured and true concentration agree within 10%. This concentration is typically defined as the upper limit of the LDR. Samples with analyte concentrations that are greater than 90% of the upper LDR limit must be diluted and re-analyzed. The LDR should be verified annually or whenever the analytical conditions are changed.

9.2.2 Method Detection Limit

A method detection limit must be confirmed annually and must be $< \frac{1}{2}$ the QL.

9.2.3 Spectral Interference Measurement and Check

The laboratory must establish and initially verify an inter-elemental spectral interference correction routine to be used during sample analysis. Criteria for determining an inter-element spectral interference is the apparent positive or negative concentration on the analyte that is outside the limits of the calibration blank for the analyte. Once established, the interferences must be measured daily. Only a portion of the correction routine must be verified daily. The test criteria and the solutions are as follows:

- For interferences from aluminum and iron, only those correction factors (positive or negative) when multiplied by 100 that exceed $\pm \frac{1}{2}$ the QL are tested daily.
- For all other interfering elements, only those correction factors (positive or negative) when multiplied by 10 that exceed $\pm \frac{1}{2}$ the QL are tested daily.
- If the correction routine is operating properly, the determined apparent analyte concentration from analysis of each interfering solution should fall within a specific concentration range. The range shall be the greater of either $\pm \frac{1}{2}$ the QL or a calculated concentration range (multiply the concentration of the interfering element by the value of the correction factor being tested and dividing by 10). If the apparent analyte concentration is outside the greater of the two ranges, the correction factor should be re-determined and samples re-analyze.
- If the samples analyzed do not contain concentrations of the interfering elements at the 10 mg/L level, daily verification is not required; however, all inter-element spectral correction factors must be verified daily.

9.2.4 Initial Calibration

An initial calibration is performed for every analytical batch using a blank and a calibration standard for each analyte.

If an ICAL fails because of one standard mix, a fresh solution of that standard may be reanalyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration standard mix), the system must be checked so that the criteria are satisfied before any samples are analyzed.

The calibration is verified by the analysis of an ICV and CB. If the criteria for those standards are not met, take corrective action as needed before continuing with analysis, including reanalysis or reparation and reanalysis of the initial calibration if necessary. The analysis may also continue but samples cannot be analyzed for the out-of-control analytes.

9.2.5 Initial and Continuing Calibration Verification

To check instrument performance and verify the accuracy and stability of the calibration, analyze an ICV and CCV standards. The ICV is analyzed immediately following initial calibration and the CCV at a frequency of one per 10 analytical samples and at the end of the analytical run. The recovery of analytes in the ICV and CCV are calculated as follows:

$$\%R = \frac{ICV / CCV}{s} \times 100$$

Where

$\%R$ = percent recovery
 ICV/CCV = measured concentration of analyte in the ICV/CCV, mg/L
 S = expected analyte concentration in the ICV/CCV, mg/L

The ICV recovery and RSD criteria are listed in Appendix C. If the %R or RSD for any analyte in the ICV falls outside of the QC criteria, the instrument must be recalibrated for at least the out-of-control analytes. Samples cannot be analyzed for the out-of-control analytes until an acceptable ICV is analyzed.

The CCV recovery criteria are listed in Appendix C. If the %R for any analyte in the CCV falls outside of the QC criteria, the instrument must be recalibrated for at least the out-of-control analytes. Once an acceptable calibration is obtained, the samples preceding the out-of-control CCV must be reanalyzed for the affected analytes.

9.2.6 Calibration Blank

The stability of the baseline must be monitored by analyzing a CB immediately

after every ICV/CCV standard. If the value of the CB result is less than $\frac{1}{2}$ the QL, the result is acceptable. If the value of the CB result equals or exceeds one-half the QL, the analysis may continue but samples cannot be analyzed for the out-of-control analytes. The cause of the high CB result must be determined and the problem corrected. The instrument must be recalibrated at least for the out-of-control analyte and all samples not bracketed by acceptable CB results must be reanalyzed.

9.2.7 Second Source Calibration Verification

Analyze a SCV daily to verify the calibration standards and acceptable instrument performance. The ICV serves as SCV for this SOP. The recovery criteria are listed in Appendix C.

9.2.8 Quantitation Limit Standard

To verify the ability to detect target analytes near the QL, a QLS must be analyzed at the beginning of the analytical run and after 40 analytical samples. If using an auto-diluter to analyze samples, use the diluter also to analyze the QLS.

The recovery of analytes in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where

$\%R$ = percent recovery

M = measured concentration of analyte, mg/L

T = true concentration of the analyte in the QL, mg/L

If the QLS recovery does not meet the criteria in Appendix C, determine the cause, take corrective action, and reanalyze the QLS.

9.2.9 Spectral Interference Check

Analyze SIC solutions daily to measure and test inter-elemental spectral correction factors. If the SIC solutions do not meet the test criteria given in Section 9.2.3 and Appendix C, the factor must be updated before samples are analyzed. If the affected samples do not contain concentrations of the interfering elements at the 10 mg/L level, daily verification is not required. If the affected samples contain concentrations of analyte at less than $\frac{1}{2}$ the QL, daily verification is not required. If the corrected concentration of the analyte

due to spectral interference is less than 10% of the total analyte concentration, daily verification is not required.

9.3 Batch QC

9.3.1 Method Blank

Analyze at least one MB with each batch of 20 or fewer field samples of the same matrix. MB values $\geq \frac{1}{2}$ the QL indicate potential laboratory or reagent contamination. Use the following guidelines to determine when samples must be reprepared, reanalyzed, and flagged as estimated:

- If the MB analyte value is $\geq \frac{1}{2}$ the QL and the sample result is less than five times the MB analyte amount, rerun the MB once to verify and if still unacceptable then the MB and all associated samples must be reprepared and reanalyzed. If agreed to by the Chemistry Team Leader, the associated sample results can also be reported but will be qualified as estimated “J” and flagged “B” and a note placed in the Work Order memo field in LIMS.
- If the MB analyte value is $\geq \frac{1}{2}$ the QL and the sample result is non-detected or is greater than five times the MB analyte concentration, report sample results without qualification.

9.3.2 LCS

Analyze one LCS standard with each batch of 20 or fewer samples of the same matrix. Recovery of analytes in the LCS is calculated as:

$$\%R = \frac{LCS}{s} \times 100$$

Where

$\%R$ = percent recovery

LCS = measured concentration of analyte in the LCS, mg/L

s = analyte concentration in the LCS, mg/L

If the recovery of the LCS does not meet the recovery criteria in Appendix C, reanalyze once to verify. If the recovery is still unacceptable, the analyte is judged to be out-of-control and the source of the problem must be identified and resolved. All samples associated with the out-of-control LCS must be reprepared and reanalyzed. In some cases, the associated sample results can also be reported with prior approval from the Laboratory QA Officer or Technical Director. The results will be qualified as estimated “J”.

9.3.3 Matrix Spike/Matrix Spike Duplicate

The MS and MSD are designed to provide information about the effect of sample matrix on the measurement system. One set of MS/MSD samples must be prepared for every 10 field samples of the same matrix in an SDG. Homogenize the routine sample selected as the QC and spike a representative aliquot with the analytes of interest prior to any sample preparation. The spiking level must be the same as that used for the LCS.

Samples identified as field blanks cannot be used for MS/MSD sample analysis. MS/MSD recoveries are calculated as:

$$\%R = \frac{C_{ms} - C}{s} \times 100$$

Where

$\%R$ = percent recovery

C_{ms} = measured concentration of analyte in the MS, corrected for sample preparation and any dilutions

C = measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions

s = expected spiked analyte concentration in the MS, corrected for sample preparation and any dilutions

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|C_{msd} - C_{ms}|}{(C_{msd} + C_{ms}) / 2} \times 100$$

Where

RPD = relative percent difference.

C_{msd} = measured concentration in the MSD, corrected for sample preparation and any dilutions.

C_{ms} = measured concentration in the MS, corrected for sample preparation and any dilutions.

If the value of C is less than four times the value of s , apply accuracy and precision criteria in Appendix C. If the value of C is greater than four times the value of s , $\%R$ is not meaningful. If the MS/MSD does not meet these criteria, examine other QC results to determine if a matrix problem exists. If laboratory performance is in control, the poor MS/MSD accuracy and precision is likely to be matrix-related. Flag any out-of-control results as estimated "J".

9.4 Method Performance

Region 9 Laboratory performance for this SOP from September 27, 2008 to August 27, 2009 for LCS data in water is summarized in the following table.

Method Performance

Analyte	Number of Measurements	Mean Recovery, %	Standard Deviation	95% Confidence Interval (2 σ)	
				Lower	Upper
Aluminum	69	101	3.03	95.4	107
Antimony	21	104	3.3	97.8	111
Arsenic	23	105	3.1	98.7	111
Barium	65	101	4.83	91.7	111
Beryllium	21	99.7	3.87	92	107
Boron	43	100	3.41	93.4	107
Cadmium	25	101	3.08	94.9	107
Calcium	72	101	3.86	93.3	109
Chromium	69	99.4	2.97	93.4	105
Cobalt	48	100	2.8	94.7	106
Copper	76	97.9	2.79	92.4	104
Iron	81	102	3.23	95.5	108
Lead	27	101	3.14	94.8	107
Lithium	23	105	2.51	99.6	110
Magnesium	73	99.7	3	93.7	106
Manganese	67	100	3.09	94.2	107
Molybdenum	65	100	2.6	95	105
Nickel	70	102	3.46	95.5	109
Potassium	46	103	4.38	94	111
Selenium	24	105	3.63	97.4	112
Silica (SiO ₂)	20	99.8	4.81	90.2	109
Silver	27	98.6	3.17	92.3	105
Sodium	44	103	3.62	95.6	110
Strontium	6	104	3.45	97.1	111
Thallium	19	101	2.58	95.4	106
Vanadium	65	101	2.78	95.1	106
Zinc	82	101	3.53	94	108

The primary sources of analytical error are:

- Interferences (See Section 6)
- Calibration standard accuracy

- Digestion equipment contamination
- Transfer pipette accuracy

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QLS, MS/MSD, and LCS) are recorded in the LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used in this SOP in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the LIMS or in the instrument run log. Project Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the Element database. The data package is produced from Element database and manual log records. Appendix H provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance
- Subsequent instrument modifications and upgrades, including major software upgrades
- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.6 SOP Distribution and Acknowledgement

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. The Lab QC Database is used to maintain the list of assigned analysts for each SOP. Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 Revisions to this SOP are summarized in Appendix I.

11 REFERENCES

EPA Region 9 Laboratory. *Business Plan*.

EPA Region 9 Laboratory. *Chemical Hygiene Plan*.

EPA Region 9 Laboratory. *Environmental Management System*.

EPA Region 9 Laboratory SOP 110. *Sample Receiving and Log-in*.

EPA Region 9 Laboratory SOP 125. *Sample Disposal*.

EPA Region 9 Laboratory SOP 130. *Glassware Cleaning Procedures*.

EPA Region 9 Laboratory SOP 403. *Sample Preparation for ICP-AES*.

EPA Region 9 Laboratory SOP 462. *Analysis of Total Suspended Solids By EPA Method 160.2*.

EPA Region 9 Laboratory SOP 706. *Laboratory Waste Management Procedure*.

EPA Region 9 Laboratory SOP 820. *Laboratory Discrepancy and Corrective Action Procedures*.

EPA Region 9 Laboratory SOP 825. *Deionized Water Monitoring*.

EPA Region 9 Laboratory SOP 830. *Notification Procedures for Results Exceeding the Safe Drinking Water Act Maximum Contaminant Level*.

EPA Region 9 Laboratory SOP 840. *Notebook Documentation and Control*.

EPA Region 9 Laboratory SOP 880. *Demonstration of Capability.*

U.S. Environmental Protection Agency. Method 200.7, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Atomic Emission Spectrometry, Revision 4.4, EMMC Version, May 1994.

Standard Methods for the Examination of Water and Wastewater, Method 2340B, Hardness by Calculation, 20th Edition, 1998.

Perkin Elmer, Optima 5000 Series Hardware Guide.

Perkin Elmer, *AS93plus User's Guide.*

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. This SOP does not include mercury as an analyte. Mercury is listed as an analyte in the reference method.
2. Aqueous samples with less than 1% undissolved solids are brought to a final volume of 50 mL. This procedure does not include the sample concentration step specified in the reference method.
3. The Region 9 Laboratory does not subtract the MB results from the LCS results for LCS recovery calculation. The reference method allows MB subtraction.
4. This SOP specifies that the MB acceptance criterion is less than one-half the QL. The reference method specifies no greater than 2.2 times MDL.
5. SIC acceptance criterion of $\frac{1}{2}$ the QL is being followed in this procedure.
6. The SIC solutions of thallium, silica, and tin listed in the reference method are not necessary for this instrument and are not analyzed.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides target analytes with the CAS number and quantitation limits for this SOP.

Analyte	Chemical Abstract Services Registry Number (CASRN)	Quantitation Limit, <i>ug/L</i>
Aluminum (Al)	7429-90-5	100
Antimony (Sb)	7440-36-0	20
Arsenic (As)	7440-38-2	20
Barium (Ba)	7440-39-3	10
Beryllium (Be)	7440-41-7	1
Boron (B)	7440-42-8	100
Cadmium (Cd)	7440-43-9	5
Calcium (Ca)	7440-70-2	100
Chromium (Cr)	7440-47-3	10
Cobalt (Co)	7440-48-4	10
Copper (Cu)	7440-50-8	10
Iron (Fe)	7439-89-6	100
Lead (Pb)	7439-92-1	20
Lithium (Li)	7439-93-2	5
Magnesium (Mg)	7439-95-4	500
Manganese (Mn)	7439-96-5	5
Molybdenum (Mo)	7439-98-7	20
Nickel (Ni)	7440-02-0	10
Potassium (K)	7440-09-7	2000
Selenium (Se)	7782-49-2	20
Silica (SiO ₂)	7637-86-9	500
Silver (Ag)	7440-22-4	10
Sodium (Na)	7440-23-5	500
Strontium (Sr)	7440-28-6	5
Thallium (Tl)	7440-28-0	20
Tin (Sn)	7440-31-5	100
Titanium (Ti)	7440-32-6	10
Vanadium (V)	7440-62-2	10
Zinc (Zn)	7440-66-6	10

APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

Parameter	Frequency	Criteria
ICV/SCV	After ICAL	95 - 105%
ICV	After ICAL	< 3% RSD
CCV	Every 10 Samples	90 - 110%
CB	After each ICV/CCV	< ½ QL
QLS	After ICAL & after every 40 samples	60 - 140%
MB	Each Batch	< ½ QL
LCS	Each Batch	85 - 115%
MS/MSD, Accuracy	Every 10 samples	70 - 130%
MS/MSD, Precision	Every 10 samples	≤ 20 RPD
SIC	After ICAL, as needed per analyte	± ½ QL or calculated acceptance window, whichever is greater

APPENDIX D. STANDARDS TABLES

Table 1. Method Analytes and Potential Interfering Elements

Analyte	Wavelength, nm	Plasma View	Potential Interfering Elements***
Al	308.215	Radial	<u>Mo</u> , Ti, <u>V</u>
Sb	206.836	Axial	Ce, <u>Cr</u> , <u>Fe</u> , <u>Mo</u> , <u>V</u>
As	188.979*	Axial	Ce, <u>Cr</u> , <u>Co</u> , <u>Mo</u>
Ba	233.527*	Radial	<u>V</u>
Be	313.107*	Radial	<u>Cr</u> , Ti
B	249.677	Radial	Co, <u>Fe</u> , Mo
Cd	226.502	Axial	<u>Fe</u> , <u>Ni</u> , Ti
Ca	315.887	Radial	Mo,
Ce	413.764	Radial	None
Cr	205.560	Radial	Ce, <u>Be</u> , Fe, Mo, Ni
Co	228.616	Radial	Ba, Cd, Fe, Ni <u>Ti</u>
Cu	324.752	Radial	<u>Fe</u> , Mn, Mo
Fe	273.955*	Radial	None
Pb	220.353	Axial	<u>Al</u> , Ce, Cu, Fe, Mo, Ti
Li	670.784	Axial**	None
Mg	279.077	Radial	Mn
Mn	260.568*	Radial	Mg, Cr, Co, Fe
Mo	202.031*	Radial	<u>V</u>
Ni	231.604	Radial	Ca, Co, Mo
K	766.490	Radial	None
Se	196.026	Axial	Ca, Ce, Mn, Ti
SiO ₂	251.611	Radial	<u>Mo</u>
Ag	328.068	Axial	<u>Fe</u> , Mn, Mo, Ti, <u>V</u>
Na	589.592*	Radial	None
Sr	421.552	Radial	None
Tl	190.801*	Axial	Ce, Cr, <u>Co</u> , <u>Mn</u> , Mo, <u>Ti</u> , <u>V</u>
Sn	189.927*	Axial	Mg
Ti	334.940	Radial	Ca, Cr
V	292.402	Radial	Fe, Mn, <u>Mo</u> , <u>Ti</u>
Zn	213.857	Radial	Ca, <u>Cu</u> , <u>Fe</u> , <u>Ni</u>

Note: *Wavelengths other than those recommended by Method 200.7

**Axial view with high resolution

***All potential interfering elements based on ½ QL interference level. Underlined potential interfering element often require daily testing per section 9.2.3

Table 2. Calibration Standard Concentrations*

Analyte	Solution	Concentration mg/L	Analyte	Solution	Concentration mg/L
As	IV	10.0	Co	III	2.0
Ca	IV	10.0	V	III	2.0
Sb	IV	5.0	Al	II	10.0
Ba	IV	1.0	Cr	II	5.0
B	IV	2.0	SiO ₂	II	10.0
Cd	IV	2.0	Sn	II	4.0
Cu	IV	2.0	Ti	II	10.0
Mn	IV	2.0	Zn	II	5.0
Se	IV	5.0	Be	I	1.0
Ag	IV	0.5	Fe	I	10.0
K	V	20.0	Mg	I	10.0
Mo	V	10.0	Ni	I	2.0
Na	V	10.0	Pb	I	10.0
Sr	V	1.0	Tl	I	5.0
Ce	III	2.0	Li**	I	2.0

Note: *Mixes are prepared as needed from individual stock standards. Prepared mixed standards may also be purchased. All calibration sources are different than the source of the ICV/SCV.

**Lithium standard is from an individual stock and is used for Li method only.

Table 3. ICV/SCV/CCV, LCS/MS/MSD Concentrations

Analyte	ICV/SCV/CCV mg/L	LCS/MS/MSD mg/L
Al	2.0	2.0
Sb	2.0	0.80
As	2.0	0.80
Ba	2.0	0.20
Be	2.0	0.20
B	2.0	0.30
Cd	2.0	0.20
Ca	2.0	1.0
Ce	2.0	2.0
Cr	2.0	0.40
Co	2.0	0.20
Cu	2.0	0.30
Fe	2.0	3.0
Pb	2.0	1.0
Li	0.5	0.20
Mg	2.0	2.0
Mn	2.0	0.20
Mo	2.0	0.40
Ni	2.0	0.50
K	10.0	10.0
Se	2.0	2.0
SiO ₂	10.0	2.0
Ag	0.5	0.075
Na	2.0	3.0
Sr	2.0	0.20
Tl	2.0	2.0
Sn	2.0	0.70
Ti	2.0	0.20
V	2.0	0.30
Zn	2.0	0.20

APPENDIX E.
INSTRUMENT PARAMETERS

Nebulizer Gas Flow setting:	0.55 - 0.60 L/min
Auxiliary Gas Flow setting:	0.2 L/min
Plasma gas Flow setting:	15 L/min
ICP RF Power setting:	1500 W
Argon Line Pressure:	> 100 psi
Resolution Setting:	Normal
Resolution Setting, Li Method:	High
Replicates:	4
Read Parameters:	5 sec. minimum, 20 sec. maximum
Rinse Time:	120 – 240 sec.
Flush Time:	70 sec.

APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

Maintenance Schedule for the PE Optima 5300 DV

Item	Frequency	Comments
Auto-sampler Rinse Station Reservoir	As needed	Fill with 2% HNO_3 / 2% HCl
Pump Tubing	Daily	Check for fatigue and wear. Replace as needed.
Drain Tubing	Daily	Check for good drainage, adjust as needed
Nebulizer Spray	Daily	Check, unclog by backflushing if needed
Torch Tip	Daily	Check for sample residues. Replace with clean glassware if needed.
Argon Dewar	Daily	Check for sufficient amount and pressure. Order as needed.
Auto-sampler and Peristaltic Pump	Daily	Wipe spills or residues.
Glassware	Weekly or needed	If excessive carryover, inspect and clean if needed.
Radial and axial windows	Monthly or as needed	If sensitivities fall or cloudiness noted replace with clean windows.
Air filters	Monthly	Clean as needed.

APPENDIX G.
DECISION TREE FOR REPORTING METALS

Aluminum (Al)	x	xxx
Antimony (Sb)	x	xxx
Arsenic (As)	x	xxx
Barium (Ba)	x	xxx
Beryllium (Be)	x	xx
Boron (B)		xx
Cadmium (Cd)	x	xxx
Calcium (Ca)		xx
Chromium (Cr)	x	xxx
Cobalt (Co)	x	xxx
Copper (Cu)	x	xxx
Iron (Fe)		xx
Lead (Pb)	x	xxx
Magnesium (Mg)		xx
Lithium (Li)		xx
Manganese (Mn)	x	xxx
Molybdenum (Mo)	x	xxx
Nickel (Ni)	x	xxx
Potassium (K)		xx
Selenium (Se)	x	xxx
Silica (SiO ₂)		xx
Silver (Ag)	x	xxx
Sodium (Na)		xx
Strontium (Sr)		xx
Thallium (Tl)	x	xxx
Thorium (Th)	x	
Tin (Sn)		xx
Titanium (Ti)		xx
Uranium (U)	x	
Vanadium (V)	x	xxx
Zinc (Zn)	x	xxx

Where:

x = reported by ICP-MS

xx = reported by ICP-AES

xxx = if all 200.7 QC passes and the concentration is above the 200.7 QL, an element may be reported from the 200.7 analysis.

APPENDIX H.

TYPICAL DATA PACKAGE FORMAT

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms

EPA Review Form

ESAT technical review guide

Discrepancy Reports (if applicable)

Work Order Memo (if applicable)

Daily folder review forms or checklists

Analysis matrix listing all analytical runs (for organics only)

Tracking Forms

Work Order(s)

COC(s)

Sample Preparation (for projects that require extraction or digestion)

Bench Sheets (and extraction logs, where used)

Sample cleanup data and records (e.g. GPC logs)

Moisture data as applicable

[Analysis Method] Data (For each method where multiple methods in package)

Bench sheet(s) where not used in Sample Preparation section

Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Alternatively, separate calibration and sample data as:

Initial Calibration Data

Sample Data

Miscellaneous Data

Other data as applicable (e.g. conductivity for perchlorate)

Standard Records

Standards records from LIMS (and logbook pages as needed)

Revision: 7, Effective: 09/17/09

**USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA**

**STANDARD OPERATING PROCEDURE 507
DETERMINATION OF TRACE ELEMENTS IN WATER BY ICP-MS**

Revision 6
Effective Date: April 23, 2007

Reviewed by: _____
Richard Bauer Date
Chemistry Team Leader/Technical Director

Reviewed by: _____
K. W. Hendrix, Laboratory QA Officer Date

Approved by: _____
Brenda Bettencourt, Laboratory Director Date

Periodic Review:

Signature	Title	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____

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APPENDIX A. DEVIATIONS FROM THE REFERENCE METHOD

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APPENDIX I. SOP DISTRIBUTION AND ACKNOWLEDGEMENT LIST

1 SCOPE AND APPLICABILITY

This SOP provides procedures for the determination of dissolved and total recoverable elements by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) in environmental samples for use in the USEPA Region 9 Laboratory, Richmond, CA. It is applicable to ground, surface, drinking, and storm runoff water samples; industrial and domestic waste waters. This SOP is based on EPA Method 200.8, *Determination of Trace Elements in Waters and Wastes by ICP – MS*, Rev. 5.4, May 1994. Deviations from the reference method are described in Appendix A. Analytes and quantitation limits (QLs) are listed in Appendix B.

Water samples with turbidity >1 NTU or where silver and/or total recoverable analytes are requested must be digested following Region 9 Laboratory SOP 403 prior to analysis. Other water samples may be analyzed directly after proper filtration and/or acid-preservation.

2 METHOD SUMMARY

This SOP describes the determination of trace elements in aqueous samples by ICP-MS by direct analysis or after digestion with nitric and hydrochloric acids. Sample solutions are introduced by pneumatic nebulization into a plasma, in which desolvation, atomization, and ionization occurs. Ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are detected by an electron multiplier. Ion intensities at each mass are recorded and compared to those obtained from external calibration standards to generate concentration values for the samples. Results are corrected for instrument drift and matrix effects using internal standards. Additional corrections are applied as necessary to correct for isobaric and polyatomic elemental interferences.

The dynamic reaction cell (DRC) simultaneously employs two techniques for the elimination of interferences, chemical resolution, and dynamic bandpass tuning (DBT). Chemical resolution involves the use of a gas within the DRC cell, which reacts with the interference to eliminate it. The DBT is applied at the same time using a bandpass mass filter which provides a high mass cut off and a low mass cut off to define a precise bandpass window, thus preventing the formation of new species that may interfere with the analysis.

3 DEFINITIONS

Analytical Sample - Any sample introduced into the ICP-MS instrument, excluding calibration standards, blanks, or QC reference samples.

Calibration Blank (CB) - A blank that is the same matrix as the calibration standards, but

without the analytes. The calibration blank is also a zero standard used to calibrate the ICP-MS instrument.

Continuing Instrument Calibration Verification (CCV) – The CCV standard is the same solution as the ICV standard and is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout the analysis sequence (after every ten samples and at end of the analytical run). The CCV is also known as the continuing instrument performance check (IPC) standard.

Dissolved Analyte - The concentration of analyte in an aqueous sample that is filtered through a 0.45-µm membrane filter assembly prior to sample acidification.

Initial Calibration Standard (ICAL) - Standards used to calibrate the instrument response with respect to analyte concentration.

Initial Instrument Calibration Verification (ICV) - A standard containing the analytes of interest that is used to verify the accuracy of the analysis. It is analyzed immediately after calibration. The ICV is also known as the initial instrument performance check (IPC) standard.

Internal Standard - An element added to all sample, extract, and standard solutions in the same known amount. Its response is measured throughout an analytical run and is used to correct for instrument drift and sample transport interferences. The internal standard should not be a sample constituent. Recommended internal standard elements are listed in Appendix D, Table 1.

Laboratory Control Sample (LCS) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is analyzed exactly like a sample and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements. The LCS is also known as a laboratory fortified blank (LFB) or blank spike (BS).

Laboratory Information Management System (LIMS) – The Element Database.

Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear. The LDR study is used to define the concentration of the highest calibration standard.

Matrix Spike (MS) - An aliquot of an analytical sample to which known quantities of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations. The MS is also known as a laboratory fortified matrix (LFM)

sample.

Matrix Spike Duplicate (MSD) - A duplicate aliquot of an analytical sample to which known quantities of the method analytes are added in the laboratory. The MSD is analyzed exactly like a sample and its purpose is to determine whether the sample matrix contributes bias to the analytical results and to determine laboratory precision. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MSD corrected for background concentrations. The MSD is also known as a laboratory fortified matrix duplicate (LFMD) sample.

Method Blank (MB) - An aliquot of reagent water or other blank matrix that is treated exactly as a sample. The MB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment. The MB is also known as a laboratory reagent blank (LRB).

Method Detection Limit (MDL) - The minimum concentration of an analyte in an environmental sample that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Quantitation Limit (QL) - The concentration at which confidence in the reported value requires no qualifying remarks. A standard is run at the QL to verify acceptable data quality.

Quantitation Limit Standard (QLS) - A standard used to check the accuracy of the analysis at the quantitation limit.

Sample Delivery Group (SDG) - A group of twenty samples or less from a project that is sent to the laboratory for analysis.

Second Source Calibration Verification (SCV) - A solution of method analytes of known concentration that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check instrument or laboratory performance with externally prepared test materials. The SCV is also known as a quality control standard (QCS).

Stock Standard Solution (SSS) - A concentrated standard containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Total Recoverable Analyte Concentration - The concentration of an analyte in an unfiltered aqueous sample after preparation by acid digestion.

Tuning Solution - A solution containing selected elements over the entire mass range of the method. It is used to tune the mass calibration and resolution of the mass spectrometer, and

to assess instrument performance prior to calibration and sample analysis.

Water Sample - For the purpose of this method, a sample taken from matrices classified as drinking, surface, ground, or storm runoff water, or industrial or domestic wastewater.

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

4.2 Equipment and Instruments

Areas of high, lethal voltages exist within the instrument. Never touch parts of the instrument that are not intended for access by the instrument operator. Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

The ICP-MS emits radio frequency and intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards. The instrument is shielded to minimize exposure to these hazards and the shields should always be in place during operation.

Always wear safety glasses for eye protection (and a full face shield if large quantities of concentrated acids are being transferred), protective clothing, and observe proper mixing when working with these reagents.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Pollution Prevention Plan* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-regulated Waste	Not applicable
ICP/MS instrument liquid waste (nitric acid, hydrochloric acid, trace metals)	Hazardous Waste	Corrosive, Toxic
Pump Oil	Hazardous Waste	Other

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples should be collected in pre-cleaned polyethylene containers. Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, and minimize waste disposal. A 500 mL sample volume should be sufficient to meet these objectives.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form.

Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to “active out”.

At the end of the day, return sample containers to the designated sample locations.

Update the LIMS database to change the container disposition to “available in.”

5.3 Preservation Verification

1. Dissolved Analyte Samples

The samples must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. Glass or plastic filtering apparatus are recommended to avoid contamination. The laboratory must perform filtration immediately if the step was not performed in the field. Acidify the filtrate with dilute (1:1) nitric acid immediately following filtration to pH<2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient).

2. Drinking Water Samples

Samples are preserved by acidifying with dilute nitric acid to pH<2 (normally, 3

mL of dilute nitric acid per liter of sample is sufficient). Preservation may be done at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, samples may be shipped to the laboratory within two weeks of collection and preserved upon receipt in the laboratory. Following acidification, the sample is mixed and held for sixteen hours and then verified to be pH<2 just prior to withdrawing an aliquot for turbidity measurement. If the sample turbidity is <1 NTU, the sample can be analyzed directly without digestion. If turbidity is >1 NTU, perform the acid digestion for total recoverable analysis.

3. Aqueous Total Recoverable Analyte Samples

Samples are preserved by acidifying with dilute nitric acid to pH<2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient). Preservation may be done at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, samples may be shipped to the laboratory within two weeks of collection and preserved upon receipt in the laboratory. Following acidification, the sample is mixed and held for sixteen hours and then verified to be pH<2 just prior to withdrawing an aliquot for digestion or 'direct analysis'. If the pH of the sample is >2, more acid must be added and the sample held for sixteen hours until verified to be pH<2.

5.4 Sample Storage

Samples must be stored at >0 and ≤ 6 °C. Retain samples for 60 days after the final analytical report is sent to the data user.

5.5 Holding Time

Samples must be analyzed within six months from collection.

6 INTERFERENCES

1. Isobaric Elemental Interferences

Isobaric elemental interferences result when isotopes of different elements have the same nominal mass-to-charge ratio and cannot be resolved with the instrument's spectrometer. One way to solve this problem is to measure a different isotope for which there is no interference. Alternatively, one can monitor another isotope of the interfering element and subtract an appropriate amount from the element being analyzed, using known isotope ratio information. Corrections for most of the common elemental interferences are programmed into the software.

All analytes listed in Appendix B have at least one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method, only antimony-123 (tellurium), molybdenum-98 (ruthenium), and selenium-82 (krypton) have isobaric elemental interferences. (Refer to Appendix D, Table 3). If alternative analytical isotopes having higher natural abundance are selected in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. Such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios should be established prior to the application of any corrections.

2. Abundance Sensitivity Interference

Abundance sensitivity interference refers to the degree of peak overlap that can occur between adjacent peaks. The interference can occur when the shoulder of a large peak significantly overlaps the peak of a neighboring minor peak, thereby contributing to its intensity. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

3. Isobaric Polyatomic Ion Interferences

Isobaric polyatomic interferences result when ions containing more than one atom have the same nominal mass-to-charge ratio as an analyte of interest and cannot be resolved by the instrument's spectrometer. Examples include ArCl^+ (mass 75), which interferes with As, and ClO^+ (mass 51) which interferes with V, which must be corrected by measuring ClO^+ at mass 53. This in turn must be adjusted for contribution from Cr at mass 53. These interferences are highly dependent on the matrix of the samples and day-to-day plasma conditions, so correction factors may be determined on the day of analysis. When possible, one should choose an interference-free isotope to measure.

The Region 9 Laboratory does not routinely calculate these correction factors and uses the recommended elemental equations for data calculations that are listed in Appendix D, Table 2. Alternatively, the Dynamic Reaction Cell (DRC) uses chemical resolution to remove polyatomic interferences using reaction gasses. The reaction gas is chosen such that it reacts with the interfering species to form a new, non-interfering species of a different mass. The new species is then mass separated prior to entry into the analyzer and the interference is effectively removed. The DRC can also use a reaction gas to react with the analyte of interest to form a new molecular species that is then analyzed at a mass that is free of the interference. An example is arsenic in the presence of oxygen in the DRC mode to form arsenic oxide, which is analyzed at mass 92, thus eliminating the ArCl^+ interference present at arsenic mass 75.

4. Physical Interferences

Physical interferences result from the physical processes associated with the transport of sample to the plasma, sample behavior within the plasma, and transmission through the interface region between the plasma and the mass spectrometer. Viscosity and surface tension differences can affect results, as can deposits on the sample and skimmer cones caused by large quantities of dissolved solids in the samples. The interferences can be compensated for by the use of internal standards that approximate the analytical behavior of the elements being determined. Additionally, it is recommended that dissolved solids in samples be kept below 0.2% (w/v).

5. Memory Interferences

Memory interferences are related to sample transport and result when there is carryover from one sample to the next. Sample carryover can result from sample deposition on the sample and skimmer cones and from incomplete rinsing of the sample solution from the plasma torch and the spray chamber between samples. These memory effects are dependent upon both the analyte being measured and sample matrix and can be minimized through the use of suitable rinse times.

The rinse times necessary for a particular analyte should be estimated prior to analysis. This can be achieved by aspirating a standard containing the analyte at a concentration ten times the highest calibration standard for the normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce the analyte signal to less than ten times the method detection limit should be noted. The minimum rinse time between samples should be set to this time. Memory interferences may also be assessed within an analytical run by using three or more replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should check for the possibility of a memory effect. If the analyte concentration in the previous sample is high enough to suspect analyte carryover, the sample should be re-analyzed after a long rinse period.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. Minor deviations may be made in specific apparatus and materials provided that they are documented and equivalency is maintained.

All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives and isolated from other laboratory glassware. Refer to Region 9 Laboratory SOP 130, *Glassware Cleaning Procedures*, for specific instructions.

7.1 Instruments and Equipment

- Perkin Elmer Elan DRC Plus Inductively Coupled Plasma Mass Spectrometer.
- Cetac Autosampler
- Cetac Autodilutor
- Gilson Minipuls3 Peristaltic Pump
- Polyscience 6105 – Refrigerated Circulator

7.2 Reagents

Reagents may contain impurities that might affect analytical data. Only materials that conform to the American Chemical Society (ACS) specifications should be used. If the purity of a reagent is in question, analyze for contamination prior to use. Record all reagent preparations in the LIMS.

- Reagent Water – All references to reagent water in this SOP refer to laboratory deionized water as described in EPA Region 9 Laboratory SOP 825.
- Hydrochloric Acid (HCl), concentrated, trace metals grade or better (e.g. Baker Instra-Analyzed)
- Hydrochloric Acid, dilute (1:1) - Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.
- Nitric Acid (HNO₃), concentrated, trace metals grade or better (e.g. Baker Instra-Analyzed)
- Nitric Acid, dilute (1:1) - Add 500 mL concentrated HNO₃ to 400 mL reagent water and dilute to 1L.
- Argon gas supply, high-purity grade, 99.99%
- DRC Reaction gas - Ammonia, electronic grade, 99.99%
- DRC Reaction gas - Oxygen, research grade

7.3 Standards

Record all standards and standard preparations in the LIMS.

7.3.1 Stock Standards

Stock standard solutions are available from commercial suppliers such as Spex or Inorganic Ventures. Multi-element solutions containing elements listed in

Appendix B are typically used.

7.3.2 Initial Calibration Standards

Prepare initial calibration standards at a minimum of three levels. Use multi-element stock solutions (Section 7.3.1) as the source and dilute to the appropriate volume with 1% (v/v) nitric acid.

For routine analysis, prepare standards to contain 10 µg/L and 20 µg/L for all elements, 100 µg/L for Be, Al, V, Cr, Mn, Co, Mo, Ag, Cd, Sb, Ba, Tl, Pb, Th, and U, and 200 µg/L for Ni, Cu, Zn, As, and Se.

For low level, direct analysis, prepare standards to contain element concentrations at 10 µg/L, 20 µg/L, and 50 µg/L for each element.

NOTE: High level standards may also be used for undiluted samples containing levels of analytes greater than 50 µg/L.

Prepare fresh calibration standards every two weeks or as needed.

7.3.3 ICV/CCV Standard

The ICV standard and CCV standard are identical and only differentiated by their place within the analytical sequence. For routine analysis, a 50 µg/L ICV/CCV is typically analyzed. For low level, direct analysis, a 20 µg/L is typically used. Prepare each solution as needed from multi-element stock solutions (Section 7.3.1) in 1% (v/v) nitric acid.

7.3.4 CB

Dilute concentrated nitric acid with reagent water to obtain a 1% (v/v) nitric acid solution.

7.3.5 MB

Prepare the MB using reagent water plus all of the reagents used in processing the samples. The MB is taken through the entire preparation and analytical sequence.

7.3.6 LCS and MS/MSD

Prepare the LCS by fortifying an aliquot of reagent water from multi-element stock solutions (Section 7.3.1). Process the LCS and MS/MSD through the entire preparation and analytical sequence.

For routine analysis, prepare the LCS by fortifying an aliquot of reagent water to contain 40 µg/L of each analyte. Prepare the MS/MSD by fortifying an aliquot of the QC sample with the stock standards to contain 40 µg/L of each analyte.

For low level, direct analysis, prepare the LCS and MS/MSD concentrations to contain 25 µg/L of each analyte.

7.3.7 SCV

Prepare SCV standards in 1% (v/v) nitric acid from multi-element stock standards from a source different from the calibration standards.

For routine analysis, prepare a standard to contain 50 µg/L of each analyte.

For low level, direct analysis, prepare a standard to contain 20 µg/L of each analyte.

7.3.8 QLS

Prepare the QLS as needed from multi-element stock solutions (Section 7.3.1) in 1% (v/v) nitric acid as shown in the following table:

QLS Concentrations		
Element	Routine Analysis, µg/L	Low-level, Direct Analysis, µg/L
Be Co Mo Ag U	0.5 µg/L	0.25 µg/L
Sb As Ba Cd Cr Ni Se	1 µg/L	0.5 µg/L
Cu Pb Mn Tl Th	2 µg/L	1 µg/L
V	4 µg/L	2 µg/L
Zn	5 µg/L	2.5 µg/L
Al	20 µg/L	10 µg/L

7.3.9 Rinse Blank

Dilute concentrated nitric acid with reagent water to obtain a 2% (v/v) nitric acid solution.

7.3.10 Internal Standard Solution

Prepare internal standards from single-element stock standards (Section 7.3.1) to contain 100 µg/L each of gallium, holmium, indium, rhodium, scandium, terbium, and yttrium and 200 µg/L lithium⁶ in 1% (v/v) nitric acid.

7.3.11 Tuning Solution

Prepare an intermediate standard to contain 1,000 µg/L of barium, beryllium, cerium, cobalt, indium, lead, magnesium, thorium, and uranium from single-element stock standards (Section 7.3.1). Prepare a working solution from the intermediate standard at 1.0 µg/L in 1% (v/v) nitric acid.

7.3.12 Dual Detector Cross Calibration Solution

The dual detector cross calibration solution is used to correlate the pulse and analog modes of the detector for extended linear ranges.

Prepare a solution of all available elements across the entire mass range using the multi-element standards (Section 7.3.1) in 1% (v/v) nitric acid at concentrations of 100 µg/L to 500 µg/L.

7.4 Supplies

- Auto-sampler tubes
- Syringe with 0.45µm disk filters
- Class A volumetric flasks, graduated cylinders, and funnels (glass and/or metal-free plastic)
- Class A volumetric pipettes
- Narrow-mouth storage bottles with screw closure, 125-mL to 1-L capacities
- Automatic pipettes capable of delivering volumes of 10 to 1,000 µL
- Metal-free disposable tips
- Wash Bottle with screw closure, 500-mL to 1,000-mL capacity

8 ANALYTICAL PROCEDURES

It is recommended that samples with unknown or unusual history be screened by ICP for elements at high concentration. Alternatively, samples may be screened using a semi-quantitative ICP/MS analysis at a 500-fold dilution.

8.1 Instrument Operation

Set-up the ICP-MS following operating instructions provided by the manufacturer and discussed below. Use operating parameters provided in Appendix E as a starting point.

Ensure that all appropriate waste containers are properly connected and labeled.

Ignite the plasma and stabilize for at least 30 minutes. During this stabilization period, run the tuning solution (described in Section 7.3.11) using indium signal to align the

torch.

Copy the operating procedure from the master file to the daily data file. Edit so that all masses which are necessary to perform elemental calculations (for interference corrections) and which can provide information concerning data quality are monitored during the analytical run.

At a minimum, masses for the elements of interest prescribed in Appendix D, Table 3 must be monitored in the same scan used for the collection of the data. For elements run in DRC mode, interference corrections calculations are not necessary. Create a new data set file and save workspace.

Initialize the autosampler and create a sample table. If the autodiluter is to be used, initialize the autodiluter and edit the autosampler table as appropriate.

8.1.1 Tuning and Mass Calibration

After the plasma system (i.e., torch box, plasma, and spray chamber) has stabilized, verify and adjust the mass calibration and resolution.

Check the spectrometer resolution with beryllium, magnesium, cobalt, indium, and lead. Also monitor argon dimmer, cerium, and thorium.

The resolution should produce a peak width of approximately 0.75 atomic mass unit (amu) at 5% peak height. For the PE Elan, the resolution of 0.625 to 0.675 at 10% peak height corresponds to approximately 0.70 to 0.75 amu peak width at 5% peak height.

Adjust the mass calibration to ensure 0.1 amu accuracy from unit mass.

8.1.2 Sensitivity and Stability Check

Analyze the tuning solution (Section 7.3.11) a minimum of five times for daily performance check. The RSD for each element must be less than 5% before the instrument can be calibrated and samples analyzed.

Instrument sensitivity should be, at a minimum, as listed below:

Mg - 6,000 counts per second (CPS)

In - 30,000 CPS

U - 20,000 CPS

To avoid interferences, it is preferable that oxide (Ce) and ++ (Ba) levels not exceed 3%. If they do, depending on the specific analysis to be performed, maintenance or instrument adjustments may be required before proceeding with

the analysis.

8.2 Calibration and Standardization

8.2.1 Internal Standardization

Internal standards are used to correct for instrument drift and physical transport interferences. Internal standards are automatically added to all samples, standards, and blanks by mixing with the sample solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil. For full mass range scans, a minimum of three internal standards must be monitored and used for calculation.

NOTE: The concentration of the internal standard should be sufficiently high that good measurement precision is obtained while minimizing the bias introduced if the internal standard is naturally present in the sample (i.e., the signal intensity contributed from naturally occurring internal standard element in the sample is insignificant).

The typical concentration of the internal standard solution contains 200 µg/L lithium⁶ and 100 µg/L of gallium, indium, rhodium, scandium, terbium, and yttrium; holmium is also included as an alternate.

The typical final concentration of the internal standard solution after mixing with the sample is approximately 20 µg/L or approximately one-fifth the initial concentration of the internal standard solution.

8.2.2 Initial Calibration

Perform an initial calibration daily or for every analytical batch, whichever is more frequent. For routine analysis and higher level direct analysis, analyze a minimum of three routine standards (Section 7.3.2) and a CB (Section 7.3.4) according to Section 8.3.2. For low-level, direct analysis, analyze a minimum of three low-level standards and a CB. Refer to Section 9.2.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Analyze the ICV, CB, and SCV according to Section 8.3.2 immediately after analyzing the initial calibration standards. Use the appropriate levels for routine or low-level analysis. If QC criteria are not met, take corrective action as described in Section 9.2 and Appendix C.

8.2.3 Continuing Calibration

Prepare the CCV (appropriate for routine or low-level analysis) and CB as

described in Sections 7.3.3 and 7.3.4 and analyze according to Section 8.3.2. Refer to Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

Digest samples with turbidity >1 NTU and/or where silver is requested following Region 9 Laboratory SOP 403 prior to analysis.

8.3.1.1 Aqueous Samples, Total Recoverable Analytes

For the determination of total recoverable analytes in water, digest samples following Region 9 Laboratory SOP 403 prior to analysis.

The digestion procedures used in SOP 403 will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

The total recoverable sample digestion procedure is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed sample aliquots must be prepared until the analysis solution contains < 0.1mg/L silver.

8.3.1.2 Aqueous Samples, Dissolved Analytes

For the determination of dissolved analytes in ground and surface waters, add a 30 mL aliquot of the filtered, acid preserved sample into a 50-mL polypropylene tube. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis.

For LCS and MS/MSD analyses, spike the samples at 25 µg/L for all analytes.

NOTE: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be digested using the procedure in Region 9 Laboratory SOP 403 prior to analysis.

8.3.1.3 Drinking Water Samples, Total Recoverable Analytes, Direct Analysis

Drinking water samples with turbidity <1 NTU must be acidified and analyzed directly without digestion. Add a 30 mL aliquot of the unfiltered, acid-preserved sample into a 50-mL polypropylene tube. Add 0.60 mL dilute nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis.

For LCS and MS/MSD analyses, spike the samples at 25 µg/L for all analytes.

NOTE: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be digested using the procedure in Region 9 Laboratory SOP 403 prior to analysis.

Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined by direct analysis. For this reason, samples for silver analysis should be digested.

8.3.2 Sample Analysis and Analytical Sequence

This section describes setting up the analytical sequence and performing the instrumental analysis. Record the analytical sequence in the instrument run log or the LIMS sequence page, if available.

Make appropriate dilutions on the basis of screening data, sample history, or other information. Samples for routine analysis are diluted two times using the autodiluter or manual dilution. Samples for low-level analysis are run without dilution.

1. Enter autosampler loading list into the data system, to include initial calibration, all required QC, and samples. If autodiluter is to be used, set-up the QLS, MB, LCS, and samples and specify autodiluter locations. For initial routine analysis, set the autodiluter for two times dilution.
2. Load the samples to be analyzed in the autosampler according to their designated positions in the loading list. The following table shows a typical analytical sequence:

Seq.	Description	Seq.	Description	Seq.	Description
1	CB	15	S2	29	S12
2	Cal Std 1	16	S3	30	CCV
3	Cal Std 2	17	S4	31	CB
4	Cal Std 3	18	CCV	32	S13
5	Cal Std 4	19	CB	33	S14
6	ICV	20	S5	34	S15
7	CB	21	S6	35	S16
8	SCV	22	S7	36	S17
9	QLS	23	S8	37	S18
10	MB	24	S9	38	S19
11	LCS	25	S10	39	S20
12	S1	26	S11	40	CCV
13	S1-MS	27	S11-MS	41	CB
14	S1-MSD	28	S11-MSD	42	QLS*

NOTE: *Analyze QLS if more than 40 analytical samples are to be analyzed.

3. Start the autosampler analytical sequence and collect results.
4. Review the results for QC compliance and off-scale results. Identify samples that must be re-analyzed in a different analytical run. Samples having analytes at concentrations higher than the highest calibration must be diluted into range and re-analyzed.
5. Compare all analyte results generated in DRC mode with the run in standard mode. If results from the two modes differ significantly, interference may be present. If interference is suspected, dilute and reanalyze in both modes.

8.3.3 Analyte Identification and Quantitation

- 8.3.3.1 If an element has more than one monitored isotope, examination of the concentration calculated for each isotope, or the isotope ratios, will provide useful information for the analyst in detecting a possible spectral interference. Consideration should be given to both primary and secondary isotopes in the evaluation of the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes. Check additional monitored masses (i.e. krypton, bromine, palladium) as indicators of potential interferences (refer to Appendix D).
- 8.3.3.2 After set-up and calibration the instrument reports results for the analyzed solution in the units of $\mu\text{g/L}$. The instrument calculations include

elemental correction calculations, internal standard correction calculations, and calibration factors.

8.3.3.3 Report results in µg/L using the following equation:

$$C = M \times \frac{V_f}{V_i} \times D$$

Where

- C = final reported concentration, in µg/L.
- M = measured concentration reported by instrument, in µg/L.
- V_f = final volume of sample solution after sample preparation, in mL.
- V_i = initial volume of sample used in sample preparation, in mL.
- D = sample analysis dilution factor, to account for any dilution performed after sample preparation. For samples analyzed by the direct analysis, include the factor introduced by the addition of 1:1 nitric acid.

8.3.4 QC Review

- Review the results of instrument QC (ICV, CCV, CB, SCV, and QLS) immediately after their analysis to verify that the results are within QC limits. See Section 9.2 for corrective action requirements and Appendix C for QC limits.
- Review the results of batch QC (MB, LCS, MS/MSD) immediately after their analysis to verify that the results are with QC limits. See Section 9.2 for corrective action requirements and Appendix C for QC limits.

8.3.5 Data Export and LIMS Entry

- Export data from the instrument into text files. Import into the LIMS using DataTool. Review final results in the LIMS.
- Report all results to two significant figures. Report detected results to one-half the QL. Flag values between one-half the QL and the QL as estimated (J).

8.4 Maintenance

Perform maintenance if the tune standard does not pass. Observe for measured mass parameter at ±0.1 amu. Observe for resolution parameter of peak width at 0.65 ±0.025. Adjust DAC parameters, if necessary.

If daily performance is unacceptable, check sample introduction (pump tubing, torch, nebulizer, cones, etc.) for wear and cleanliness. Clean or replace as necessary. If daily performance is still unacceptable, perform Optimizations procedure as described in Elan Software Guide.

Refer to Appendix F for preventative maintenance operations and schedules.

9 QUALITY CONTROL

9.1 Demonstration of Capability

The EPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

A demonstration of capability must be performed prior to using an analytical procedure. A new demonstration must be performed if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880 for more details.

9.2 Instrument QC

9.2.1 Initial Calibration

An initial calibration is performed daily or for each batch of analysis using a blank and a minimum of three calibration standards. A linear calibration forced through zero is used for calculation. Refer to Appendix C for acceptance criteria.

If an ICAL fails because of one standard, a fresh solution of that standard may be reanalyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that the criteria are satisfied before any samples are analyzed.

The calibration is verified by the analysis of an ICV, CB, and SCV. If the criteria for those standards are not met, take corrective action as needed before continuing with analysis, including reanalysis or re-preparation and reanalysis of the initial calibration if necessary. The analysis may also continue but samples cannot be analyzed for the out-of-control analytes.

9.2.2 Initial and Continuing Calibration Verification

To check instrument performance and verify the accuracy and stability of the calibration, analyze an ICV and CCV standard. The ICV is analyzed immediately following initial calibration and the CCV at a frequency of one per 10 analytical samples and at the end of the analytical run. The recovery of analytes in the ICV and CCV are calculated as follows:

$$\% R = \frac{M}{T} \times 100$$

Where

%R = percent recovery of the standard.

M = measured concentration of the analyte, µg/L.

T = true concentration of the analyte in the ICV/CCV, µg/L.

The ICV recovery criteria are listed in Appendix C. If the %R for any analyte in the ICV falls outside of the QC criteria, the instrument must be re-calibrated for at least the out-of-control analytes. Samples cannot be analyzed for the out-of-control analytes until an acceptable ICV is analyzed.

The CCV recovery criteria are listed in Appendix C. If the %R for any analyte in the CCV falls outside of the QC criteria, the instrument must be re-calibrated for at least the out-of-control analytes. Once an acceptable calibration is obtained, the samples preceding the out-of-control CCV must be re-analyzed for the affected analytes.

9.2.3 Calibration Blank

The stability of the baseline must be monitored by analyzing a CB immediately after every ICV/CCV standard. If the value of the CB result is less than ½ the QL, the result is acceptable. If the value of the CB result equals or exceeds one-half the QL, the analysis may continue but samples cannot be analyzed for the out-of-control analytes. The cause of the high CB result must be determined and the problem corrected. The instrument must be re-calibrated at least for the out-of-control analyte and all samples not bracketed by acceptable CB results must be re-analyzed.

9.2.4 Second Source Calibration Verification

Analyze a SCV daily to verify the calibration standards and acceptable instrument performance. If the measured concentrations are not within ±10% of the true values, the method performance is unacceptable. The source of the problem must be identified and corrected before proceeding with analyses.

The recovery of analytes in the SCV is calculated as:

$$\% R = \frac{M}{T} \times 100$$

Where

- %R = percent recovery of the standard.
- M* = measured concentration of the analyte, µg/L.
- T* = true concentration of the analyte in the SCV, µg/L.

9.2.5 Quantitation Limit Standard

To verify the ability to detect target analytes near the QL, a QLS must be analyzed at the beginning of the analytical run and after each 40 analytical samples. If using an autodiluter to analyze samples, use the diluter also to analyze the QLS. The recovery of analytes in the QLS is calculated as:

$$\% R = \frac{M}{T} \times 100 \times D$$

Where

- %R = percent recovery of the standard.
- M* = measured concentration of the analyte, µg/L.
- T* = true concentration of the analyte in the QLS, µg/L.
- D* = sample analysis dilution factor, to account for any dilution performed after sample preparation.

If the QLS recovery does not meet the criteria in Appendix C, determine the cause, take corrective action, and re-analyze the QLS.

9.3 Batch QC

9.3.1 Method Blank

Analyze at least one MB with each batch of 20 or fewer field samples of the same matrix. MB values $\geq \frac{1}{2}$ the QL indicate potential laboratory or reagent contamination. Use the following guidelines to determine when samples must be re-prepared, re-analyzed, and flagged as estimated:

- If the MB analyte value is $\geq \frac{1}{2}$ the QL and the sample result is less than five times the MB analyte amount, rerun the MB once to verify and if still unacceptable then the MB and all associated samples must be re-prepared

and re-analyzed. The associated sample results can also be reported but will be qualified as estimated “J”.

- If the MB analyte value is $\geq \frac{1}{2}$ the QL and the sample result is non-detected or is greater than five times the MB analyte concentration, report sample results without qualification.

9.3.2 LCS

Analyze one LCS with each batch of 20 or fewer samples of the same matrix. Recovery of analytes in the LCS is calculated as:

$$\% R = \frac{M}{T} \times 100 \times D$$

Where

- %R = percent recovery of the standard.
- M* = measured concentration of the analyte, µg/L.
- T* = true concentration of the analyte in the LCS, µg/L.
- D* = sample analysis dilution factor, to account for any dilution performed after sample preparation.

If the recovery of the LCS does not meet the recovery criteria in Appendix C, re-analyze once to verify. If the recovery is still unacceptable, the analyte is judged to be out- of-control and the source of the problem must be identified and resolved. All samples associated with the out-of-control LCS must be re-prepared and re-analyzed.

9.3.3 Matrix Spike/Matrix Spike Duplicate

The MS and MSD are designed to provide information about the effect of sample matrix on the measurement system. One set of MS/MSD samples must be prepared for every 10 field samples of the same matrix in an SDG. Homogenize the routine sample selected as the QC and spike a representative aliquot with the analytes of interest prior to any sample preparation. The spiking level must be the same as that used for the LCS.

Samples identified as field blanks cannot be used for MS/MSD sample analysis. MS/MSD recoveries are calculated as:

$$\% R = \frac{C_{ms} - C}{s} \times 100$$

Where

- $\%R$ = percent recovery.
- C_{ms} = measured concentration of analyte in the MS, corrected for sample preparation and any dilutions.
- C = measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions.
- s = expected spiked analyte concentration in the MS, corrected for sample preparation and any dilutions.

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|C_{msd} - C_{ms}|}{(C_{msd} + C_{ms}) / 2} \times 100$$

Where

- RPD = relative percent difference.
- C_{msd} = measured concentration in the MSD, corrected for sample preparation and any dilutions.
- C_{ms} = measured concentration in the MS, corrected for sample preparation and any dilutions.

If the value of C is less than four times the value of s , apply accuracy and precision criteria in Appendix C. If the value of C is greater than four times the value of s , $\%R$ is not calculated. If the MS/MSD does not meet these criteria, examine other QC results to determine if a matrix problem exists. If laboratory performance is in control, the poor MS/MSD accuracy and precision is likely to be matrix-related. Flag any out-of-control results as estimated "J".

9.4 Sample QC

Internal Standard Response - Monitor the signal intensity for the internal standard masses throughout the analytical run. This information is useful in detecting instrument drift, sensitivity shift; dissolved solids content, and inherent internal standard (i.e., a natural constituent in a sample). The absolute intensity of any one internal standard must not deviate more than 60 - 125% from its original intensity in the calibration blank. If deviations greater than these are observed, examine the internal standard intensities with the following actions:

- If the intensities of the internal standards for the ICV, CCV, or CB are out-of-control, recalibrate and re-analyze the analytes affected by the out-of-control internal standards in the affected samples.
- If the intensities of the internal standards for the ICV, CCV, and CB are within

control limits but sample internal standards are out-of-control, rerun the sample or rerun at an appropriate dilution for the analytes affected by the out-of-control internal standard.

- Report results from the original, undiluted, or least diluted sample where the internal standards are within the acceptance limits.

9.5 Method Performance

Region 9 Laboratory performance for this SOP from January 2006 to February 2007 is summarized in the following table.

Method Performance				
Analyte	QC Type	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2 σ)
Aluminum (Al)	LCS	37	99.7	87.9 - 112
Antimony (Sb)	LCS	36	101	96.8 - 106
Arsenic (As)	LCS	50	101	92.7 - 109
Barium (Ba)	LCS	32	98.3	92.1 - 104
Beryllium (Be)	LCS	34	96.3	87.9 - 105
Cadmium (Cd)	LCS	40	98.9	94.2 - 104
Chromium (Cr)	LCS	42	103	91.5 - 115
Cobalt (Co)	LCS	31	97.3	87.1 - 107
Copper (Cu)	LCS	44	98.9	86.2 - 112
Lead (Pb)	LCS	57	99.5	89.9 - 109
Manganese (Mn)	LCS	43	98.5	89.8 - 107
Molybdenum (Mo)	LCS	33	99.7	93.1 - 106
Nickel (Ni)	LCS	38	97.8	90 - 106
Selenium (Se)	LCS	34	98.1	90.7 - 106
Silver (Ag)	LCS	34	98.7	89.5 - 108
Thallium (Tl)	LCS	34	97.4	87.4 - 108
Thorium (Th)	LCS	7	91.7	78.1 - 105
Uranium (U)	LCS	13	95.6	81.5 - 110
Vanadium (V)	LCS	33	96.6	86.9 - 106
Zinc (Zn)	LCS	45	100	90 - 111

The primary sources of analytical error are:

- Calibration standard accuracy
- Digestion equipment contamination
- Transfer pipette accuracy

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QLS, MS/MSD, and LCS) are recorded in the LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used in this SOP in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the LIMS or in the instrument run log. Case Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the LIMS. The data package is produced from LIMS database and manual log records. Appendix G provides decision tree for reporting metals. Appendix H provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control. Document all preventive or routine maintenance performed, as well as repairs or corrective or remedial actions in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*. Also, document major changes or upgrades to instrument hardware and software in the maintenance logbook.

10.6 SOP Distribution and Acknowledgement

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. Document using the SOP Distribution and Acknowledgement List as shown in Appendix I.

11 REFERENCES

EPA Region 9 Laboratory SOP 110, *Sample Receiving and Login*.

EPA Region 9 Laboratory SOP 125, *Sample Disposal*.

EPA Region 9 Laboratory SOP 130, *Glassware Cleaning Procedures*.

EPA Region 9 Laboratory SOP 403, *Aqueous Sample Preparation for ICP-AES and ICP-MS*.

EPA Region 9 Laboratory SOP 462, *Analysis of Total Suspended Solids By EPA Method 160.2*.

EPA Region 9 Laboratory SOP 820, *Laboratory Discrepancy and Corrective Action Procedures*.

EPA Region 9 Laboratory SOP 830, *Notification Procedures for Results Exceeding the Safe Drinking Water Act Maximum Contaminant Level*.

EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

EPA Region 9 Laboratory SOP 880, *Demonstration of Capability*.

Perkin Elmer, *ELAN 6100 DRC Software Kit and Elan 6100 DRC Hardware Guide*.

U.S. Environmental Protection Agency Method 200.8, *Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, EMMC Version, May 1994*.

U.S. Environmental Protection Agency SW846 Method 6020, *Inductively Coupled Plasma-Mass Spectrometry, Revision 1, January 1998*.

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. This SOP does not include mercury as an analyte. Mercury is listed as an analyte in the reference method.
2. The MS/MSD and LCS are spiked at 40 µg/L for selenium; the referenced method specifies 200 to 500 µg/L.
3. This SOP specifies analysis of a MSD for precision; the reference method specifies analysis of a laboratory duplicate.
4. A linear dynamic range (LDR) standard is specified in the reference method but not specified in this SOP. The Region 9 Laboratory requires any sample with a concentration above the highest calibration standard be diluted and reanalyzed.
5. This SOP includes gallium for internal standard based on the manufacture's recommendation. Gallium is not listed as an internal standard in the reference method.
6. This SOP specifies that the MB acceptance criterion is less than one-half the QL. The reference method specifies no greater than 2.2 times MDL.
7. The antimony, indium, and molybdenum elemental equations used for calculations are taken from the instrument software and differ slightly from those specified in the reference method.
8. The SOP specifies that arsenic results be reported from arsenic oxide (AsO mass 91) using the Dynamic Reaction Cell (DRC) mode and not arsenic at mass 75 as the reference method specifies.
9. The SOP specifies that thallium results be reported from thallium 203 and not thallium 205 as the reference specifies.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides the target analyte list for this SOP with the CAS number and quantitation limits.

Analyte	Chemical Abstracts Registry Number (CASRN)	QL, Routine Analysis, Water, µg/L	QL, Low-Level Analysis, Water, µg/L
Aluminum (Al)	7429-90-5	20	10
Antimony (Sb)	7440-36-0	1	0.5
Arsenic (As)	7440-38-2	1	0.5
Barium (Ba)	7440-39-3	1	0.5
Beryllium (Be)	7440-41-7	0.5	0.25
Cadmium (Cd)	7440-43-9	1	0.5
Chromium (Cr)	7440-47-3	1	0.5
Cobalt (Co)	7440-48-4	0.5	0.25
Copper (Cu)	7440-50-8	2	1
Lead (Pb)	7439-92-1	2	1
Manganese (Mn)	7439-96-5	2	1
Molybdenum (Mo)	7439-98-7	0.5	0.25
Nickel (Ni)	7440-02-0	1	0.5
Selenium (Se78)*	7782-49-2	2	1
Selenium (Se82)	7782-49-2	1	0.5
Silver (Ag)	7440-22-4	0.5	0.25
Thallium (Tl)	7440-28-0	2	1
Thorium (Th)	7440-29-1	2	1
Uranium (U)	7440-61-1	0.5	0.25
Vanadium (V)	7440-62-2	4	2
Zinc (Zn)	7440-66-6	5	2.5

NOTE: *Se at mass 78 is only reported when bromine is detected in concentration that interferes with Se at mass 82.

APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

Parameter	Frequency	Criteria
Correlation Coefficient	Each ICAL	≥ 0.995
ICV	After ICAL	90 - 110%
CCV	Every 10 Samples	90 - 110%
CB	After each ICV/CCV	$< \frac{1}{2}$ QL
SCV	After ICAL	90 - 110%
QLS	After ICAL & after every 40 analytical samples	60 - 140%
MB	Each Batch	$< \frac{1}{2}$ QL
LCS	Each Batch	85 - 115%
MS/MSD, Accuracy	Every 10 samples	70 - 130%
MS/MSD, Precision	Every 10 samples	≤ 20 RPD
Internal Standard	Every analysis	60-125% of initial CB

Instrument Sensitivity and Stability Check:

- For daily performance check, the RSD for each element must be $< 5\%$.
- Sensitivity should be, at a minimum, Mg - 6,000 CPS, In – 30,000 CPS, and U – 20,000 CPS.
- Oxide (Ce) and ++ (Ba) levels, approximately 3% or lower are preferred.

APPENDIX D.
INTERNAL STANDARD TABLES, ELEMENT ISOTOPE, & EQUATION

Table 1. Internal Standards and Limitations of Use

Internal Standard	Mass	Possible Limitation
⁶ Lithium	6	a
<u>Scandium</u>	45	Polyatomic Ion Interference
<u>Yttrium</u>	89	
Rhodium	103	a, b
<u>Indium</u>	115	Isobaric Interference by Sn
<u>Terbium</u>	159	
Holmium	165	
Gallium	71	c

NOTES:

Internal standards recommended for use with this method are shown in underlined text.

Internal standards typically used by the Region 9 Laboratory are shown in **bold** text.

- a May be present in environmental samples.
- b In some instruments, Yttrium may form measurable amounts of YO⁺ (105 amu) and YOH⁺ (106 amu). If this is the case, care should be taken in the use of the cadmium elemental correction equation.
- c Gallium is recommended by the manufacturer of the Elan DRC instrument being used at the EPA Region 9 Laboratory.

Table 2. Recommended Element Equations for Data Calculations - Standard Mode

Element	Elemental Equation	Note
Al	$(1.000)(^{27}\text{C})$	
Sb	$(1.000)(^{123}\text{C}) - (0.127189)(^{125}\text{C})$	1
As	$1.000(^{75}\text{C}) - (3.127)[(^{77}\text{C}) - (0.815)(^{82}\text{C})]$	2
Ba	$1.000(^{137}\text{C})$	
Be	$1.000(^9\text{C})$	
Cd	$1.000(^{111}\text{C}) - (1.073)[(^{108}\text{C}) - (0.712)(^{106}\text{C})]$	3
Cr	$1.000(^{52}\text{C})$	4
Co	$1.000(^{59}\text{C})$	
Cu63	$1.000(^{63}\text{C})$	
Cu65	$1.000(^{65}\text{C})$	5
Pb	$1.000(^{206}\text{C}) + 1.000(^{207}\text{C}) + 1.000(^{208}\text{C})$	6
Mn	$1.000(^{55}\text{C})$	
Mo	$1.000(^{98}\text{C}) - 0.11058(^{101}\text{C})$	7
Ni60	$1.000(^{60}\text{C})$	
Ni62	$1.000(^{62}\text{C})$	8
Se78	$1.000(^{78}\text{C}) - 0.1869(^{76}\text{C})$	9
Se82	$1.000(^{82}\text{C})$	10
Ag	$1.000(^{107}\text{C})$	
Tl	$1.000(^{203}\text{C})$	
Th	$1.000(^{232}\text{C})$	
U	$1.000(^{238}\text{C})$	
V	$1.000(^{51}\text{C}) - (3.127)[(^{53}\text{C}) - (0.113)(^{52}\text{C})]$	11
Zn	$1.000(^{66}\text{C})$	
Ga	$1.000(^{71}\text{C})$	
Ho	$1.000(^{165}\text{C})$	
In	$1.000(^{115}\text{C}) - 0.014032(^{118}\text{C})$	12
Li ⁶	$1.000(^6\text{C})$	
Rh	$1.000(^{103}\text{C})$	
Sc	$1.000(^{45}\text{C})$	
Tb	$1.000(^{159}\text{C})$	
Y	$1.000(^{89}\text{C})$	

NOTES:

- C Calibration blank subtracted counts at specified mass.
 1 Isobaric correction for Te
 2 Isobaric correction for ArCl, Se
 3 Correction for MoO, Sn.

- 4 The background for ClOH will normally be small and can be estimated from the reagent blank.
- 5 Used as alternate mass when ArNa interference apparent at Cu63.
- 6 Allowance for isobaric variability of lead isotopes
- 7 Isobaric elemental correction for Ru
- 8 Used as alternate mass when CaO and CaOH interferences at Ni60.
- 9 Used as alternate mass when HBr interference apparent at Se82, Isobaric correction for Ar2 dimer.
- 10 Some Ar supplies contain Kr as an impurity. Se is corrected for ^{82}Kr by background subtraction.
- 11 Correction for chloride interference with adjustment for ^{53}Cr . ClO 51/53 ratio may be determined from the reagent blank. Isobaric mass 52 must be from Cr only, not ArC^+ .
- 12 Isobaric correction for Sn

Table 3. Recommended Analytical Isotope and Additional Masses that must be monitored

Element of Interest	Isotope
Aluminum	<u>27</u>
Antimony	121, <u>123</u>
Arsenic	<u>75</u>
Barium	135, <u>137</u>
Beryllium	<u>9</u>
Cadmium	106, 108, <u>111</u> , 114
Chromium	<u>52</u> , 53
Cobalt	<u>59</u>
Copper	<u>63</u> , 65
Lead	<u>206</u> , <u>207</u> , <u>208</u>
Manganese	<u>55</u>
Molybdenum	95, 97, <u>98</u>
Nickel	<u>60</u> , 62
Selenium	76, 77, 78, <u>82</u>
Silver	<u>107</u> , 109
Thallium	<u>203</u> , 205
Thorium	<u>232</u>
Uranium	<u>238</u>
Vanadium	<u>51</u>
Zinc	<u>66</u> , 67, 68
Bromine	79, 81
Krypton	83
Palladium	105
Ruthenium	101
Tellurium	125
Tin	118

NOTE: Isotopes recommended for analytical determination are underlined.

Table 4. Recommended Analytical Isotopes For DRC Analysis

Element of Interest	Isotope
Arsenic as Arsenic Oxide	<u>91</u>
Chromium	<u>52</u>

NOTE: Isotopes recommended for analytical determination are underlined.

Table 5. Internal Standard Groups - Standard Mode

Element	Internal Standard Group	Internal Standard
Be	1	Li ⁶
Al	2	Sc
V	2	
Cr	2	
Mn	2	
Co	2	
Ni	2	
Cu	2	
Zn	3	Y
As	3	
Se	3	
Mo	4	In
Ag	4	
Cd	4	
Sb	4	
Ba	5	Tb
Tl	5	
Pb	5	
U	5	
Th	5	

Table 6. Internal Standards - DRC Mode

Element	Internal Standard Group	Internal Standard
Cr	6	Ga
As as AsO	7	Rh

APPENDIX E.
RECOMMENDED INSTRUMENT PARAMETERS

Nebulizer Gas Flow:	0.85 - 1.05 mL/min (~0.90 typical)
Auxiliary Gas Flow:	1.20 mL/min
Plasma gas Flow:	12.0 mL/min
ICP RF Power:	1,100 - 1,500 watts (1,350 typical)
Pulse Stage Voltage:	900 - 2,500 (increases with age of detector to meet sensitivity parameters)
Analog Stage Voltage:	1,600 - 2,500 (increases with age of detector to meet sensitivity parameters)
Argon Line Pressure:	51 psi \pm 1

APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

Maintenance Schedule for the Elan ICP-MS

Item	Frequency	Comments
Auto-sampler Rinse Station Reservoir	As needed	Fill with 2% HNO ₃ .
Pump Tubing	Daily	Check for fatigue and wear. Replace as needed.
Cones	Daily Weekly	Inspect for sample residues. Wipe clean or replace with clean cone as needed. Remove and inspect condition of cones. Replace if needed.
Torch Tip	Daily	Check for sample residues. Replace with clean glassware if needed.
Argon Dewar	Daily	Check for sufficient amount and pressure. Order as needed.
Autodiluter	Daily	Rinse thoroughly with reagent water after each use.
Auto-sampler and Peristaltic Pump	Weekly	Wipe spills or residues.
Nebulizer Spray	Weekly	Check, unclog or replace if needed.
Glassware	Weekly	Inspect and clean if needed.
Glassware & Cone alignment	Weekly	Perform X-Y alignment, if needed.
Air filters	Monthly	Clean or replace as needed.
Chiller Coolant	Monthly	Check level and top off as needed.
Vacuum Oil	Monthly	Check level and color, replace with fresh one if needed.

APPENDIX G.
DECISION TREE FOR REPORTING METALS

Aluminum (Al)	x	xxx
Antimony (Sb)	x	
Arsenic (As)	x	
Barium (Ba)	x	xxx
Beryllium (Be)	x	xxx
Boron (B)		xx
Cadmium (Cd)	x	
Calcium (Ca)		xx
Chromium (Cr)	x	
Cobalt (Co)	x	xxx
Copper (Cu)	x	xxx
Iron (Fe)		xx
Lead (Pb)	x	
Magnesium (Mg)		xx
Manganese (Mn)	x	xxx
Molybdenum (Mo)	x	
Nickel (Ni)	x	xxx
Potassium (K)		xx
Selenium (Se)	x	
Silica (SiO ₂)		xx
Silver (Ag)	x	
Sodium (Na)		xx
Strontium (Sr)		xx
Thallium (Tl)	x	
Thorium (Th)	x	
Tin (Sn)		xx
Titanium (Ti)		xx
Uranium (U)	x	
Vanadium (V)		xx
Zinc (Zn)	x	xxx

Where:

x = reported by ICP-MS

xx = reported by ICP-AES

xxx = if all 200.7 QC passes and the concentration is above the 200.7 QL, an element may be reported from the 200.7 analysis.

APPENDIX H. TYPICAL DATA PACKAGE FORMAT

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms

Daily folder review forms or checklists
Other review forms as applicable

Tracking Forms

Work Order(s)
COC(s)

Sample Preparation (for projects that require extraction or digestion)

Bench Sheets (and extraction logs, where used)
Sample cleanup data and records (e.g. GPC logs)
Moisture data as applicable
Analysis matrix (for organics)

[Analysis Method] Data (For each method where multiple methods in package)

Bench sheet(s) where not used in Sample Preparation section
Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Alternatively, separate calibration and sample data as:

Initial Calibration Data
Sample Data

Miscellaneous Data

Other data as applicable (e.g. conductivity for perchlorate)

Standard Records

Standards records from LIMS (and logbook pages as needed)

APPENDIX I.
SOP DISTRIBUTION AND ACKNOWLEDGEMENT LIST

STANDARD OPERATING PROCEDURE: 507
Revision: 6, Effective: 04/23/07

DETERMINATION OF TRACE ELEMENTS IN WATER BY ICP-MS

I have received, read, and understood the above referenced SOP and agree to comply with the SOP when performing the subject procedure until the effective date of future revisions.

NAME	DATE DISTRIBUTED	SIGNATURE	DATE
_____	_____	_____	_____
_____	_____	_____	_____
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**USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA**

**STANDARD OPERATING PROCEDURE 515
DETERMINATION OF MERCURY IN WATER BY CVAA SPECTROMETRY**

Revision 6
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1 SCOPE AND APPLICABILITY

This SOP describes the sample preparation steps and the instrumental analytical procedure for mercury by cold vapor atomic absorption (CVAA) in environmental samples. It is applicable to drinking, ground, surface, sea and brackish water, domestic and industrial wastes, and leachates. This SOP is based on EPA Method 245.1, *Determination of Mercury in Water by CVAA Spectrometry*, Revision 3, May 1994. Deviations from the reference method are described in Appendix A. Analyte and quantitation limit (QL) are listed in Appendix B.

2 METHOD SUMMARY

An aliquot of a water sample is transferred to a hot block digestion vessel. The sample is digested with nitric acid, sulfuric acid, and a dilute potassium permanganate-potassium persulfate solution for two hours at 95 °C. The digestion oxidizes all forms of mercury to Hg (II). The Hg (II) in the digested water sample is reduced with stannous chloride to elemental mercury that is sparged from the sample and detected by atomic absorption. The measurement step is performed using an automated mercury analyzer.

3 DEFINITIONS

Analytical Sample - Any sample in which mercury is being determined, excluding standards, method blanks, or QC reference samples.

Calibration Blank (CB) - A blank that is the same matrix as the calibration standards, but without the analyte.

Continuing Instrument Calibration Verification (CCV) - The CCV standard is the same solution as the ICV standard and is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout the analysis sequence (after every ten samples and at end of the analytical run). The CCV is also known as the continuing instrument performance check (IPC) standard.

Initial Instrument Calibration Standard (ICAL) - A standard prepared from the stock standard. The ICAL standards are used to calibrate the instrument response with respect to analyte concentration.

Initial Instrument Calibration Verification (ICV) - A standard containing the analyte of interest that is used to verify the accuracy of the analysis. It is analyzed immediately after

calibration. The ICV is also known as the initial instrument performance check (IPC) standard.

Laboratory Control Sample (LCS) - An aliquot of reagent water or other blank matrix to which a known quantity of the method analyte is added. The LCS is analyzed exactly like a sample and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements. The LCS is also known as a laboratory fortified blank (LFB) or blank spike (BS).

Laboratory Information Management System (LIMS) - The Element Database.

Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear. The LDR study is used to define the concentration of the highest calibration standard.

Matrix Spike (MS) - An aliquot of an analytical sample to which a known quantity of the method analyte is added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations. The MS is also known as a laboratory fortified matrix (LFM) sample.

Matrix Spike Duplicate (MSD) - A duplicate aliquot of an analytical sample to which a known quantity of the method analyte is added in the laboratory. The MSD is analyzed exactly like a sample and its purpose is to determine whether the sample matrix contributes bias to the analytical results and to determine laboratory precision. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MSD corrected for background concentrations. The MSD is also known as a laboratory fortified matrix duplicate (LFMD) sample.

Method Blank (MB) - An aliquot of reagent water or other blank matrix that is treated exactly as a sample. The MB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment. The MB is also known as a laboratory reagent blank (LRB).

Method Detection Limit (MDL) - The minimum concentration of an analyte in an environmental sample that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Quantitation Limit (QL) - The concentration at which confidence in the reported value requires no qualifying remarks. A standard is run at the QL to verify acceptable data quality.

Quantitation Limit Standard (QLS) - A standard used to check the accuracy of the analysis at the quantitation limit.

Sample Delivery Group (SDG) - A group of twenty samples or less from a project that is sent to the laboratory for analysis.

Second Source Calibration Verification (SCV) - A solution of method analyte of known concentration that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check instrument or laboratory performance with externally prepared test materials. The SCV is also known as a quality control standard (QCS).

Stock Standard Solution (SSS) - A concentrated standard containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Water Sample - For the purpose of this method, a sample taken from matrices classified as drinking, surface, ground, or storm runoff water, or industrial or domestic wastewater.

4 SAFETY & HEALTH

All laboratory personnel must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-regulated Waste	Not applicable
Mercury instrument waste (mercury, nitric acid, sulfuric acid, potassium permanganate, potassium persulfate, etc.)	Hazardous Waste	Corrosive, Toxic

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples should be collected in pre-cleaned polyethylene containers. Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, and minimize waste disposal. A 100 mL sample should be sufficient to meet these objectives.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form.

Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to “active out” and the location to the appropriate room number. At the end of the day, return sample containers to the “Home” locations. Update the LIMS database using the “return to home location” feature and update container disposition to “available in”. Verify that your initials are recorded whenever you update the LIMS custody information.

5.3 Preservation Verification

Samples are preserved by acidifying with dilute nitric acid to pH < 2 (normally, 3 mL of dilute nitric acid per liter of sample is sufficient). Preservation may be done at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, samples must be shipped to the laboratory as soon as possible after collection and acid preserved upon receipt in the laboratory.

5.4 Sample Storage

Samples must be stored at > 0 and ≤ 6 °C. Retain samples for 60 days after the final analytical report is sent to the data user.

5.5 Holding Time

Samples must be analyzed within 28 days from collection.

6 INTERFERENCES

1. Interferences have been reported for water samples containing sulfide, chloride, copper, and tellurium. Organic compounds that have broadband UV absorbance (around 253.7 nm) are confirmed interferences. The concentration levels for interfering compounds are difficult to define. This suggests that quality control procedures (Section 9) must be strictly followed.
2. Low level mercury sample preparation, digestion, and analysis may be subject to environmental contamination if performed in areas with ambient backgrounds where mercury was previously employed as an analytical reagent in analyses such as total Kjeldahl nitrogen (TKN) or chemical oxygen demand (COD). The EPA Region 9 Laboratory does not currently use any mercury containing reagents, but caution must be taken should new procedures be developed.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

- Cetac M-7500 Mercury Analyzer - includes optical cell, mercury lamp, peristaltic pump, nafion dryer, sample and reagent tubing, ASX-500 autosampler, and Cetac M-7500 software, or equivalent.
- Environmental Express Hot Block Digestion System, or equivalent
- Analytical Balance - capable of weighing accurately to ± 0.001 g
- ASTM Class 1 weights
- Pipettes - calibrated fixed volume and digital variable volume, Eppendorf or equivalent, with appropriate trace metals-free plastic tips.
- Pipettors - for dispensing reagents and acids
- Stirrer plate and stirring bars

7.2 Reagents

Reagents may contain impurities that might affect analytical data. Only materials that conform to the American Chemical Society (ACS) specifications should be used. If the purity of a reagent is in question, analyze for contamination prior to use. Record all reagents and reagent preparations in the LIMS.

- Reagent water - All references to reagent water in this SOP refer to laboratory deionized water as described in EPA Region 9 Laboratory SOP 825.
- Hydrochloric acid (HCl), concentrated, ACS reagent grade or better
- Hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), ACS reagent grade or better
- Nitric Acid (HNO_3), concentrated, ACS reagent grade or better
- Potassium permanganate (KMnO_4), ACS reagent grade or better
- Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), ACS reagent grade or better
- Sodium chloride (NaCl), ACS reagent grade or better
- Sulfuric Acid (H_2SO_4), concentrated, ACS reagent grade or better
- Stannous chloride (SnCl_2), ACS reagent grade or better
- Argon gas supply, high-purity grade, 99.99%

7.2.1 5% Potassium Permanganate Solution

Dissolve 25 g potassium permanganate in 500 mL of reagent water. Prepare fresh annually.

7.2.2 5% Potassium Persulfate Solution

Dissolve 25 g potassium persulfate in 500 mL of reagent water. Prepare fresh annually.

7.2.3 12% Sodium Chloride-Hydroxylamine Hydrochloride Solution

Dissolve 60 g of hydroxylamine hydrochloride and 60 g of sodium chloride in 500 mL of reagent water. Prepare fresh annually.

7.2.4 10% Stannous Chloride in 10% HCl

Dissolve 100 g of stannous chloride in 100 mL HCl and dilute to 1L with reagent water. Place a stirring bar into the solution. Prepare fresh monthly.

7.2.5 5% HCl and 2% HNO_3 Solution

Add 100 mL of HCl and 40 mL of HNO_3 acid to approximately 1,500 mL reagent water, mix, and dilute to 2,000 mL with reagent water.

7.2.6 Diluent

This solution is used to dilute samples with mercury concentration above the calibration range of the instrument and will not be digested. Prepare this solution by transferring 200 mL of reagent water in a container, add 5 mL of concentrated nitric acid, 10 mL of concentrated sulfuric acid, 30 mL of 5% potassium permanganate solution, 16 mL of 5% potassium persulfate solution, and 10 mL of 12% sodium chloride-hydroxylamine hydrochloride solution. Cap container and mix.

7.3 Standards

Record all standard and standard preparations in LIMS.

7.3.1 Stock Standards

- 10 µg/mL or lower Mercury Primary Stock Standard - Perkin Elmer Life and Sciences or equivalent. This standard will be used to prepare the calibration standards, ICV, CCV, QLS, LCS, and MS/MSD solutions. Follow the manufacturer's supplied expiration date.
- 10 µg/mL or lower Mercury Secondary Stock Standard - Inorganic Ventures or equivalent. This standard will be used to prepare the SCV solution. Follow the manufacturer's supplied expiration date.

7.3.2 Working Standards

NOTE: This section assumes that 10 µg/mL stock standards are diluted to the indicated final concentrations. The analyst must adjust the volume of stock standard used to attain the final concentration if a different concentration stock standard is used.

- Mercury Primary Daily Standard, 20 µg/L

Prepare a 20 µg/L primary daily standard by pipetting 0.2 mL of the 10 µg/mL stock standard into a 100-mL Class-A volumetric flask containing 50 mL of reagent water. Add 1 mL concentrated HNO₃, dilute to volume with reagent water and mix. Prepare daily.

- Mercury Secondary Daily Standard, 20 µg/L

Prepare a 20 µg/L secondary daily standard by pipetting 0.2 mL of the 10 µg/mL stock standard into a 100-mL Class-A volumetric flask containing

50 mL of reagent water. Add 1 mL concentrated HNO₃, dilute to volume with reagent water and mix. Prepare daily.

7.3.3 Calibration Standards, ICV / CCV Standard, CB, QLS

These standards are prepared in Class-A volumetric flasks, brought up to volume with reagent water, and processed as described in Section 8.3.1 without heating.

	Vol. of 20 µg/L Daily Standard (mL)	Final Volume (mL)	Final Concentration (ng/L)
Cal Std 1	0	50	0
Cal Std 2 / QLS	0.075	50	30
Cal Std 3	0.125	50	50
Cal Std 4	0.25	50	100
Cal Std 5	0.75	50	300
Cal Std 6	1.25	50	500
ICV / CCV	0.5	50	200
CB	0	50	0

7.3.4 SCV

This standard is prepared in a Class-A volumetric flask, brought up to volume with reagent water, and processed as described in Section 8.3.1 without heating.

	Vol. of 20 µg/L Secondary Daily Standard (mL)	Final Volume (mL)	Final Concentration (ng/L)
SCV	0.75	50	300

7.3.5 MB

Transfer a 20-mL aliquot of reagent water to a digestion tube and process as described in Section 8.3.1 with heating.

7.3.6 LCS

Transfer a 20-mL aliquot of reagent water to a digestion tube and add 0.2 mL of the primary daily standard. Process as described in Section 8.3.1 with heating.

	Vol. of 20 µg/L Primary Daily Standard (mL)	Final Volume (mL)	Final Concentration (ng/L)
LCS	0.2	20	200

7.3.7 MS / MSD

Transfer a 20-mL aliquot of a well-mixed designated QC sample into a digestion tube, add the right amount of spike, and mix well. Process as described in Section 8.3.1 with heating.

	Vol. of 20 µg/L Primary Daily Standard (mL)	Volume of QC Sample (mL)	Concentration of Spike Added (ng/L)
MS/MSD	0.2	20	200

7.4 Supplies

- Disposable plastic or borosilicate autosampler vials, 16 x 100 mm
- 50-mL digestion tubes from Environmental Express (P/N SC499), or equivalent.
- Volumetric Class-A Flasks - 1000-mL, 500-mL, 100-mL, 50-mL, and 25-mL
- Volumetric Class-A Pipettes - 50-mL, 25-mL, 10-mL, and 5-mL
- Wash bottles

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set-up the instruments following the recommended operating conditions provided by the manufacturer. Use operating parameter provided in Appendix D as a starting point. Appendix F provides the instrumental startup information.

Ensure that all appropriate waste containers are properly connected and labeled.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

Perform an initial calibration daily or for every batch. Analyze a minimum of five calibration standards and a blank to establish a linear curve. Refer to Section 9.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Analyze the ICV, CB, and SCV immediately after analyzing the initial calibration standards. If QC criteria are not met, take corrective action as described in Section 9.2 and Appendix C.

8.2.2 Continuing Calibration

The accuracy and stability of the calibration shall be verified by the periodic analysis of the CCV and CB standard. Refer to Section 9.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

1. Set-up a Batch from Element database, print a copy of the bench sheet, and initiate a Mercury Digestion Log before beginning any preparations.
2. On a laboratory cart or bench top in the designated sample prep area, arrange the samples in order according to laboratory ID. Print extract label using LIMS. Label a 50-mL digestion tube for each sample and QC sample.
3. Shake the sample, measure and transfer a 20-mL aliquot of the well-mixed sample to the digestion tube. Record the volume in the digestion log.

NOTE:

- TCLP and CA WET Extracts, dilute the sample 10x prior to digestion.
 - SPLP Extract, determine client's required reporting limit and dilute (or not) accordingly.
 - Laboratory Waste, dilute the sample at least 20x prior to digestion.
4. Add 1.0 mL of concentrated sulfuric acid and 0.5 mL of concentrated nitric acid. Swirl the digestion tube to mix.
 5. Add 3 mL of the 5% potassium permanganate solution and swirl the digestion tube to mix. The solution should turn to a purplish color.

An excess of potassium permanganate must be maintained at all times throughout the digestion. Samples containing high concentrations of oxidizable organic substances may require additional potassium permanganate. A visual check for the presence of excess permanganate is the deep purple color. This purple color must be maintained throughout the digestion procedure. A by-product of the oxidation is dark brown to black manganese dioxide that can mask or obscure the purple color. If in doubt of the purple color, allow the manganese dioxide to settle and tilt the bottle slightly to observe clear solution.

NOTE: If additional potassium permanganate was added to any sample, the same amount of potassium permanganate must also be added to all

standards and samples to keep the volumes consistent. The calibration curve is generated assuming that the volumes of samples and standards are constant. The addition of any additional potassium permanganate to a sample would dilute that sample by the volume added; this SOP does not factor in any differences in sample and reagent volume.

6. Add 1.6 mL of the 5% potassium persulfate solution and swirl the digestion tube to mix.
7. Place the cap on the tube but not tightened to allow pressure to vent but minimizing evaporative loss. Digest the samples for 2 hours at 95 ± 5 °C.
8. At the end of 2 hours, remove the tubes from the hot block and allow to cool to room temperature.

NOTE: The QC standard and sample solutions must exhibit a purple permanganate color at this point. If any solutions do not exhibit the purple color, additional potassium permanganate must be added to all standards and samples, and the 2-hour digestion repeated.

9. Add 1 mL of the 12% sodium chloride-hydroxylamine hydrochloride solution and mix well.

NOTE: The solution should become clear and colorless. If the solution remains purple in color, continue to add sodium chloride-hydroxylamine solution in 1-mL increments until the purple color disappears. If additional sodium chloride- hydroxylamine solution was added to any sample, add the same amount of solution to all standards and samples.

NOTE: The dark brown to black residue of manganese dioxide, MnO_2 , which forms from reduction of the permanganate will also be dissolved by the hydroxylamine solution and must be completely dissolved before analysis. Additional hydroxylamine solution may be required to completely dissolve the manganese dioxide. If additional hydroxylamine solution was added to any sample, add the same amount of solution to all standards and samples.

10. The digestates are now ready for analysis. The completed bench sheet and Mercury Digestion Log must be peer-reviewed for completeness and correctness and signed off by the reviewer.

8.3.2 Sample Analysis and Analytical Sequence

This section describes setting up the analytical sequence and performing the instrumental analysis. Record the analytical sequence in the instrument run log or the LIMS sequence page, if available.

Include all batch QC samples as described in Section 9.3.

1. Enter sample sequence in the instrument software. Refer to Appendix E for details regarding entering the sequence.
2. Load the samples to be analyzed in the autosampler according to their designated positions in the sequence file, as in the following example:

Seq.	Description	Seq.	Description	Seq.	Description
1	Cal Std 1	15	S1-MSD	29	S11-MSD
2	Cal Std 2	16	S2	30	S12
3	Cal Std 3	17	S3	31	CCV
4	Cal Std 4	18	S4	32	CB
5	Cal Std 5	19	CCV	33	S13
6	Cal Std 6	20	CB	34	S14
7	ICV	21	S5	35	S15
8	CB	22	S6	36	S16
9	SCV	23	S7	37	S17
10	QLS	24	S8	38	S18
11	MB	25	S9	39	S19
12	LCS	26	S10	40	S20
13	S1	27	S11	41	CCV
14	S1-MS	28	S11-MS	42	CB

3. Start autosampler analytical sequence.
4. Review the results for QC compliance and off-scale results. If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of the diluent and re-analyze.

8.3.3 Analyte Identification and Quantitation

The Cetac M-7500 software reports results for the analyzed solutions in units of ng/L. LIMS database reports aqueous results in µg/L using the following equation:

$$C = M \times D / 1000$$

Where

- C = final reported concentration, in $\mu\text{g/L}$.
- M = measured concentration reported by instrument, in ng/L .
- D = dilution factor, to account for dilution performed after sample preparation.

8.3.4 QC Review

- Review the results of instrument QC (ICV, CCV, CB, SCV, and QLS) immediately after their analysis to verify that the results are within QC limits. See Section 9.2 for corrective action requirements and Appendix C for QC limits.
- Review the results of batch QC (MB, LCS, MS/MSD) immediately after their analysis to verify that the results are within QC limits. See Section 9.3 for corrective action requirements and Appendix C for QC limits.

8.3.5 Data Export and LIMS Entry

- Export data from the instrument into text files. Import into the LIMS using DataTool. Review final results in the LIMS.
- Report all results to two significant figures. Report detected results to one-half the QL. Flag values between one-half the QL and the QL as estimated (J).

8.4 Maintenance

Refer to manufacturer's maintenance requirements as appropriate for this instrument.

As a minimum requirement, inspect the pump tubing daily for fatigue and wear. Replace if too worn or if left clamped overnight.

If a decrease in absorbance is observed, check the pump tubing, the Gas/Liquid separator (GLS), and make sure that the nafion dryer has not been used for more than 300 hours. Nafion dryer normally lasts 3 - 6 months but do not replace if peak shape is still good.

Refer to Appendix G for preventive maintenance operations and schedules.

9 QUALITY CONTROL

9.1 Demonstration of Capability

The EPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880 for more details.

9.2 Instrument QC

9.2.1 Initial Calibration

An initial calibration is performed daily or for each batch of analysis using a blank and a minimum of five calibration standards. A linear calibration is used for calculation. Refer to Appendix C for acceptance criteria.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that the criteria are satisfied before any samples are analyzed.

The calibration is verified by the analysis of an ICV, CB, and SCV. If the criteria for those standards are not met, take corrective action as needed before continuing with analysis, including re-analysis or re-preparation and re-analysis of the initial calibration if necessary.

9.2.2 Initial and Continuing Calibration Verification

To check instrument performance and verify the accuracy and stability of the calibration, analyze an ICV and CCV standard. The ICV is analyzed immediately following initial calibration and the CCV at a frequency of one per 10 analytical samples and at the end of the analytical run. The recovery of mercury in the ICV and CCV are calculated as follows:

$$\% R = \frac{M}{T} \times 100$$

Where

%R = percent recovery of the standard.

M = measured concentration of mercury, ng/L.

T = true concentration of mercury in the ICV/CCV, ng/L.

The ICV recovery criteria are listed in Appendix C. If the %R for the ICV falls outside of the QC criteria, re-analyze to verify. If it is still out, the cause of the poor recovery must be determined and the problem corrected. Samples cannot be analyzed until an acceptable ICV is analyzed.

The CCV recovery criteria are listed in Appendix C. If the %R for the CCV falls outside of the QC criteria, the cause of the poor recovery must be determined and the problem corrected. All samples not bracketed by acceptable CCV must be re-analyzed.

NOTE: If it is suspected that the ICV or CCV were prepared incorrectly, it may be re-prepared and re-analyzed. If it passes, the analysis may continue.

9.2.3 Calibration Blank

The stability of the baseline must be monitored by analyzing a CB immediately after every ICV/CCV standard. If the value of the CB result is less than ½ the QL, the result is acceptable. If the value of the CB result equals or exceeds ½ the QL, the cause of the high CB result must be determined and the problem corrected. The instrument must be re-calibrated and all samples not bracketed by acceptable CB results must be re-analyzed.

NOTE: If it is suspected that there is contamination in the sample tube used for the CB, the blank may be re-poured and re-analyzed. If it passes, the analysis may continue.

9.2.4 Second Source Calibration Verification

Analyze a SCV daily to verify the calibration standards and acceptable instrument performance. If the SCV recovery does not meet the criteria in Appendix C, the method performance is unacceptable. The source of the problem must be identified and corrected before proceeding with analyses.

The recovery of mercury in the SCV is calculated as:

$$\% R = \frac{M}{T} \times 100$$

Where

- %R = percent recovery of the standard.
- M = measured concentration of mercury, ng/L.
- T = true concentration of the mercury in the SCV, ng/L.

9.2.5 Quantitation Limit Standard

To verify the ability to detect target analyte near the QL, a QLS must be analyzed at the beginning of the analytical run and after 40 analytical samples. The recovery of mercury in the QLS is calculated as:

$$\% R = \frac{M}{T} \times 100$$

Where

- %R = percent recovery of the standard.
- M = measured concentration of mercury, ng/L.
- T = true concentration of the mercury in the QLS, ng/L.

If the QLS recovery does not meet the criteria in Appendix C, determine the cause, take corrective action, and re-analyze the QLS.

9.3 Batch QC

9.3.1 Method Blank

Analyze at least one MB daily or with each batch of 20 or fewer field samples of the same matrix. MB values $\geq \frac{1}{2}$ the QL indicate potential laboratory or reagent contamination.

Use the following guidelines to determine when samples must be re-prepared, re-analyzed, and flagged as estimated:

- If the MB analyte value is $\geq \frac{1}{2}$ the QL and the sample result is less than five times the MB analyte amount, rerun the MB once to verify and if still unacceptable then the MB and all associated samples must be re-prepared and re-analyzed. The associated sample results can also be reported but will be qualified as estimated “J” and flagged “B” and a note placed in the Work Order memo field in LIMS.
- If the MB analyte value is $\geq \frac{1}{2}$ the QL and the sample result is non-detected or is greater than five times the MB analyte concentration, report sample results without qualification.

9.3.2 LCS

Analyze one LCS standard daily or with each batch of 20 or fewer samples of the same matrix. Recovery of mercury in the LCS is calculated as:

$$\% R = \frac{M}{T} \times 100$$

Where

%R = percent recovery of the standard.

M = measured concentration of the mercury, ng/L.

T = true concentration of the mercury in the LCS, ng/L.

If the recovery of the LCS does not meet the recovery criteria in Appendix C, re-analyze once to verify. If the recovery is still unacceptable, the analyte is judged to be out-of-control and the source of the problem must be identified and resolved. All samples associated with the out-of-control LCS must be re-prepared and re-analyzed.

9.3.3 Matrix Spike / Matrix Spike Duplicate

The MS and MSD are designed to provide information about the effect of sample matrix on the measurement system. One set of MS/MSD samples must be prepared for every 10 field samples of the same matrix in an SDG. Homogenize the routine sample selected as the QC and spike a representative aliquot with the analyte of interest prior to any sample preparation.

Samples identified as field blanks cannot be used for MS/MSD sample analysis. MS/MSD recoveries are calculated as:

$$\% R = \frac{C_{ms} - C}{s} \times 100$$

Where

%R = percent recovery.

C_{ms} = measured concentration of mercury in the MS, corrected for sample preparation and any dilutions, ng/L.

C = measured concentration of mercury in the routine sample corrected for sample preparation and any dilutions, ng/L.

s = expected spiked analyte concentration in the MS, corrected for sample preparation and any dilutions, ng/L.

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|C_{msd} - C_{ms}|}{(C_{msd} + C_{ms}) / 2} \times 100$$

Where

- RPD = relative percent difference.
 C_{msd} = measured concentration in the MSD, corrected for sample preparation and any dilutions, ng/L.
 C_{ms} = measured concentration in the MS, corrected for sample preparation and any dilutions, ng/L.

If the value of C is less than four times the value of s , apply accuracy and precision criteria in Appendix C. If the value of C is greater than four times the value of s , $\%R$ is not calculated. If the MS/MSD does not meet these criteria, examine other QC results to determine if a matrix problem exists. If laboratory performance is in control, the poor MS/MSD accuracy and precision is likely to be matrix-related. Flag any out-of-control results as estimated "J".

9.4 Method Performance

The following table summarizes method performance for the period 03/04/08 to 03/04/09.

Method Performance

Analyte	Matrix	QC Type	Number of Measurements	Mean Recovery, %	Std Dev (σ)	95% Confidence Interval (2σ)
Mercury	Water	LCS	56	100	5.8	88.4 - 112

The primary sources of analytical error are:

- Calibration standard accuracy
- Instrument calibration
- Pipette accuracy
- Contaminated glassware
- Digestion equipment contamination
- Sample tube contamination

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QLS, SCV, MS/MSD, and LCS) are recorded in the LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the Element database or in the instrument Run Log. Project Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the Element database. The data package is produced from Element database and manual log records. Appendix E provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance
- Subsequent instrument modifications and upgrades, including major software upgrades
- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.6 SOP Distribution and Acknowledgement

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. The Lab QC Database is used to maintain the list of assigned analysts for each SOP. Analyst training is documented via the Training

Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix H.

11 REFERENCES

USEPA Region 9 Laboratory. *Business Plan*.

USEPA Region 9 Laboratory. *Chemical Hygiene Plan*.

USEPA Region 9 Laboratory. *Environmental Management System*.

USEPA Region 9 Laboratory. SOP 110, *Sample Receiving and Login*.

USEPA Region 9 Laboratory. SOP 125, *Sample Disposal*.

USEPA Region 9 Laboratory. SOP 130, *Glassware Cleaning Procedures*.

USEPA Region 9 Laboratory. SOP 706, *Laboratory Waste Management Procedure*.

USEPA Region 9 Laboratory. SOP 820, *Laboratory Discrepancy and Corrective Action Procedures*.

USEPA Region 9 Laboratory. SOP 830, *Notification Procedures for Results Exceeding the Safe Drinking Water Act Maximum Contaminant Level*.

USEPA Region 9 Laboratory. SOP 840, *Notebook Documentation and Control*.

USEPA Region 9 Laboratory. SOP 880, *Demonstration of Capability*.

U.S. Environmental Protection Agency Method 245.1, *Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrophotometry, Revision 3.0, May 1994*.

Cetac M-7500 Operator's Manual, Version 1.02, Feb. 2002.

Mercury Digestions with the Environmental Express Hot Block based on EPA Method 245.1, Environmental Express.

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. This SOP uses automated instruments which require only a small digested sample aliquot (approximately 5 mL) to perform the mercury analysis. The reference method requires purging the headspace in the digestion vessel, the addition of stannous chloride solution to the entire digested sample, and then analysis of the digested sample. It is a destructive technique in that the entire digested sample is used. Samples that are over-range require re-digestion and dilution in a subsequent digestion batch. This SOP allows for dilution of over-range samples since only 5 mL of digested sample was used during the initial analysis
2. This SOP specifies the analysis of MSD for precision, while the reference method specifies the analysis of a laboratory duplicate.
3. A linear dynamic range (LDR) is specified in the reference method but not in this SOP. The Region 9 Laboratory requires any sample with a concentration above the highest calibration standard to be diluted and re-analyze.
4. This SOP specifies that the MB acceptance criterion is less than $\frac{1}{2}$ the QL and not the MDL as the reference method specifies.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides the target analytes list for this SOP with the CAS number and quantitation limits.

Analyte	Chemical Abstracts Registry Number (CASRN)	Quantitation Limit
Mercury	7439-97-6	30 ng/L (0.03 µg/L)

APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

Parameter	Frequency	Criteria
Correlation Coefficient	Each ICAL	≥ 0.995
ICV	After ICAL	95 - 105%
CCV	Every 10 samples and end of run	90 - 110%
CB	After each ICV/CCV	$< \frac{1}{2}$ QL
QLS	Each batch and after 40 analytical samples	60 - 140%
SCV	After ICAL	90 - 110%
MB	Each batch of 20 or fewer samples	$< \frac{1}{2}$ QL
LCS	Each Batch of 20 or fewer samples	85 - 115%
MS/MSD, Accuracy	Every 10 samples	70 - 130%
MS/MSD, Precision	Every 10 samples	≤ 20 RPD

APPENDIX D.
RECOMMENDED INSTRUMENT PARAMETERS

Typical Cetac M-7500 Mercury Analyzer Operating Parameters

Parameter	Setting
Argon Flow Rate	40 mL/min
Pump Rate	50%
Sample Uptake Time	45 sec.
Number of Replicates	4

APPENDIX E.
TYPICAL INSTRUMENT STARTUP PROCEDURE

TYPICAL STARTUP PROCEDURE FOR Cetac M-7500

1. Follow the QuickTrace M-7500 Mercury Analyzer Operator's Manual for specific details.
2. To start the instrument from a completely cold condition, turn on the QuickTrace M-7500 software, instrument, lamp, the carrier gas (making sure the main gas supply is on), and ASX-500 Auto-sampler. A minimum of 2 hours warm-up time is required.
3. Clean and rinse the 2-L rinse bottle with reagent water and refill with trace metal grade 5% HCL / 2% HNO₃ solution.
4. Place the auto-sampler rinse tubing into the rinse bottle.
5. Prepare a fresh 10% SnCl₂ in 10% HCl solution if old solution is yellow or precipitated. The reagent flow is approximately 1.5 mL/min at 50% pump speed.
6. Verify that the sample capillary (inlet insert) is 0.5 mm above the Gas/Liquid separator (GLS) center post.
7. Open vents on waste container.
8. Inspect peristaltic pump tubing for wear and flat spots (replace if necessary). Place the peristaltic pump tubing in their appropriate shoes and holder clips (top yellow tubing with yellow tab is for sample, second from the top yellow tubing with black tab is for reagent, and the bottom two yellow tubing with yellow tab is for drain). Do not lock shoe clamps at this time. NOTE: Never adjust tension on tubing.
9. Place the reagent tubing in a beaker of reagent water and using the M-7500 controls start the peristaltic pump.
10. Lock down the peristaltic shoe clamps after 1 minute to allow the tubing to stretch evenly prior to locking.
11. Wet the gas-liquid separator (GLS) center post with carrier gas flowing at a flow rate of 40 mL/min. Wet the GLS center post by performing this procedure at the beginning of each day. Using the quick release mechanisms, fully release the clamp tension on the lower two tube (drain) channels. Using the sample and reagent tubes, pump reagent water. The GLS should begin to fill with water, allow the liquid level to reach the top of the GLS center post. *Do not let the liquid level overflow into the nafion dryer.* Re-engage the quick-release clamps on the drain pump tubes, once the GLS has emptied, sample analysis can start.

12. Inspect liquid flows. The GLS drain should be flowing smoothly with no build up or pulsing of liquid. The waste line from the peristaltic pump to the waste container should be with no vibrations. If this is not the case upon inspection, stop immediately and change GLS drain line or waste line.
13. Inspect the rinse station for a convex liquid bubble adhering to the sample probe. If this is not the case, change the rinse pump peristaltic tubing.
14. Attach the GLS exhaust tube to the GLS.
15. Place the reagent tubing in the reagent bottle.
16. Verify that the carrier gas flow of the method matches what is listed in the M-7500 controls, if the flow is not the same make the necessary change and click set gas. This will stabilize the gas flow prior to zeroing the optics.
17. Open the worksheet *Low Level Mercury*. Enter the filename for today's analytical run: current year, month, date, and run # (e.g.: 09030401). Enter it in the box with the message *Enter new worksheet name* and then click *OK*.
18. Type standard and sample IDs under the *Sample Label Column*. Change the sample type (e.g.: QLS is Contract Required Detection Limit). Then Save file.
19. Transfer the calibration standards (0, 30, 50, 100, 300, and 500 ng/L) into the first 6 positions of the standard rack, ICV/CCV in position 7, and SCV in position 8. The CB is the same as Cal 0 which is in position 1.
20. Pour the samples into clean auto-sampler vials and place into the sample rack, making sure they are in the right position as entered in the *Sample Label Column*.
21. Zero the M-7500 using the auto zero.
22. Prime the optional ADX-500 Auto-diluter with matrix diluent, if planning to use.
23. Peak profile the highest standard and verify baseline and sample integration times.
24. Define the *Time Profile* by reading a test Absorbance Signal by clicking the *Sample* button on the *Conditions* tab. Click on the position of the highest calibration standard (S6) and click *OK*. The instrument will read the absorbance after the instrument auto-zeroes. Once this has been done, it may be necessary to set cursors, with the mouse, to mark the Signal Profile Chart for the exact times at which the Baseline Correction Points should be acquired and between which points (start/stop) the sample peak readings should be taken. Whenever running an initial Time Profile, use the highest concentration standard.
25. Start the overall analysis process using the *Go* button on the *Menu Bar*. The correlation coefficient of the curve must be ≥ 0.995 or the instrument must be re-calibrated.

26. The instrument will switch to *Stand-by mode* after the last sample of the sequence is analyzed. Click *OK* when the message *System has entered Standby* appears. Print data.
27. Review results for QC compliance and off-scale results. Identify samples that must be re-analyzed. Samples having mercury concentrations greater than 500 ng/L must be diluted into calibration range with an appropriate amount of the diluent and re-analyzed.
28. When analysis is done, run reagent water through the reagent and sample tube for several minutes. Next, withdraw the 5% HCl / 2% HNO₃ solution uptake tube and the reagent tube manually and continue pumping until the drain line runs empty. Use the M-7500A Software Controls to turn off the pump once the tube is empty. Unclass the pump tubes and turn off the gas, auto-sampler, lamp, and instrument.

APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

Maintenance Schedule for the Cetac M-7500

Item	Frequency	Comments
Auto-sampler Rinse Station Reservoir	Daily	Ensure that both the reservoir and rinse bottles are filled with solution
Pump Tubing	Daily	Check for fatigue and wear. Replace as needed.
GLS	Daily	Check that liquid flow to and from the GLS are smooth and is completely wet during operation.
GLS	Weekly or as needed	Remove the GLS and clean if residue is building up.
Auto-sampler Cabinet, Peristaltic Pump, and Auto-sampler Arm	Weekly or as needed	Wipe spills or residues with clean wet towel.
Cell Windows	As needed	Clean the cell windows if dirty or if cannot re-zero.
Fan filter	As needed	Remove, wash, dry, and re-install the fan filter on rear of instrument panel as needed.
Sample Probe	Monthly	Inspect, replace if leaking or show signs of deterioration.
Nafion Dryer	3 – 6 months	Replace if a decrease in absorbance is observed after checking the pump tubing and GLS.
GLS Inlet Tubing	Annually or as needed	Replace
GLS Drain Restrictor	Annually or as needed	Replace

**APPENDIX G.
TYPICAL DATA PACKAGE FORMAT**

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

ESAT Cover memorandum
TDF
Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms

EPA Review Form
ESAT Technical Review Guide
LIMS Memo Field Printout (if applicable)
Discrepancy Reports (if applicable)
Daily folder review forms or checklists
Analysis matrix (for organics)

Tracking Forms

Work Order(s)
COC(s)

Sample Preparation (for projects that require extraction or digestion)

Bench Sheets (and extraction logs, where used)
Sample cleanup data and records (e.g. GPC logs)
Moisture data as applicable

[Analysis Method] Data (For each method where multiple methods in package)

Bench sheet(s) where not used in Sample Preparation section
Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Alternatively, separate calibration and sample data as:

Initial Calibration Data
Sample Data

Miscellaneous Data

Other data as applicable (e.g. conductivity for perchlorate)

Standard Records

Standards records from LIMS (and logbook pages as needed)

STANDARD OPERATING PROCEDURE: 515
Revision: 6, Effective: 04/24/09

[illegible]

**USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA**

**STANDARD OPERATING PROCEDURE 531
ANALYSIS OF PERCHLORATE BY ION CHROMATOGRAPHY**

Revision 5
Effective Date: August 21, 2009

Reviewed by: _____
Richard Bauer Date
Chemistry Team Leader/Technical Director

Reviewed by: _____
K. W. Hendrix, Laboratory QA Officer Date

Approved by: _____
Brenda Bettencourt, Laboratory Director Date

Periodic Review:

Signature	Title	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____

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APPENDIX A. DEVIATIONS FROM THE REFERENCE METHOD

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APPENDIX H. REVISION HISTORY

1 SCOPE AND APPLICABILITY

This SOP covers the determination of perchlorate in reagent water, surface water, ground water, drinking water, and solids leached with reagent water using ion chromatography following EPA Method 314.0, *Determination of Perchlorate in Drinking Water Using Ion Chromatography*, Rev. 1.0, November 1999. Although not specifically tested, this method is potentially applicable to mixed domestic water and industrial wastewaters. Deviations from the reference method are described in Appendix A. Analyte and quantitation limit (QL) are listed in Appendix B.

2 METHOD SUMMARY

A volume of sample is injected into and passed through a series of ion-exchange columns. The perchlorate anion is separated on the basis of its relative affinity to a low capacity, strongly basic anion exchanger. The separated perchlorate anion is directed into a strongly acidic cation suppressor where it is converted to the highly conductive acid form. The potassium hydroxide eluent is converted to a weakly conductive acid. The separated anion in its acid form is detected by electrical conductivity and is identified on the basis of retention time as compared to the external standards. Quantitation is based on peak area and a quadratic calibration is used to determine concentrations in environmental samples.

3 DEFINITIONS

Analytical Sample - Any sample in which perchlorate is being determined, excluding standards, method blanks, or QC reference samples.

Calibration Blank (CB) - A blank that is the same matrix as the calibration standards, but without the analyte.

Continuing Instrument Calibration Verification (CCV) - A standard containing the analytes of interest, which is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout the analysis sequence (after every ten samples and at the end of the analytical run). The CCV is also known as continuing calibration check standard (CCCS) and end calibration check standard (ECCS).

Initial Instrument Calibration Standard (ICAL) - Standards used to calibrate the instrument response with respect to analyte concentration.

Instrument Performance Check Solution (IPC) - A solution containing a specific amount of perchlorate and other common anions (namely chloride, sulfate, and carbonate) used to evaluate the performance of the instrument system with respect to a defined set of criteria.

Laboratory Control Sample (LCS) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is analyzed exactly like a sample and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements. The LCS is also known as a laboratory fortified blank (LFB) or blank spike (BS).

Laboratory Information Management System (LIMS) - The Element database.

Method Blank (MB) - An aliquot of reagent water or other blank matrix that is treated exactly as a sample. The MB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment. The MB is also known as laboratory reagent blank (LRB).

Matrix Conductivity Threshold (MCT) - The highest permitted conductance of an unknown sample matrix, measured prior to conducting the analysis, which is used to determine when sample matrix dilution is required. The conductance of a sample matrix is proportional to the common anions present in the matrix (which contribute to the level of total dissolved solids [TDS]), which can greatly affect the integrity of this analysis. The value for this threshold is dependent on the conditions, hardware, and state of the hardware employed. Matrix conductivity is measured in microsiemens/cm ($\mu\text{S}/\text{cm}$) or microMhos/cm ($\mu\text{Mhos}/\text{cm}$) which are considered equivalent terms.

Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Matrix Duplicate (MD) - An aliquot of sample prepared and analyzed separately with identical procedures. Analysis of the sample and MD indicates precision associated with the laboratory procedures, but not with sample collection, preservation, or storage procedures. The MD is also known as laboratory duplicate (LD).

Matrix Spike (MS) - An aliquot of an analytical sample to which known quantities of the method analytes are added. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations. The MS is also known as laboratory fortified matrix (LFM).

Matrix Spike Duplicate (MSD) - A duplicate aliquot of an analytical sample to which known quantities of the method analytes are added. The MSD is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results and to determine laboratory precision. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the

MSD corrected for background concentrations. The MSD is also known as laboratory fortified matrix duplicate (LFMD).

Peak Area to Height Ratio (A/H) - The ratio of the peak area divided by the peak height which is used as a tool to monitor analytical performance. This ratio is used to establish and monitor the MCT and represents an objective means of assessing analytical performance when analyzing high conductivity matrices. A gradual distortion of the baseline is typically observed in the retention time window for perchlorate as the matrix conductivity increases (consistent with elevated levels of common anions) which will more significantly influence peak height relative to the influence on peak area. As the distortion of the baseline increases, this ratio increases, and the integrity of the measured perchlorate will be compromised.

Quantitation Limit (QL) - The concentration at which confidence in the reported value requires no qualifying remarks. A standard is analyzed at the QL to verify the previously established calibration curve.

Quantitation Limit Standard (QLS) - A standard used to check the accuracy of the analysis at the quantitation limit. The QL is also known as ICCS (initial calibration check standard).

Second Source Calibration Verification (SCV) - A solution of method analyte of known concentration that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check the initial calibration. The SCV is also known as quality control sample (QCS).

Solid Sample - For the purpose of this method, a sample taken from matrices classified as soil, solid, sludge, or sediment.

Stock Standard Solution (SSS) - A concentrated standard containing the method analyte prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Water Sample - For the purpose of this method, a sample taken from matrices classified as drinking, surface, ground, or storm runoff water, or industrial or domestic wastewater.

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN for additional information.

Safety precautions must be taken when handling solutions and samples. Protective clothing including lab coats, safety glasses, and gloves must always be worn. Contact lenses must not be worn. If solutions come into contact with your eyes, flush with water continuously for 15 minutes. If solutions come in contact with your skin, wash thoroughly with soap and water. ESAT personnel should contact the Health and Safety and Environmental Compliance Task Manager and EPA staff should see the Team Leader or the Laboratory Safety, Health and Environmental Compliance Manager to determine if additional treatment is required.

Perchlorates are oxidizing compounds and will render organic matter easily flammable. When perchlorates are mixed with finely divided organic matter, they may be explosive.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-regulated Waste	Not applicable
Solid/soil sample waste	Hazardous Waste	Toxic
Perchlorate instrument waste	Hazardous Waste	Corrosive

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples should be collected in pre-cleaned plastic or glass bottles. Volume collected

should be sufficient to ensure a representative sample, allow for replicate analysis, and minimize waste disposal. A 100 mL sample volume of water or 20 g of solid sample should be sufficient to meet these objectives.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form.

Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to “active out” and the location to the appropriate room number. At the end of the day, return sample containers to the “Home” locations. Update the LIMS database using the “return to home location” feature and update container disposition to “available in”. Verify that your initials are recorded whenever you update the LIMS custody information.

5.3 Sample Storage

Samples should be received and stored at $> 0^{\circ}\text{C}$ to $\leq 6^{\circ}\text{C}$. If not already noted in the LIMS login record, record any discrepancies in the LIMS memo field.

Retain samples for 60 days after the final analytical report is sent to the data user.

5.4 Holding Time

Samples must be analyzed within 28 days from collection.

6 INTERFERENCES

1. Interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in an ion chromatogram. These interferences can lead to false positive results for the target analyte as well as reduced detection limits as a consequence of elevated baseline noise.
2. Interferences can be divided into three different categories: (a) direct chromatographic co-elution, where an analyte response is observed at very near the same retention time as the target anion; (b) concentration dependant co-elution, which is observed when the response of higher than typical concentrations of the neighboring peak overlap into the retention time window of the target anion; and, (c) ionic character displacement, where retention times may significantly shift due to the influence of high ionic strength matrices (high mineral content or hardness) overloading the exchange sites in the column and significantly shortening target analyte retention times.

3. Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependant co-elution or ionic character displacement, but it must be emphasized that sample dilution will alter the reported quantitation limit by a proportion equivalent to that of the dilution.
4. Sample matrices with high concentrations of common anions such as chloride, sulfate, and carbonate can make the analysis problematic by destabilizing the baseline in the retention time window for perchlorate. This is evidenced by observing the protracted tailing following the initial elution of the more weakly retained anions (chloride, sulfate, and carbonate), which extends into the perchlorate retention time window. Monitoring the conductivity of the matrix can indirectly assess these common anion levels. Consequently, all sample matrices must be monitored for conductivity prior to analysis. When laboratory determined MCT is exceeded, procedures incorporating sample dilution must be performed.
5. Samples that contain particles larger than 0.45 micron require filtration to prevent damage to instrument columns and flow systems. If, after filtration, the sample is still turbid or colored, filter again using a 0.20 micron filter.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

- Ion Chromatograph System - The Dionex Ion Chromatograph System including the Advance Chromatography Module, Eluent Degas Module, an Auto-Regen System (includes a Pump, Anion Cartridge, and a Regenerant Reservoir), Conductivity Cell Detector, Dionex Advance Computer Interface, and Dionex PeakNet 6/Chromeleon 6 Data System, or equivalent that meets the requirements of the method.
- Dionex AS40 Auto-sampler
- EG40 Eluent Generator using Dionex EluGenCartridge (potassium hydroxide), or equivalent
- Suppressor - Dionex AMMS 300 4-mm, or equivalent
- Anion Guard Column - Dionex IonPac AG16 4-mm, or equivalent
- Anion Separator Column - Dionex IonPac AS16 4-mm, or equivalent
- Analytical Balance - capable of weighing accurately to ± 0.001 g
- Class S weights

- Drying oven - capable of being controlled at 105 ± 5 °C
- Desiccator
- An Eppendorf air-displacement pipetter - Capable of delivering volumes ranging from 50 to 1000 μ L with an assortment of high quality disposable pipet tips, or equivalent.
- Conductivity bridge - ranges from 1 to 200,000 μ mhos per centimeter with automated temperature compensation (VWR Model EC 2052 Catalog No. 23198-013), or equivalent
- Conductivity cell with 1.0 constant or micro dipping type cell with 1.0 constant (VWR Catalog No. 23198-020), or equivalent
- Stirrer Plate and Stirring Bars

7.2 Reagents

Reagents may contain impurities that affect analytical data. Only materials that conform to the American Chemical Society (ACS) reagent grade specifications should be used. If the purity of a reagent is in question, analyze for contamination prior to use. Record all reagent preparations in the LIMS database.

- Reagent water - All references to reagent water in this SOP refer to laboratory deionized water as described in EPA Region 9 Laboratory SOP 825.
- Degassed reagent water - Reagent water that has been purged with helium.
- Conductivity Solution - A 1,000 μ mhos/cm solution (VWR Catalog No. 23226-603), or equivalent. Follow the manufacturer's supplied expiration date.
- Eluent Solution - An EG40 Eluent Generator using Dionex EluGenCartridge (EGC II KOH, P/N 058900)
- Potassium perchlorate (KClO_4), reagent grade
- Sodium carbonate (Na_2CO_3 , CASRN [497-19-8]), reagent grade
- Sodium chloride (NaCl , CASRN [7647-14-5]), reagent grade
- Sodium sulfate (Na_2SO_4 , CASRN [7757-82-6]), reagent grade
- Sulfuric Acid (H_2SO_4), concentrated, reagent grade
- Nitrogen gas, high purity

7.3 Standards

Record all standard and standard preparations in the LIMS database.

7.3.1 Stock Standards

Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105 °C for 30 minutes) and are stable for 12 months when stored at > 0 °C to ≤ 6 °C.

- 1,000 $\mu\text{g/L}$ Primary Stock Standard - Custom standard solution purchased from ERA (Custom Standard USEPA Region 9 Perchlorate 1000 $\mu\text{g/L}$). Follow the manufacturer's supplied expiration date.
- 1,000 $\mu\text{g/L}$ Secondary Stock Standard - Custom standard solution purchased from SpexCertiPrep (Custom Standard 1000 $\mu\text{g/L}$ Cat. # VUSEPACA-3-500). Follow the manufacturer's supplied expiration date.
- Perchlorate Stock Standard - Prepare a 1,000 mg/L standard by dissolving 0.1393 g KClO_4 in reagent water and dilute to volume in a 100-mL volumetric flask. Then prepare a 1,000 $\mu\text{g/L}$ standard by pipetting 0.1 mL of the 1,000 mg/L perchlorate standard into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh yearly.

7.3.2 Calibration Standards, CCV Standard, QLS, LCS

A minimum of six calibration standards are required for non-linear calibration fit. All standards are to be diluted to volume with reagent water. Prepare fresh daily.

Standard Name	Volume of 1000 $\mu\text{g/L}$ Std., mL	Final Volume, mL	Final Conc., $\mu\text{g/L}$
Cal Std 1/ QLS	0.2	100	2
Cal Std 2	0.5	100	5
Cal Std 3/ LCS	1.0	100	10
Cal Std 4	1.5	100	15
Cal Std 5/ CCV	2.5	100	25
Cal Std 6	5.0	100	50

7.3.3 IPC Standard

The IPC is used to verify the laboratory determined MCT and the state of the IC system to quantitate perchlorate in highly ionic matrices. This solution contains perchlorate at approximately 5 times the QL concentration and mixed common anions, which reflects a conductance near (within $\pm 10\%$) the laboratory specified MCT. The Region 9 Laboratory uses a solution containing 10 $\mu\text{g/L}$ perchlorate and 500 mg/L mixed anions (chloride, sulfate, and carbonate). NOTE: Use appropriate concentration of mixed anions if MCT changes.

This IPC solution is prepared by pipetting 5.0 mL of the 1,000 $\mu\text{g/L}$ perchlorate standard and 10 mL of the 25 mg/mL mixed anions standard into a 500-mL volumetric flask and diluting to volume with reagent water. Measure the conductivity of this solution on a daily basis. If the measured conductance of

this solution has shifted by more than 10% from the original measured value, prepare a fresh solution.

7.3.4 SCV Standard

The SCV standard is obtained from a source external to the laboratory and different from the source of the calibration standards. The Region 9 Laboratory uses a custom solution from Spex CertiPrep with a concentration 1,000 $\mu\text{g/L}$ perchlorate.

A 20 $\mu\text{g/L}$ SCV standard is prepared by pipetting 2.0 mL of the 1,000 $\mu\text{g/L}$ standard into a 100-mL volumetric flask and diluting to volume with reagent water. Prepare fresh daily.

7.3.5 Regenerant Solution

A regenerant solution of 50 mN H_2SO_4 is prepared by adding 5.6 mL of concentrated H_2SO_4 to approximately 2,000 mL of reagent water and bringing it to a final volume of 4 liters. Prepare fresh yearly.

7.3.6 Mixed Common Anions Stock Solution

Containing the anions chloride, sulfate, and carbonate each at 25 mg/mL anion concentration. This solution is used to prepare simulated common anion samples in the determination of the MCT and the IPC. Prepare fresh yearly.

Dissolve the following salts in reagent water to a final volume of 25 mL:

1.1 g Sodium Carbonate = 0.62 g CO_3

1.0 g Sodium Chloride = 0.61 g Cl

0.93 g Sodium Sulfate = 0.63 g SO_4

7.4 Supplies

- Volumetric Class A Flasks - 1000 mL, 500 mL, 250 mL, 100 mL, and 25 mL
- Volumetric Class A Pipettes - 10 mL, 5 mL, and 4 mL
- Plastic or Teflon spray bottle
- Disposable Beaker Cups, 20-mL volume
- Disposable Syringe Filters, 0.20 micron and 0.45 micron
- 10-mL Disposable Syringes with Luer-lock fittings
- Polyvials, 5-mL capacity with filter caps (Dionex P/N 38141), or equivalent
- Clean sand (used for blank solid matrix)

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set-up the ion chromatograph following operating instructions provided by the manufacturer. Use operating parameters provided in Appendix E as a starting point. Appendix D provides instrumental startup information.

Ensure that all appropriate waste containers are properly connected and labeled.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

Perform an initial calibration using a minimum of six calibration standards to establish a quadratic curve. Analyze calibration standards as described in Section 8.3.4. Refer to Section 9.3.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Analyze a calibration blank immediately after the initial calibration. If the value of the CB is less than one-half the QL, the calibration is acceptable. If the value of the blank result equals or exceeds one-half the QL, the cause of the high CB result must be determined, the problem corrected, and the instrument re-calibrated.

Analyze a SCV standard to confirm the initial calibration. Meet QC criteria and take corrective action as needed as described in Section 9.3.1 and Appendix C.

NOTE: Update retention time windows in the instrument software after each initial calibration. Five percent of Standard 5 retention times should generally be used to define calibration retention time windows. Print a record of the retention time windows and retain for inclusion in the data package.

8.2.2 Continuing Calibration

At the beginning of each analytical sequence right after the IPC, verify calibration with a CCV standard. Prepare the CCV as described in Section 7.3.22 and analyze according to Section 8.3.4. Follow requirements and take corrective action as described in Section 9.3.2.

NOTE: After the first CCV analysis, update retention times in the instrument software to correspond to the first CCV and adjust retention time window to five percent of the retention times.

8.3 Analysis

8.3.1 Conductivity Check

Prior to conducting any field sample analysis, the conductivity of the sample must be determined. When the conductance of a field sample is above the conductivity of the MCT, sample dilution must be performed and the resulting conductivity must be at or below the conductivity of the MCT. The procedure for determining conductivity of the sample is in Appendix D.

8.3.2 Water Sample Preparation

1. Prepare MS, MSD, and LCS samples. For MS and MSD, fortify the source sample with primary stock or working standards. Prepare the LCS by fortifying reagent water with primary stock or working standards. MS/MSD and LCS spike levels in the following table are recommended for most projects:

Parameter	Recommended MS/MSD & LCS Spiking Levels, $\mu\text{g/L}$
Perchlorate	10

2. Filter samples that are turbid or contain particulates to prevent damage to instrument columns and flow systems. Filter samples following this procedure:
 - 1) Transfer an aliquot of well-mixed unfiltered sample into a disposable beaker cup.
 - 2) Withdraw approximately 5 mL of the sample into a disposable syringe.
 - 3) Attach a 0.45-micron disposable syringe filter to the syringe.
 - 4) Apply pressure to the plunger and filter the sample through the syringe filter and into a 5-mL vial.
 - 5) Repeat the procedure until the 5-mL vial is filled close to the 5-mL mark.
 - 6) If the sample is still turbid or colored, filter the sample again using a 0.20 micron filter.
 - 7) Discard the remaining sample from the beaker cup into the liquid waste container and the syringe assembly into a solid waste container.

NOTE: MB and LCS samples must be filtered if any sample in the batch is filtered. Record any sample filtrations in the comments section of the LIMS bench sheet or the instrument run log.

3. Dilute samples with conductivity reading that exceeds the laboratory MCT.

4. Fill 5-mL polyvials with each well-mixed sample. Attach a filter cap to each vial and push down the filter cap with the supplied tool until it is flush with the top of the vial. Label the contents of the vial.

8.3.3 Solid Sample Preparation

1. For homogenization of solid samples, follow SOP 150, *Soil and Sediment Homogenization*.
2. Weigh out approximately 2.0 g of each solid sample. Sample weights may be adjusted to meet project requirements, if necessary. Add reagent water equal to ten times the weight of solid material taken as sample. (Example: To 2.2 g of solid sample, add 22 mL of reagent water).
3. Prepare MS, MSD, and LCS samples. For MS and MSD samples, fortify the mixture from the source sample with primary stock or working standards. Prepare the LCS by fortifying blank solid matrix with primary stock or working standards. The following table provides MS/MSD and LCS spike levels suitable for most projects:

Parameter	Routine MS/MSD & LCS Spiking Levels, $\mu\text{g/L}$
Perchlorate	10

4. Mix each sample with a shaker table or a magnetic stirrer for 10 to 15 minutes. Filter the resulting mixture with a 0.45-micron filter or a 0.20 micron as needed as described in Section 8.3.2.
5. Fill 5-mL polyvials with each well-mixed sample filtrate. Attach a filter cap to each vial and push down the filter cap with the supplied tool until it is flush with the top of the vial. Label the contents of the vial.
6. From a separate sample aliquot, determine percent solids following SOP 460, *Percent Solids Determination*.

8.3.4 Analytical Sequence and Sample Analysis

This section describes setting up the analytical sequence and performing the instrumental analysis. Record the analytical sequence in the instrument run log (or the LIMS sequence page, if available).

Include all batch QC samples as described in Section 9.4.

1. Enter sample sequence in the instrument software. (Refer to Appendix D for details regarding entering the sequence). Load the samples to be analyzed in the autosampler according to their designated positions in the sequence file.
2. The following table shows an example of a typical sample sequence. If not calibrating the instrument, start with Seq. #9.

Seq.	Description	Seq.	Description	Seq.	Description
1	Cal Std 1	14	S1	27	S11
2	Cal Std 2	15	S1-MS	28	S12
3	Cal Std 3	16	S1-MSD	29	S13
4	Cal Std 4	17	S2	30	S14
5	Cal Std 5	18	S3	31	S15
6	Cal Std 6	19	S4	32	CCV
7	CB	20	S5	33	S16
8	SCV	21	CCV	34	S17
9	IPC	22	S6	35	S18
10	CCV	23	S7	36	S19
11	QLS	24	S8	37	S20
12	MB	25	S9	38	CCV
13	LCS	26	S10		

3. If samples are filtered, analyze filtered MB and LCS. Alternatively, analyze MD as specified in Section 9.4.4.
4. Start the autosampler (Dionex AS40) by pressing the 'Hold/Run' button until the light on the side of the word 'Run' is lighted. Initiate the analysis by clicking on the 'Start' button in the Batch list section of the software. The analysis will stop automatically by inserting a 'Sample' positioned at the end of the sequence file and changing the Program name (PerchlorateProgram) under the 'Program' column to 'StopMethod', and re-saving the edited sequence file.
5. If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and re-analyze.
6. If a sample result exceeds 800 µg/L, positive results obtain immediately following the high sample must be confirmed to demonstrate that carryover does not impact the quantitated value.

8.3.5 Analyte Identification and Quantitation

8.3.5.1 Peak Identification

Review all chromatograms to ensure that the correct peaks are integrated. The instrument is typically set to identify peaks as target analytes if the retention times are within $\pm 5\%$ of retention times from the first CCV.

8.3.5.2 For water samples, report results in $\mu\text{g/L}$ using the following equation:

$$C = M \times D$$

Where

- C = final reported concentration, in $\mu\text{g/L}$
- M = measured concentration reported by software, in $\mu\text{g/L}$
- D = sample analysis dilution factor, to account for any dilution

8.3.5.3 For solid samples, report results in mg/kg using the following equation:

$$C = M \times \frac{V_f}{V_i} \times D \times 100 / S$$

Where

- C = final reported concentration, in mg/kg
- M = measured concentration reported by software, in $\mu\text{g/L}$
- V_f = final volume of sample solution after sample preparation, in liters
- V_i = initial weight of sample used in sample preparation, in kilograms
- D = sample analysis dilution factor, to account for any dilution
- S = Percent of solids in the sample used.

8.3.5.4 Manual Integration

Where the chromatography software integrates the signal inconsistently, follow SOP 835, *Chromatographic Integration Procedures*. All manual chromatographic integration must be initialed and dated by the analyst, noted in the run log, and approved by the supervisor, Chemistry Technical Director, Quality Assurance Officer, or designees.

8.3.6 QC Review

- Review results of instrument QC (IPC, CCV, QLS) immediately after their analysis to verify that the results are within QC limits. See Section 9.3 for corrective action requirements and Appendix C for QC limits.
- Review results of batch QC (MB, LCS, MS/MSD/MD). See Section 9.4 for corrective action requirements and Appendix C for QC limits.

8.3.7 Data Export and LIMS Entry

- Export data from the instrument into text files. Import into the LIMS using DataTool. Review final results in the LIMS.
- Report all results to two significant figures. Report detected results to one-half the QL. Flag values between one-half the QL and the QL as estimated (J).

8.4 Maintenance

Column maintenance prolongs column life and reduces retention time shifts. Shorter retention time and smaller peaks are indications that a column is degrading and maintenance is necessary. Refer to manufacturer's requirements for column maintenance.

Monitor retention time shift. Retention time drift, as indicated by the first CCV, of >5% is an indication that instrument maintenance may need to be performed.

Routine instrument maintenance is summarized in Appendix F.

9 QUALITY CONTROL

The following sections describe quality control measures, criteria, frequency, and corrective action. Appendix C summarizes QC measures and criteria.

9.1 Demonstration of Capability

The EPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880, *Demonstration of Capability*, for more details.

9.2 Matrix Conductivity Threshold (MCT)

The MCT is an individual laboratory defined value which must be determined once prior to using the method or when using a new instrument and repeated when major changes has occur on the instrument. MCT is determined by preparing a series of sequentially increasing common anion fortified reagent water samples each containing a constant perchlorate concentration. Initially, a reagent water-prepared LCS, containing no common anions, must be analyzed which contains a concentration of 10 $\mu\text{g/L}$ perchlorate, which is approximately 5 times the QL. Next, the series of sequentially increasing anionic solutions are prepared, each containing perchlorate at a concentration of 10 $\mu\text{g/L}$, which also contains the individual common anions of chloride, sulfate, and carbonate, all included at uniform increasing concentrations of 200, 300, 400, 500, 600, 800, and 1000 mg/L for each anion.

1. Prepare the mixed common anion stock solution containing chloride, sulfate, and carbonate, each at 25 mg/mL.
2. Prepare the LCS at a perchlorate concentration of 10 $\mu\text{g/L}$.
3. Prepare the series of common anion fortified reagent water samples by adding 0.20 mL, 0.30 mL, 0.40 mL, 0.50 mL, 0.60 mL, 0.80 mL, and 1.00 mL of the mixed common anion stock solution into separate 25 mL volumetric flasks. Next, add 0.25 mL of the 1,000 $\mu\text{g/L}$ perchlorate standard to each 25 mL volumetric flask and dilute to volume with reagent water to yield a final perchlorate concentration of 10 $\mu\text{g/L}$.
4. Measure and record the conductance of each of these prepared solutions on a calibrated conductivity meter (this meter must be calibrated as described in Appendix E prior to measuring conductance). To use as a relative reference conductance, the 400 mg/L mixed anion sample, which contains chloride, sulfate,

and carbonate at 400 mg/L, should display a conductance of between 3,200 $\mu\text{S}/\text{cm}$ and 3,700 $\mu\text{S}/\text{cm}$.

5. Analyze each solution, recording the peak area to height (A/H) ratio and the quantified concentration of perchlorate.
6. The A/H ratio and quantified perchlorate concentration for the LCS and the 200 mg/L mixed common anion solution should be consistent but as the common anion levels increase, the A/H ratio will also begin to increase as the peak height is distorted and reduced. With increasing common anion concentration, the peak area will also eventually begin to be reduced and quantitation impacted, but this is typically secondary, with the A/H ratio predicting this pending quantitation problem.
7. Calculate the A/H ratio percent difference ($\text{PD}_{\text{A/H}}$) between the A/H ratio for the LCS (A/H_{LCS}) and the A/H ratios for each mixed common anion solutions (A/H_{MA}) using the following equation:
$$\text{PD}_{\text{A/H}} = |(\text{A/H}_{\text{LCS}} - \text{A/H}_{\text{MA}})| / \text{A/H}_{\text{LCS}} * 100$$
8. As the conductivity of the matrices increases, the $\text{PD}_{\text{A/H}}$ will also increase. The MCT is established at the conductance level of the highest mixed anion solution that yields a $\text{PD}_{\text{A/H}}$ value below 20%.
9. As a final step, confirm the perchlorate QL in a mixed common anion solution which reflects a conductance near (within $\pm 10\%$) that specified as the MCT. This solution must contain perchlorate at the laboratory QL, as well as the common anions chloride, sulfate, and carbonate, prepared consistent with the instruction for mixed anion solutions in this section and at a concentration estimated to generate a conductance near the MCT. The conductance of this solution must be measured at within $\pm 10\%$ of the MCT and following the analysis; the recovered perchlorate must be between 70 - 130% of the QL concentration. If the QL recovery fails this criterion, the MCT must be lowered by 10% and the QL verification repeated.
10. Prior to conducting any field sample analysis, the conductivity of that sample must be determined. When the conductance of a field sample is above the MCT, sample dilution must be performed.

9.3 Instrument QC

9.3.1 Initial Calibration

An initial calibration is performed by analysis of a minimum of six standards. Calibration is calculated using a quadratic fit. The coefficient of determination

for the initial calibration must be ≥ 0.995 for the calibration to be valid. The calibration is verified by analyzing a SCV standard. The SCV recovery requirement is 90% to 110% of the expected value.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that all criteria are satisfied before any samples are analyzed.

If the calibration does not meet coefficient of determination and SCV criteria, the analysis shall be terminated, the problem corrected, and a new calibration curve prepared.

9.3.2 Continuing Calibration Verification

To verify the accuracy and stability of the calibration, analyze a CCV standard prior to analyzing each analytical batch and thereafter at a frequency of one CCV standard per 10 field samples for the duration of the analytical batch. Analyze a closing CCV standard at the end of the analytical batch.

The recovery of analyte in the CCV is calculated as follows:

$$\% R = \frac{M}{T} \times 100$$

Where

$\%R$ = percent recovery of the standard

M = measured concentration of analyte, $\mu\text{g/L}$

T = true concentration of the analyte in the CCV, $\mu\text{g/L}$

If the CCV recovery is not within 85 - 115%, the analysis shall be terminated. The cause of the poor recovery must be determined and the problem corrected. All samples not bracketed by acceptable CCV results must be re-analyzed.

NOTE: If it is suspected that the CCV was prepared incorrectly, it may be re-prepared and re-analyzed. If it passes, the analysis may continue.

9.3.3 Instrument Performance Check Solution

The MCT must be verified through the analysis of an IPC. The IPC is three tiered and is used to verify the state of the IC system, over time, to quantitate perchlorate in highly ionic matrices. This must be conducted with each analytical run.

- 9.3.3.1 Prepare a solution containing a mixed common anion, which reflects a conductance near (within $\pm 10\%$) that specified as the MCT and a perchlorate concentration at approximately 5 times the QL. Region 9 Laboratory uses a solution containing 10 $\mu\text{g/L}$ of perchlorate and 500 mg/L of the mixed common anions (chloride, sulfate, and carbonate). NOTE: Use appropriate concentration of anions when MCT changes.
- 9.3.3.2 Confirm the conductance of the IPC and analyze as the initial sample in the analysis batch. If after several weeks of storage, the measured conductance of this solution has shifted by more than 10% from the original measured value, prepare a fresh IPC solution. Following the analysis, calculate the $\text{PD}_{\text{A/H}}$ by comparing the peak area to height ratio of the IPC mixed anion standard ($\text{A}/\text{H}_{\text{MA}}$) for this analytical run to the value that was derived for the LCS ($\text{A}/\text{H}_{\text{LCS}}$) in the previous analytical run. As the first tier criteria, the value for the $\text{PD}_{\text{A/H}}$ must be less than 25% before proceeding with the analytical run.
- 9.3.3.3 As the second tier criteria, the measured recovery for perchlorate in the IPC must be within 80 - 120%.
- 9.3.3.4 As the third tier and final criteria for the IPC, the laboratory must closely monitor the perchlorate retention time. When a new solution of eluent is prepared and sudden shifts of more than 5% are observed in the perchlorate retention time, some type of instrument problem may be present and the column may require cleaning or replacement. The laboratory should retain a record of retention times to provide evidence of an analytical column's continued performance.

9.3.4 Quantitation Limit Standard

To verify the ability to detect target analytes near the QL, a QLS must be analyzed at the beginning of the analytical run (typically just after the CCV) and after every 40 analytical runs. The recovery of analytes in the QL is calculated as:

$$\% R = \frac{M}{T} \times 100$$

Where

- $\%R$ = percent recovery of the standard
 M = measured concentration of the analyte, $\mu\text{g/L}$
 T = true concentration of the analyte in the QLS, $\mu\text{g/L}$

If the QLS recovery does not meet criteria in Appendix C, determine the cause, take corrective action, and re-analyze the QLS.

9.4 Batch QC

9.4.1 Method Blank

Analyze at least one MB daily or with each batch of 20 or fewer field samples of the same matrix. MB values $\geq \frac{1}{2}$ QL indicate potential laboratory contamination. Use the following guidelines to determine when samples must be re-prepared and re-analyzed:

- a) If the MB analyte value $\geq \frac{1}{2}$ QL and the sample result is less than five times the MB analyte amount, rerun the MB once to verify and if still unacceptable then the MB and all associated samples must be re-prepared and re-analyzed. The associated sample results can also be reported but will be qualified as estimated "J".
- b) If the MB analyte value $\geq \frac{1}{2}$ QL and the sample result is greater than five times the MB analyte concentration or is non-detected, report sample result.

9.4.2 LCS

Analyze one LCS standard daily or with each batch of 20 or fewer field samples of the same matrix. If the LCS recovery does not meet criteria, rerun once to verify, if still does not meet criteria provided in Appendix C, determine the cause, take corrective action, and re-analyze the LCS and associated samples. LCS recovery is calculated as:

$$\% R = \frac{C_m}{C_t} \times 100$$

Where

- $\%R$ = percent recovery
 C_m = measured analyte concentration in the LCS
 C_t = true analyte concentration in the LCS

9.4.3 Matrix Spike/Matrix Spike Duplicate

The MS and MSD are designed to provide information about the effect of sample matrix on the measurement system. One set of MS/MSD samples must be analyzed for every 20 or fewer routine samples of the same matrix in an SDG. If the analyte concentration of the MS/MSD source sample is more than

four times the MS/MSD spike level, a MD sample is analyzed and reported instead of the MS/MSD samples.

Samples identified as field blanks cannot be used for MS and MSD sample analysis. MS/MSD recoveries are calculated as:

$$\% R = \frac{C_{ms} - C}{s} \times 100$$

Where

- $\%R$ = percent recovery
- C_{ms} = measured concentration of analyte in the MS, corrected for sample preparation and any dilutions
- C = measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions
- s = expected spike concentration in the MS, corrected for sample preparation and any dilutions

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|C_{msd} - C_{ms}|}{(C_{msd} + C_{ms}) / 2} \times 100$$

Where

- RPD = relative percent difference
- C_{msd} = measured concentration in the MSD, corrected for sample preparation and any dilutions
- C_{ms} = measured concentration in the MS, corrected for sample preparation and any dilutions

If the value of C is less than four times the value of s , apply accuracy and precision criteria in Appendix C. If the MS/MSD do not meet these criteria, examine other QC results to determine if a matrix problem exists. If laboratory performance is in control, the poor MS accuracy or precision is likely to be matrix-related. Flag any out-of-control results as estimated (J).

9.4.4 Matrix Duplicate

Sample homogeneity can affect the quality and interpretation of the data. MD results can be used to assess sample homogeneity.

A matrix duplicate is analyzed only if the original sample concentration is more than four times the matrix spike level. A sample and a matrix duplicate are

diluted, if needed, and analyzed for every MS and MSD that falls outside of the calibration range.

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|C_{md} - C|}{(C_{md} + C) / 2} \times 100$$

Where

- RPD = relative percent difference
 C_{md} = measured concentration in the MD, corrected for sample preparation and any dilutions
 C = measured concentration in the routine sample, corrected for sample preparation and any dilutions

The RPD for any analyte must be ≤ 15 for samples with analyte levels $\geq QL$. If the control limits are exceeded, flag all associated analyte results as estimated (J).

9.5 Method Performance

The following table summarizes method performance by matrix for the period 01/01/08 to 05/18/09.

Method Performance

Analyte	Matrix	QC Type	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2σ)
Perchlorate	Water	LCS	37	100	89.6 - 111
Perchlorate	Solid	LCS	13	102	88.1 - 116

The primary sources of analytical error are:

- Standard's accuracy
- Instrument calibration
- Analytical balance
- Vial contamination
- Pipette calibration

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, SCV, CCV, QLS, MS/MSD, and LCS) are recorded in the LIMS database. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the LIMS database or in the instrument Run Log or sequence record. Project Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the LIMS database. The data package is produced from Element database and manual log records. Appendix G provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance.
- Subsequent instrument modifications and upgrades, including major software upgrades.
- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.6 SOP Read and Understood

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. The Lab QC Database is used to maintain the list of assigned analysts for each SOP. Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix H.

11 REFERENCES

Dionex Corporation, 1999. *DX-600 Operations and Maintenance Manual*.

Record 269, Dionex Chromatography Database 4.2.0, Dionex Corp., Sunnyvale, California 94806.

U.S. Environmental Protection Agency Method 314.0, November 1999. *Determination of Perchlorate in Drinking Water Using Ion Chromatography, Environmental Monitoring Systems Laboratory, Revision 1.0*.

USEPA Region 9 Laboratory. *Business Plan*.

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USEPA Region 9 Laboratory. SOP 130, *Glassware Cleaning Procedures*.

USEPA Region 9 Laboratory. SOP 150, *Soil and Sediment Homogenization*.

USEPA Region 9 Laboratory. SOP 460, *Percent Solids Determination*.

USEPA Region 9 Laboratory. SOP 706, *Laboratory Waste Management Procedure*.

USEPA Region 9 Laboratory. SOP 820, *Laboratory Discrepancy and Corrective Action Procedures*.

USEPA Region 9 Laboratory. SOP 835, *Chromatographic Integration Procedures*.

USEPA Region 9 Laboratory. SOP 840, *Notebook Documentation and Control*.

USEPA Region 9 Laboratory. SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency*.

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. The reference method applies to aqueous samples only. The SOP extends the method to include solid matrices.
2. The SOP specifies potassium hydroxide as the eluent per manufacturer recommendation, rather than NaOH as specified in the method.
3. The SOP specifies that LCS and MS/MSD samples are spiked at 10 $\mu\text{g/L}$. Spike concentrations are not varied to reflect the range of concentrations observed in field samples as specified in the reference method.
4. The SOP uses a 5% retention time window based on the first CCV of each batch. The reference method calculates a window of 3σ based on variations of standards analyzed over several days.
5. The reference method specifies that alternate medium and high level CCVs be analyzed for batches of more than 10 field samples. The SOP requires a single, medium level CCV for all batches. The SOP also requires that a QLS, which is equivalent to a low level CCV, be analyzed with each batch of 20 or fewer samples. Samples analyzed at the Region 9 Laboratory typically do not contain high levels of perchlorate. Therefore, a high level CCV provides little value.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides the target analytes list for this SOP with the CAS number and quantitation limits.

<u>Analyte</u>	<u>Chemical Abstracts</u> <u>Registry Number (CASRN)</u>	<u>Water Quantitation</u> <u>Limit, µg/L</u>	<u>Soil Quantitation</u> <u>Limit, mg/kg</u>
Perchlorate	14797-73-0	2.0	0.02

APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

Parameter	Frequency	Criteria
Coefficient of Determination	Each ICAL	$r^2 \geq 0.995$
SCV	After each ICAL	90 - 110%
IPC	Beginning of each batch	80 - 120%
CCV	Beginning and every 10 samples	85 - 115%
CB	After each calibration	$< \frac{1}{2}$ QL
MB	Each batch	$< \frac{1}{2}$ QL
QLS	Each batch	75 - 125%
LCS	Each batch	85 - 115%
MS/MSD, accuracy	Every 20 samples	80 - 120%
MS/MSD, MD precision	Every 20 samples	≤ 15 RPD
CCV Retention Time Drift	Each batch	$\pm 5\%$ ICAL Std 5
Retention Time Window	Each batch	$\pm 5\%$ first CCV

APPENDIX D. INSTRUMENT INFORMATION

A. Instrument Startup

1. Turn on the computer system and the printer connected to the DX-600. Log into the network. Double click on the server monitor icon and click on the start button to turn on the Chromeleon 6.6 server. This will allow communication between the instrument and the computer. When the server is running, the message in the status box on the computer monitor should say 'Chromeleon Server is running idle.'
2. Double click on the Chromeleon icon to get into the Browser section of the software. Go to the last analyzed sequence and double click on the "Conductivity_Detector_EluGen_Pump_AS40_LC30" control panel to view. Turn on the pump by clicking on the IP25 connected box. Click on the ON button to turn the eluent flow, type "50.00" mM in the eluent generator concentration box and press enter. Turn on the helium flow to the regenerant (50 mN sulfuric acid) solution by setting the gas regulator to approximately 8.5 to 10 psi. Turn the regenerant flow on by clicking on the "Regen Valve ON" button on the control panel at the computer. The system pressure should not be at or above 3000 psi. The baseline reading should be approximately 5 μ S or below prior to starting an analytical sequence. Depending on how long the instrument was not used, it may take a minimum of 1 hour to a maximum of 8 hours for the instrument to stabilize.
3. Setup a sequence by clicking on a sequence file that contains the last calibration performed on the instrument. The sequence files are located in C:\Chromel\Data\DCXKH531_local\DX600_Perchlorate\DX-600 Data\sequence#. The sequence number is a seven-digit number containing the last 2 digits of the year, the month, the day, and the run number (1), ex 0907221. Re-save the accessed file as today's sequence file. Ensure that the small box "Save Raw Data" is checked prior to clicking the save button. Under the status column for each position in the sequence to be analyzed, change "Finished" to "Single". This will enable the computer system to acquire the data for the standards and samples to their designated position in the sequence file. Ensure that the status column for the calibration standards (std1 thru std6) remains 'Finished', which will prevent the computer from writing over the calibration data. If a new calibration is to be analyzed with the QC standards and samples, every entry in the status column should be 'single.' Check for errors within the sequence file by clicking on Batch, Edit, Add, click on the sequence file you wish to run, click open, click on the data file that was just added, click on ready check, when it says OK, click on the OK box.
4. Load the standards and samples to be analyzed according to their designated position in the sequence file. Start the autosampler (Dionex AS40) by pressing the Hold/Run button until the light on the side of the word Run is lighted.

5. The analysis is started by clicking on the start button in the Batch list section of the software. The analysis will stop automatically by inserting a sample positioned at the end of the sequence file and changing the Program name to "stopmethod.pgm", and re-saving the edited sequence file.
6. For each sample injected through the autosampler, the sample loop is flushed with the sample for approximately 2 minutes prior to sample analysis/data acquisition.

B. Conductivity Check Procedure - Prior to conducting any field sample analysis, the conductivity of that matrix must be determined using the following procedure:

1. Allow samples and standards to reach room temperature. The EC Model 2052 is designed to compensate for temperatures in the 5 - 45 °C range but the readings are more accurate near 25 °C. Turn the conductivity meter knob to the ATC position. Allow the meter to warm up for 2-3 minutes.
2. Fill a porcelain dish with standard potassium chloride solution and immerse the cell in the solution. The electrodes in the cell need to be submerged and the electrode chamber must be freed of trapped air. Tap the cell to remove any bubbles, and dip it two or three times to assure proper wetting. Hold the cell away from the bottom and sides of the dish and make certain it is immersed approximately 1.5 inches. Allow the cell to equilibrate in the solution for 20 seconds.
3. Rotate the range switch to the lowest range position which gives a reading (within the range). An over-range value is indicated by a "1" followed by blanks. An under-range value is indicated by a reading followed by a small letter "U".
4. Read the displayed conductance. Record the specific conductance in the Specific Conductance Run Log. The units are determined by the range switch.
5. The standard solution must read within 5% of the theoretical value. If the specific conductance recorded for the standard does not meet this criteria the meter calibration must be adjusted using the STANDARDIZE control on the front of the meter. (If a meter other than the Model 2052 is used refer to the manufacturer's manual for calibration procedures.) Once the meter has been adjusted, return to Step 2 and verify the instrument calibration before proceeding with the analysis of samples.

NOTE: In the event that the meter will not calibrate or fails to maintain calibration, the cell may require replacement. Refer to the manufacturer's operating manual for instructions.

6. Raise the conductivity cell from the sample (and above the dish) and rinse both the inside and outside of the cell with reagent water. Collect the rinsing in the dish and dispose of the waste sample and rinses in an appropriate waste container. Do not wipe the cell to clean it as this may damage the surface.

7. Determine the specific conductance of all samples using the procedure described above. Samples which exceed the laboratory MCT must be diluted and conductivity re-determined to make sure sample conductivity is below the MCT.

APPENDIX E.
RECOMMENDED INSTRUMENT PARAMETERS

DX600 Detector Parameters

Detector Type: Electro Chemical Detector
Data Collection time (minutes): 16.5
Data Collection Rate: 5.00 Hz
Real time plot scale maximum (μS): 2650
Real time plot scale minimum (μS): -500

DX600 Integration Data Events

Time	Description
0.00	Inhibit integration On
0.00	Minimum Area 0.003 [Signal]*min
7.00	Peak Slice 51.62 s
7.00	Minimum Height 0.007 [Signal]*min
7.00	Minimum Width 0.25 min
10.00	Peak Purity Threshold 2.00%
10.00	Sensitivity 0.002 [Signal]*min
12.00	Valley to Valley On
12.00	Tailing Sensitivity Factor 1.8
12.00	Fronting Sensitivity Factor 1.8
13.20	Inhibit Integration Off

DX600 Calibration Parameters

External or internal calibration: EXTERNAL
Number of replicates for calibration: 1
Rejection: Manual
Level Weighting: Equal
Sample Loop: 1000 μL
Calibration standard volume: 1.00 mL
Default sample volume: 1.00 mL
Amount units: $\mu\text{g/L}$

APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

Maintenance Schedule for the DX-600

Item	Frequency	Comments
Filter in the DI water container for the KOH cartridge	As needed	Check filters for discoloration when replacing DI water, replace if needed.
KOH Eluent Cartridge	As needed	Replace when ion count falls below 1.25%. The system displays warning at 10% ion count. A new cartridge has 100% ion count and at 0% ion count, the system will not run until the KOH cartridge is replaced.
Pump	Daily	Prime prior to starting the instrument to prevent air bubbles from entering columns.
High System Pressure	As needed	Check individual pressure of guard and analytical columns.
Guard Column	As needed	Condition guard column if pressure is more than $\frac{1}{4}$ of the analytical column, if still high, replace. Replace guard column if the perchlorate peak deteriorates.
Analytical Column	As needed	Condition analytical column if pressure is more than 4 times of the guard column, if still high replace.
Low System Pressure and/ or Leak Alarm	As needed	Tighten or replace leaky lines or fittings.
Pump seals	Annually	Replace
Inlet frit of guard column	As needed	Replace if system pressure has increased by more than 200 psi and there's solid residue on frit.
Suppressor	As needed	Replace if peak resolutions are not well defined and the baseline noise interfere with peak quantitation.
Check valve cartridges	Annually	Replace
Injection Valve	Annually	Rebuild with new rotor seal and stator phase.
Autosampler tip assembly	Annually	Replace

APPENDIX G. TYPICAL DATA PACKAGE FORMAT

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms

- EPA Review Form
- ESAT technical review guide
- Discrepancy Reports (if applicable)
- Work Order Memo (if applicable)
- Daily folder review forms or checklists
- Analysis matrix listing all analytical runs (for organics only)

Tracking Forms

- Work Order(s)
- COC(s)

Sample Preparation (for projects that require extraction or digestion)

- Bench Sheets (and extraction logs, where used)
- Sample cleanup data and records (e.g. GPC logs)
- Moisture data as applicable
- Analysis matrix (for organics)

[Analysis Method] Data (For each method where multiple methods in package)

- Bench sheet(s) where not used in Sample Preparation section
- Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Alternatively, separate calibration and sample data as:

- Initial Calibration Data
- Sample Data

Miscellaneous Data

- Other data as applicable (e.g. conductivity for perchlorate)

Standard Records

Standards records from LIMS (and logbook pages as needed)

STANDARD OPERATING PROCEDURE: 531
Revision: 5, Effective: 08/21/09

[illegible]

PROPOSED GROUNDWATER METHOD DETECTION LIMITS

Specific Method	Analysis	Matrix	Analyte	MDL	Quantitation Limit	Units
8081B/SOP330	OC Pesticides	Water	alpha-BHC	0.02	0.05	ug/L
8081B/SOP330	OC Pesticides	Water	beta-BHC	0.02	0.05	ug/L
8081B/SOP330	OC Pesticides	Water	delta-BHC	0.02	0.05	ug/L
8081B/SOP330	OC Pesticides	Water	gamma-BHC (Lindane)	0.02	0.05	ug/L
8081B/SOP330	OC Pesticides	Water	Heptachlor	0.02	0.05	ug/L
8081B/SOP330	OC Pesticides	Water	Aldrin	0.02	0.05	ug/L
8081B/SOP330	OC Pesticides	Water	Heptachlor epoxide	0.02	0.05	ug/L
8081B/SOP330	OC Pesticides	Water	Endosulfan I	0.02	0.05	ug/L
8081B/SOP330	OC Pesticides	Water	Dieldrin	0.05	0.10	ug/L
8081B/SOP330	OC Pesticides	Water	4,4'-DDE	0.05	0.10	ug/L
8081B/SOP330	OC Pesticides	Water	Endrin	0.05	0.10	ug/L
8081B/SOP330	OC Pesticides	Water	Endosulfan II	0.05	0.10	ug/L
8081B/SOP330	OC Pesticides	Water	4,4'-DDD	0.05	0.10	ug/L
8081B/SOP330	OC Pesticides	Water	Endosulfan sulfate	0.05	0.10	ug/L
8081B/SOP330	OC Pesticides	Water	4,4'-DDT	0.05	0.10	ug/L
8081B/SOP330	OC Pesticides	Water	Methoxychlor	0.25	0.50	ug/L
8081B/SOP330	OC Pesticides	Water	Endrin ketone	0.05	0.10	ug/L
8081B/SOP330	OC Pesticides	Water	Endrin aldehyde	0.05	0.10	ug/L
8081B/SOP330	OC Pesticides	Water	alpha-Chlordane	0.02	0.05	ug/L
8081B/SOP330	OC Pesticides	Water	gamma-Chlordane	0.02	0.05	ug/L
8270D/SOP375	PAH-Low	Water	Naphthalene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	2-Methylnaphthalene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	1-Methylnaphthalene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	Acenaphthylene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	Acenaphthene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	Fluorene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	Phenanthrene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	Anthracene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	Fluoranthene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	Pyrene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	Benzo(a)anthracene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	Chrysene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	Benzo(b)fluoranthene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	Benzo(k)fluoranthene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	Benzo(a)pyrene	25	50	ng/L

Specific Method	Analysis	Matrix	Analyte	MDL	Quantitation Limit	Units
8270D/SOP375	PAH-Low	Water	Indeno(1,2,3-cd)pyrene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	Dibenz(a,h)anthracene	25	50	ng/L
8270D/SOP375	PAH-Low	Water	Benzo(g,h,i)perylene	25	50	ng/L
8082A/SOP335	PCBs	Water	Aroclor 1016	0.10	0.20	ug/L
8082A/SOP335	PCBs	Water	Aroclor 1221	0.20	0.40	ug/L
8082A/SOP335	PCBs	Water	Aroclor 1232	0.10	0.20	ug/L
8082A/SOP335	PCBs	Water	Aroclor 1242	0.10	0.20	ug/L
8082A/SOP335	PCBs	Water	Aroclor 1248	0.10	0.20	ug/L
8082A/SOP335	PCBs	Water	Aroclor 1254	0.10	0.20	ug/L
8082A/SOP335	PCBs	Water	Aroclor 1260	0.10	0.20	ug/L
8082A/SOP335	PCBs	Water	Aroclor 1262	0.10	0.20	ug/L
8082A/SOP335	PCBs	Water	Aroclor 1268	0.10	0.20	ug/L
8270D/SOP315	SVOCs	Water	1,4-Dioxane	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Phenol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	Bis(2-chloroethyl)ether	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	2-Chlorophenol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	1,3-Dichlorobenzene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	1,4-Dichlorobenzene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Benzyl alcohol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	1,2-Dichlorobenzene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	2-Methylphenol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	Bis(2-chloro-1-methylethyl) ether	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	3&4-Methylphenol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	N-Nitrosodipropylamine	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Hexachloroethane	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Nitrobenzene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Isophorone	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	2-Nitrophenol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	2,4-Dimethylphenol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	Bis(2-chloroethoxy)methane	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	2,4-Dichlorophenol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	1,2,4-Trichlorobenzene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Naphthalene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	4-Chloroaniline	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	Hexachlorobutadiene	0.5	1.0	ug/L

Specific Method	Analysis	Matrix	Analyte	MDL	Quantitation Limit	Units
8270D/SOP315	SVOCs	Water	4-Chloro-3-methylphenol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	2-Methylnaphthalene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Hexachlorocyclopentadiene	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	2,4,6-Trichlorophenol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	2,4,5-Trichlorophenol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	2-Chloronaphthalene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	2-Nitroaniline	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	Dimethyl phthalate	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Acenaphthylene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	2,6-Dinitrotoluene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	3-Nitroaniline	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	Acenaphthene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	2,4-Dinitrophenol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	4-Nitrophenol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	Dibenzofuran	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	2,4-Dinitrotoluene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Diethyl phthalate	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Fluorene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	4-Chlorophenyl phenyl ether	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	4-Nitroaniline	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	4,6-Dinitro-2-methylphenol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	Diphenyl amine	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	4-Bromophenyl phenyl ether	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Hexachlorobenzene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Pentachlorophenol	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	Phenanthrene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Anthracene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Carbazole	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Di-n-butyl phthalate	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Fluoranthene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Pyrene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Butyl benzyl phthalate	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Benzo(a)anthracene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	3,3'-Dichlorobenzidine	2.5	5.0	ug/L
8270D/SOP315	SVOCs	Water	Chrysene	0.5	1.0	ug/L

Specific Method	Analysis	Matrix	Analyte	MDL	Quantitation Limit	Units
8270D/SOP315	SVOCs	Water	Bis(2-ethylhexyl) phthalate	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Di-n-octyl phthalate	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Benzo(b)fluoranthene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Benzo(k)fluoranthene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Benzo(a)pyrene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Indeno(1,2,3-cd)pyrene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Dibenz(a,h)anthracene	0.5	1.0	ug/L
8270D/SOP315	SVOCs	Water	Benzo(g,h,i)perylene	0.5	1.0	ug/L
8015B/SOP385	TPH - Extractable	Water	TPH as Diesel	120	250	ug/L
8015B/SOP385	TPH - Extractable	Water	TPH as Motor Oil	500	1000	ug/L
8015C/SOP380	TPH - Purgeable	Water	TPH as Gasoline	25	50	ug/L
524.2/SOP354	VOCs	Water	Dichlorodifluoromethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Chloromethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Vinyl chloride	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Bromomethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Chloroethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Trichlorofluoromethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,1-Dichloroethene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Dibromomethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Bromodichloromethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	cis-1,3-Dichloropropene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	4-Methyl-2-pentanone (MIBK)	2.0	4.0	ug/L
524.2/SOP354	VOCs	Water	Toluene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	trans-1,3-Dichloropropene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,1,2-Trichloroethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Tetrachloroethene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,3-Dichloropropane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	2-Hexanone	2.0	4.0	ug/L
524.2/SOP354	VOCs	Water	Chlorodibromomethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,2-Dibromoethane (EDB)	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Chlorobenzene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,1,1,2-Tetrachloroethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Ethylbenzene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	m&p-Xylene	0.5	1.0	ug/L
524.2/SOP354	VOCs	Water	o-Xylene	0.2	0.5	ug/L

Specific Method	Analysis	Matrix	Analyte	MDL	Quantitation Limit	Units
524.2/SOP354	VOCs	Water	Styrene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Bromoform	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Isopropylbenzene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Bromobenzene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,1,2,2-Tetrachloroethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,2,3-Trichloropropane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,1,2-Trichloro-1,2,2-trifluoroethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Acetone	2.0	4.0	ug/L
524.2/SOP354	VOCs	Water	Dichloromethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	tert-Butyl alcohol	5.0	10	ug/L
524.2/SOP354	VOCs	Water	trans-1,2-Dichloroethene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	tert-Butyl methyl ether (MTBE)	1.0	2.0	ug/L
524.2/SOP354	VOCs	Water	1,1-Dichloroethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Diisopropyl ether	1.0	2.0	ug/L
524.2/SOP354	VOCs	Water	Ethyl tert-butyl ether	1.0	2.0	ug/L
524.2/SOP354	VOCs	Water	2,2-Dichloropropane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	cis-1,2-Dichloroethene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	2-Butanone (MEK)	2.0	4.0	ug/L
524.2/SOP354	VOCs	Water	Bromochloromethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Chloroform	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,1,1-Trichloroethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Carbon tetrachloride	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,1-Dichloropropene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Benzene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,2-Dichloroethane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	tert-Amyl methyl ether	1.0	2.0	ug/L
524.2/SOP354	VOCs	Water	Trichloroethene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,2-Dichloropropane	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Propylbenzene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	2-Chlorotoluene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	4-Chlorotoluene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,3,5-Trimethylbenzene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	tert-Butylbenzene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,2,4-Trimethylbenzene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	sec-Butylbenzene	0.2	0.5	ug/L

Specific Method	Analysis	Matrix	Analyte	MDL	Quantitation Limit	Units
524.2/SOP354	VOCs	Water	1,3-Dichlorobenzene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	p-Isopropyltoluene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,4-Dichlorobenzene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,2-Dichlorobenzene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Butylbenzene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,2-Dibromo-3-chloropropane	1.0	2.0	ug/L
524.2/SOP354	VOCs	Water	1,2,4-Trichlorobenzene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Hexachlorobutadiene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	Naphthalene	0.2	0.5	ug/L
524.2/SOP354	VOCs	Water	1,2,3-Trichlorobenzene	0.2	0.5	ug/L
245.1/SOP515	Mercury	Water	Mercury	0.015	0.030	ug/L
200.7/SOP505	Metals by 200.7	Water	Aluminum	50	100	ug/L
200.7/SOP505	Metals by 200.7	Water	Antimony	10	20	ug/L
200.7/SOP505	Metals by 200.7	Water	Arsenic	10	20	ug/L
200.7/SOP505	Metals by 200.7	Water	Barium	5.0	10	ug/L
200.7/SOP505	Metals by 200.7	Water	Beryllium	0.50	1.0	ug/L
200.7/SOP505	Metals by 200.7	Water	Boron	50	100	ug/L
200.7/SOP505	Metals by 200.7	Water	Cadmium	2.5	5.0	ug/L
200.7/SOP505	Metals by 200.7	Water	Calcium	50	100	ug/L
200.7/SOP505	Metals by 200.7	Water	Chromium	5.0	10	ug/L
200.7/SOP505	Metals by 200.7	Water	Cobalt	5.0	10	ug/L
200.7/SOP505	Metals by 200.7	Water	Copper	5.0	10	ug/L
200.7/SOP505	Metals by 200.7	Water	Iron	50	100	ug/L
200.7/SOP505	Metals by 200.7	Water	Lead	10	20	ug/L
200.7/SOP505	Metals by 200.7	Water	Magnesium	250	500	ug/L
200.7/SOP505	Metals by 200.7	Water	Manganese	2.5	5.0	ug/L
200.7/SOP505	Metals by 200.7	Water	Molybdenum	10	20	ug/L
200.7/SOP505	Metals by 200.7	Water	Nickel	5.0	10	ug/L
200.7/SOP505	Metals by 200.7	Water	Potassium	1000	2000	ug/L
200.7/SOP505	Metals by 200.7	Water	Selenium	10	20	ug/L
200.7/SOP505	Metals by 200.7	Water	Silica (SiO ₂)	250	500	ug/L
200.7/SOP505	Metals by 200.7	Water	Silver	5.0	10	ug/L
200.7/SOP505	Metals by 200.7	Water	Sodium	250	500	ug/L
200.7/SOP505	Metals by 200.7	Water	Thallium	10	20	ug/L

Notes:						
BHC	Hexachlorocyclohexane					
DDD	Dichlorodiphenyldichloroethane					
DDE	Dichlorodiphenyldichloroethene					
DDT	Dichlorodiphenyltrichloroethane					
MDL	Method detection limit					
mg/L	Milligrams per kilogram					
ng/L	Nanograms per kilogram					
OC	Organochlorine					
PAH	Polycyclic aromatic hydrocarbons					
PCB	Polychlorinated biphenyl					
SOP	Standard Operating Procedure					
SVOC	Semivolatile organic compounds					
TPH	Total petroleum hydrocarbons					
ug/L	Micrograms per kilogram					
VOC	Volatile organic compounds					

ATTACHMENT 3
GROUNDWATER FIELD SOPS

SOP APPROVAL FORM

TETRA TECH EM INC.

ENVIRONMENTAL STANDARD OPERATING PROCEDURE

MONITORING WELL INSTALLATION

SOP NO. 020

REVISION NO. 4

Last Reviewed: April 2009



Quality Assurance Approved

May 21, 2009

Date

1.0 BACKGROUND

Groundwater monitoring wells are designed and installed for a variety of reasons, including (1) detecting the presence or absence of contaminants, over both the short and the long term, (2) collecting groundwater samples representative of in situ aquifer chemical characteristics, (3) conducting aquifer testing, and (4) measuring water levels for determining groundwater potentiometric head and groundwater flow direction.

This standard operating procedure (SOP) focuses on common methods and minimum standards for oversight and documentation of monitoring well installation for Tetra Tech EM Inc. (Tetra Tech) projects. Detailed specifications for well design and installation may vary in response to site-specific conditions; however, some elements of well installation are common to most situations. Well installation conducted according to this SOP will have complete and approved construction specifications, usually in a work plan or site-specific field sampling plan. In most cases, Tetra Tech will provide oversight and documentation of the well installation process conducted by a drilling subcontractor. This SOP is based on widely recognized methods described by the U.S. Environmental Protection Agency (EPA) and American Society for Testing and Materials (ASTM). In addition, monitoring wells should be designed and installed in a manner consistent with all local and state regulations. Detailed specifications for well installation should be identified within a site-specific work plan, sampling plan, or quality assurance project plan (QAPP).

An experienced and knowledgeable person (preferably a hydrogeologist) will need to locate the well and supervise its installation so that the samples ultimately collected will be representative of the groundwater. Personnel installing wells should work under the supervision of a registered professional, and the requirements of the state where the work is being performed should be followed as to the specific requirements for the registered professional and his or her level of involvement and oversight.

The following types of monitoring well materials, installation procedures, and record-keeping requirements are included in this SOP:

Monitoring well materials

- Casing materials
- Well screen materials
- Filter pack materials
- Annular sealant (bentonite pellets or chips)
- Grouting materials
- Surface completion and protective casing materials

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- Concrete surface pad and bumper posts
- Uncontaminated water

Monitoring well installation procedures

- Well screen and riser placement
- Filter pack placement
- Temporary casing retrieval
- Annular seal placement
- Grouting
- Surface completion and protective casing (aboveground and flush-mount)
- Concrete surface pad and bumper posts
- Permanent and multiple casing well installation

Record-keeping procedures

- Surveying
- Permits
- Well construction and borehole logging
- Monitoring well identification

Well installation methods will depend to some extent on the borehole drilling method. Specific boring or drilling protocols are detailed in other SOPs. The boring method, in turn, will depend on site-specific geology, hydrogeology, and project requirements. Drilling methods commonly used for well installation include hollow-stem augering, cable tool, mud-rotary, air rotary, air casing hammer, sonic, and rock coring.

1.1 PURPOSE

This SOP establishes the requirements and procedures for monitoring well installation and associated documentation. The performance objectives for monitoring well installation are as follows:

- Ensure that the monitoring well will provide water samples representative of in situ aquifer conditions.
- Ensure that the monitoring well construction will last for the duration of the project.
- Ensure that the monitoring well will not serve as a conduit for vertical migration of contaminants, particularly vertical migration between discrete aquifers.
- Ensure that the well construction details are documented in a standardized format.

1.2 SCOPE

This SOP applies to the oversight and documentation of monitoring well installation. Although some of the procedures may apply to the installation of water supply wells, this SOP is not intended to cover the design and construction of such wells. The SOP identifies several well drilling methods related to monitoring well installation, but the scope of this SOP does not include drilling methods.

Other relevant SOPs include SOP 002 for decontamination of drilling and well installation equipment, SOP 026 for borehole logging, SOP 005 for soil sampling, SOP 021 for monitoring well development, SOPs 010 and 015 for groundwater sampling from monitoring wells, and SOP 014 for measuring static water levels within monitoring wells.

1.3 DEFINITIONS

Annulus: The space between the monitoring well casing or conductor casing and the wall of the well boring.

Bentonite seal: A colloidal clay seal separating the sand pack from the annular grout seal.

Centralizer: A stainless steel or plastic spacer that keeps the well screen and casing centered in the borehole.

Filter pack: Clean sand or gravel placed between the borehole wall and the well screen to prevent formation material from entering the screen.

Grout seal: A fluid mixture of (1) bentonite and water, (2) cement, bentonite, and water, or (3) cement and water placed above the bentonite seal between the casing and the borehole wall to secure the casing in place and keep water from entering the borehole.

Tremie pipe: A rigid pipe used to place the well filter pack, bentonite seal, or grout seal. The tremie pipe is lowered to the bottom of the well or area to be filled and pulled up ahead of the material being placed.

Well casing: A solid piece of pipe, typically polyvinyl chloride (PVC) or stainless steel, used to keep a well open in either unconsolidated material or unstable rock.

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Well screen: A PVC or stainless steel pipe with openings of a uniform width, orientation, and spacing used to keep materials other than water from entering the well and to stabilize the surrounding formation.

1.4 REFERENCES

- American Society for Testing and Materials. 2004. Standard Practice for Design and Installation of Ground Water Monitoring Wells in Aquifers. D5092-04. West Conshohocken, Pennsylvania.
- California Department of Toxic Substances Control. 1995. Monitoring Well Design and Construction for Hydrogeologic Characterization. Guidance for Groundwater Investigations. July.
- Driscoll, F.G. 1986. *Groundwater and Wells (Second Edition)*. Johnson Division, UOP, Inc. St. Paul, Minnesota.
- U.S. Environmental Protection Agency (EPA). 1991. Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells. Office of Research and Development, Environmental Monitoring Systems Laboratory. Washington, DC. EPA/600-4-89/034. March. <http://www.epa.gov/swrust1/cat/wwelldct.pdf>
- EPA. 1992. RCRA Ground Water Monitoring Technical Enforcement Guidance Document. Office of Solid Waste and Emergency Response. Washington, DC. OSWER-9950-1. November.
- EPA. 1994. Monitor Well Installation. Environmental Response Team SOP #2048 (Rev. #0.0, 03/18/96). <http://www.ert.org>

1.5 REQUIREMENTS AND RESOURCES

To conduct oversight and document the installation of a monitoring well, the person at the drill site should be a geoscientist or engineer who has relevant professional training and experience. The site geoscientist is responsible for oversight and documentation of all well installation activities. The site geoscientist shall understand the project objectives and regularly communicate from the field with the project manager or technical project team members. The site geoscientist shall verify that all permits are obtained, and that the well locations are cleared for overhead and underground utilities or other obstructions.

Well installation requires a completed boring with stable or supported walls. The type of drilling rig needed to complete the boring and the well construction materials required for monitoring well installation will depend on the drilling method used, the geologic formations present, and chemicals of concern in groundwater. The rig and support equipment used to drill the borehole is usually used to install the well.

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Under most conditions, the following items are also required for the proper installation of monitoring wells:

- Tremie pipe and funnel
- Bentonite pellets or chips
- Grouting supplies
- Casing materials
- Well screen materials
- Filter pack materials
- Surface completion materials (protective casing, lockable and watertight well cover, padlock)
- Electronic water level sounding device for water level measurement
- Measuring tape with weight for measuring the depth of the well and determining the placement of filter pack materials
- Decontamination equipment and supplies
- Site-specific work plan, field sampling plan, health and safety plan, and QAPP
- Monitoring Well Completion Record (see Figure 1 for example)

2.0 MONITORING WELL INSTALLATION PROCEDURES

For reference, this section presents standard procedures for monitoring well installation and is divided into three subsections. Section 2.1 addresses monitoring well construction materials, while Section 2.2 describes typical monitoring well installation procedures. Section 2.3 addresses record-keeping requirements associated with monitoring well installation. Monitoring well design and installation procedures described in work plans, sampling plans, and QAPPs should be fully consistent with the procedures outlined in this SOP as well as any applicable local and state regulations and guidelines.

2.1 MONITORING WELL CONSTRUCTION MATERIALS

Monitoring well construction materials should be specified in the site-specific work plan as well as in the statement of work for any subcontractors assisting in the well installation. The riser, well screen, and filter pack and annular sealant placement equipment should be certified as clean by the manufacturer and delivered to and maintained in clean condition at the site. Where this is not possible, all materials or tools should be steam cleaned or high-pressure water cleaned with water from a source of known chemistry immediately prior to installation (see Tetra Tech SOP No. 002). Samples of the filter pack, annular seal, and mixed grout should be retained as a quality control measure until at least one round of groundwater sampling and analysis is completed.

This section generally discusses material specifications for the following well construction components:

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- Casing and well screen
- Filter pack
- Annular sealant (bentonite pellets or chips)
- Grout
- Tremie pipes
- Surface completion components (protective casing, lockable and watertight cap, and padlock)
- Concrete surface pad
- Uncontaminated water

Figures 2A and 2B shows the construction details of a typical monitoring well, with above grade or flush mounted surface completion, respectively.

2.1.1 Casing Materials

The material type and minimum wall thickness of the casing should be adequate to withstand the forces of installation. The ends of each casing section should be either flush-threaded or beveled for welding. Schedule 40 or Schedule 80 PVC casing is typically used for monitoring well installation. Either type of casing is appropriate for monitoring wells with depths less than 100 feet below ground surface (bgs). If the well is deeper than 100 feet bgs, Schedule 80 PVC should be used.

Stainless steel used for well casing is typically Type 304 and is of 11-gauge thickness.

2.1.2 Well Screen Materials

Well screens should be new, machine-slotted or continuous wrapped wire-wound, and composed of materials best suited for the monitoring environment based on site characterization findings. Well screens are generally constructed of the same materials used for well casing (PVC or stainless steel). The screen should be plugged at the bottom with the same material as the well screen. Alternatively, a short (1- to 2-foot) section of casing material with a bottom (sump) should be attached below the screen. This assembly must be able to withstand installation and development stresses without becoming dislodged or damaged. The length of the slotted area should reflect the interval to be monitored.

The minimum internal diameter of the well screen should be chosen based on the particular application. A minimum inside diameter of 2 inches is usually needed to allow for the introduction and withdrawal of sampling devices. Typical monitoring well screen diameters are 2 inches and 4 inches.

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The slot size of the well screen should be determined relative to (1) the grain size of particles in the aquifer to be monitored and (2) the gradation of the filter pack material. This determination is often made in the field based on the grain size and distribution of borehole material encountered.

2.1.3 Filter Pack Materials

The primary filter pack consists of a granular material of known chemistry and selected grain size and gradation. The filter pack is installed in the annulus between the well screen and the borehole wall. The grain size and gradation of the filter pack are selected to stabilize the hydrologic unit adjacent to the screen and to prevent formation material from entering the well during groundwater sampling. The procedure for determining the grain size and gradation of the filter pack is to be presented in each site-specific field sampling plan or work plan. After development, a properly filtered monitoring well is relatively free of turbidity.

A secondary filter pack is a layer of material placed in the annulus directly above the primary filter pack and separates the filter pack from the annular sealant. The secondary filter pack should be uniformly graded fine sand, with 100 percent by weight passing through a No. 30 U.S. Standard sieve, and less than 2 percent by weight passing through a No. 200 U.S. Standard sieve.

2.1.4 Annular Sealant (Bentonite Pellets or Chips)

The materials used to seal the annulus may be prepared as a slurry or used as dry pellets, granules, or chips. Sealants should be compatible with ambient geologic, hydrogeologic, and climatic conditions and any man-induced conditions anticipated to occur during the life of the well.

Bentonite (sodium montmorillonite) is the most commonly used annular sealant and is furnished in sacks or buckets in powder, granular, pelletized, or chip form. Bentonite should be obtained from a commercial source and should be free of impurities that may adversely impact the water quality in the well. Pellets are compressed bentonite powder in roughly spherical or disk shapes. Chips are large, coarse, irregularly shaped units of bentonite. The diameter of the pellets or chips should be less than one-fifth the width of the annular space into which they will be placed in order to reduce the potential for bridging. Granules consist of coarse particles of unaltered bentonite, typically smaller than 0.2 inch in diameter. Bentonite slurry is prepared by mixing powdered or granular bentonite with water from a source of known chemistry.

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2.1.5 Grouting Materials

The grout backfill that is placed above the bentonite annular seal is ordinarily liquid slurry consisting of either (1) a bentonite (powder, granules, or both) base and water, (2) a bentonite and Portland cement base and water, or (3) a Portland cement base and water. Often, bentonite-based grouts are used when flexibility is desired during the life of the well installation (for example, to accommodate freeze-thaw cycles). Cement- or bentonite-based grouts are often used when cracks in the surrounding geologic material must be filled or when adherence to rock units or a rigid setting is desired.

Each type of grout mixture has slightly different characteristics that may be appropriate under various physical and chemical conditions. However, quick-setting cements containing additives are not recommended for use in monitoring well installation because additives may leach from the cement and influence the chemistry of water samples collected from the well.

2.1.6 Tremie Pipe

A tremie pipe is used to place the filter pack, annular sealant, and grouting materials into the borehole. The tremie pipe should be rigid, have a minimum internal diameter of 1.0 inch, and be made of PVC or steel. The length of the tremie pipe should be sufficient to extend to the full depth of the monitoring well.

2.1.7 Surface Completion and Protective Casing Materials

Protective casings that extend above the ground surface should be made of aluminum, steel, stainless steel, cast iron, or a structural plastic. The protective casing should have a lid with a locking device to prevent vandalism. Sufficient clearance, usually 6 inches, should be maintained between the top of the riser and the top of the protective casing. A watertight well cap should be placed on the top of the riser to seal the well from surface water infiltration in the event of a flood. A weep hole should be drilled in the casing a minimum of 6 inches above the ground surface to enable water to drain out of the annular space.

Flush-mounted monitoring wells (wells that do not extend above ground surface) require a watertight protective cover of sufficient strength to withstand heavy traffic. The well riser should be fitted with a locking watertight cap.

2.1.8 Concrete Surface Pad and Bumper Posts

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A concrete surface pad should be installed around each well when the outer protective casing is installed. The surface pad should be formed around the well casing. Concrete should be placed into the formed pad and into the borehole (on top of the grout), typically to a depth of 1 to 3 feet bgs (depending on state, federal, and local regulations). The protective casing is then installed into the concrete. As a general guideline, if the protective casing is 4 inches in diameter, the concrete pad should be 3 feet square and 4 inches thick. If the well casing is 8 inches in diameter, the pad should be 4 feet square and 6 inches thick. Round concrete pads are also acceptable.

The finished pad should be sloped so that drainage flows away from the protective casing and off the pad. The finished pad should extend at least 1 inch above grade, with the edge tapered to match the existing grade.

If the monitoring well is located in a high-traffic area and finished at surface grade, a traffic-bearing, flush-mounted cover should be used whenever possible. For wells finished with protective casing above grade, a minimum of three bumper posts (bollard) should be installed around the pad to protect the well. The bumper posts, consisting of steel pipes 3 to 4 inches in diameter and at least 5 feet long, should be installed in a radial pattern around the protective casing, beyond the edges of the cement pad. The base of the bumper posts should be installed 2 feet bgs in a concrete footing; the tops of the posts should be capped or filled with concrete. Bumper posts are not required for flush-mounted monitoring wells.

2.1.9 Uncontaminated Water

Water used in the drilling process, to prepare grout mixtures and to decontaminate the well screen, riser, and annular sealant injection equipment, should be obtained from a source of known chemistry or municipal tap water. The water should not contain constituents that could compromise the integrity of the monitoring well installation.

2.2 MONITORING WELL INSTALLATION PROCEDURES

This section describes the procedures used to install a single-cased monitoring well, with either temporary casing or hollow-stem augers to support the walls of the boring in unconsolidated formations. The procedures are described in the order in which they are conducted, and include (1) placement of well screen and riser pipe, (2) placement of filter pack, (3) progressive retrieval of temporary casing, (4) placement of annular seal, (5) grouting, (6) surface completion and installation of protective casing, and (7) installation of concrete pad and bumper posts.

The additional steps necessary to install a well with permanent or multiple casing strings are described at the end of this section.

2.2.1 Well Screen and Riser Placement

Screen length, depth, and monitoring well diameter will depend on site-specific considerations such as intended well use, contaminants of concern, and hydrogeology. Some specific considerations include the following:

1. Water table wells should have screens of sufficient length and diameter to monitor the water table and provide sufficient sample volume under high and low water table conditions.
2. Wells with low recharge should have screens of sufficient length and diameter so that adequate sample volume can be collected.
3. Wells should be screened over sufficiently short intervals to allow for monitoring of discrete migration pathways.
4. Where light nonaqueous-phase liquids (LNAPL) or contaminants in the upper portion of a hydraulic unit are being monitored, the screen should be set so that the upper portion of the water-bearing zone is below the top of the screen.
5. Where dense nonaqueous-phase liquids (DNAPL) are being monitored, the screen should be set within the lower portion of the water-bearing zone, just above a relatively impermeable lithologic unit.
6. The screened interval should not extend across an aquiclude or aquitard.
7. If contamination is known to be concentrated within a portion of a saturated zone, the screen should be constructed in a manner that minimizes the potential for cross-contamination within the aquifer.
8. If downhole geophysical surveys are to be conducted, the casing and screen must be of sufficient diameter and constructed of the appropriate material to allow for effective use of the geophysical survey tools.
9. If aquifer tests are to be conducted in a monitoring well, the slot size must allow sufficient flux to produce the required drawdown and recovery. The diameter of the well must be sufficient to house the pump and monitoring equipment, and allow sufficient water flux (in combination with the screen slot size) to produce the required drawdown or recovery.

After the total depth of the boring is confirmed and the well screen depth interval and the height of the aboveground completion are determined, the screen slot size and well pack material are determined based

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on the specifications described in the work plan. The well-screen slot size can only be selected after the filter pack grain size is specified. In monitoring wells, the well screen should retain 90 to 100 percent of the filter pack sands. Cumulative weight percent vs. grain size in thousandths of an inch (standard size for screen slots) of the selected filter sand is used to select the appropriate screen size.

Next, the screen and riser are assembled from the bottom up as it is lowered down the hole. The following procedures should be followed:

1. Measure the total depth of the boring using a weighted tape.
2. Determine the length of screen and casing materials required to construct the well.
3. Assemble the well parts from the bottom up, starting with the well sump or cap, well screen, and then the riser pipe. Progressively lower the assembled length of pipe.
4. The length of the assembled pipe should not extend above the top of the drill rig or be longer than the lateral extent of fall protection surrounding the drill rig as a safety precaution.

The well sump or cap, well screen, and riser should be certified clean by the manufacturer or should be decontaminated before assembly and installation. Flush joints should be tightened, and welds should be watertight and of good quality. The riser should extend above grade and be capped temporarily to prevent entrance of foreign materials during the remaining well completion procedures.

When the well screen and riser assembly is lowered to the predetermined level, it may float and require a method to hold it in place. For borings drilled using cable tool or air-rotary drilling methods, centralizers should be attached to the riser at intervals of between 20 and 40 feet.

2.2.2 Filter Pack Placement

The filter pack is placed after the well screen and riser assembly has been lowered into the borehole. The steps below should be followed:

1. Determine the volume of the annular space in the filter pack interval. The filter pack should extend from the bottom of the borehole to at least 2 feet above the top of the well screen to allow for compaction during well development.
2. Assemble the required material (sand pack and tremie pipe).
3. Lower a clean or decontaminated tremie pipe down the annulus to within 1 foot of the base of the hole.

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4. Pour the sand down the tremie pipe using a funnel; pour only the quantity estimated to fill the first foot.
5. Check the depth of sand in the hole using a weighted tape.
6. Pull the drill casing up ahead of the sand to keep the sand from bridging.
7. Continue with this process (steps 4 through 6) until the filter pack is at the appropriate depth.

If bridging of the filter pack occurs, break out the bridge prior to adding additional filter pack material.

For wells less than 30 feet deep installed inside hollow-stem augers, the sand may be poured in 1-foot lifts without a tremie pipe.

Sufficient measurements of the depth to the filter pack material and the depth of the bottom of the temporary casing should be made to ensure that the casing bottom is always above the filter pack. The filter pack should extend 2 feet above the well screen (or more if required by state or local regulations). However, the filter pack should not extend across separate hydrogeologic units. The final depth interval, volume, and type of filter pack should be recorded on the Monitoring Well Completion Record (Figure 1).

A secondary filter pack may be installed above the primary filter pack to prevent the intrusion of the bentonite grout seal into the primary filter pack. A measured volume of secondary filter material should be added to extend 1 to 2 feet above the primary filter pack. As with the primary filter pack, the secondary filter pack must not extend into an overlying hydrologic unit. An on-site geoscientist should evaluate the need for a secondary filter pack by considering the gradation of the primary filter pack, the hydraulic head difference between adjacent units, and the potential for grout intrusion into the primary filter pack.

The secondary filter material is poured into the annular space through tremie pipe as described above. Water from a source of known chemistry may be added to help place the filter pack into its proper location. The tremie pipe or a weighted line inserted through the tremie pipe can be used to measure the top of the secondary filter pack as work progresses. The amount and type of secondary filter pack used should be recorded on the Monitoring Well Completion Record (Figure 1).

2.2.3 Temporary Casing Retrieval

The temporary casing or hollow-stem auger should be withdrawn in increments. Care should be taken to minimize lifting the well screen and riser assembly during withdrawal of the temporary casing or auger.

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It may be necessary to place the top head of the rig on the riser to hold it down. To limit borehole collapse in formations consisting of unconsolidated materials, the temporary casing or hollow-stem auger is usually withdrawn until the lowest point of the casing or auger is at least 2 feet, but no more than 5 feet, above the filter pack. When the geologic formation consists of consolidated materials, the lowest point of the casing or auger should be at least 5 feet, but no more than 10 feet, above the filter pack. In highly unstable formations, withdrawal intervals may be much less. After each increment, the depth to the primary filter pack should be measured to check that the borehole has not collapsed or that bridging has not occurred. Should collapse occur, re-drilling of the borehole to remove collapsed material will be necessary.

2.2.4 Annular Seal Placement

A bentonite pellet, chip, or slurry seal should be placed between the borehole and the riser on top of the primary or secondary filter pack. This seal retards the movement of grout into the filter pack. The thickness of the bentonite seal will depend on state and local regulations, but the seal should generally be between 3 and 5 feet thick.

The bentonite seal should be installed using a tremie pipe, lowered to the top of the filter pack and slowly raised as the bentonite pellets or slurry fill the space. Care must be taken so that bentonite pellets or chips do not bridge in the augers or tremie pipe. The depth of the seal should be checked with a weighted tape or the tremie pipe.

If a bentonite pellet or chip seal is installed above the water level, water from a known source should be added to allow proper hydration of the bentonite. Sufficient time should be allowed for the bentonite seal to hydrate. The volume and thickness of the bentonite seal should be recorded on the Monitoring Well Completion Record (Figure 1).

2.2.5 Grouting

Grouting procedures vary with the type of well design. The volume of grout needed to backfill the remaining annular space should be calculated and recorded on the Monitoring Well Completion Record (Figure 1). The use of alternate grout materials, including grouts containing gravel, may be necessary to control zones of high grout loss. Bentonite grouts should not be used in arid regions because of their propensity to desiccate. Typical grout mixtures include the following:

- **Bentonite grout:** about 1 to 1.25 pounds of bentonite mixed with 1 gallon of water.

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- **Cement-bentonite grout:** about 5 pounds of bentonite and one 94-pound bag of cement mixed with 7 to 8 gallons of water.
- **Cement grout:** one 94-pound bag of cement mixed with 6 to 7 gallons of water.

The grout should be installed by gravity feed or pumping through a tremie pipe. The grout should be mixed in batches in accordance with the appropriate requirements and then pumped into the annular space until full-strength grout flows out at the ground surface without evidence of drill cuttings or fluid. The tremie pipe should then be removed to allow the grout to cure.

The riser should not be disturbed until the grout sets and cures for the amount of time necessary to prevent a break in the seal between the grout and riser. For bentonite grouts, curing times are typically around 24 hours; curing times for cement grouts are typically 48 to 72 hours. However, the curing time required will vary with grout content and climatic conditions. The curing time should be documented in the Monitoring Well Completion Record (Figure 1).

2.2.6 Surface Completion and Protective Casing

Aboveground completion of the monitoring well should begin once the grout has set (no sooner than 24 hours after the grout was placed). The protective casing is lowered over the riser and set into the cured grout. The protective casing should extend below the ground surface to a depth below the frost line (typically 3 to 5 feet, depending on local conditions). The protective casing is then cemented in place. A minimum of 6 inches of clearance should be maintained between the top of the riser and the protective casing. A 0.5-inch diameter drainage or weep hole should be drilled in the protective casing approximately 6 inches above the ground surface to enable water to drain out of the annular space between the casing and riser. A watertight cap should be placed on top of the riser to seal the well from surface water infiltration in the event of a flood. A lock should be placed on the protective casing to prevent vandalism.

For flush-mounted monitoring wells, the well cover should be raised above grade approximately 1 inch, and the surrounding concrete pad sloped so that water drains away from the cover. The flush-mount completion should be installed in accordance with applicable state and local regulations. Figures 2A and 2B show above grade and flush mounted completion details.

2.2.7 Permanent and Multiple Casing Well Installation

When wells are installed through multiple saturated zones, special well construction methods should be used to assure well integrity and limit the potential for cross-contamination between geologic zones.

Generally, these types of wells are necessary if relatively impermeable layers separate hydraulic units. Two procedures that may be used are described below.

In the first procedure, the borehole is advanced to the base of the first saturated zone. Conductor casing is then anchored in the underlying impermeable layer (aquitar) by advancing the casing at least 1 foot into the aquitar and grouting the annular space between the conductor casing and borehole from the bottom of the casing to the surface. After the grout has cured, a smaller diameter borehole is drilled through the conductor casing. This procedure is repeated until the zone of interest is reached. After the zone is reached, a conventional well screen and riser are set. A typical well constructed in this manner is shown on Figure 3.

A second acceptable procedure involves driving a casing through several saturated layers while drilling ahead of the casing. However, this method is not acceptable when the driven casing may structurally damage a competent aquitar or aquiclude and result in cross-contamination of the two saturated layers. This method should also be avoided when highly contaminated groundwater or nonaqueous-phase contamination may be dragged down into underlying uncontaminated hydrologic units.

2.3 RECORD -KEEPING PROCEDURES

Record-keeping procedures associated with monitoring well installation are described in the following sections. These include procedures for surveying, obtaining permits, completing well construction records, and identifying monitoring wells. Upon completion of the well installation the paperwork must be checked for completeness and technical accuracy by another qualified person as soon as practical.

2.3.1 Surveying

Although not a part of this SOP, the latitude, longitude, and elevation at the top of the riser should be determined for each monitoring well. A permanent notch or black mark should be made on the north side of the riser. The top of the riser and ground surface elevations should be surveyed to the nearest one-hundredth of a foot.

2.3.2 Permits and Well Construction Records

Local and state regulations should be reviewed prior to monitoring well installation, and any required well permits should be in-hand before the driller is scheduled.

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Monitoring well installation activities should be documented in both the field logbook and on the Monitoring Well Completion Record (Figure 1). Additionally, boring logs should be completed (SOP 026) and, if necessary, filed with the appropriate regulatory agency within the appropriate time frame.

2.3.3 Monitoring Well Identification

Each monitoring well should have an individual well identification number or name as specified in the field work plan. The well identification may be stamped in the metal surface upon completion or permanently marked by using another method. Current state and local regulations should be checked for identification requirements (such as township, range, section, or other identifiers in the well name).

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FIGURE 1
MONITORING WELL COMPLETION RECORD

DRILLING INFORMATION	SURFACE COMPLETION ABOVE GROUND W/ CRASH POSTS	MONITORING WELL
RIG TYPE _____		MONITORING WELL ID _____
DRILLING BEGAN:		PROJECT _____
DATE _____ TIME _____		SITE _____
		BOREHOLE ID _____
BORING DIAMETER (in) _____		TOP OF CASING (ft) _____
BORING DEPTH (ft) _____		GROUND SURFACE ELEVATION (ft) _____
WELL INSTALLATION BEGAN:		
DATE _____ TIME _____		
WELL DEPTH (ft) _____		
ANNULAR SEAL		BENTONITE/SAND SLURRY
PORTLAND CEMENT (lbs) _____		BENTONITE (lbs) _____
BENTONITE (lbs) _____		SAND (lbs) _____
WATER (gal) _____		WATER (gal) _____
FROM (ft) _____ TO (ft) _____		FROM (ft) _____ TO (ft) _____
BENTONITE SEAL		CASING
TYPE _____		TYPE _____
BENTONITE (lbs) _____		DIAMETER (in) _____
WATER (gal) _____		
FROM (ft) _____ TO (ft) _____		STATIC WATER LEVEL (ft) _____
FINE SAND		WELL SCREEN
SAND SIZE _____		TYPE _____
SAND (lbs) _____		DIAMETER (in) _____
FROM (ft) _____ TO (ft) _____		SLOT SIZE (in) _____
FILTER PACK		FROM (ft) _____ TO (ft) _____
SAND SIZE _____		SUMP
SAND (lbs) _____		FROM (ft) _____ TO (ft) _____
FROM (ft) _____ TO (ft) _____		BOREHOLE BACKFILL
CENTRALIZERS		TYPE _____
INTERVALS _____		FROM (ft) _____ TO (ft) _____

All measurements are in feet below ground surface except for well casing stickup

Notes _____

FIGURE 2A

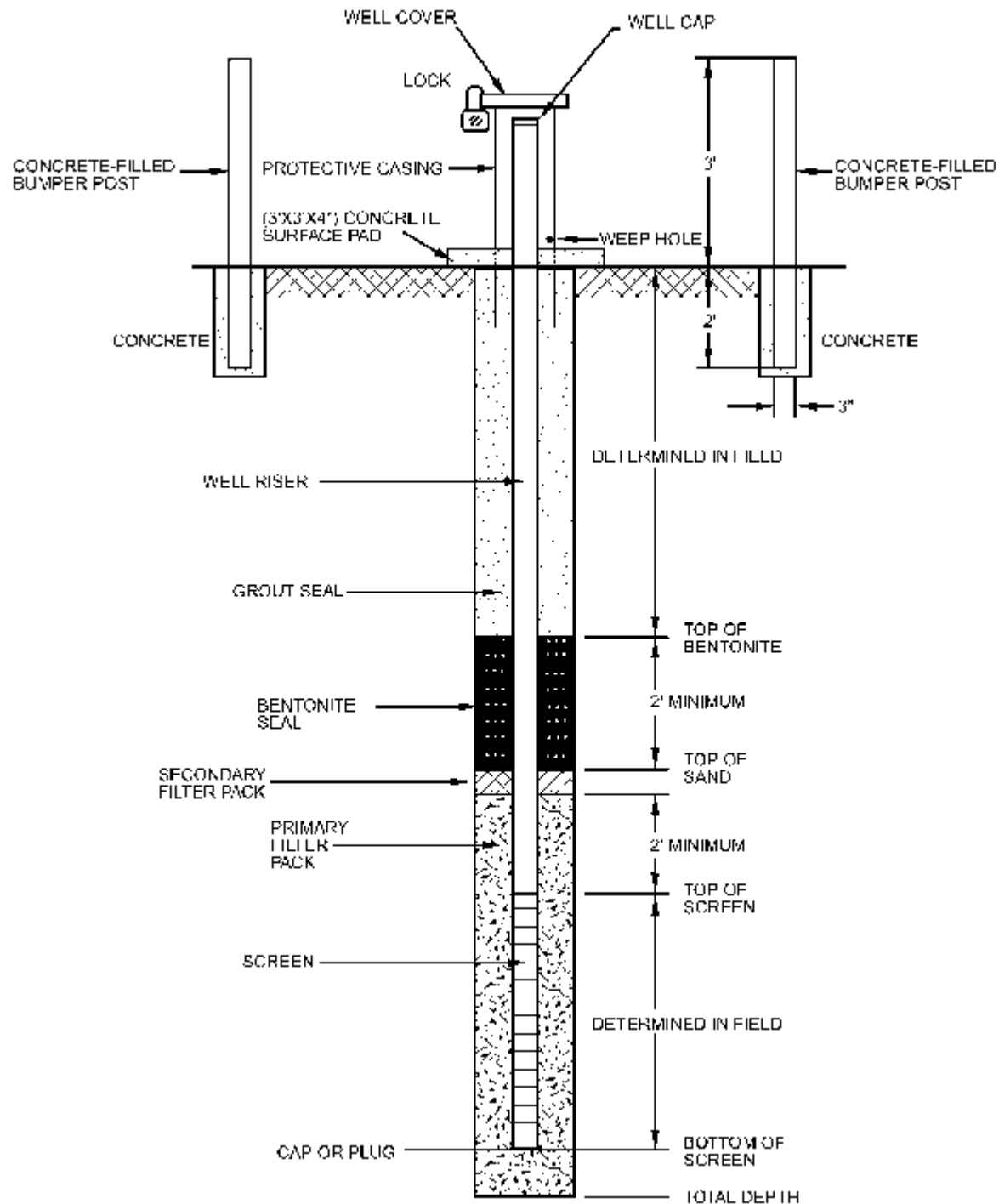


FIGURE 2B
MONITORING WELL TYPICAL CONSTRUCTION DETAILS –
FLUSH MOUNTED COMPLETION

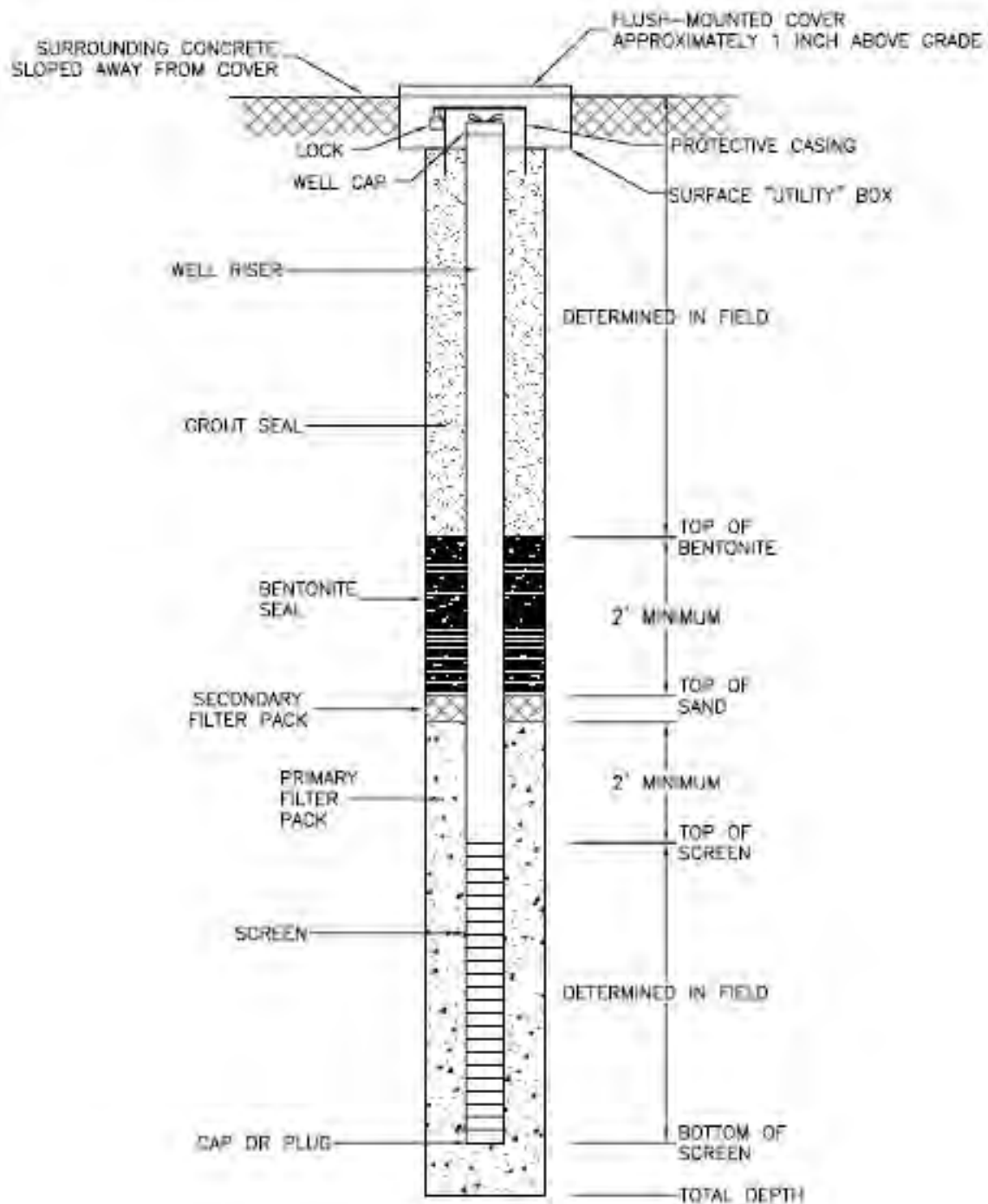
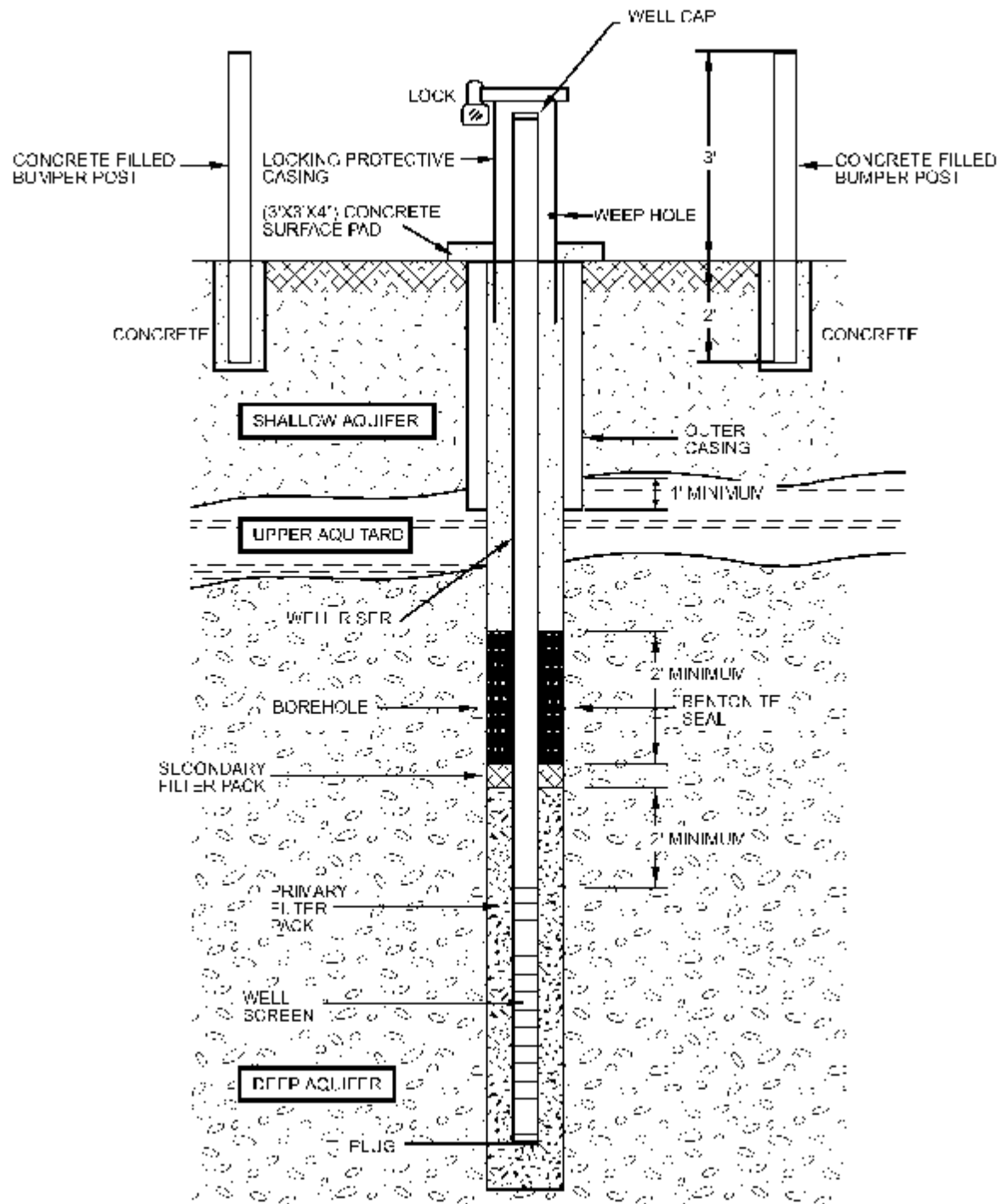


FIGURE 3
MULTIPLE CASING WELL CONSTRUCTION DIAGRAM



SOP APPROVAL FORM

TETRA TECH EM INC.
ENVIRONMENTAL STANDARD OPERATING PROCEDURE

MONITORING WELL DEVELOPMENT

SOP NO. 021

REVISION NO. 4

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Quality Assurance Approved

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Date

1.0 BACKGROUND

All drilling methods impair the ability of an aquifer to transmit water to a drilled hole. This impairment is typically a result of disturbance of soil grains (smearing) or the invasion of drilling fluids or solids into the aquifer during the drilling process. The impact to the hydrologic unit surrounding the borehole must be remediated so that the well hydraulics and samples collected from the monitoring well are representative of the aquifer.

Well development should be conducted as an integral step of monitoring well installation to remove the finer-grained material, typically clay and silt, from the geologic formation near the well screen and filter pack. Monitoring well installation is discussed in standard operating procedure (SOP) No. 020. The fine-grained particles may interfere with water quality analyses and alter the hydraulic characteristics of the filter pack and the hydraulic unit adjacent to the well screen. Well development improves the hydraulic connection between water in the well and water in the formation. The most common well development methods are mechanical surging, overpumping, air-lift pumping, backwashing, surge bailing, and well jetting; these methods can be used individually or in combination to achieve the most effective well development.

The health and safety plan for the site should be followed to avoid exposure to chemicals of concern. Water, sediment, and other waste removed from a monitoring well should be disposed of in accordance with applicable federal, state, and local requirements.

1.1 PURPOSE

This SOP establishes the requirements and procedures for monitoring well development. Well development improves the hydraulic characteristics of the filter pack and borehole wall by performing the following functions:

- Reducing the compaction and the intermixing of grain sizes produced during drilling by removing fine material from the pore spaces.
- Removing the filter cake or drilling fluid film that coats the borehole as well as much or all of the drilling fluid and natural formation solids that have invaded the formation.
- Creating a graded zone of sediment around the screen, thereby stabilizing the formation so that the well can yield sediment-free water.

1.2 SCOPE

In most cases, well development is conducted by a drilling contractor with oversight and documentation by Tetra Tech. This SOP applies to the development of newly installed monitoring wells. The SOP identifies the most commonly used well development methods. Selection of a particular method or combination will depend on site conditions, equipment limitations, and other factors. The method selected and the rationale for selection should be described in the site-specific sampling plan or work plan. All modifications to proposed well development methods should be documented in a field logbook and/or Well Completion Record.

1.3 DEFINITIONS

Aquifer: A geologic formation, group of formations, or part of a formation that is saturated and capable of storing and transmitting water.

Aquitard: A geologic formation, group of formations, or part of a formation through which virtually no water moves.

Bailer: A cylindrical sampling device with valves on either end, used to extract water from a well or borehole.

Bentonite seal: A colloidal (extremely fine particle that will not settle out of solution) clay seal separating the sand pack from the surface seal.

Drilling fluid: A fluid (liquid or gas) that may be used in drilling operations to remove cuttings from the borehole, to clean and cool the drill bit, and to maintain the integrity of the borehole during drilling.

Filter pack: A clean, uniform sand or gravel placed between the borehole wall and the well screen to prevent formation material from entering the screen.

Grout seal: A fluid mixture of (1) cement and water or (2) cement, bentonite, and water that is placed above the bentonite seal between the casing and the borehole wall to secure the casing in place and keep water from entering the borehole.

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Hydraulic conductivity: A measure of the ease with which water moves through a geologic formation. Hydraulic conductivity, K, is typically measured in units of distance per time in the direction of groundwater flow.

Hydrologic units: Geologic strata that can be distinguished on the basis of capacity to yield and transmit fluids. Aquifers and confining units are types of hydrologic units.

Oil air filter: A filter or series of filters placed in the airflow line from an air compressor to reduce the oil content of the air.

Oil trap: A device used to remove oil from the compressed air discharged from an air compressor.

pH: The negative base-10 log of the hydrogen-ion activity in moles per liter.

Riser: The pipe extending from the well screen to or above the ground surface.

Specific conductance: A measure of the ability of the water to conduct an electric current. Specific conductance is related to the total concentration of ionizable solids in the water and is inversely proportional to electrical resistance.

Static water level: The elevation of the top of a column of water in a monitoring well or piezometer that is not influenced by pumping or conditions related to well installation, hydrologic testing, or nearby pumping.

Surging: An uneven flow and strong momentum given to a fluid, as water in a tank, resulting in a rapid, temporary rise in pressure.

Transmissivity: The volume of water transmitted per unit width of an aquifer over the entire thickness of the aquifer flow, under a unit hydraulic gradient.

Turbidity: Muddy looking water created by having sediment or foreign particles stirred up or suspended.

Well screen: A cylindrical pipe with openings of a uniform width, orientation, and spacing used to keep materials other than water from entering the well and to stabilize the surrounding formation.

1.4 REFERENCES

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1.5 REQUIREMENTS AND RESOURCES

To conduct oversight of and document monitoring well development, the person at the drill site should be a geoscientist who has relevant professional training and experience. The site geoscientist is responsible for oversight and documentation of all well development activities. The site geoscientist shall understand the project objectives and regularly communicate from the field with the project manager or technical project team members.

The type of equipment used for well development will depend on the well development method. Well development methods and the equipment required are discussed in Section 2.1 of this SOP. In general, monitoring wells should be developed shortly after they are installed but no sooner than 24 to 48 hours after the placement of the grout seal, depending on the grout cure rate and well development method to be used. Most drilling or well development rigs have pumps, air compressors, bailers, surge blocks, and other equipment that can be used to develop a monitoring well.

All downhole equipment should be properly decontaminated before and after each well is developed. See SOP No. 002 (General Equipment Decontamination) for details.

2.0 WELL DEVELOPMENT PROCEDURES

This section describes common well development methods, factors to be considered in selecting a well development method, procedures for initiating well development, well development duration, and calculations typically made during well development. In addition to this, procedures described in any work plans for well development should be fully consistent with local and state regulations and guidelines.

2.1 WELL DEVELOPMENT METHODS

Well development methods vary with the physical characterization of hydrologic units in which the monitoring well is screened, and the drilling method used. The most common methods include mechanical surging, overpumping, air-lift pumping, backwashing, surge bailing, and well jetting. These methods may be effective alone or may need to be combined (for example, overpumping combined with backwashing). Factors such as well design and hydrogeologic conditions will determine which well development method will be most practical and cost effective. Commonly used well development methods are described in Sections 2.1.1 through 2.1.6.

The use of chemicals for monitoring well development should be avoided as much as possible. Introduction of chemicals may significantly alter groundwater chemistry in and around the well.

2.1.1 Mechanical Surging

The mechanical surging method forces water to flow in and out of the well screen by operating a plunger (or surge block) in the casing, similar to a piston in a cylinder. A typical surge block is shown on Figure 1. For shallow wells with limited bentonite or grout seal heights, care should be taken to avoid damaging the seal by surging. The surge block should fit snugly in the well casing to increase the surging action. The surge block is attached to a drill rod or drill stem and is of sufficient weight to cause the block to drop rapidly on the down stroke, forcing water contained in the borehole into the aquifer surrounding the well. In the recovery stroke or upstroke, water is lifted by the surge block, allowing water and fine sediments to flow back into the well from the aquifer. Down strokes and recovery strokes are usually 3 to 5 feet in length.

The surge block should be lowered into the water column above the well screen. The water column will effectively transmit the action of the block to the filter pack and hydrologic unit adjacent to the well screen. Development should begin above the screen and move progressively downward to prevent the surge block from becoming sand locked in the well. The initial surging action should be relatively gentle, allowing any material blocking the screen to break up, go into suspension, and then move into the well. As water begins to move easily both in and out of the screen, the surge block is usually lowered in increments to a level just above the screen. As the block is lowered, the force of the surging movement should be increased. In wells equipped with long screens, it may be more effective to operate the surge block in the screen to concentrate its action at various levels.

A pump or bailer should be used periodically to remove dislodged sediment that may have accumulated at the bottom of the well during the surging process. The pump or bailer should be moved up and down at the bottom of the well to suspend and collect as much sediment as possible.

The accumulation of material developed from a specific screen interval can be measured by sounding the total depth of the well before and after surging. Continue surging until little or no sand accumulates.

2.1.2 Overpumping

Overpumping involves pumping the well at a rate substantially higher than it will be pumped during well purging and groundwater sampling. This method is most effective on coarse-grained formations and is usually conducted in conjunction with mechanical surging or backwashing. Overpumping is commonly implemented using a downhole submersible pump lowered to the bottom of the well. In cases where the water table is less than 25 feet from the top of the casing, it is possible to overpump the well with a centrifugal pump at the ground surface. The intake pipe is lowered into the water column at a depth sufficient to ensure that the water in the well is not drawn down to the pump intake level. The inflow of water at the well screen is not dependent on the location of the pump intake as long as it remains submerged.

Overpumping will induce a high velocity water flow, resulting in the flow of sand, silt, and clay into the well, opening clogged screen slots, and cleaning formation voids and fractures. The movement of these particles at high flow rates should eliminate particle movement at the lower flow rates used during well purging and sampling. The bridging of particles against the screen because of the flow rate and direction created by overpumping may be overcome by using mechanical surging or backwashing in conjunction with this method.

2.1.3 Air Lift Pumping

Air lift pumping uses a two-pipe system consisting of an air injection pipe and a discharge pipe. In this well development method, an air lift pump is operated by cycling the air pressure on and off for short periods of time. This operation provides a surging action that can dislodge fine-grained particles in the vicinity of the well screen. Subsequently applying a steady, low pressure removes the fines drawn into the well by the surging action.

The bottom of the air lift should be at least 10 feet above the top of the well screen. Air is injected through an inner pipe at sufficient pressure to bubble out directly into the surrounding discharge pipe. The bubbles formed by the injected air cause the column of water in the discharge pipe to be lifted upward and allow water from the aquifer to flow into the well. This arrangement prevents injected air from entering the well screen. Pumping air through the well screen and into the filter pack and adjacent hydrologic unit should be avoided because it can cause air entrainment, inhibiting future sampling efforts and possibly altering groundwater chemistry.

The air injected into the well should be filtered using an oil-air filter and oil trap to remove any compressor lubricant entrained in the air. Air pressures required for this well development method are relatively low; an air pressure of 14.8 pounds per square inch should move a 30-foot column of water. For small-diameter, shallow wells where the amount of development water is likely to be limited, tanks of inert gas (such as nitrogen) can be used as an alternative to compressed air.

2.1.4 Backwashing

Effective development procedures should cause flow reversals through the screen openings that will agitate the sediment, remove the finer fraction, and then rearrange the remaining formation particles. Backwashing overcomes the bridging that results from overpumping by allowing the water that is pumped to the top of the well to flow back through the submersible pump and out through the well screen. The backflow portion of the backwashing cycle breaks down bridging, and the inflow then moves the fine material toward the screen and into the well.

Some wells respond satisfactorily to backwashing techniques, but the surging effect is not vigorous enough to obtain maximum results in many cases.

A variation of backwashing may be effective in low-permeability formations. After the filter pack is installed around the monitoring well screen, clean water is circulated down the well casing, out through the well screen and filter pack, and up through the open borehole before the grout or bentonite seal is placed in the annulus. Flow rates should be controlled to prevent floating the filter pack. Because of the low hydraulic conductivity of the formation, negligible amounts of water will infiltrate into the formation. Immediately after this procedure, the bentonite seal should be installed, and the nonformation water should be pumped out of the well and filter pack.

2.1.5 Surge Bailing

Surge bailing can be an effective well development method in relatively clean, permeable formations where water flows freely into the borehole. A bailer made of stainless steel or polyvinyl chloride and slightly smaller than the well casing diameter is allowed to fall freely through the borehole until it strikes the groundwater surface. The contact of the bailer produces a downward force and causes water to flow outward through the well screen, breaking up bridging that has developed around the screen. As the bailer fills and is rapidly withdrawn from the well, the drawdown created causes fine particles to flow through the well screen and into the well. Subsequent bailing can remove these particles from the well. Lowering the bailer to the bottom of the well and using rapid short strokes to agitate and suspend solids that have settled to the well bottom can enhance removal of sand and fine particles. Bailing should continue until the water is free of suspended particles.

2.1.6 Well Jetting

Well jetting can be used to develop monitoring wells in both unconsolidated and consolidated formations. Water jetting can open fractures and remove drilling mud that has penetrated the aquifer. The discharge force of the jetting tool is concentrated over a small area of the well screen. As a result, the tool must be rotated constantly while it is raised and lowered in a very small increments to be sure that all portions of the screen are exposed to the jetting action.

Jetting is relatively ineffective on the fine screens typically used in monitoring wells (slot sizes from 0.01 to 0.02 inch). In addition, jetting requires the introduction of external water into the well and surrounding formation. This water should be obtained from a source of known chemistry. Water introduced for development should be completely removed from the aquifer immediately after development.

The use of compressed air as a jetting agent should not be employed for development of monitoring wells. Compressed air could entrain air in the formation, introduce oil into the formation, and damage the well screen.

2.2 FACTORS TO CONSIDER WHEN SELECTING A WELL DEVELOPMENT METHOD

It is important to check federal, state, and local regulatory requirements for monitoring well development requirements. This SOP may be changed to accommodate applicable regulations, site conditions, or equipment limitations where applicable.

The type of geologic material, the design, completion of the well, and the type of drilling method used are all factors to be considered during the development of a monitoring well.

Monitoring well development should usually be started slowly and gently and then performed with increasing vigor as the well is developed. Most well development methods require the application of sufficient energy to disturb the filter pack, thereby freeing fine particles and allowing them to be drawn into the well. The coarser particles then settle around and stabilize the screen.

Development of wells completed in fine sand and silt strata should involve methods that are relatively gentle so that strata material will not be incorporated into the filter pack. Vigorous surging for development can produce mixing of the fine strata and filter pack and produce turbid samples from the formation. In addition, development methods should be carefully selected based upon the potential contaminants present, the quantity of wastewater generated, and requirements for containerization or treatment of wastewater.

For small diameter and small volume wells, a development bailer can be used in place of a submersible pump in the pumping method. Similarly, a bailer can be used in much the same fashion as a surge block in small diameter wells.

Any time an air compressor is used for well development, it should be equipped with an oil-air filter or oil trap to minimize the introduction of oil into the screened area. The presence of oil could affect the organic constituent concentrations of the water samples collected from the well.

The presence of light nonaqueous-phase liquids (LNAPL) can impact monitoring well development. Water jetting or vacuum-enhanced well development may assist in breaking down the smear zone in the LNAPL. Normal development procedures are conducted in the water-saturated zone and do not affect the LNAPL zone.

2.3 INITIATING WELL DEVELOPMENT

Newly completed monitoring wells should be developed as soon as practical, but no sooner than 24 to 48 hours after grouting is completed if rigorous well development methods are used. Development may be initiated shortly after well installation if the development method does not interfere with the grout seal. State and local regulations should be checked for guidance. The following general well development steps can be used with any of the methods described in Section 2.1.

1. Assemble the necessary equipment on a plastic sheet around the well. This may include a water level meter (or oil-water interface probe if LNAPL or dense nonaqueous-phase liquids [DNAPL] are present); personal protective equipment; pH, conductivity, temperature, and turbidity meters; air monitoring equipment; Well Development Data Sheets (see Figure 2); a watch; and a field logbook.
2. Open the well and take air monitoring readings at the top of the well casing and in the breathing zone. See SOP No. 003 (Organic Vapor Air Monitoring) for additional guidance.
3. Measure the depth to water and the total depth of the monitoring well. See SOP No. 014 (Static Water Level, Total Well Depth, and Immiscible Layer Measurement) for additional guidance.
4. Measure the initial pH, temperature, turbidity, and specific conductance of the groundwater from the first groundwater that comes out of the well. Note the time, initial color, clarity, and odor of the water. Record the results on a Well Development Data Sheet (see Figure 2) or in a field logbook. See SOPs No. 011 (Field Measurement of Water Temperature), 012 (Field Measurement of pH), 013 (Field Measurement of Specific Conductance), and 088 (Field Measurement of Water Turbidity) for additional guidance.
5. Develop the well using one or more of the methods described in Section 2.1 until the well is free of sediments and the groundwater turbidity has reached acceptable levels. Record the development method and other pertinent information on a Well Development Data Sheet (see Figure 2) or in a field logbook.
6. Containerize any groundwater produced during well development if groundwater contamination is suspected. The containerized water should be sampled and analyzed to determine an appropriate disposal method.
7. Do not add water to assist in well development unless the water is from a source of known chemical quality and the addition has been approved by the project manager. If water is added, five times the amount of water introduced should be removed during development.
8. Continue to develop the well, repeating the water quality measurements for each borehole volume. Development should remove a minimum of 3 well volumes and continue if necessary until water quality parameters are stable to within 10 percent. Development should also continue until all the water added during development (if any) is removed or the water has a turbidity of less than 50 nephelometric turbidity units. This level may only be attainable after allowing the well to settle and testing at low flow sampling rates.

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9. At the completion of well development, measure the final pH, temperature, turbidity, and specific conductance of the groundwater. Note the color, clarity, and odor of the water. Record the results on a Well Development Data Sheet (see Figure 2) or in a field logbook. In addition to the final water quality parameters, the following data should be noted on the Well Development Data Sheet: well identification, date(s) of well installation, date(s) and time of well development, static water level before and after development, quantity of water removed and time of removal, type and capacity of pump or bailer used, and well development technique.

All contaminated water produced during development should be containerized in drums or storage vessels properly labeled with the date collected, generating address, well identification, and consultant contact number.

2.4 DURATION OF WELL DEVELOPMENT

Well development should continue until representative water is free of drilling fluids, cuttings, or other materials introduced during well construction. When pH, temperature, turbidity, and specific conductance readings stabilize and the water is visually clear of suspended solids, the water is representative of formation water. The minimum duration of well development should vary in accordance with the method used to develop the well. For example, surging and pumping the well may provide a stable, sediment-free sample in a matter of minutes, whereas bailing the well may require several hours of continuous effort to obtain a clear sample.

An on-site project geoscientist should make the final decision as to whether well development is complete. This decision should be documented on a Well Development Data Sheet (see Figure 2) or in a field logbook. Upon completion of the well development, the data sheet must be checked for completeness and technical accuracy by another qualified person as soon as practical.

2.5 CALCULATIONS

It is necessary to calculate the volume of water in the well. Monitoring well diameters are typically 2, 3, 4, or 6 inches. The height of the water column (in feet) in the well can be multiplied by the following conversion factors to calculate the volume of water in the well casing.

Well Diameter (inches)	Volume (gal/foot)
2	0.1631

3	0.3670
4	0.6524
6	1.4680

3.0 POTENTIAL PROBLEMS

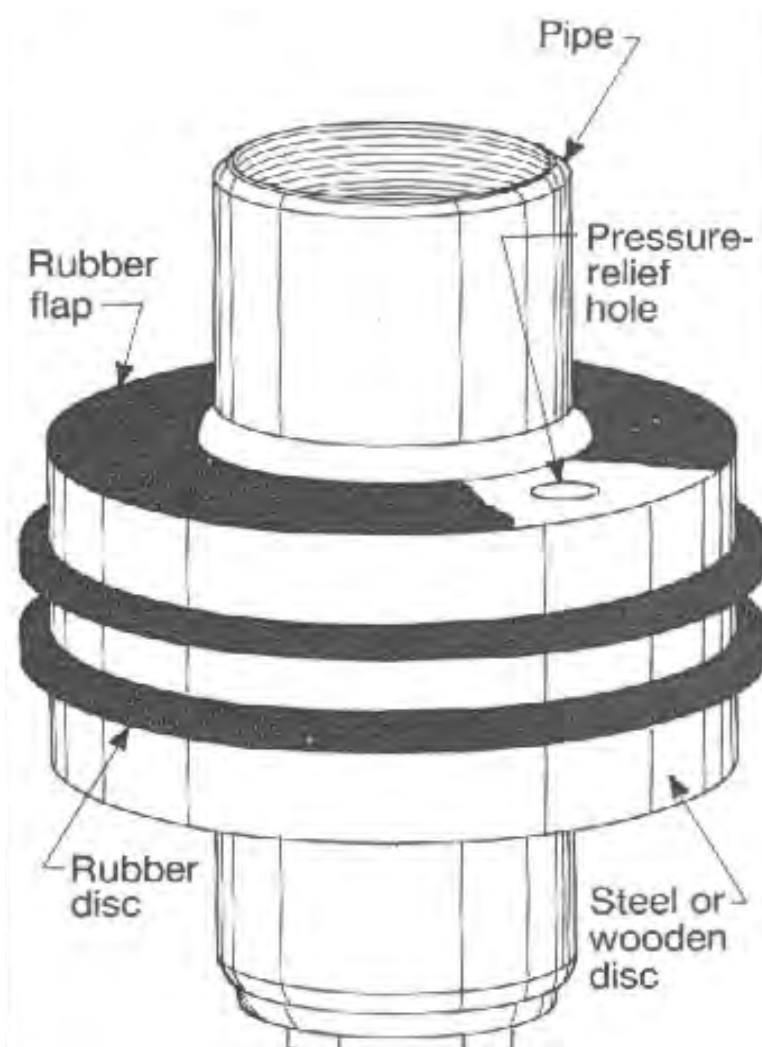
The following potential problems can occur during development of monitoring wells:

- In some wells the pH, temperature, and specific conductance may stabilize, but the water remains turbid. When this occurs, the well may still contain construction materials (such as drilling mud in the form of a mud cake) and formation soils that have not been washed out of the borehole. Excessive or thick drilling mud cannot be flushed out of a borehole with one or two well volumes of flushing. Continuous flushing over a period of several days may be necessary to complete well development. If the well is completed in a silty zone, it may be necessary to sample with low flow methods or filtering. If, after several attempts, all parameters have stabilized except turbidity, the well may be considered developed with the exception noted in the field log and/or Well Completion Report.
- Mechanical surging and well jetting disturb the formation and filter pack more than other well development methods. In formations with high clay and silt contents, surging and jetting can cause the well screen to become clogged with fines. If an excessive amount of fines is produced, sand locking of the surge block may result. Well development with these methods should be initiated gently to minimize disturbance of the filter pack and to prevent damage to the well screen.
- Effective overpumping may involve the discharge of large amounts of groundwater. This method is not recommended when groundwater extracted during well development is contaminated with hazardous constituents. If the hazardous constituents are organic compounds, this problem can be partially overcome by passing the groundwater through an activated carbon filter.
- When a well is developed by mechanical surging or bailing, rapid withdrawal of the surge block or bailer can result in a large external pressure outside of the well. If the withdrawal is too rapid and this pressure is too great, the well casing or screen can collapse.
- A major disadvantage of well jetting is that an external supply of water is needed. The water added during well jetting may alter the hydrochemistry of the aquifer; therefore, the water added in this development procedure should be obtained from a source of known chemistry. In addition, the amount of water added during well development and the amount lost to the formation should be recorded.

- The use of air in well development can chemically alter the groundwater, either directly through chemical reaction or indirectly as a result of impurities introduced through the air stream. In addition, air entrainment within the formation can interfere with the flow of groundwater into the monitoring well. Consequently, air should not be injected in the immediate vicinity of the well screen.

FIGURE 1

SCHEMATIC DRAWING OF A SURGE BLOCK



Last Reviewed: June 2009

Sheet ____ of ____

[illegible]

SOP APPROVAL FORM

TETRA TECH EM INC.
ENVIRONMENTAL STANDARD OPERATING PROCEDURE

USING THE GEOPROBE SYSTEM

SOP NO. 054

REVISION NO. 1

Last Reviewed: December 1999



Quality Assurance Approved

March 28, 1994

Date

1.0 BACKGROUND

This standard operating procedure (SOP) details all procedures for using the Geoprobe System, a hydraulically operated sampling probe, and its specialized sampling tools. The procedures described within this SOP include soil gas sampling, groundwater sampling, and soil sampling procedures as well as procedures for installing piezometers and vapor sampling implants. This SOP also describes general procedures for rod removal, backfilling, and decontamination which are common elements to all sampling procedures. This SOP No. 054 replaces former draft SOP No. 054 (Geoprobe Soil Gas Sampling) and draft SOP No. 055 (Geoprobe Groundwater Sampling).

Use of the Geoprobe System is only one of many sampling techniques used by Tetra Tech EM Inc. (Tetra Tech); however, it is a preferred sampling method when certain conditions prevail. Specifically, Geoprobe sampling should be considered when sampling is limited to relatively shallow depths and any of the following are factors: (1) costs must be kept very low, (2) the time period is short to perform the sampling, (3) maneuverability is important, and (4) the required sampling volume is limited.

Prior to the use of the Geoprobe equipment, all buried utility lines and other underground structures must be marked because this equipment can penetrate buried piping and tanks. A diagram of the Geoprobe system is shown in Figure 1.

1.1 PURPOSE

The purpose of SOP No. 054 is to establish positioning, preparing, and sampling procedures; piezometer and vapor sampling implant installation procedures; rod removal procedures; backfilling procedures; and decontamination procedures to guide field personnel.

1.2 SCOPE

The procedures outlined in SOP No. 054 are applicable to all Tetra Tech personnel involved in soil gas, soil, or groundwater sampling using the Geoprobe System or any of its specialized equipment. It also is applicable to all personnel using the Geoprobe System to install piezometers and vapor sampling implants. This SOP, in fact, applies to all uses of the Geoprobe System.

1.3 DEFINITIONS

Because Geoprobe Systems is a corporation specializing in an innovative sampling process, many of the terms used to describe its equipment are specialized and specific. For this reason, familiarity with hydraulic system, soil sampling, soil gas sampling, and groundwater sampling terms is necessary. These terms are discussed below.

1.3.1 Hydraulic System Terms

The following terms are principally used to discuss the basic operation of the hydraulic punch and its major components. If terms are encountered while using this SOP that are not listed below, check Sections 1.3.2, 1.3.3, and 1.3.4 below.

Hydraulic Punch: The principal part of the Geoprobe System, the hydraulic punch, looks very much like a small mobile drilling rig and is usually attached to a truck or van. The punch's hydraulic system uses the weight of the vehicle for support and a hydraulic system installed in the vehicle to advance sampling tools into the soil (see Figure 1).

Hammer: The hydraulic hammer pounds the rods and accessories into the soil once the hydraulic punch is unable to push it farther (see Figure 1).

Control Panel: The control panel is located near the hydraulic punch and contains the levers that control the movement of the punch (see Figure 2).

Probe Lever: This lever is found on the control panel and causes the hydraulic punch to push the drive rod and accessories into the soil. Overall, this lever controls the vertical movement of the punch (see Figure 2).

Hammer Lever: This lever is found on the control panel and engages the hydraulic hammer when the hammer release valve is moved to its extended position (see Figure 2).

Hammer Release Valve: This lever is found on the front of the hydraulic punch and allows the hammer to work when in its extended position. If the valve is not extended, pushing the hammer lever will not engage the hammer.

Foot Lever: This lever is found on the control panel and lowers the foot of the hydraulic punch so that it rests on the ground to stabilize the punch (see Figure 2).

Extend Lever: This lever is found on the control panel and controls the horizontal movement of the hydraulic punch. The lever extends the punch out of the van or truck. It also enables the hydraulic punch to extend about 2 feet from the rear of the vehicle (see Figure 2).

Fold Lever: This lever is found on the control panel and folds and unfolds the hydraulic punch so that it can be easily moved and stored (see Figure 2). This lever enables the hydraulic punch to move from the horizontal position to the vertical position.

Electrical Control Switch: This switch is found on the control panel and turns on the Geoprobe System's hydraulic system. None of the other levers work until this switch is turned on. It has slow, fast, and off speed positions (see Figure 2).

Vacuum System Panel: The vacuum system panel is located near the right rear of the vehicle and contains the vacuum system controls, the hydraulic oil cooling switch, and the remote ignition (see Figure 2).

Remote Ignition: This device is found on the vacuum system panel and allows one to start the vehicle's engine from near the hydraulic punch instead of walking around the vehicle and climbing into the vehicle's cab (see Figure 2).

Hydraulic Oil Cooling Switch: This switch is found on the vacuum system panel and turns on the auxiliary cooling system for the hydraulic oil (see Figure 2).

Vacuum/Volume (Vac/Vol) Pump Switch: This switch is found on the vacuum system panel and allows pressure to build up in the vacuum tank (see Figure 2).

Vacuum Line Valve: This valve is found on the vacuum system panel and opens and closes the vacuum line (see Figure 2).

Sample Line Gauge: This gauge is found on the vacuum system panel and registers the sample line pressure in inches of mercury (see Figure 2).

Drive Rod: The Geoprobe drive rod (sometimes called a probe rod) is a high-strength-steel, hollow tube with a 1-inch outer diameter. Though the rods come in 1-foot, 2-foot, and 3-foot lengths, the standard length is 3 feet. Each rod is threaded on both ends and has a male end and a female end (see Figure 3).

Drive Cap: This cap is a steel cap screwed onto the male end of the drive rod so that the rod can be pushed or hammered into the soil without damaging its threads. The drive cap is always installed to the top of the drive rod before advancing probe rods or sampling tools (see Figure 3).

Pull Cap: This cap is a steel cap that screws onto the male end of the drive rod and is used to pull the drive rod from the soil once the sample has been collected (see Figure 3).

Anvil: This piece of steel is placed inside the hydraulic punch at the point where the hammer actually makes contact. The anvil transfers the force of the hammer to the drive cap (see Figure 3).

Rotary-Impact Carbide-Tipped Drill Bit: This 18-inch or 24-inch steel drill bit fits directly into the hydraulic punch and is used to drill through concrete or hard asphalt. The bit does not spin with appreciable torque but is driven by the hammer, spinning only slightly to clear itself of debris (see Figure 3).

Chain-Assisted Pull Cap: This modified pull cap is attached to the hydraulic punch with a chain. It is most useful when the drive rod, for one reason or another, is not aligned directly underneath the hydraulic punch. With this cap, the rod can still be pulled using the punch (see Figure 3).

Rod Extractor: This tool threads onto a drive rod and is sent down into the hole made by a drive rod that has broken in the soil. The rod extractor, which looks a little like a drill bit, is then hammered into the broken rod and is used to pull the broken rod from the soil (see Figure 3).

Rod Pull Plate: This steel plate has a hole in its center through which a drive rod can be fitted. It is used to extract drive rods when installing piezometers, soil gas implants, or to expose the screen to groundwater when using a screen point sampler (see Figure 3).

O-Ring: An O-ring is a rubber ring used to seal sections of drive rods or various other Geoprobe tools so that, once together, they are air- and water-tight.

Teflon Tape: This inert, sticky tape can be used to create air-tight seals when pieces of the drive rod or accessories are threaded together. The tape can replace an O-ring.

1.3.2 Soil Sampling Terms

These terms are usually used when discussing soil sampling using the Geoprobe System. Sometimes, though, the terms are used when discussing other sampling techniques. If terms are encountered while using this SOP that are not listed below, check Sections 1.3.1 above and Sections 1.3.3 and 1.3.4 below.

Shelby Tube: This tube is used to collect large samples of cohesive soils. Its greatest disadvantages are that it cannot be used to sample from depths greater than about 10 feet and has no mechanism to stay closed until reaching the proper depth (see Figure 4).

Shelby-Tube-Drive Head: This 2-inch diameter piece of steel attaches to the Shelby tube using hex bolts. The Shelby-tube-drive head consists of two parts: a standard 2-inch Shelby tube drive head and a Geoprobe drive rod adapter. This allows the 2-inch wide Shelby tube to be driven by the hydraulic punch, which is actually designed for 1-inch diameter drive rods (see Figure 4).

Hex Bolts: These are the bolts used to attach a Shelby tube to a drive head (see Figure 4).

Extruder Latch: This device secures the Shelby tube to the extruder rack during the extrusion process that removes the soil from the tube (see Figure 4).

Extruder Piston: This piston is threaded onto a drive rod, and with the help of the hydraulic punch, extrudes the soil sample from the Shelby tube (see Figure 4).

Probe-Drive Systems: This sampling system allows samples to be collected at deeper depths than the Shelby tube system. Each probe-drive sampler remains closed until it reaches the depth desired and then is opened by those operating the punch by removing a stop pin (see Figure 5). The sampler is then pushed through the soil at the desired depth and removed. Three types of probe-drive samplers exist: the standard sampler, the Kansas sampler, and the large bore probe-drive sampler.

Standard Probe-Drive Sampler: This probe-drive sampler has a diameter of 1 inch and lengths of 10 or 24 inches. Its greatest difference from the other probe-drive sampler is that it does not have a removable cutting shoe (see Figure 5).

Stop Pin: This pin stops the point of a probe-drive sampler from retracting into the sampler tube. Once it is removed, the sample can be collected (see Figure 5).

Piston Rod: This rod connects the drive head of a probe-drive sampler to the sampler's point. Once the stop pin is removed, this rod slides through the sampler, allowing the point to retract inside the tube (see Figure 5).

Drive Head: This head is the top of a probe-drive sampler, which allows the piston rod to slide straight up the sample tube after the piston stop has been removed and the drive rod is advanced (see Figure 5).

Cutting Shoe: This portion of the probe-drive sampler cuts through the soil once the point is allowed to retract inside. The Kansas samplers and large-bore sampler have removable cutting shoes (see Figure 5).

Extruder Rack: This device holds soil samplers in place during extrusion. The Shelby tube extruder rack is shown in Figure 4, and the standard probe-drive extruder rack is shown in Figure 5.

Extension Rod: This long, thin, threaded, solid rod is dropped through a drive rod to the probe-drive sampler so that the stop pin can be removed. Often more than one extension rod (an extension rod string) must be put together to reach the stop pin (see Figure 5).

Extension Rod Handle: This small metal handle screws to the top of the extension rod string so that it can be turned easily while being used to remove the stop pin (see Figure 5).

Large-Bore Probe-Drive Sampler: This probe-drive sampler is 1-1/8 inches in diameter and 24 inches long. Its larger width allows for the collection of larger samples. The diameter also allows for acetate or brass liners to be used in sample collection. These liners can make viewing the sample easier and preparing it for analysis simpler.

Kansas Sampler: This specially designed probe-drive sampler has a removable cutting shoe to enable easy extraction of soil and to allow the shoe to be replaced without replacing the complete sampler.

Kansas Stainless Sampler: This sampler has a stainless-steel sampling tube. It works in the same way as the Kansas sampler.

1.3.3 Soil Gas Sampling Terms

The following terms are used principally to discuss soil gas sampling. A few terms, though, are used while discussing groundwater sampling as well. If unfamiliar terms not listed below are encountered while using this SOP, check Sections 1.3.1 and 1.3.2 above and Section 1.3.4 below.

Expendable Point: These points fit into an expendable point holder that has been threaded into the lead drive rod. When the drive rod is pulled back, these points do not move with it, leaving a gap from which soil gas can be collected. The points are ultimately left in the ground (see Figure 6).

Expendable Point Holder: This holder threads into the leading drive rod. It is used for driving expendable points (see Figure 6).

Retractable Point Holder: This holder lifts off its point, leaving a gap so that soil gas can be drawn, but unlike expendable points, the holder does not separate completely and ultimately is retrieved with the lead drive rod (see Figure 6).

Gas Sampling Cap: When using the standard soil gas sampling method, the gas sampling cap replaces the drive cap on top of the drive rod and allows tubing to be connected to the drive rod. A soil gas sample is drawn through the probe rod through this cap and into a sample container (see Figure 6).

Post-Run Tubing (PRT) System: This system collects soil gas drawn directly through a tube instead of through the drive rod itself. The system involves one of two specially designed point holders, each threaded on top so that an adapter that has been attached to the tube can be screwed into it after being advanced down the drive rod string. The two point holders differ in that one uses a retractable point and the other uses an expendable point (see Figure 7).

PRT Expendable Point Holder: This holder is threaded into the leading probe rod and is used for driving expendable points (see Figure 7).

PRT Adapter: The PRT adapter attaches the tubing through which the soil gas is to be drawn to the point holder, which has been driven to the proper sampling depth (see Figure 7).

Polyethylene Tubing: This tubing is the preferred tubing for connecting the PRT system to the sample container. Its stiff nature, however, sometimes makes it difficult to attach to the sample container and a coupler of Tygon tubing is necessary (see Figure 7).

Tygon Tubing: This tubing is the preferred tubing for connecting soil gas sampling containers to the drive rod and vacuum system. It often is also necessary as a coupler sample between the stiff polyethylene tubing used with PRT sampling systems and the sample container.

Glass Bulb: This bulb of glass has valves on each side and a neoprene septum through which gas can be withdrawn. The bulb is used to collect soil gas and can be used as the container in which the gas is taken for analysis (see Figure 8).

Tedlar Bag: This small bag has a valve on it. It is placed in an air-tight chamber, the air in the chamber is evacuated, and the bag fills with soil gas. The bags can then be taken for analysis.

Tedlar Bag Chamber: Tetra Tech uses these modified, air-tight kitchen containers as vacuum chambers. These chambers are modified with nipples on each side, which enable it to be attached to a vacuum pump, to a Tedlar bag, and to the Tygon tubing.

1.3.4 Groundwater Sampling Terms

The following terms are used to discuss groundwater sampling. If unfamiliar terms not listed below are encountered while using this SOP, check Sections 1.3.1, 1.3.2, and 1.3.3 above.

Mill-Slotted Well Point: This 3-foot long tube has 15 mill-cut slots in it, each 2 inches long and 0.020 inches wide. Only the bottom 2 feet of this tube is slotted, and sometimes mill-slotted well points come in two parts: a 2-foot slotted section and a 1-foot unslotted section. The slots allow groundwater to enter (see Figure 9).

Geoprobe Screen Point Sampler: This sampler has a 19-inch screen that encases a perforated stainless-steel sleeve. Once in place, the screen allows the water to enter the tube and prevents coarse sediment from entering the tube (see Figure 9).

Thieving Tube: This tube is used to extract the water from either mill-slotted well points or Geoprobe screen point samplers, Tetra Tech uses polyethylene tubing as thieving tubes. This tubing is lowered into the water, capped on top, and then extracted. The result is much like putting a straw into a glass of water, sealing the straw with a finger and lifting it. This method is used primarily for the collection of groundwater samples to be analyzed for volatile organic compounds. A check valve can also be attached to the thieving tube which seals the bottom and holds the groundwater within the tube.

Check Valve: This stainless steel valve has a small ball which, when attached to a thieving tube, floats to the top of the groundwater table and then sinks, ultimately sealing the thieving tube with groundwater. Oscillating the thieving tube will allow groundwater to rise within the tube for larger retrieval volume.

Well Mini-Bailer: This specially designed bailer drops through the drive rods and into the groundwater in the mill-slotted well point or screen point. A small ball in the bailer floats to the top and then sinks, ultimately sealing the bailer after it fills with about 40 milliliters of groundwater.

1.4 REFERENCES

The following references were used to prepare this SOP:

Driscoll, F.G. 1987. *Groundwater and Wells*. Second Edition. Johnson Division. St. Paul, Minnesota.

Fisher Scientific. 1991. "The Fisher Catalog of Scientific Instruments."

Geoprobe Systems. 1990. "8-M Operations Manual." July 27.

Geoprobe Systems. 1991. "Accessory Tools Catalog."

Geoprobe Systems. 1992. "Equipment and Tools Catalog."

2.0 POSITIONING, PREPARING AND SAMPLING PROCEDURES

The Geoprobe System uses a hydraulic punch that is usually installed in the back of a van or truck to first push and then to hammer its hollow drive rod through soils. Depending on which tools are attached to the end of the drive rod and which sampling equipment is attached to it, the Geoprobe can be used to remove soil, soil gas, or groundwater. It can also be used to drill through cement or concrete and can aid in the installation of piezometer wells and vapor sampling implants. The following sections detail the procedures for positioning the Geoprobe unit, preparing the sampling system, and sampling with the Geoprobe unit.

2.1 POSITIONING THE GEOPROBE UNIT

Before the Geoprobe System can be used, the Geoprobe hydraulic punch and accessories must be properly positioned near the sampling site. The hydraulic punch and other equipment also needs to be prepared. In cases where concrete or other hard surfaces hinder sampling, the Geoprobe must be used to reach soil. This section details methods to perform these activities.

To position and unload the Geoprobe System use the following procedures:

1. Drive the vehicle containing the Geoprobe System to the sampling location and align the center of the rear of the vehicle with the point at which the sample will be taken. The rear bumper should be 1 to 2 feet from the sampling point so that the foot of the hydraulic punch can be extended out over it.
2. Shut off the vehicle.
3. Put it in park.
4. Set the emergency brake before proceeding.
5. One person only should operate the hydraulic punch and the assembly and disassembly of probe rods and accessories. A second person is usually necessary to handle the samples and to decontaminate equipment. All personnel present must wear steel-toed shoes, gloves, and eye protection. When drilling through concrete or using the hydraulic hammer, ear protection is also necessary.
6. Once ready to take the sample, start the engine using the remote ignition located in the right rear of the vehicle. As a safety device, the remote ignition will not work unless the vehicle is in park.
7. Activate the hydraulic system by turning on the electrical control switch. The vehicle's engine must be running for the hydraulic system to work.
8. Slowly extend the Geoprobe out of the vehicle using the extend lever. Always use the slow speed on the hydraulic controls when positioning the hydraulic punch. The punch and mast should be far enough out of the van or truck so that the mast will not strike the roof when it is unfolded.
9. Unfold the hydraulic punch out of the vehicle using the fold lever. Once the punch has been lined up perpendicular to the ground surface, lower the foot of the punch using the foot lever until the vehicle itself is raised about 1 foot on its springs. This stabilizes the vehicle and punch. **Never lift the vehicle completely off the ground using the foot lever.** Doing so destabilizes the vehicle and hydraulic punch and may cause damage to equipment or injury to those nearby. Also, as pressure is placed on the rod, tools, and accessories, the foot of the punch may begin to lift. Do not allow it to lift farther than 6 inches from the ground. Allowing it to lift farther than 6 inches may throw the vehicle off balance and cause the rod to bend or break.

The Geoprobe System is now positioned. If it is necessary to drill through concrete or hard asphalt, use the following procedures:

1. Raise the hydraulic punch using the probe lever and then deactivate the hydraulic system by turning the electrical control switch to off. The hydraulic system should always be turned off when the hydraulic controls are not being used.
2. Place the drill bit into the hydraulic hammer. The bit is not used with a drive rod or anvil.
3. Activate the hammer rotation control knob, which is located on the hydraulic hammer, by turning the knob counter-clockwise. This allows the drill bit to rotate when the hammer lever on the control panel is pressed.
4. Activate the hammer release valve, which is located on the hydraulic hammer, by pulling the lever out and down.
5. To drill through solid surfaces, both the probe and hammer mechanisms of the hydraulic punch must be used. The hammer mechanism drives the drill bit in a percussion fashion and causes it to turn slightly. The probe mechanism allows the hammer and bit to be raised and lowered so that the bit can clear itself of debris. Once ready to begin, turn on the hydraulic system.
6. Fully depress the hammer lever. This lever needs to remain depressed throughout the drilling procedure and keeps the bit pounding and rotating.
7. Put pressure on the bit by pressing the probe lever down. Using this lever, advance the bit in small increments through the concrete or other hard surface. If advanced too quickly, the bit will bind and stop rotating. Should this happen, raise the punch slightly to allow the bit to rotate. If too little pressure is placed on the bit, too little percussion will occur, and drilling will be slow.
8. Continue drilling, in small increments, until soil has been reached. At that time prepare for sampling.

2.2 PREPARING THE SAMPLING SYSTEM

Before the hydraulic punch is used to sample, decisions must be made concerning which type of sample will be taken, whether several samples will be taken at varying depths, and which type of Geoprobe sampling equipment will be used. The following sections discuss preparation procedures for soil sampling, soil gas sampling, and groundwater sampling.

2.2.1 Soil Sampling

The samplers attached to the hydraulic punch for soil sampling come in two forms. The first type is the 2-inch diameter Shelby tube system that is common to other soil sampling methods. The second system

uses various specially designed probe-drive systems that remain completely sealed while being pushed or driven to a particular depth. They then are opened to allow a sample to be collected. The Shelby tube and probe-drive systems are discussed below.

Shelby Tube System

The Shelby tube is a thin-walled steel tube, 2 inches in diameter and 30 inches long, with four mounting holes around its top. It allows large amounts of soil to be sampled at once, but the soil must be relatively cohesive. Because the tube remains open at all times, the tube cannot be driven to great depths and must be removed and replaced after coring 30 inches of soil. Usually, the Shelby tube system is chosen when large amounts of soil are needed at depths no deeper than 10 feet. Rocky or sandy soils are not conducive to this sampling method.

To prepare for sampling using Shelby tubes, use the following procedures:

1. First attach a Shelby tube to the Shelby-tube-drive head by putting the head's hex bolts through the holes in the tube.
2. Next, screw a Geoprobe drive rod adapter into the top of the drive head to allow the 2-inch-wide Shelby tube to be driven by the hydraulic punch and hammer, which are actually made for 1-inch outer diameter drive rods.
3. A drive cap is then screwed onto the top of Geoprobe drive rod adapter. The tube is now ready to be attached to the hydraulic punch.
4. To attach the tube, raise the hydraulic punch using the probe lever and then turn off the Geoprobe hydraulic system.
5. Lift the hammer latch and insert the anvil inside.
6. Place the assembled Shelby tube sampler so that it is aligned under the anvil.

The hydraulic punch is now ready to drive a Shelby tube and collect a sample core. For collecting soil cores at depths of greater than 30 inches, attach sections of probe rod to an assembled Shelby tube sampler and drive the sampler down the same hole using a new Shelby tube for each 30-inch increment in depth.

Probe-Drive Systems

All of the probe-drive systems work in essentially the same way. A sampler is attached to a hollow drive rod, inserted into the hydraulic punch, and punched or hammered into the soil. Once the sampler reaches the depth at which the sample is to be taken, a stop pin in the sampler is removed using an extension rod that has been dropped through the inside of the hollow drive rod. The release of the stop pin allows the point of the sampler to retract inside the sample tube as the sampler is further advanced into the soil. The probe is then punched through the soil where the sample is to be taken. The rod and probe are then pulled to the surface for sample extraction.

Currently, three types of samplers are used in the probe-drive systems: the standard probe-drive sampler, the Kansas sampler, and the large bore probe-drive sampler. Preparation of each is slightly different. Each is discussed separately below.

Standard Probe-Drive Samplers

The standard probe-drive sampler comes in 10- and 24-inch lengths. The proper length is determined by the size of the sample desired. The point of this sampler is connected to a piston rod that will slide through its length. At its top, the piston rod is connected to the drive head, which keeps it centered and holds the piston stop pin, which stops the piston from sliding.

To prepare the standard probe-drive sampler, use the following procedures:

1. Insure that the sampler is assembled and complete, and that the piston stop pin which is reverse threaded is tightly locked so that the sampler point will not slide into the sampling tube.
2. Attach a shortened Geoprobe drive rod to the sampler so that the total length is nearly the standard 3 feet. If the 10-inch sampler is used, a 2-foot drive rod should be attached, and if the 24-inch sampler is used, a 1-foot drive rod should be attached.
3. Screw a drive cap onto the top of the shortened drive rod. The sampler is now ready for attachment to the hydraulic punch.
4. To insert the probe-drive sampler, raise the hydraulic punch using the probe lever, and then turn the hydraulic system off.

5. Lift the hammer latch and insert the anvil inside.
6. Place the assembled standard probe-drive sampler and shortened drive rod directly under the anvil so that the drive cap touches the anvil and the point of the sampler is aimed at the place where the sample is to be taken. The standard probe-drive sampler and the hydraulic punch should both be vertical.

Kansas Samplers

The Kansas sampler is much like the standard probe-drive sampler. However, it has a removable hardened cutting shoe near its point that allows it to penetrate rockier soils and to be easily replaced and decontaminated. Kansas samplers come in two versions: the Kansas Stainless Sampler, which has a stainless-steel tube, and the Kansas Sampler, which has an alloy steel tube.

To prepare a Kansas sampler, use the following procedures:

1. Ensure that the hardened cutting shoe is in place.
2. Assemble and install the Kansas sampler in the same manner as the standard probe-drive sampler (see Procedures 2 through 7 above).

Large Bore Samplers

The large bore sampler, similar to both types of Kansas samplers, has a removable cutting shoe and works in the same manner. It is slightly larger than the Kansas samplers, usually 24 inches long and 1-1/8 inches wide. The larger bore allows for the use of acetate or brass liners. The soil, therefore, can be removed easily by removing the liner. The acetate liner allows for easy visual examination of the core and can be easily sliced away so that the sample can be prepared for the laboratory. The brass liners come in four 6-inch sections that allow for easy separation and packaging of 6-inch soil samples. Some laboratories accept full 6-inch brass liners, allowing the samples to be collected with a very minimal disturbance to the soil matrix.

To prepare a large-bore sampler, use the following procedures:

1. Place the desired liner into the sampler by unscrewing the cutting shoe and sampler drive head from the two ends and then inserting the liner.
2. Assemble the sampler and attach a 12-inch drive rod to the sampler.
3. Screw a drive cap onto the top of the drive rod.
4. Place the assembled sampler and drive rod under the hydraulic punch in the manner detailed in the section above for preparing standard probe-drive samplers (see Procedures 5, 6, and 7 above).

2.2.2 Soil Gas Sampling

Two main methods are used to collect soil gas using the Geoprobe system: the standard method and the PRT system.

To use the standard method, the drive rods are decontaminated and assembled in an air-tight manner as they are punched into the soil. To ensure an air-tight seal, either Teflon tape or an O-ring can be placed on the male threads of the drive rods. The probe rods are driven approximately 6 inches below the area from where the sample is to be taken. The rods are then lifted approximately 6 inches leaving the expendable point and a small opening between the point and the end of the rod behind. A gas sampling cap is then attached to the top of the rod, a vacuum pump removes the necessary volume of gas, and the sample is collected.

To collect soil gas samples using the PRT system, polyethylene tubing attached to a stainless steel adapter is pushed through the drive rod after the rod is in place. The tubing and adapter is then reverse threaded onto the top of the PRT expendable point holder, and the gas is collected through the tubing. This method increases the accuracy of soil gas sampling, eliminates the potential for leaks in the rod, and simplifies probe rod decontamination.

Standard Method

Only decontaminated drive rods can be used with the standard method. Rods should be decontaminated using the procedures in Section 6.0 of this SOP.

To prepare a decontaminated drive rod for soil gas sampling using the standard method, use the following procedures:

1. Screw an expendable point holder into the female end of a 3-foot drive rod. (Note: a retractable point can also be used with this method; however, decontamination requirements almost always preclude its use.)
2. Place an expendable point into this holder.
3. Screw a drive cap onto the male end of the drive rod.
4. Place the rod into the hydraulic punch.
5. Turn on the hydraulic system.
6. Install the anvil within the hydraulic punch's hammer by lifting the hammer latch and inserting it.
7. Place the assembled drive rod directly under the anvil so that the drive cap faces the anvil and the expendable point is aimed at the desired sampling location.
8. Push sampler and hydraulic punch through the soil to gather the sample.

PRT System

Two types of PRT systems are available. The first uses an expendable point holder and expendable point like the standard method. The second uses a retractable point holder that lifts off of the drive-point without actually separating from it. Both systems allow the threading of a PRT adapter and tubing through the drive rod so that the gas can be taken from the depth required without being sucked through the drive rod.

To prepare the drive rod and sampler for PRT soil gas sampling, use the following procedures:

1. Select the desired PRT sampler (either one with an expendable point or one with a retractable point) and ensure that the PRT adapter easily screws into the threads on top of the sampler. This step is necessary to ensure that the adapter will fit easily when it is affixed from above ground.
2. If using the sampler with an expendable point, attach the point.

3. Screw the sampler to the end of a shortened drive rod so that the total length of the sampler is nearly 3 feet.
4. Screw the drive cap to the other end of the drive rod.
5. Attach the drive rod and sampler to the hydraulic punch using the same procedures detailed in the standard method (see Procedures 4, 5, and 6 above).

2.2.3 Groundwater Sampling

The Geoprobe System offers two systems for collecting groundwater, each with several groundwater sampling options. The first method involves the use of a mill-slotted well point. The second method uses a specially designed Geoprobe screen point sampler.

Mill-Slotted Well Points

The mill-slotted well point is a 2- or 3-foot length of hollow steel tubing with 15-millcut slots in it, each 2 inches long and 0.020 inches wide. Once in place, groundwater enters the tube through these slots. To prepare the mill-slotted well point, use the following procedures:

1. Screw a solid drive point into the female end of the sampler.
2. If a 2-foot well point is being used, screw the sampler to a 1-foot length of drive rod.
3. Screw a drive cap to the other end of the well point or 1-foot drive rod.
4. Place the sampler and rod into the hydraulic punch by raising the punch as much as necessary and turn hydraulic system off.
5. Install the anvil within the hydraulic punch's hammer by lifting the hammer latch and inserting it.
6. Place the mill-slotted well point sampler under the anvil with the drive cap near the anvil and the point aimed at the sampling location.

Geoprobe Screen Point Sampler

The Geoprobe screen point sampler has a 19-inch screen encased in a perforated stainless-steel sleeve. The screen remains encased in the sleeve until the screen point sampler reaches the desired depth. The

rod is then pulled back approximately 19 inches, leaving the screen exposed to the formation. Flexible tubing can be pushed through the drive rod and attached to the sampler using the adapters for the PRT soil gas system, enabling groundwater to be removed without touching the drive rod. Decontaminating the drive rod is subsequently easier.

To prepare a Geoprobe screen point sampler, use the following procedures:

1. Close the screen on the sampler.
2. Attach its expendable point.
3. Attach the sampler to a shortened drive rod so that the assembly is nearly 30 inches long.
4. Place the sampler into the hydraulic punch using the methods detailed for mill-slotted well points (see Procedures 4, 5, and 6 above).

2.3 SAMPLING

Sampling procedures for the Geoprobe hydraulic punch are similar for all samplers and sampling media. This section presents general procedures that apply to all samplers and sample types, and specific operating procedures for soil, soil gas, and groundwater.

2.3.1 General Procedures

All control panel switches have a slow and fast position. All switches should initially be set at the slow position when positioning the punch and the sampling tools. In all cases, the hydraulic system should be shut off when not in operation and when adapters and additional drive rods are put into place. The hydraulic punch should be turned off any time it is not actually in operation.

The Geoprobe hydraulic punch is designed with a key safety feature that will shut it off if the controls are released. If the operator senses that something is wrong, he or she must release the controls and stop operating the punch until all is well. At no time should the foot of the punch be allowed to lift higher than 6 inches off the ground because the punch will destabilize and may bend the drive rod or sampling tube.

Also, at no time should part of a human body be placed on top of a drive cap while the cap is near the anvil or under the foot of the hydraulic punch.

Once the assembled sampler or drive rod is under the anvil, both it and the hydraulic punch should be vertical. Positioning the drive rod and sampler is critical in order to drive the rod vertically. Not positioning the sampler or drive rod vertically will result in problems when attaching subsequent drive rods needed to reach the proper depth and with rod retrieval.

To begin probing in soils of normal texture, use the following procedures:

1. Activate the hydraulic punch and push down on the probe lever on the control panel so that the probe slowly lowers itself. Always use the slow control on the first rod or sampler.
2. Continue to press on the probe lever until the rod or sampler is completely forced into the soil. The point of the rod will then be nearly 3 feet into the soil.

Soils and other materials are often too hard for the hydraulic punch's probe mechanism to penetrate.

When this occurs, the hammer on the hydraulic punch should be used in accordance with the following procedures:

1. Ensure that the hammer rotation valve is closed.
2. Use the hydraulic punch to put pressure on the rod, sampler, and soil. When the probe rod refuses to move, the foot of the hydraulic punch will begin lifting off the ground. Never allow the foot to lift more than 6 inches off the ground, but never use the hammer with the foot resting on the ground surface.
3. If the probe foot lifts off the ground, the hydraulic punch may no longer be perpendicular. If this occurs, use the machine's fold lever, which is located on the control panel, to correct the punch's position.
4. Press the hammer lever on the control panel. The rod should now advance. Never use the hammer unless there is downward pressure on the drive cap because doing so may damage the equipment.
5. Stop hammering periodically and check to see if the probe rods can be advanced using the probe mechanism only.

When samples are to be taken at depths of greater than 3 feet, additional drive rods must be added to those already in the ground. Shelby tube soil sampling procedures for adding rods are discussed in Section 2.3.2. For all other sampling methods, use the following procedures to add drive rods:

1. Using the probe lever, raise the hydraulic punch off the portion of the drive rod protruding from the ground.
2. Unscrew the drive cap from the drive rod.
3. If using the standard method of collecting soil gas or other sampling methods that will draw the sample through the length of the entire drive rod, wrap the threads of the drive rod with Teflon tape or push an O-ring over the threads to make the drive rod string air- and water-tight.
4. Screw another drive rod onto the first drive rod protruding from the ground. Tighten the rods together with a pipe wrench.
5. Screw a drive cap onto the top of the new drive rod.
6. Place the hydraulic punch over the new drive rod and push the rod farther into the ground.

As the rod string is pushed farther into the ground, it will sometimes begin to loosen. The rods should remain tight so that the threads are not damaged. Occasionally, stop probing and twist the rod string with a pipe wrench to ensure that all of the joints remain tightly sealed.

2.3.2 Soil Sampling

This section presents procedures used to sample soils using either the Shelby tube sampling method or any of the probe-drive systems. In all cases, sampling tools should never be advanced farther than their length once they are opened because the sampler will overfill. If the sampler overfills, it could be damaged or expand, causing it to fall off the drive head.

Shelby Tube Sampling Procedures

Because the Shelby tube does not remain closed until it reaches the desired sampling depth and because it is not connected to a drive rod but to a Shelby drive head, sampling procedures for Shelby tubes differ greatly from soil sampling with other methods. New drive rods cannot be continuously added. Sampling

at depths of greater than 30 inches requires a step-like procedure. For example, to sample to a depth of 90 inches, three Shelby tubes are needed. The first is advanced from 0 to 30 inches and then removed. The second is pushed through the hole made by the first and advanced to a depth of 60 inches and removed. The third is also pushed through the 60-inch deep hole and advanced from 60 to 90 inches.

Samplers must be ready to change sampling methods if necessary. For example, if soils are not cohesive, they tend to drop out of the Shelby tube as it is pulled from the ground. Also, if the soils are not cohesive, they tend to collapse into the hole left by the initial tube before the second and third tubes can be pushed into place. For this reason, use of the Shelby tube method is impractical at depths of greater than 10 feet. Rocky soils are also difficult to sample with a Shelby tube sampler because they tend to destroy the sampler while it is being driven into the ground.

To sample using the Shelby tube method, use the following procedures:

1. Turn on the hydraulic system and slowly press the Shelby tube into the soil using the probe lever on the control panel.
2. Once the tube has reached the sampling depth or has been extended to nearly its full 30-inch length, stop the hydraulic punch and raise it off the drive cap and Shelby tube drive head.
3. Unscrew the drive cap.
4. Screw on a pull cap.
5. Lower the hydraulic punch and lift the hammer latch. Remove the anvil. Place the latch around the pull cap so that the latch will hold the cap to the hydraulic hammer.
6. Using the probe lever, raise the hydraulic punch to pull the Shelby tube from the ground.

If the desired sampling depth is greater than 30 inches, additional Shelby tubes and probe rods must be used. The tubes are then prepared for probing using the methods presented in Sections 2.2.1 and 2.3.1 above. To advance the Shelby tube deeper, the tubes are pushed through the hole left by the first tube using the method detailed above.

Once a Shelby tube core has been retrieved from a sampling point, it must be extruded from the Shelby tube sampler using the following procedures:

1. Lower the hydraulic punch using the probe lever so that its mast will not strike the top of the van as it is folded.
2. Lift the foot of the hydraulic punch using the foot lever.
3. Slowly and carefully fold the hydraulic punch using the fold lever.
4. Once the punch is horizontal, the Shelby tube extruder bracket can be placed onto the punch's foot. This bracket will hold the Shelby tube in place and allow the punch to push the soil out of the tube.
5. Screw an extruder piston onto a drive rod and a drive cap on the drive rod's other end.
6. Place the drive rod into place under the horizontal drive punch.
7. Place the full Shelby tube into the extruder rack and secure it with the extruder latch.
8. A pan or container should be held at the end of the Shelby tube to collect sample material as it is extruded.
9. The probe lever activates the hydraulic punch and pushes the soil from the Shelby tube.

Tetra Tech's SOPs on packaging and documenting samples, SOPs Nos. 016, 017, 018, and 019, should be used to prepare the sample for analysis.

Probe-Drive System Sampling Procedures

All three types of probe-drive samplers work in essentially the same way. The sampler is advanced to just before the proper sampling depth and then the drive point is released by removing a stop pin using solid extension rods that have been dropped through the hollow drive rod. The point is then pushed back into the body of the sampler as the sampler fills with the soil sample.

In addition to the general procedures listed in the Section 2.3.1, the probe must be stopped at just before the desired sampling depth so that the stop pin can be removed. Pushing the probe too far will require starting over.

To use the probe-drive sampling system to sample soil, use the following procedures:

1. Attach additional drive rods as discussed in the general procedures in Section 2.3.1.
2. Stop the hydraulic probe just before the desired sampling depth.
3. Raise the hydraulic punch, turn off the hydraulic system, and remove the drive cap.
4. Insert an extension rod into the drive rod and screw additional extension rods together until the assembly reaches the same depth as the sampler.
5. Attach a small extension rod handle to the top of the extension rod.
6. Rotate the extension rod handle clockwise until the leading extension rod has turned the stop pin and disengaged it.
7. Pull and unscrew each extension rod from the hollow drive rod. The stop pin should be attached to the bottom of the extension rod string. If not, repeat Procedures 1 through 6.
8. To sample, mark the drive rod with tape or chalk about 10 inches above the ground if a 10-inch sampler is used or 24 inches from the ground if a 24-inch sampler is used.
9. Replace the drive cap and start the hydraulic system.
10. Drive the rod until the tape or chalk mark touches the ground. Be careful not to overdrive the sampler. Doing so could compact the soil in the sampler or cause it to balloon outward, making soil removal and extrusion difficult.
11. Raise the hydraulic punch and replace the drive cap with the pull cap. Remove the anvil.
12. Latch the pull cap underneath the hydraulic hammer latch and pull the rods out of the ground, disassembling the rod as needed.
13. Check to ensure that a soil sample is now in the sampler.

Once a soil sample has been removed from the ground, it can be extruded using the Geoprobe. The tools supplied by Geoprobe Systems for extruding soil from probe-drive samplers do not require the Geoprobe to be folded and horizontal. If liners are used with large-bore samplers, extrusion is usually unnecessary. When extrusion is necessary for probe-drive samplers, use the following procedures:

1. Raise the foot of the hydraulic punch off the ground using the foot lever on the control panel.
2. Attach the extruder rack onto the foot of the punch so that its crossbeam rests on top of it.

3. Completely disassemble the sampler. In all cases, remove the piston, point, and drive head of the sampler. If using the Kansas and large-bore samplers, unscrew the removable cutting shoe as well.
4. Insert the sample tube into the extruder with its cutting end up.
5. Insert a disposable wooden dowel or the reusable steel piston above the soil and below the hydraulic punch so that pressure on the dowel or piston from the punch will push the soil out of the bottom of the sample tube.
6. Position proper sampling jars or trays under the sample tube and very slowly use the probe lever to force the soil out of the tube. Injury can result if the soil is quickly forced from the tube.

The soil sample is now ready for packaging or on-site laboratory analysis. For large-bore samplers, the soil may be contained in a plastic sleeve that can be sliced away once the soil is to be packaged or in a brass sleeve that may be capped on both ends and shipped to the laboratory as is. Tetra Tech's SOPs on packaging and documenting samples for analysis should be followed when collecting samples using the Geoprobe System.

2.3.3 Soil Gas Sampling Procedures

The standard method and the PRT system are used for collecting soil gas using the Geoprobe System. The standard method requires the drive rods to be sealed together with either O-rings or Teflon tape to ensure an air-tight seal so that soil gas from depths other than the bottom of the drive-rod string cannot penetrate the system.

The PRT system draws soil gas through continuous tubing that is dropped through the drive rod after the drive rod has reached the desired level. The tubing is then attached directly to the point holder at the end of the drive-rod string.

For both methods, the drive rod should be driven to the desired depth. The drive cap should be replaced by the drive pull cap, and the rod should be pulled back out of the hole approximately 6 inches. This 6-inch void is the area where the soil gas sample is collected from. A pipe wrench or vise-grip pliers should be attached to the pipe just above the foot of the hydraulic punch so that the wrench or pliers rests on the foot to stop the drive rod from working its way back down into the hole.

Tygon tubing should be replaced between each sample for both sampling methods to avoid cross contamination.

The standard method and the PRT system sampling procedures are presented below. In addition, procedures for collecting soil gas in Tedlar bags, glass bulbs, and adsorption tubes is also presented below.

Standard Method

To gather a sample using the standard method, raise the hydraulic punch as mentioned above and replace the drive cap with a gas sampling cap. This cap is designed to fit the drive rods and is used to connect them by tube to a vacuum supply. Once the tubing has connected the gas sampling cap to the vacuum supply, remove the volume of air necessary to ensure that none of the gas being drawn was in the rod during probing, and then collect the sample in either Tedlar bags, glass bulbs, or adsorption tubes as discussed below.

PRT System

To use the PRT system (with either an expendable or a retractable point) to collect soil gas samples use the following procedures:

1. Secure the PRT adapter to the end of a piece of polyethylene tubing 1 to 2 feet longer than the total length of the drive-rod string. The adapter must fit tightly within the tubing. If it does not, tape it into place. Also, ensure that the O-ring is in place on the threaded end of the adapter.
2. Remove the drive cap from the probing rod and lower the adapter into it, holding on to the tubing.
3. Grasp the excess tubing and apply downward pressure. Turn the tubing counter-clockwise to engage the adapter threads on the sampler holder.
4. Pull up lightly on the tubing to test engagement of threads. If the adapter has not engaged, try again. If it repeatedly does not engage, soil may have intruded into the drive rod either during probing or, in the case of the retractable point, when the rod was pulled back to leave the point opening. Use the threaded extrusion rods to clean out the threads.

5. In most cases, the adapter will easily screw into place. The sampler is now ready to collect samples in either Tedlar bags, glass bulbs, or adsorption tubes using the procedures presented below. After the sample is collected and the sampler and tube is removed from the ground, the O-ring should be checked to ensure that a good seal exists between the sampler and adapter. If the O-ring is tightly smashed, the seal should be good.
6. Discard polyethylene tubing and use new polyethylene tubing for each sample.

Tedlar Bags

Soil gas can be collected for chemical analysis in a 500-cubic-centimeter Tedlar gas sampling bag by inducing a vacuum on the exterior of the bag. The following procedures should be used to collect soil gas samples in Tedlar bags:

1. For the PRT system, connect a short (6- to 12-inch) piece of Tygon tubing to the free end of the polyethylene tubing protruding out of the drive rod. For the standard method, connect the Tygon tubing to the soil gas sampling cap.
2. Attach the other end of the Tygon tubing to one end of the Tedlar bag chamber. Tetra Tech uses modified, plastic, air-tight kitchen containers for these chambers. They are inexpensive and work well.
3. Connect another piece of Tygon tubing 2 feet to 3 feet long to the other end of the Tedlar bag chamber and to the nipple on the bottom of the vacuum system panel.
4. Place the lid on the Tedlar bag chamber.
5. Turn the vacuum/volume (vac/vol) pump switch on and allow pressure to build in the vacuum tank. Make sure that the vacuum line valve is closed before turning on the pump switch.
6. Open the vacuum line valve and purge three times the volume of ambient air out of the Tedlar bag chamber and PRT tubing or probe rods. The equations for determining purge volumes are as follows:

Probe rods or tubing

$$V = \pi r^2 H$$

where

V = Volume

π = 3.14159

r = Radius of tube or rod

H = Length of tube or rod

Vacuum chamber

$$V = LWH$$

where

V = Volume

L = Length of chamber

W = Width of chamber

H = Height of chamber

7. Close the line valve.
8. Clamp the Tygon tubing shut with hemostats.
9. Remove the lid from the Tedlar bag chamber.
10. Connect a Tedlar gas sampling bag to the fitting inside the Tedlar bag chamber and open the valve on the gas sampling bag.
11. Place the lid back on the Tedlar bag chamber, seal it tightly, and remove the hemostats.
12. Turn the vac/vol pump switch on and open the vacuum line valve to create a vacuum in the chamber. The Tedlar bag should fill once the vacuum is created. The rate at which the Tedlar gas sampling bag fills depends on the permeability of the soil. The minimum amount of soil gas needed for analysis is approximately 0.5 liter. If less than 0.5 liter is collected after 4 minutes of sampling, raise the soil gas probe 0.5 foot and continue to evacuate the vacuum chamber for another minute. If the minimum required volume of soil gas is not collected, repeat the procedure. If the minimum required volume of soil gas is still not collected, abandon the collection process. All steps conducted should be accurately recorded in the logbook even if no samples are satisfactorily collected.
13. After the soil gas sample is collected in the Tedlar bag, clamp the Tygon tubing with hemostats.
14. Turn off the vacuum pump.
15. Remove the vacuum chamber lid.
16. Close the valve on the Tedlar gas sampling bag and remove the bag from the chamber. Label the Tedlar bag with the appropriate information.

Glass Bulbs

The following procedures should be used to collect soil gas in glass bulbs:

1. Turn the vac/vol pump switch on and allow pressure to build in the vacuum tank. Make sure that the vacuum line valve is closed before starting the vacuum pump. The inside scale of the vacuum tank gauge is calibrated in inches of mercury. The outside scale is calibrated for volume in liters (at standard temperature and pressure). Obtain the desired vacuum and turn the vacuum pump off.
2. Connect a short (6- to 12-inch) piece of Tygon tubing to the sample cap or PRT protruding from the drive rod.
3. Connect one end of the labeled glass bulb to the Tygon tubing.
4. Connect another piece of Tygon tubing 3 feet to 5 feet long to the other end of the glass bulb and to the nipple on the bottom of the vacuum system panel.
5. Open the two stopcocks on the glass bulb.
6. Turn off the vacuum pump.
7. Turn the vacuum line valve to its open position.
8. Purge three times the volume of ambient air within the rods, bulb, and tubing. Equations for figuring out volumes are presented in the Tedlar bag discussion.
9. Turn the vacuum line valve to its closed position. Allow the pressure in the sample train to equalize (the sample line gauge should read zero).
10. Close the stopcocks on the glass bulb.
11. Remove the glass bulb and label it with the appropriate information.

Adsorption Tubes

The following procedure should be used to collect soil gas in adsorption tubes:

1. Connect a short (6- to 12-inch) piece of Tygon tubing to the sample cap or PRT protruding from the drive rod.
2. Connect this piece of tubing to the nipple on the bottom of the vacuum system panel and purge three volumes of air from the drive rod or PRT system as described in the discussion of the Tedlar bag method.
3. Use hemostats to clamp the Tygon tubing attached to the drive rod or PRT.
4. Insert the adsorption tube between the Tygon tubing from the drive rod or PRT and the Tygon tubing attached to the vacuum system panel.

5. Remove the hemostats and draw the required volume of air through the adsorption tube.
6. Remove the adsorption tube and place the appropriate caps on the tube ends.
7. Clearly label package, and ship the samples as required by the laboratory or Tetra Tech and U.S. Environmental Protection Agency (EPA) SOPs.

Soil Gas Sampling Pointers

If the needle on the vacuum line valve does not move, the soil at the sampling depth may be saturated, pore space may be too tight to yield a sample, or sampling train may be plugged. If the needle moves back to zero very quickly, either the soil at the sampling depth is very permeable or a leak is present in the sampling train.

In some soils, the needle may return to zero very slowly. The time it takes for the needle to return to zero is called the “recovery” time. Recovery time should be noted for each sample taken. This information will allow relative comparison of soil permeability. Recovery times of greater than 10 minutes should be considered suspect. The effect of leakage in the sampling system increases with longer recovery times. After 10 minutes, the operator should consider either changing the sampling depth, location, or length of pullback from the sampling tip, or switching entirely from soil gas sampling to grab sampling and analysis of soil.

2.3.4 Groundwater Sampling

The two options for sampling groundwater using the Geoprobe System follow procedures similar to those presented in Sections 2.3.2 and 2.3.3 above. The sections below detail procedures for using mill-slotted well point samplers and Geoprobe screen point samplers to sample groundwater.

Mill-Slotted Well Point Sampler

Once the mill-slotted well point reaches groundwater, the water will begin to flow through the slots. When the sample is to be analyzed for volatile organic compounds, do not use a vacuum to suck groundwater from the drive rod. If the sample is to be analyzed for other parameters such as metals, semivolatiles, pesticides, or explosives, using a vacuum on the drive rod is acceptable. In all cases,

polyethylene tubing can be used as a thieving rod by lowering its end into the drive rod, capping or sealing the tube's top, and then removing it. The preferred method for collecting samples for volatile organic analysis is to use a well mini-bailer. To collect groundwater samples with a mini-bailer, use the following procedures:

1. Raise the hydraulic punch, turn off the hydraulic system, and remove the drive cap.
2. Lower a well mini-bailer into the drive rod until it reaches the bottom. As it reaches the bottom, the check ball on the bailer's end will float in the groundwater and then slowly sink to the bottom.
3. Allow a couple of seconds for the ball to sink and set.
4. Pull the well mini-bailer out of the drive rod. The bailer should contain about 20 milliliters of groundwater.
5. Package and document the samples in accordance with Tetra Tech SOPs No. 016, 017, 018, and 019, or a similar EPA-approved procedure.

If a bailer is not required and volatile organic samples are not being collected, a foot valve sampler, vacuum trap, or peristaltic pump can be used to collect samples. Once the sample has been removed and packaged, the mill-slotted well point can be removed and decontaminated.

Geoprobe Screen Point Sampler

The Geoprobe screen point sampler contains a screen and screen plug that allows water to enter the rod. To collect groundwater samples with a Geoprobe screen point sampler, use the following procedures:

1. Push the sampler below the depth necessary to reach groundwater.
2. Raise the hydraulic punch and replace the drive cap with a pull cap. Also, remove the anvil.
3. Latch the pull cap under the hammer latch, and use the probe lever to lift the drive rod about 18 inches. Because the sampler has an expendable point, the point should stay at the deepest depth, and the screen and screen connector should fall out of the bottom of the sampler. Sometimes, however, the screen stays within the sampler and is lifted the 18 inches with the drive rod.
4. To ensure that the screen is exposed, attach a vice grip or pipe wrench to the rod above the foot of the hydraulic punch and raise the hydraulic punch. Then remove the pull cap

and place an extension rod through the tubing to push the screen into place. Additional extension rods can be attached to reach the desired depth.

To remove the groundwater sample for volatile organic analysis, with a well mini-bailer, follow steps 1 through 5 under the mill-slotted well point section above. Tubing can be used as a thieving rod with or without a check valve to collect groundwater samples as well. If the sampler is supplied with the optional PRT expendable point holder, then a PRT adapter can be pushed through the drive rod and threaded into place by following the PRT system Procedures previously discussed. A vacuum trap system or peristaltic pump can then be used to withdraw the sample. The PRT system method, however, should never be used when the sample is to be analyzed for volatile organic compounds because it involves using a vacuum to remove the sample.

3.0 PIEZOMETER AND VAPOR SAMPLING IMPLANT INSTALLATION PROCEDURES

The Geoprobe System's ability to quickly probe into soil allows for easy installation of both piezometers and vapor sampling implants. Both installation procedures are discussed below.

3.1 PIEZOMETER INSTALLATION

Piezometers are tubes that extend to groundwater and enable easy sampling of groundwater on a routine basis (see Figure 10). In addition to installing the piezometer, piezometers must be protected from the weather and from contamination. A well-head protector must therefore be installed around them. In some soil types, preparing the well-head protector may be the first step to installing a piezometer. For this reason, the directions below should be read completely before beginning piezometer installation. If a post-hole digger is to be used for well-head protector installation, Procedure 5 should be performed first. The piezometer should then be advanced through this hole.

To install temporary or permanent piezometers, use the following procedures:

1. Use the hydraulic punch to drive the temporary casing to the desired piezometer installation depth. Use the general procedures outlined in Section 2.3.1 above for details on driving the piezometer casing. The different temporary casings that can be used are described below. Geoprobe Systems also manufactures special drive caps, expendable points, and pull caps that fit these types and sizes of pipe.

- a) 1-7/16-inch outside diameter by 1-3/16-inch inside diameter, RW-flush threaded pipe can be used as a temporary casing. This casing can be driven to an approximately 25- to 30-foot depth. Two sizes of piezometer wells can be installed inside of the temporary casing: (1) 3/4-inch outside diameter by 1/2-inch inside diameter, polyvinyl chloride (PVC) pipe, or (2) 1-inch outside diameter by 3/4-inch inside diameter, PVC pipe.
 - b) 1-13/16-inch outside diameter by 1-1/2-inch inside diameter, EW-flush threaded pipe can be used as a temporary casing. This casing can be driven to an approximately 15- to 20-foot depth. Three sizes of piezometer wells can be installed inside of the temporary casing: (1) 3/4-inch outside diameter by 1/2-inch inside diameter PVC pipe, or (2) 1-inch outside diameter by 3/4-inch inside diameter, PVC pipe, or (3) 1-1/2-inch outside diameter by 1-inch inside diameter, PVC pipe.
 - c) 1-1/4-inch outside diameter by 1-inch inside diameter, NPT-threaded pipe can be used as a temporary casing. This casing can be driven to an approximately 25- to 30-foot depth. Only 3/4-inch outside diameter by 1/2-inch inside diameter, PVC pipe piezometer wells can be installed inside of the temporary casing. If using NPT-threaded pipe, couplers are needed to attach each section of pipe.
2. Once the piezometer casing is at the proper depth, remove the drive cap and install the selected size piezometer pipe inside of the temporary casing.
 3. Using a pull plate, remove the temporary casing.
 4. If the hole stays open, attempt to install a sand pack around the slotted portion of the piezometer, and then place dry granular bentonite on top of the sand pack as a seal. One foot of bentonite is recommended for a good seal.
 5. Dig an 8-inch nominal-diameter hole around the piezometer pipe. This hole should extend to a depth of 1.5 to 2 feet. A post-hole digger can be used for this procedure if the hole is dug prior to driving the temporary casing. The bottom 6 inches of this hole should be filled with dry granular or slurry bentonite. The remainder of the hole should be filled with concrete. A steel, locking, aboveground or flush-mount well protector should be inserted into the wet concrete to provide well-head security. A concrete pad can also be constructed around the steel well-head protector.

3.2 VAPOR SAMPLING IMPLANT INSTALLATION

Figure 11 presents diagrams of vapor sampling implants. To install vapor sampling implants, first punch a drive rod to the desired depth using an expendable point holder and an expendable point. Once at the desired sampling depth, use the following procedures:

1. Disengage the expendable point and retract the probe rod about 1 foot by raising the hydraulic punch, replacing the drive cap with a pull cap, removing the anvil, latching the pull cap onto the hydraulic hammer using its latch, and raising the hydraulic punch again using the probe lever.
2. Lock the rod into place so that it does not sink back into the hole by using vice grip pliers or a pipe wrench.
3. Unlatch the pull cap and raise the hydraulic punch again, leaving room to work freely.
4. Remove the pull cap.
5. Attach appropriate stainless-steel tubing to the vapor implant. If tubing is precut, allow 48 inches more than the required depth of the implant.
6. Insert the implant and tubing down the inside diameter of the probe rods until it stops. Note the length of the tubing inserted to ensure that the desired depth has been reached. Allow the excess tubing to extend out of the drive rod's top.
7. Pour glass beads down the inside diameter of the probe rod using a funnel to create a permeable layer around the implant.
8. Use the tubing extending from the drive rod to stir the beads into place. Do not lift up on the tubing while doing so.
9. Position the remaining tubing through the hole on a rod pull plate, and then place the drive rod through that hole.
10. Attach the plate to the hydraulic punch using its chain and slowly pull the rod up another 18 to 24 inches. While the punch pulls the rod, push down on the tubing so that it stays in place.
11. Pour bentonite seal mixture down the inside diameter of the probe rod. Stir the mixture using the tubing as before. The initial mixture may also be topped with distilled water to initiate the bentonite seal depending on the site and on the role the vapor implant is to play.
12. Pull the drive rod from the hole using the probe rod pull plate already attached, and then plug the hole using granular bentonite or a bentonite slurry mixture.

The vapor sampling implant should now be in place and the stainless steel tubing connected to it should be protruding from the ground. The vapor implant tubing should be protected by a well-head protector in the same manner as the top of the piezometer. Procedure 5 in Section 3.1 describes well-head protector installation.

4.0 ROD REMOVAL PROCEDURES

Throughout the above discussions, it has occasionally been necessary to remove drive rods and samplers. The standard removal procedures involve raising the hydraulic punch, turning off the hydraulic system, replacing the drive cap with a pull cap, removing the anvil, and then latching the pull cap under the hammer latch. The hydraulic punch can then be used to pull the rod from the ground.

Two deviations to this procedure often occur. The first deviation is necessary when sampling tubes are to be left inside the hole as the drive rod is removed, especially when soil gas implants or piezometers have been installed. Because of the presence of these sampling tubes, a pull cap cannot be screwed onto the top of the drive rod. Instead, a rod pull plate is used. This plate is a piece of steel with a hole in it large enough for a drive rod to fit through it. The plate has a hook on one end. The tubing and rod are pushed through the plate, and the pull plate is attached to the latch on the hydraulic punch by a chain. As the punch pulls up, the plate shifts, and the inside of the hole binds on the rod. This binding usually holds the rod to the plate and results in the rod being pulled up as the punch is raised.

The second deviation occurs when the rods have not been pushed perpendicular to the ground. In these cases, a specially designed chain-assisted pull cap is used. This cap looks like a pull cap but has a chain on it that fits under the latch of the hammer. Once the cap is screwed to the drive rod and latched to the probe, raising the probe raises the rod.

In a few cases, drive rods break while in the ground. To retrieve these rods, a rod extractor is used. This extractor looks something like a drill bit and is screwed to the end of a probe rod. A hammer is then used to pound the extractor into the top of the broken rod. The extractor joins the broken rod to the second drive rod so that they can be pulled out together.

5.0 BACKFILLING PROCEDURES

Unless otherwise specified in the site-specific sampling plan, holes made by sampling with Geoprobe System tools are to be backfilled with dry, fine, granular bentonite. Water may be added to activate the bentonite. Tops of the holes may then be filled with soil or concrete as necessary for each particular site.

6.0 DECONTAMINATION PROCEDURES

Between holes, the probe rods and sampling tools must be decontaminated. Because no provisions for decontamination are included in the Geoprobe System, a separate decontamination station must be provided. A wire brush, a barrel brush for reaming out the rods, and soft brushes will clean sticky soil from the probe rods and sampling tools. Follow Tetra Tech SOP No. 002 decontamination procedures when sampling soil or groundwater.

When sampling for soil gas by the standard method, Geoprobe rods and samplers are heated approximately 15 to 20 minutes by a 100,000-British thermal unit heater until they are too hot to touch with the bare hand. They are then allowed to cool before reuse. Do not heat the rods too much or the rod metal will fatigue.

When sampling for soil gas by the PRT method, the probe rods do not have to be decontaminated. However, the PRT expendable point holder and PRT adapter do need to be decontaminated. They can be heated on the dash of the vehicle with the defrost system or scrubbed in Alconox and water. Equipment blank samples can be collected, if necessary, as part of the quality control process.

Sampling plans may have different decontamination requirements. Most plans also require rinsate sample collection as part of the quality control process.

FIGURE 1
GEOPROBE SYSTEM

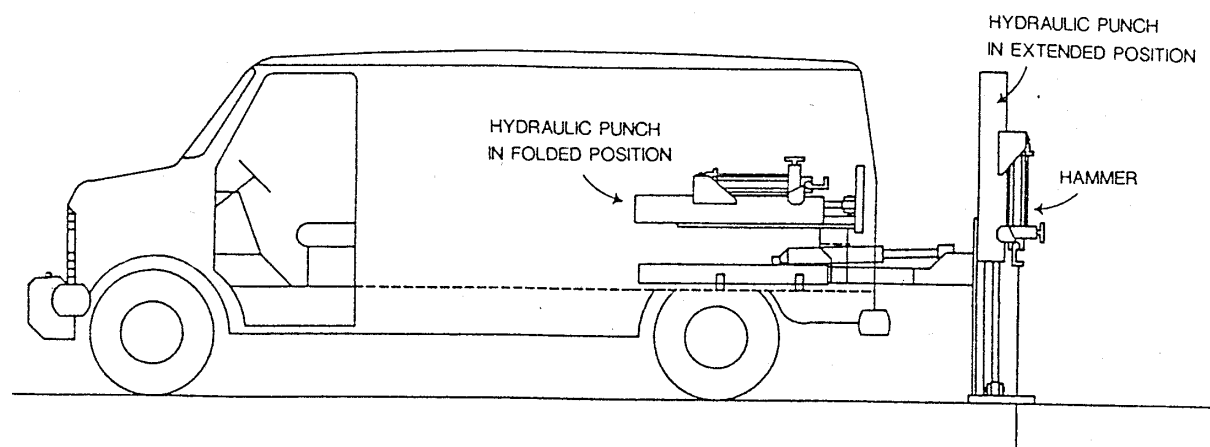
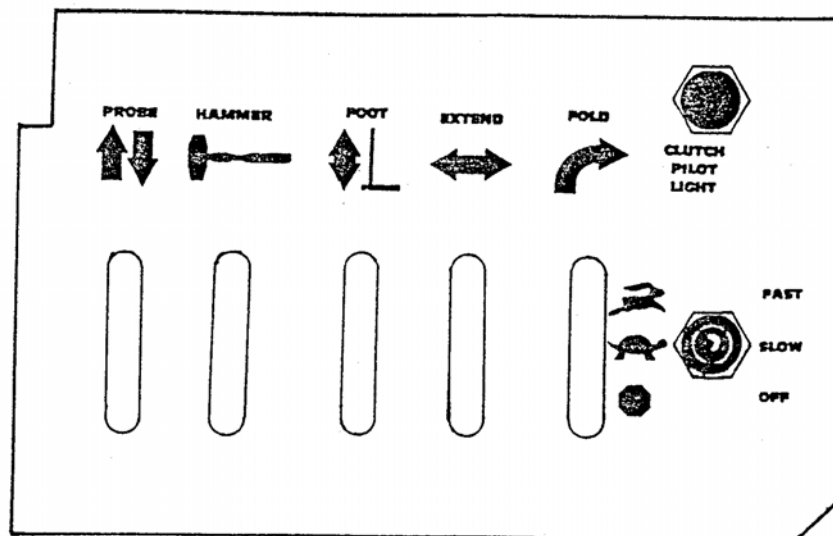
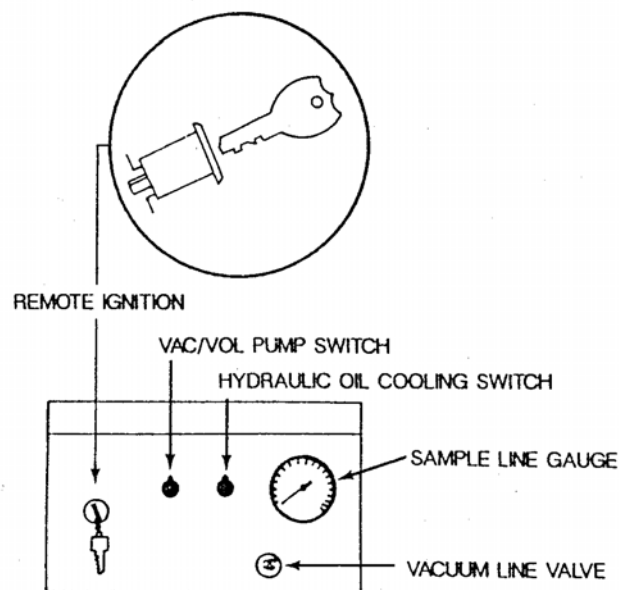


FIGURE 2
CONTROL AND VACUUM SYSTEM PANELS



CONTROL PANEL



VACUUM SYSTEM PANEL

FIGURE 3
GENERAL ACCESSORY TOOLS

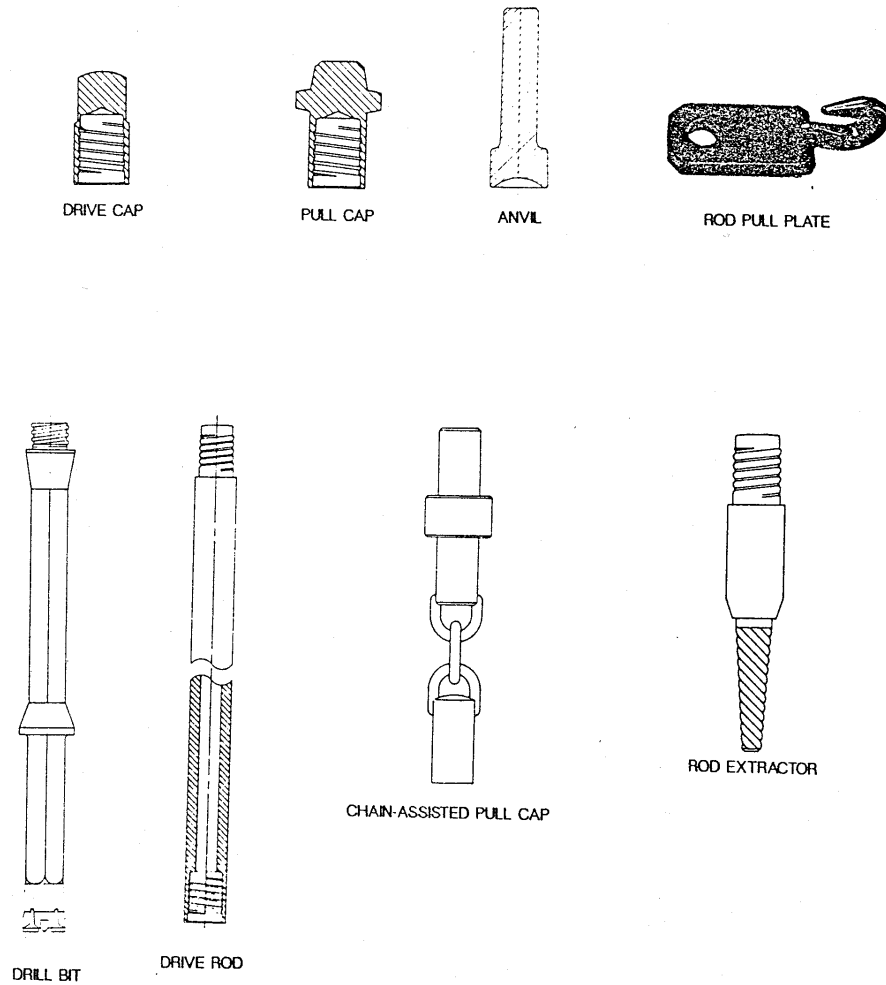


FIGURE 4
SHELBY TUBE ACCESSORIES

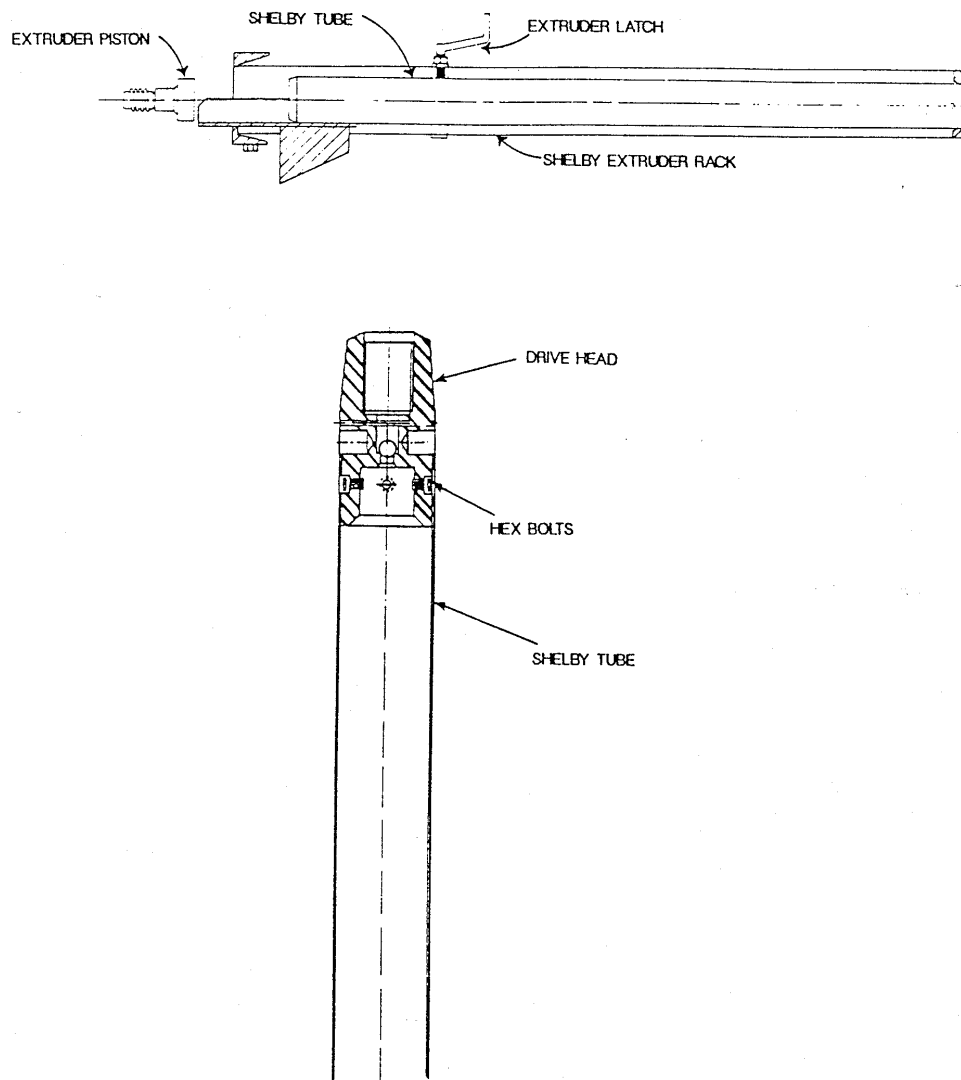


FIGURE 5
PROBE-DRIVE SYSTEM

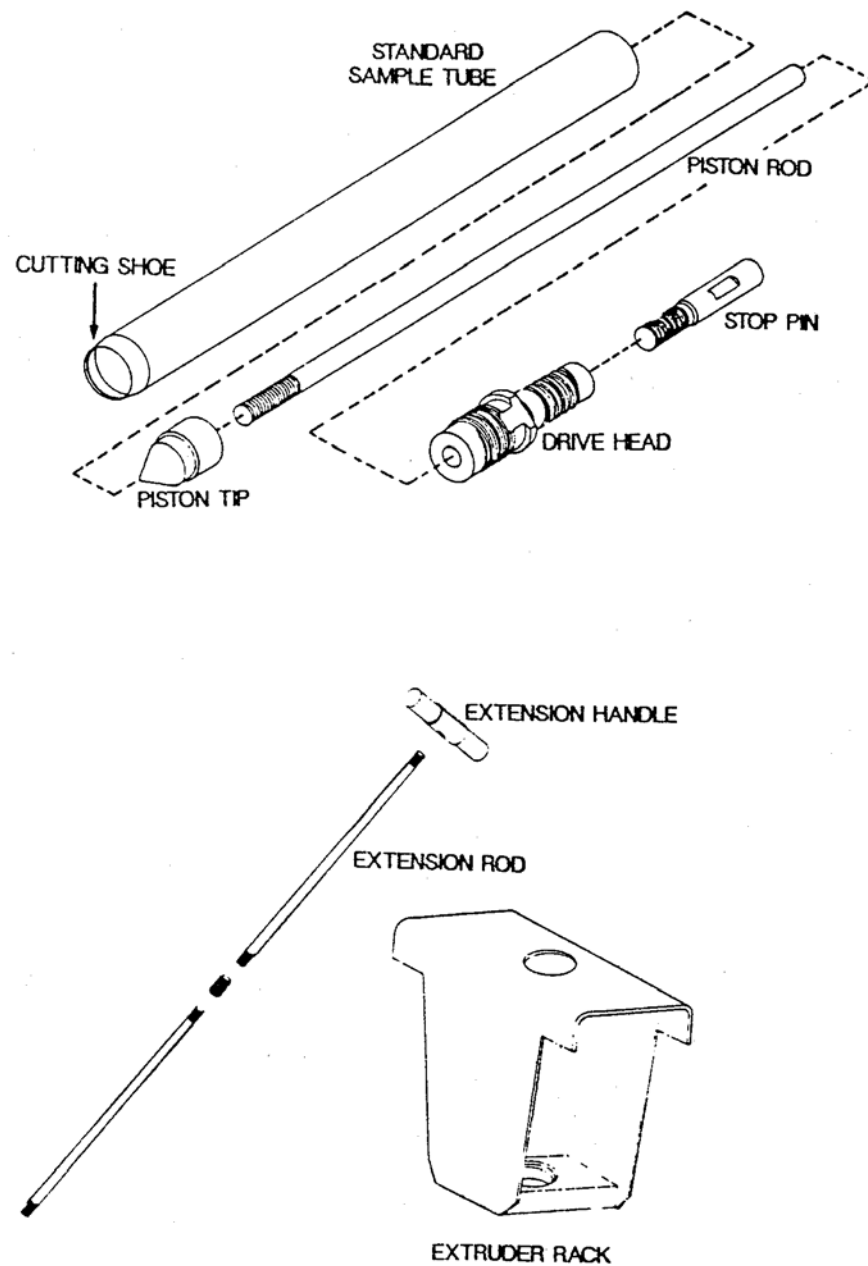
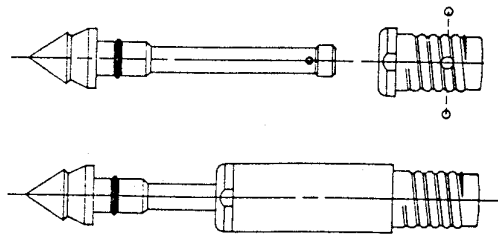
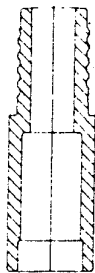


FIGURE 6

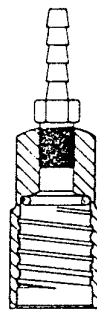
STANDARD SOIL GAS TOOLS



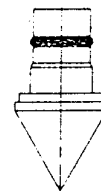
RETRACTABLE POINT HOLDER



EXPENDABLE POINT HOLDER



GAS SAMPLING CAP



EXPENDABLE POINT

FIGURE 7

POST-RUN TUBING (PRT) SYSTEM

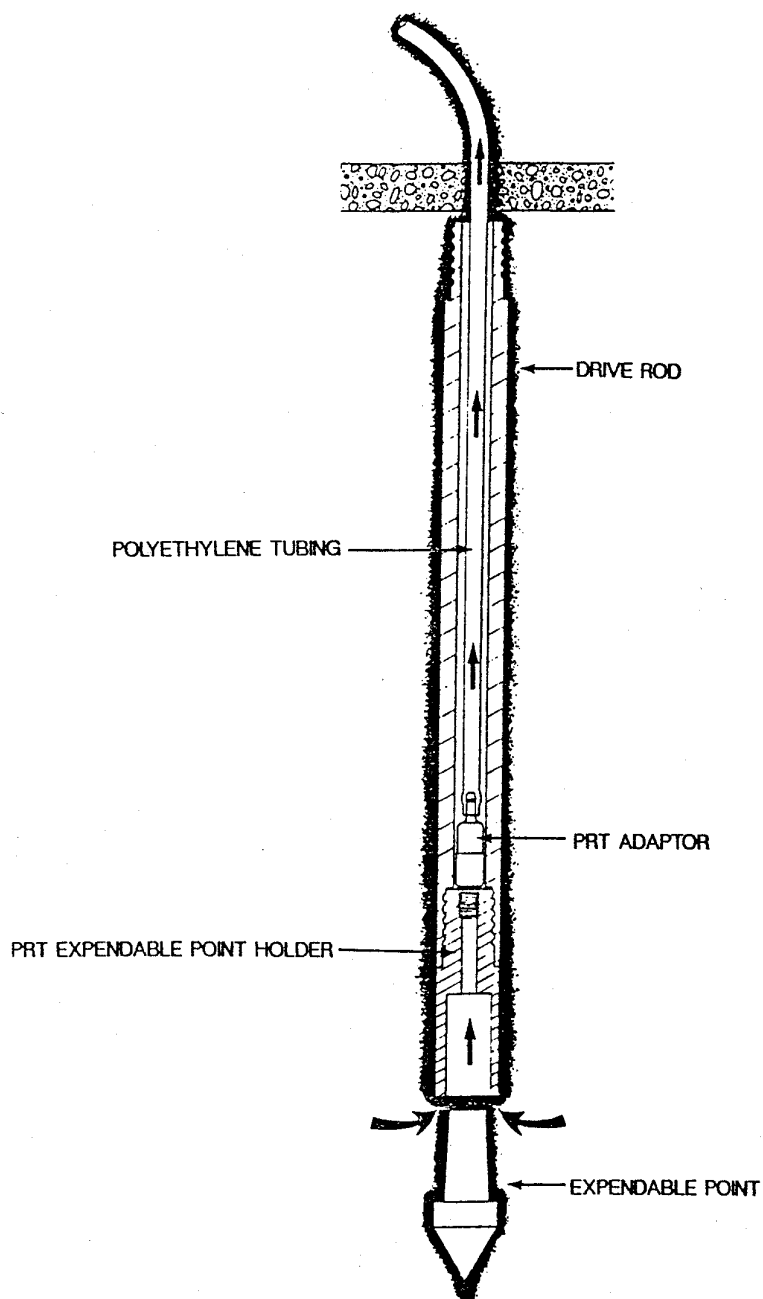
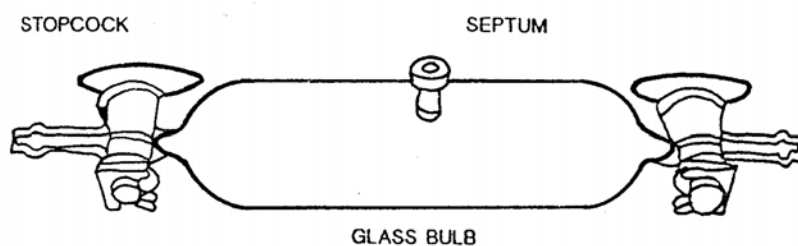


FIGURE 8

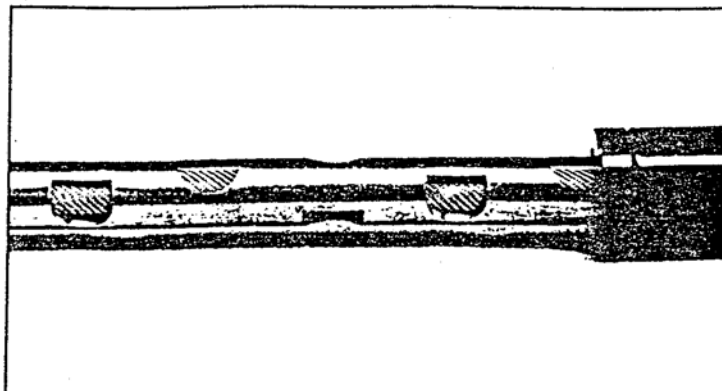
SOIL GAS SAMPLE CONTAINER



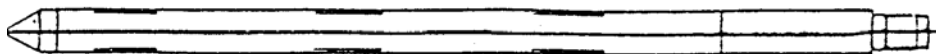
Note: Tedlar bags are also used for collection of soil gas samples; however, they are not shown on this figure.

FIGURE 9

GROUNDWATER SAMPLING TOOLS



SCREEN POINT SAMPLER IN OPEN POSITION



MILL-SLOTTED WELL POINT

FIGURE 10

PIEZOMETER INSTALLATION

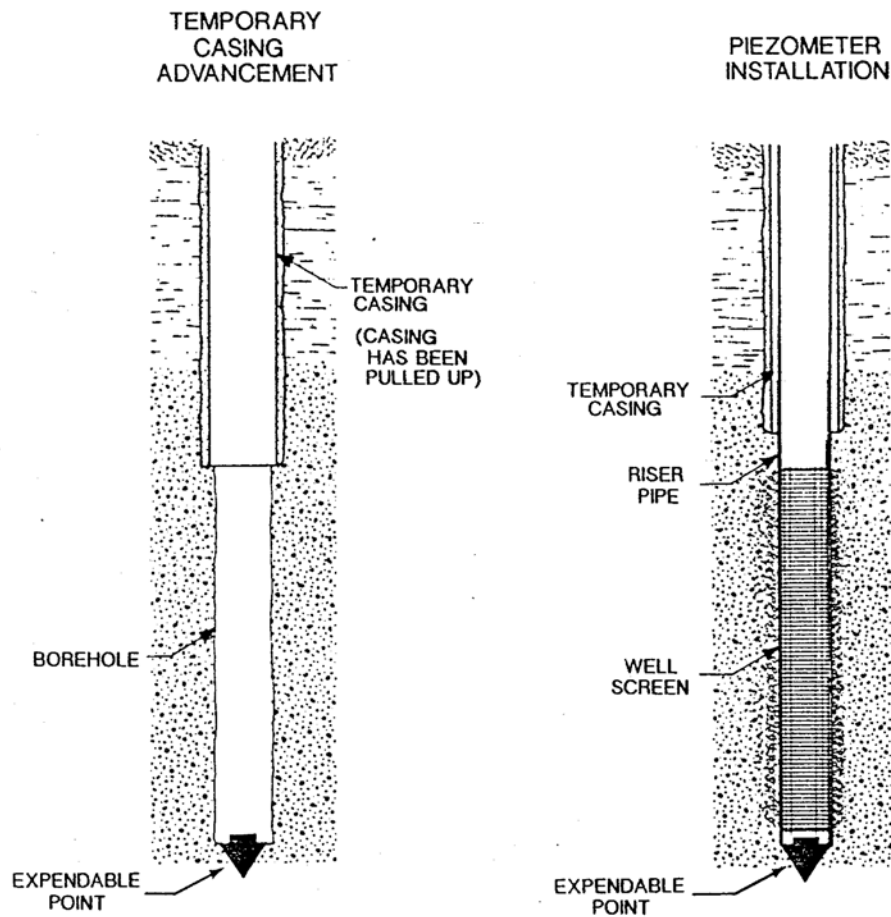
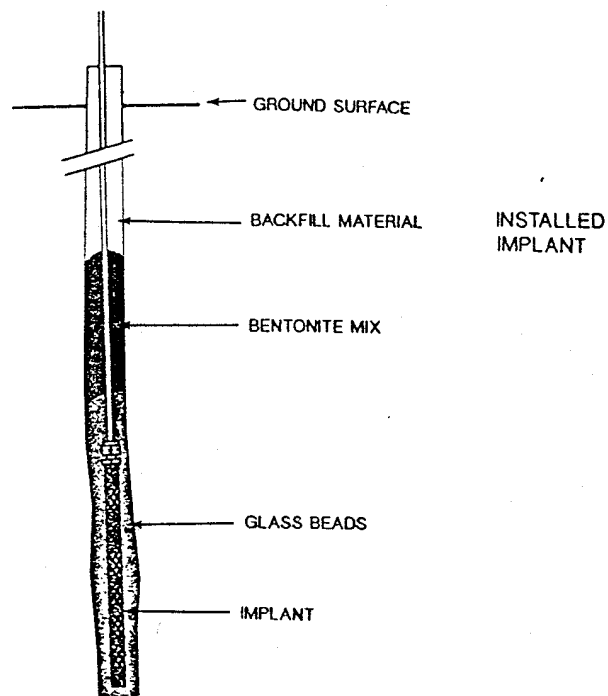
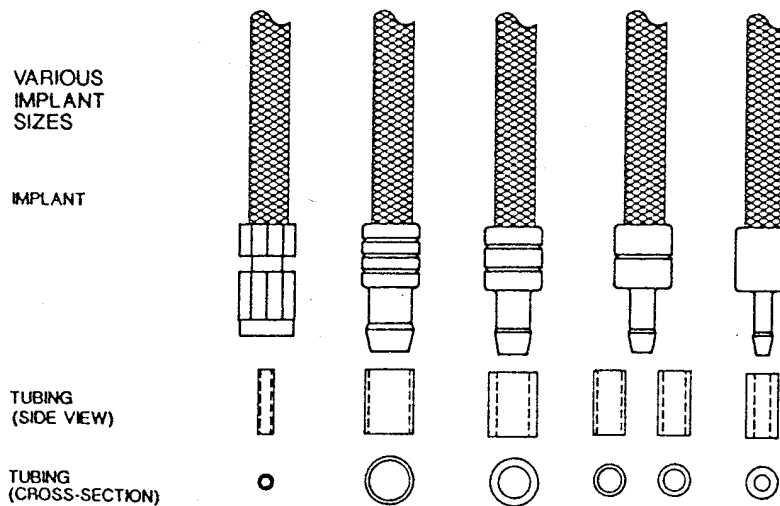


FIGURE 11

VAPOR SAMPLING IMPLANTS



SOP APPROVAL FORM

TETRA TECH EM INC.

ENVIRONMENTAL STANDARD OPERATING PROCEDURE

GENERAL EQUIPMENT DECONTAMINATION

SOP NO. 002

REVISION NO. 3

Last Reviewed: June 2009



Quality Assurance Approved

6-19-09

Date

1.0 BACKGROUND

All nondisposable field equipment must be decontaminated before and after each use at each sampling location to obtain representative samples and to reduce the possibility of cross-contamination.

1.1 PURPOSE

This standard operating procedure (SOP) establishes the requirements and procedures for decontaminating equipment in the field.

1.2 SCOPE

This SOP applies to decontaminating general nondisposable field equipment. To prevent contamination of samples, all sampling equipment must be thoroughly cleaned prior to each use.

1.3 DEFINITIONS

Alconox: Nonphosphate soap, obtained in powder detergent form and dissolved in water

Liquinox: Nonphosphate soap, obtained in liquid form for mixing with water

1.4 REFERENCES

U.S. Environmental Protection Agency (EPA). 1992a. “Guide to Management of Investigation-Derived Wastes.” Office of Solid Waste and Emergency Response. Washington D.C. EPA 9345.3-03FS. January.

EPA. 1992b. “RCRA Ground-Water Monitoring: Draft Technical Guidance.” Office of Solid Waste. Washington, DC. EPA/530-R-93-001. November.

EPA. 1994. “Sampling Equipment Decontamination.” Environmental Response Team SOP #2006 (Rev. #0.0, 08/11/94). <http://www.ert.org/mainContent.asp?section=Products&subsection=List>

1.5 REQUIREMENTS AND RESOURCES

The equipment required to conduct decontamination is as follows:

- Scrub brushes
- Large wash tubs or buckets
- Squirt bottles
- Alconox or Liquinox
- Tap water
- Distilled water
- Plastic sheeting
- Aluminum foil
- Methanol or hexane
- Isopropanol (pesticide grade)
- Dilute (0.1 N) nitric acid

2.0 PROCEDURE

The procedures below discuss decontamination of personal protective equipment (PPE), drilling and monitoring well installation equipment, borehole soil sampling equipment, water level measurement equipment, general sampling equipment, and groundwater sampling equipment.

2.1 PERSONAL PROTECTIVE EQUIPMENT DECONTAMINATION

Personnel working in the field are required to follow specific procedures for decontamination prior to leaving the work area so that contamination is not spread off site or to clean areas. All used disposable protective clothing, such as Tyvek coveralls, gloves, and booties, will be containerized for later disposal. Decontamination water will be containerized in 55-gallon drums (refer to Section 3.0).

Personnel decontamination procedures will be as follows:

1. Select an area removed from sampling locations that is both downwind and downgradient. Decontamination must not cause cross-contamination between sampling points.
2. Maintain the same level of personal protection as was used for sampling.

3. Wash neoprene boots (or neoprene boots with disposable booties) with Liquinox or Alconox solution and rinse with clean water. Remove booties and retain boots for subsequent reuse.
4. Wash outer gloves in Liquinox or Alconox solution and rinse in clean water. Remove outer gloves and place into plastic bag for disposal.
5. Remove Tyvek or coveralls. Containerize Tyvek for disposal and place coveralls in plastic bag for reuse.
6. Remove air purifying respirator (APR), if used, and place the spent filters into a plastic bag for disposal. Filters should be changed daily or sooner depending on use and application. Place respirator into a separate plastic bag after cleaning and disinfecting.
7. Remove disposable gloves and place them in plastic bag for disposal.
8. Thoroughly wash hands and face in clean water and soap.

2.2 DRILLING AND MONITORING WELL INSTALLATION EQUIPMENT DECONTAMINATION

All drilling equipment should be decontaminated at a designated location on site before drilling operations begin, between borings, and at completion of the project. Decontamination may be conducted on a temporary decontamination pad constructed at satellite locations within the site area in support of temporary work areas. The purpose of the decontamination pad is to contain wash waters and potentially contaminated soil generated during decontamination procedures. Decontamination pads may be constructed of concrete, wood, or plastic sheeting, depending on the site-specific needs and plans. Wash waters and contaminated soil generated during decontamination activities should be considered contaminated and thus, should be collected and containerized for proper disposal.

Monitoring well casing, screens, and fittings are assumed to be delivered to the site in a clean condition. However, they should be steam cleaned and placed on polyethylene sheeting on-site prior to placement downhole. The drilling subcontractor will typically furnish the steam cleaner and water.

The drilling auger, bits, drill pipe, any portion of drill rig that is over the borehole, temporary casing, surface casing, and other equipment used in or near the borehole should be decontaminated by the drilling subcontractor as follows:

1. Select an area removed from sampling locations that is both downwind and downgradient. Decontamination must not cause cross-contamination between sampling points.
2. Maintain the same level of personal protection as was used for sampling.
3. Remove loose soil using shovels, scrapers, wire brush, etc.
4. Steam clean or pressure wash to remove all visible dirt.
5. If equipment has directly or indirectly contacted contaminated media and is known or suspected of being contaminated with oil, grease, polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), or other hard to remove organic materials, rinse equipment with pesticide-grade isopropanol.
6. To the extent possible, allow components to air dry.
7. Wrap or cover equipment in clear plastic until it is time to be used.
8. All wastewater from decontamination procedures should be containerized.

2.3 BOREHOLE SOIL SAMPLING DOWNHOLE EQUIPMENT DECONTAMINATION

All soil sampling downhole equipment should be decontaminated before use and after each sample as follows:

1. Select an area removed from sampling locations that is both downwind and downgradient. Decontamination must not cause cross-contamination between sampling points.
2. Maintain the same level of personal protection as was used for sampling.
3. Prior to sampling, scrub the split-barrel sampler and sampling tools in a wash bucket or tub using a stiff, long bristle brush and Liquinox or Alconox solution.
4. After sampling, steam clean the sampling equipment over the rinsate tub and allow to air dry.
5. Place cleaned equipment in a clean area on plastic sheeting and wrap with aluminum foil.
6. Containerize all water and rinsate; disposable single-use sampling equipment should also be containerized.
7. Decontaminate all equipment placed down the hole as described for drilling equipment.

2.4 WATER LEVEL MEASUREMENT EQUIPMENT DECONTAMINATION

Field personnel should decontaminate the well sounder and interface probe before inserting and after removing them from each well. The following decontamination procedures should be used:

1. Select an area removed from sampling locations that is both downwind and downgradient. Decontamination must not cause cross-contamination between sampling points.
2. Maintain the same level of personal protection as was used for sampling.
3. Wipe the tape and probe with a disposable Alconox- or Liquinox-impregnated cloth or paper towel.
4. If immiscible layers are encountered, the interface probe may require steam cleaning or washing with pesticide-grade isopropanol.
5. Rinse with deionized water.

2.5 GENERAL SAMPLING EQUIPMENT DECONTAMINATION

All nondisposable sampling equipment should be decontaminated using the following procedures:

1. Select an area removed from sampling locations that is both downwind and downgradient. Decontamination must not cause cross-contamination between sampling points.
2. Maintain the same level of personal protection as was used for sampling.
3. To decontaminate a piece of equipment, use an Alconox wash; a tap water wash; a solvent (isopropanol, methanol, or hexane) rinse, if applicable, or dilute (0.1 N) nitric acid rinse, if applicable; a distilled water rinse; and air drying. Use a solvent (isopropanol, methanol, or hexane) rinse for grossly contaminated equipment (for example, equipment that is not readily cleaned by the Alconox wash). The dilute nitric acid rinse may be used if metals are the analyte of concern.
4. Place cleaned equipment in a clean area on plastic sheeting and wrap with aluminum foil.
5. Containerize all water and rinsate.

2.6 GROUNDWATER SAMPLING EQUIPMENT

The following procedures are to be employed for the decontamination of equipment used for groundwater sampling. Decontamination is not necessary when using disposable (single-use) pump tubing or bailers. Bailer and downhole pumps and tubing decontamination procedures are described in the following sections.

2.6.1 Bailers

1. Select an area removed from sampling locations that is both downwind and downgradient. Decontamination must not cause cross-contamination between sampling points.
2. Maintain the same level of personal protection as was used for sampling.
3. Evacuate any purge water in the bailer.
4. Scrub using soap and water and/or steam clean the outside of the bailer.
5. Insert the bailer into a clean container of soapy water. Thoroughly rinse the interior of the bailer with the soapy water. If possible, scrub the inside of the bailer with a scrub brush.
6. Remove the bailer from the container of soapy water.
7. Rinse the interior and exterior of the bailer using tap water.
8. If groundwater contains or is suspected to contain oil, grease, PAH, PCB, or other hard to remove organic materials, rinse equipment with pesticide-grade isopropanol.
9. Rinse the bailer interior and exterior with deionized water to rinse off the tap water and solvent residue, as applicable.
10. Drain residual deionized water to the extent possible.
11. Allow components to air dry.
12. Wrap the bailer in aluminum foil or a clean plastic bag for storage.
13. Containerize the decontamination wash waters for proper disposal.

2.6.2 Downhole Pumps and Tubing

1. Select an area removed from sampling locations that is both downwind and downgradient. Decontamination must not cause cross-contamination between sampling points.
2. Maintain the same level of personal protection as was used for sampling.
3. Evacuate any purge water in the pump and tubing.
4. Scrub using soap and water and/or steam clean the outside of the pump and, if applicable, the pump tubing.
5. Insert the pump and tubing into a clean container of soapy water. Pump/run a sufficient amount of soapy water to flush out any residual well water. After the pump and tubing are flushed, circulate soapy water through the pump and tubing to ensure that the internal components are thoroughly flushed.
6. Remove the pump and tubing from the container.
7. Rinse external pump components using tap water.
8. Insert the pump and tubing into a clean container of tap water. Pump/run a sufficient amount of tap water through the pump to evacuate all of the soapy water (until clear).
9. If groundwater contains or is suspected to contain oil, grease, PAH, PCB, or other hard to remove organic materials, rinse the pump and tubing with pesticide-grade isopropanol.
10. Rinse the pump and tubing with deionized water to flush out the tap water and solvent residue, as applicable.
11. Drain residual deionized water to the extent possible.
12. Allow components to air dry.
13. For submersible bladder pumps, disassemble the pump and wash the internal components with soap and water, rinse with tap water, isopropanol (if necessary), and deionized water, and allow to air dry.
14. Wrap pump and tubing in aluminum foil or a clean plastic bag for storage.
15. Containerize the decontamination wash waters for proper disposal.

3.0 INVESTIGATION-DERIVED WASTE

Investigation-derived waste (IDW) can include disposable single-use PPE and sampling equipment, soil cuttings, and decontamination wash waters and sediments. Requirements for waste storage may differ from one facility to the next. Facility-specific directions for waste storage will be provided in project-specific documents, or separate direction will be provided by the project manager. The following guidelines are provided for general use:

1. Assume that all IDW generated from decontamination activities contains the hazardous chemicals associated with the site unless there are analytical or other data to the contrary. Waste solution volumes could vary from a few gallons to several hundred gallons in cases where large equipment required cleaning.
2. Containerized waste rinse solutions are best stored in 55-gallon drums (or equivalent containers) that can be sealed until ultimate disposal at an approved facility.
3. Label IDW storage containers with the facility name and address, date, contents, company generating the waste, and an emergency contact name and phone number.
4. Temporarily store the IDW in a protected area that provides access to the containers and allows for spill/leak monitoring, sampling of containers, and removal following determination of the disposal method.

SOP APPROVAL FORM

TETRA TECH EM INC.

ENVIRONMENTAL STANDARD OPERATING PROCEDURE

**GROUNDWATER SAMPLE COLLECTION
USING LOW-FLOW SAMPLING METHODOLOGY**

SOP NO. 015

REVISION NO. 1

Last Reviewed: July 2009

K. Riesing

Quality Assurance Approved

July 28, 2009

Date

1.0 BACKGROUND

Groundwater sample collection is an integral part of site characterization at many contaminant release investigation sites. Often, a requirement of groundwater contaminant investigation is to evaluate contaminant concentrations in the aquifer. Since data quality objectives of most investigations require a laboratory setting for chemical analysis, samples must be collected from the aquifer and submitted to a laboratory for analysis. Therefore, sample collection and handling must be conducted in a manner that minimizes alteration of chemical characteristics of the groundwater.

In the past, most sample collection techniques followed federal and state guidance that included removal of water in the casing of a monitoring well (purging), followed by sample collection. The water in the casing was removed so that groundwater from the formation could flow into the casing and be available for sample collection. Sample collection was commonly completed with a bailer, bladder pump, controlled flow impeller pump, or peristaltic pump. Samples were preserved during collection. Often, samples to be analyzed for metals were filtered through a 0.45-micron filter prior to preservation and placement into the sample container.

Research conducted by several investigators has demonstrated that movement of contaminants while sorbed onto colloid particles constitutes a significant component of contaminant transport. Colloid mobility in an aquifer is a complex, aquifer-specific transport issue, and its description is beyond the scope of this standard operating procedure (SOP). However, concentrations of suspended colloids have been measured during steady-state conditions and during purging activities. Investigation results indicate standard purging procedures may cause a significant increase in suspended colloids, which in turn may bias analytical results.

Low-flow sample collection, sometimes referred to as micropurge, low-stress, or minimal drawdown groundwater sample collection, is a groundwater sampling method that minimizes increased colloid mobilization by removing water from a well at the screened interval at a rate that preserves or minimally disrupts steady-state flow conditions in the aquifer. During low-flow sampling, groundwater is discharged from the aquifer at a rate that the aquifer will yield without creating a cone of depression around the sampled well (i.e., a rate of discharge less than or equal to the rate of recharge). Research indicates that colloid mobilization will not increase above steady-state conditions during low-flow

**Title: Groundwater Sample Collection Using
Low-Flow Sampling Methodology**

**Revision No. 1, July 2009
Last Reviewed: July 2009**

discharge. Therefore, the sample collected by this method is more likely to represent steady-state groundwater chemistry.

1.1 PURPOSE

The purpose of this SOP is to describe the procedures to be used to collect a groundwater sample from a well using low-flow sampling methodology. The following sections describe the equipment to be used and the methods to be followed to promote uniform sample collection techniques. Sampling is to be conducted by field personnel who are experienced in sample collection and handling for environmental investigations.

1.2 SCOPE

This SOP applies to groundwater sampling using low-flow sampling methodology. It is intended to be used as an alternate SOP to SOP No. 010 (Groundwater Sampling), which provides guidance for the general aspects of groundwater sampling. This SOP provides procedures to be used for various methods of low-flow sample collection. The specific type of sampling pump to be used should be specified in the project-specific work plan or field sampling plan.

1.3 DEFINITIONS

Colloid: Suspended particles that range in diameter from 5 nanometers to 0.2 micrometers.

Dissolved oxygen: The ratio of the concentration or mass of oxygen in water relative to the partial pressure of gaseous oxygen above the liquid, which is a function of temperature, pressure, and the concentration of other solutes.

Flow-through cell: A device connected to the discharge line of a groundwater purge pump that allows regular or continuous measurement of selected parameters of the water and minimizes contact between the water and air.

pH: The negative base-10 log of the hydrogen-ion activity in moles per liter.

**Title: Groundwater Sample Collection Using
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Reduction and oxidation potential: A numerical index of the intensity of oxidizing or reducing conditions within a system, with the hydrogen-electrode potential serving as a reference point of zero volts.

Specific conductance: The reciprocal of the resistance in ohms measured between opposite faces of a centimeter cube of aqueous solution at a specified temperature.

Turbidity: A measurement of the suspended particles in a liquid that have the ability to reflect or refract part of the visible portion of the light spectrum.

1.4 REFERENCES

U.S. Environmental Protection Agency (EPA), Office of Research and Development. April 1996. *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures*. Publication: EPA/540/S-95/504. <http://www.epa.gov/ahaazvuc/download/issue/lwflw2a.pdf>

EPA, Office of Solid Waste and Emergency Response. May 2002. *Ground-Water Sampling Guidelines for Superfund and RCRA Project Managers*. Publication: EPA542-S-02-001. http://www.epa.gov/tio/tsp/download/gw_sampling_guide.pdf

1.5 REQUIREMENTS AND RESOURCES

The following equipment is required to complete low-flow groundwater sample collection:

- Water level indicator
- Adjustable flow rate pump (bladder, piston, peristaltic, or impeller)
- Power source for the pump (such as a battery or generator, or compressed air source)
- Discharge flow controller
- Flow-through cell
- pH probe
- Dissolved oxygen (DO) probe
- Turbidity meter
- Oxidation and reduction (Redox or Eh) probe

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- Specific conductance (SC) probe (optional)
- Temperature probe (optional)
- Meter to display data for the probes
- Calibration solutions for pH, SC, turbidity, and DO probes, as necessary
- Container of known volume for flow measurement or calibrated flow meter
- Data recording and management system

2.0 PROCEDURE

The following procedures and criteria were modified from EPA guidance titled *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures* (1996) and *Ground-Water Sampling Guidelines for Superfund and RCRA Project Managers* (2002). These references may be consulted for a more detailed description of low-flow sampling theory.

Low-flow groundwater sampling is most commonly accomplished with low discharge-rate pumps, such as bladder pumps, piston pumps, controlled velocity impeller pumps, or peristaltic pumps. Bailers and high-capacity submersible pumps are not considered acceptable low-flow sample collection devices. The purged water is monitored (in a flow-through cell or other constituent monitoring device) for chemical and optical parameters that indicate steady-state flow conditions between the sample extraction point and the aquifer. Samples are collected when steady-state conditions are indicated.

Groundwater discharge equipment may be permanently installed in the monitoring well as a dedicated system, or it can be installed in each well as needed. Most investigators agree that dedicated systems will provide the best opportunity for collecting samples most representative of steady-state aquifer conditions, but the scope and budget of a particular investigation will dictate equipment selection.

2.1 EQUIPMENT CALIBRATION

Prior to sample collection, the monitoring equipment used to measure pH, Eh, DO, turbidity, and SC should be calibrated or checked according to manufacturers' directions (see SOP No. 061 for more details regarding measurement of groundwater indicator parameters). Typically, calibration activities are completed at the field office at the beginning of sampling activities each day. The pH meter calibration

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should bracket the pH range of the wells to be sampled (acidic to neutral pH range [4.00 to 7.00] or neutral to basic pH range [7.00 to 10.00]). The DO meter should be calibrated to one point (air-saturated water) or two points (air-saturated water and water devoid of all oxygen).

The SC meter and turbidity meter cannot be calibrated in the field; they are checked against a known standard. The offset of the measured value of the calibration standard can be used as a correction value. Similarly, the Eh probe cannot be calibrated in the field, but is checked against a known standard, such as Zobell solution. The instrument should display a millivolt (mv) value that falls within the range set by the manufacturer. Because Eh is temperature dependent, the measured value should be corrected for site-specific variance from standard temperature (25 °C). The Eh probe should be replaced if the reading is not within the manufacturer's specified range. All calibration data should be recorded on the Low-Flow Groundwater Sampling Data Sheet (example included as Figure 1), on a personal digital assistant (PDA), or in a logbook.

2.2 WELL PURGING

The well to be sampled should be opened, and groundwater in the well allowed to equilibrate to atmospheric pressure. Equilibration should be determined by measuring depth to water below the marked reference on the wellhead (typically the top of the well casing) over two or more 5-minute intervals. Equilibrium conditions exist when the measured depth to water varies by less than 0.01 foot over two consecutive readings. Total depth of well measurement should be made following sample collection, unless the datum is required to place nondedicated sample collection equipment. Depth to water and total well depth measurements should be made in accordance with procedures outlined in SOP No. 014 (Static Water Level, Total Well Depth, and Immiscible Layer Measurement).

If the well does not have a dedicated sample collection device, a new or previously decontaminated portable sample collection device should be placed within the well. If nondedicated sampling equipment is used, the least contaminated wells should be purged and sampled first and most contaminated wells should be purged and sampled last (if past sampling data are available to make this determination). The intake of the device should be positioned at the midpoint of the well screen interval. The device should be installed slowly to minimize turbulence within the water in the casing and minimize mixing of stagnant water above the screened interval with water in the screened interval. Following installation, the flow controller should be connected to the sample collection device, and the flow-through cell connected

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to the outlet of the sample collection device. The calibrated groundwater chemistry monitoring probes should be installed in the flow-through cell. If a flow meter is used, it should be installed ahead of the flow-through cell.

If the well has a dedicated sample collection device, the controller for the sample collection device should be connected to the sample collection device. The flow meter and flow-through cell should be connected in line to the discharge tube, and the probes installed in the flow-through cell. Hook-up to the appropriate power source should be the last step prior to activating the pump to ensure all connections are completed prior to starting the pump.

The controller should be activated and groundwater extracted (purged) from the well. The purge rate should be monitored, and should not exceed the capacity of the well. The well capacity is defined as the maximum discharge rate that can be obtained with less than 0.1 meter (0.33 foot) drawdown. Typically, the discharge rate will be less than 0.5 liters per minute (L/min) (0.13 gallons per minute). The maximum purge rate should not exceed 1 L/min (0.25 gallons per minute), and should be adjusted to achieve minimal drawdown.

Water levels, effluent chemistry, and effluent flow rate should be continuously monitored while purging the well. Purging should continue until the measured chemical and optical parameters are stable. Stable parameters are defined as monitored chemistry values that do not fluctuate by more than the following ranges over three successive readings at 3- to 5-minute intervals:

- pH ± 0.1 unit
- SC ± 3 percent
- Eh ± 10 mv
- Turbidity ± 10 percent, when greater than 10 nephelometric turbidity units(NTU)
- DO ± 10 percent, or 0.3 milligrams per liter (mg/L)

Purging will continue until these stabilization criteria have been met or three well casing volumes have been purged. If three casing volumes of water have been purged and the stabilization criteria have not been met, a comment should be made on the data sheet that sample collection began after three well casing volumes were purged.

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The volume of water in the well is based on the following formula:

$$V = \pi r^2 h \times 7.48$$

where

- V = static volume of water in the well (gallons)
- r = inside radius of the well (feet)
- h = length of water in the well (total well depth minus depth to water) (feet)
- 7.48 = conversion factor (cubic feet to gallons)

Common well sizes and corresponding volumes are listed below.

- 1-inch well = $h \times 0.041$ gal/ft
- 2-inch well = $h \times 0.163$ gal/ft
- 3-inch well = $h \times 0.367$ gal/ft
- 4-inch well = $h \times 0.652$ gal/ft

If a stabilized drawdown in the well cannot be maintained within 0.33 feet and the water level is approaching the top of the screened interval, reduce the flow rate, or turn the pump off for 15 minutes, and allow for recovery. Under no circumstances should the well be pumped dry. Resume pumping at a lower flow rate; if the water draws down to the top of the screened interval again, turn pump off and allow for recovery. If two tubing volumes (including the volume of water in the pump and flow cell) have been removed during purging, then sampling can proceed next time the pump is turned on. This information should be noted in the field notebook or groundwater sampling log. Slow-recovering wells should be identified and purged at the beginning of the workday to maximize field work efficiency. If possible, samples should be collected from these wells within the same workday and no later than 24 hours after the end of purging.

The final pH, SC, Eh, turbidity, and DO values should be recorded. All data should be recorded on the Low-Flow Groundwater Sampling Data Sheet (Figure 1), a PDA, or in a logbook.

2.3 SAMPLE COLLECTION

Following purging, the flow-through cell shall be disconnected, and groundwater samples should be collected directly from the discharge line. Discharge rates should be adjusted so that groundwater is dispensed into the sample container with minimal aeration of the sample. Samples collected for volatile organic compound analysis should be dispensed into the sample container at a flow rate equal to or less than 100 milliliters per minute. Samples should be preserved and handled as described in the investigation field sampling plan or quality assurance project plan. Depending on the project-specific types of analyses required, the preferred order of sample collection is as follows:

1. Volatile organic compounds (VOC)
2. Purgeable organic halogens (POX)
3. Total organic halogens (TOX)
4. Cyanide
5. Extractable organics
6. Purgeable organic carbon (POC)
7. Total metals
8. Dissolved metals
9. Total organic carbon (TOC)
10. Phenols
11. Sulfate and chloride
12. Nitrate and ammonia
13. Radionuclides

See SOP No. 010 (Groundwater Sampling) for more information on groundwater sample collection.

SOP APPROVAL FORM

TETRA TECH EM INC.

ENVIRONMENTAL STANDARD OPERATING PROCEDURE

**FIELD MEASUREMENT OF GROUNDWATER
INDICATOR PARAMETERS**

SOP NO. 061

REVISION NO. 2

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Date

**Title: Field Measurement of Groundwater
Indicator Parameters**

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1.0 BACKGROUND

Various water quality monitoring systems can be used for determining groundwater indicator parameters in the field. Commonly measured field indicator parameters include pH, specific conductance, temperature, oxidation-reduction potential (ORP), dissolved oxygen (DO) and turbidity. Groundwater field measurements are typically collected in conjunction with groundwater sampling or monitoring well development (see SOPs 010, 015, and 021).

Various types of water quality systems exist including down-hole systems and flow through cells. Tetra Tech used several common water quality meters including various types of In-Situ, YSI, Hydac, and Horiba meters (see Figure 1 at the end of this SOP). The sampling team should select the type of meter or monitoring system based on site-specific conditions including data collection needs, the types of wells being sampled, and the sampling procedures used. Multiple parameter systems should be used when multiple field parameters are to be measured.

1.1 PURPOSE

This standard operating procedure (SOP) establishes the general requirements and procedures for using various water quality monitoring systems for determining groundwater pH, specific conductance, temperature, ORP, DO and turbidity in the field.

1.2 SCOPE

This SOP applies to general procedures for calibrating and operating water quality monitoring systems in the field. The project work plan or field sampling plan should identify the types of systems to be used and the actual project-specific field parameters to be measured. For each type of water quality system, the manufacturer's manual should be consulted for specific operating instructions.

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1.3 DEFINITIONS

Single Parameter System: A meter or monitoring system consisting of a single probe designed to measure a single indicator parameter.

Multiple Parameter System: A meter or monitoring system consisting of multiple probes capable of measuring multiple indicator parameters.

Open Container Measurements: Field measurements performed in an open container such as a cup, a jar, or a bucket where an air/water interface exists.

Flow-Through Chamber or Cell: A plastic cell or chamber connected to the sample pump discharge tubing so that a continuous flow of water passes across the probes. Additional tubing is used to route water from the flow-through cell to a waste container or final discharge point.

Down-Hole Monitoring System: A meter or monitoring system where probes are submerged by inserting them into the well. The probes are attached to the meter (located at the well head or ground surface) by one or more cables.

pH: A measure of the acidity or alkalinity of a solution. The pH scale ranges from 0 to 14 with strongly acidic solutions at the low end, strongly basic solutions at the high end, and “pure” or neutral water at 7. Field measurements of pH are recorded in standard units.

Specific Conductance: The ability of a solution to conduct electricity; a measure of the solution’s ionic activity and content. The higher the concentration of ionic (dissolved) constituents, the higher the conductivity. Conductivity of the same water changes substantially with temperature. Specific conductivity is generally found to be a good measure of the concentration of total dissolved solids (TDS) and salinity. Conductivity is measured by placing two electrodes (with opposite electrical charge) in the water. For a known electrical current, the voltage drop across the electrodes reveals the solution’s resistance. Since the resistance of aqueous solution changes with temperature (resistance drops with increasing temperature), the resistance is corrected to the resistance of the solution at 25 °C. Field measurements are recorded in units of microsiemens per centimeters (µS/cm).

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Temperature: The degree of hotness or coldness of the solution being measured. Field measurements are typically recorded in degrees Celsius (°C).

ORP: ORP, or redox potential, is the tendency of a chemical species to acquire electrons and be reduced. In aqueous solutions, the reduction potential is the tendency of the solution to either gain or lose electrons when new chemical species are introduced. A solution with a higher (more positive) reduction potential than the new species will have a tendency to gain electrons from the new species (to be reduced by oxidizing the new species) and a solution with a lower (more negative) reduction potential will have a tendency to lose electrons to the new species (to be oxidized by reducing the new species). Just as the transfer of hydrogen ions between chemical species determines the pH of an aqueous solution, the transfer of electrons between chemical species determines the reduction potential of an aqueous solution. Like pH, the reduction potential represents an intensity factor. It does not characterize the capacity of the system for oxidation or reduction, in much the same way that pH does not characterize the buffering capacity. Field measurements are typically recorded in millivolts (mV).

DO: Dissolved oxygen (or oxygen saturation) is a relative measure of the amount of oxygen dissolved or carried in a given medium. In aquatic environments, dissolved oxygen is a relative measure of the amount of oxygen (O₂) dissolved in the water. Field measurements are typically recorded in milligrams per liter (mg/L).

Turbidity: Turbidity is the cloudiness or haziness of a fluid caused by individual particles (suspended solids). Fluids can contain suspended solid matter consisting of particles of many different sizes. While some suspended material will be large enough and heavy enough to settle rapidly to the bottom of the container if a liquid sample is left to stand, very small particles will settle only very slowly or not at all if the sample is regularly agitated or the particles are colloidal. These small solid particles cause the liquid to appear turbid. Field measurements are typically recorded in Nephelometric Turbidity Units (NTU).

1.4 REFERENCE

Essential Handbook of Ground-Water Sampling by Gillian Nielsen, 2007.

Tetra Tech EM Inc. July 2009. SOPs 010, 015, and 021

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1.5 REQUIREMENTS AND RESOURCES

The following items are typically required to measure groundwater pH, specific conductance, temperature, ORP, DO, and turbidity using this SOP:

- Single or multiple parameter water quality measuring system
- Specific conductance calibration solutions
- Buffer solutions of pH 4, 7, and 10 for pH calibration
- Distilled or deionized water
- Rinse bottle
- 50-milliliter (mL) sample cups or beakers
- Sample tubing and connectors (specific to each type of system)
- Waste container to collect purge water
- Logbook or field data sheets

2.0 PROCEDURES

The procedures outlined in this SOP are general and may apply to various types of water quality monitoring systems to measure groundwater pH, specific conductance, temperature, ORP, DO and turbidity in the field. General procedures for testing and calibrating the monitoring systems are presented first, followed by procedures for using the instruments and making field measurements. Each particular monitoring system should be identified in the project work plan or field sampling plan and should be operated in accordance with the manufacturer's instruction manual.

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2.1 TESTING AND CALIBRATION PROCEDURES

Each field meter or monitoring system should be calibrated according to manufacturer's specifications. In general, equipment should be thoroughly cleaned then calibrated and tested before the start-up of sampling at each site. Equipment should be calibrated and tested using manufacturer provided solutions and standards. Care should be taken to rinse the probes between testing and calibration to prevent cross contaminating solutions. Solutions should be poured from the manufacturer's container into another container to prevent compromising the entire solution provided by the manufacturer. Calibration and testing of field equipment should be documented each time it is performed in field logbooks (or field data sheets, if applicable). If testing and calibration measurements are out of tolerance, the instrument must be serviced or repaired.

2.2 FIELD MEASUREMENT PROCEDURES

Each field meter or monitoring system should be operated according to manufacturer's specifications. The actual field procedures will vary depending on the type of monitoring system being used (open container systems, flow-through cell systems, or down-hole systems) and the types of field parameters being measured. In addition, most systems include a data logging option. A description of open container, flow-through cell, and down-hole measurement processes are discussed below, followed by a general procedural summary and a summary of common errors associated with field measurements of indicator parameters.

2.2.1 Open Container Measurements

Open container measurements consist of collecting groundwater and placing it in a cup or container for field measurements using a hand held system. This method of field measurements is commonly used when bailing wells, but can also be used when pumping wells. Prior to field measurements, the equipment must be cleaned and calibrated following manufacturer's specifications. Field measurements should then be made at the frequency and for the indicator parameters specified in the project work plan or field sampling plan. To make open container field measurements, samplers collect groundwater from the well and place in a cup or container large enough to adequately submerge the probe or probes, as specified in the manufacturer's operations manual. For open containers, measurements should be taken in the following order: temperature, specific conductance, pH, and turbidity. Open container systems are not recommended for low-flow sampling as flow-through systems are more appropriate. The probes and

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cup or container should be thoroughly rinsed after each field measurement and between sampling locations.

2.2.2 Flow-Through Cell Measurements

Flow-through cell systems consist of measuring groundwater parameters as a continuous flow of water passes across the probes through a cell or chamber, and is primarily used when pumping wells and using low-flow sampling procedures. Prior to field measurements, the equipment must be cleaned and calibrated following manufacturer's specifications. Field measurements should then be made at the frequency and for the indicator parameters specified in the project work plan or field sampling plan.

The flow-through cell or chamber is placed "in line" between the discharge tubing of the pump and the container used to collect purged water. The outlet from the pump must be connected to the sample chamber input. The sample chamber outlet must then be connected or routed to a waste container (or to another designated discharge point). Tubing, fittings, and adaptors are generally required and may be provided by the manufacturer. Pump discharge tubing and chamber inlets and outlets are typically 1/2 or 3/8 inch diameter.

After the cell or chamber is connected to the pump discharge tubing and waste collection container, the sensors should be inserted into the sensor mounting plate in their respective ports. Any unused sensor ports must have plugs installed to close off the sample chamber. The probe cables are then connected to the meter following manufacturer's specifications.

With the system connected, the sampler should turn on the pump according to the manufacturer's instructions and then turn on the water quality monitor. Before recording any values, the sample chamber should be full, all air should be voided, and all of the displayed values should be stable. The probes and sample chamber should be thoroughly rinsed between sampling locations.

2.2.3 Down-Hole Measurements

Down-hole measurement systems consist of inserting the probes (or a multi-parameter sensor housing) inside a well to obtain field measurements, and is primarily used when pumping wells. Prior to field measurements, the equipment must be cleaned and calibrated following manufacturer's specifications.

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Field measurements should then be made at the frequency and for the indicator parameters specified in the project work plan or field sampling plan.

The probes or sensor are attached to a hand held meter or control unit by a cable and lowered inside the well to be sampled. Limiting factors when using down-hole systems include probe or sensor diameters and available cable lengths. The probes should be thoroughly decontaminated between sampling locations...

2.2.4 General Procedures for Field Measurements of Indicator Parameters

The following section discusses general procedures that typically apply to making field measurements of indicator parameters using various types of field instruments. Each particular type of meter or monitoring system should be identified in the project work plan or field sampling plan and should be operated in accordance with the manufacturer's instruction manual.

1. Inspect the instrument and batteries prior to the field effort.
2. Check the integrity of the buffer solutions used for field calibration since frequent replacement is necessary as a result of degradation upon exposure to the atmosphere.
3. If applicable, make sure all electrolyte solutions within the electrode(s) are at proper levels and no air bubbles are present within the electrode(s).
4. Calibrate the meter and electrode(s) on a daily use basis (or as recommended) following manufacturer's instructions and record data in field logbook or on field data sheets.
5. Immerse the electrode(s) in the sample. Stabilization may take several seconds to several minutes. If the parameter values continues to drift, the sample temperature may not be stable, a physical reaction (e.g., degassing) may be occurring in the sample, or the meter or electrode may be malfunctioning. The failure of the measurements to stabilize should be clearly noted in the logbook or field data sheet. For DO, provide for sufficient flow past the membrane by gently stirring the sample. Probes without stirrers placed in wells (down-hole measurements) may be gently moved up and down to achieve the required mixing.
6. Read and record the value of each parameter being measured making sure units of measure are clearly recorded.
7. Rinse the electrode(s) with deionized water.
8. Store the electrode(s) in accordance with manufacturer's instructions

2.2.5 Common Errors or Problems Associated With Field Measurements

The project work plan or field sampling plan should clearly identify the types of parameters to be measured, the measurement frequency, and “stabilization” requirements. It is essential to ensure that the type of monitoring system selected is compatible with the monitoring well sampling or development methods to be utilized. Some common errors to avoid are identified below:

- No, or incorrect equipment calibration
- Incorrect or expired calibration standards
- Poor equipment maintenance
- Inadequate training or unfamiliarity with equipment
- No record of units of measure and “+” or “-“ values for ORP
- Too much time taken to measure temperature sensitive parameters
- DO and ORP measured in closed systems (flow-through cell or down-hole) instead of closed cell systems

FIGURE 1

**THE HORIBA U-10 WATER QUALITY MONITORING SYSTEM
THE IN-SITU TROLL 9500 LOW-FLOW SYSTEM
THE YSI HAND HELD 556 METER**



Horiba U-10



In-Situ Troll



YSI 556

SOP APPROVAL FORM

TETRA TECH EM INC.

ENVIRONMENTAL STANDARD OPERATING PROCEDURE

**STATIC WATER LEVEL, TOTAL WELL DEPTH,
AND IMMISCIBLE LAYER MEASUREMENT**

SOP NO. 014

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K. Miesing

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**Title: Static Water Level, Total Well Depth, and
Immiscible Layer Measurement**

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1.0 BACKGROUND

Measurement of static water level, total well depth, and any immiscible layers is necessary before a well can be sampled and groundwater flow direction can be determined. If an immiscible layer is present, its depth and thickness must be determined. In addition, the static water level and total depth of a monitoring well are often needed to determine a purging volume prior to sampling.

1.1 PURPOSE

This standard operating procedure (SOP) provides guidelines for field personnel measuring: (a) static water levels, (b) total water depths, and (c) immiscible layers in monitoring wells or piezometers.

1.2 SCOPE

This SOP describes the methodologies for measuring static water level, total well depth, and immiscible layer depth and thickness.

1.3 DEFINITIONS

Electrical Water Level Meter: An electrical probe used to determine the depth to fluid. The probe has a light or sound alarm connected to an open circuit. The circuit is closed and the alarm is activated when the probe contacts a conducting fluid such as water.

Immiscible Layer: A liquid phase that cannot be uniformly mixed or blended with water. Heavy immiscible phases or dense nonaqueous-phase liquids (DNAPL) sink in water; light immiscible phases or light nonaqueous-phase liquids (LNAPL) float on water.

Interface Probe: An electrical probe used to determine the presence and thicknesses of LNAPL or DNAPL in the water column of a monitoring well.

Ionization Detector: A photoionization detector (PID) or a flame ionization detector (FID) is used to measure the level of volatile organic compounds (VOC) in the gaseous phase. Ionization detectors are generally not compound-specific and thus measure only total volatile organic compounds. A PID generally cannot detect as complete a range of compounds as the FID. This difference is the result of the relative ionization energies of the two detectors. Most PIDs cannot detect methane, but FIDs can. The

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Photovac and Minirae are examples of PIDs; the Foxboro organic vapor analyzer (OVA) is an example of an FID.

Static Water Level: The level of water in a monitoring well or piezometer left open and allowed to stabilize by equilibrating to existing atmospheric pressure prior to measuring. The static water level can be measured as the depth to water or as the elevation of water relative to a reference mark or datum.

Total Well Depth: The distance from the ground surface to the bottom of a monitoring well or piezometer

1.4 REFERENCES

Tetra Tech EM Inc. 2009. SOP No. 002, General Equipment Decontamination

U.S. Environmental Protection Agency (USEPA). 2007. "Groundwater Level and Well Depth Measurement." Region 4, Field Branches Quality System and Technical Procedures. November 1. <http://www.epa.gov/region4/sesd/fbqstp/Groundwater-Level-Measurement.pdf>

U.S. EPA. 2000. "Manual Water Level Measurement." Environmental Response Team. SOP #2043 (Rev. #0.0, 02/11/00). <http://www.dem.ri.gov/pubs/sops/wmsr2043.pdf>

1.5 REQUIREMENTS AND RESOURCES

The equipment required for measuring static water levels, total well depths, and immiscible layers is as follows:

- Electrical water level meter
- Interface probe
- PID or FID
- Decontamination supplies (wash and rinse solutions, buckets, paper towels, etc.)
- Keys or wrenches for well locks and well caps
- Light source such as a flashlight or mirror to inspect inside well vaults

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- Appropriate level of personal protective equipment (PPE) as specified in the site-specific health and safety plan
- Appropriate signage and traffic control to protect personnel during monitoring activities

2.0 PROCEDURES

This section provides general guidance followed by specific procedures for measurement of static water level, total well depth, and immiscible layer.

Procedures for measuring the depth to water and the depth to the bottom of a monitoring well should be identified in the planning stage of field work. Also at this stage, measuring devices should be chosen, and an individual should be assigned to take and record measurements.

All measurement instruments should be decontaminated before and after use and between measurement locations. Refer to SOP No. 002, General Equipment Decontamination. In addition, as a general rule wells with the lowest known contaminant concentrations should be measured first followed by progressively more contaminated wells. This technique helps avoid cross-contamination from a more contaminated water source to a less contaminated water source resulting in inaccurate or false sample analytic results.

Before initiating any measuring activities, the ambient air at a monitoring well head should be monitored for possible emissions of VOCs using a PID or an FID. The site-specific health and safety plan for on-site activities should provide action levels and the rationale for selection of the appropriate ionization detector.

The sampling team should wear appropriate respiratory protection equipment when necessary. The sampling team should approach wells from the upwind side and systematically survey the inside of the well casing, the area from the casing to the ground, the area from above the well casing to the breathing zone, and the area around the well for VOCs. VOC monitoring for comparison to action levels should occur in the breathing zone(s) rather than from within the well casing. If PID or FID readings of VOCs are above action levels, the sampling team should retreat to a safe area and determine if engineering controls, increased PPE, or both are necessary to reduce exposure to VOCs above action levels listed in the site-specific health and safety plan.

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Sampling team should be careful when opening a well to check for insects or reptiles within the protective casing and use appropriate work gloves when reaching inside. The site-specific health and safety plan should be consulted for information on insects or reptiles that may be present in the project area.

2.1 STATIC WATER LEVEL MEASUREMENT

An electric water level meter is typically used to measure static water levels. The electrical probe of the meter is lowered into the monitoring well until the light or sound alarm is activated indicating the probe has touched the water surface. To ensure accuracy, the well or piezometer should be opened to allow groundwater in the well to equilibrate with atmospheric pressures before measuring depth to water. Ideally, static groundwater measurements will be collected prior to purging or sampling activities. The static water level is read directly from the graduated tape on the meter to the nearest 0.01-foot. Two to three measurements should be taken over several minutes to ensure water levels are not fluctuating. If water levels continue to fluctuate, the groundwater has not equilibrated or become static. Measurements should continue until static water levels readings are obtained before recording a final measurement. If the monitoring well top is not flush with the ground surface, the distance between the static water level and the top of the riser pipe should be measured; the height of the riser pipe above ground surface should then be subtracted from the first measurement to determine the depth to static water below ground surface. Surveyed elevations should be used if available to establish the water level elevation. The well number, measurement date and time, and individual readings should be recorded in a field logbook.

2.2 TOTAL WELL DEPTH MEASUREMENT

Total well depth can also be measured using an electric water level meter. The electrical probe of the indicator is lowered into the monitoring well until resistance is met, indicating that the probe has reached the bottom of the well. During measurement, the probe should be positioned in the well so that resistance is met, but there is no slack in the measuring tape. The total well depth is read directly from the graduated tape on the indicator to the nearest 0.01-foot. Measurements become less accurate with increased depth as the length of measuring tape deployed increases and the distance under the water column increases making it more difficult to determine if the bottom of the well has reached. In this circumstance, a weighted water level meter or measuring tape may be necessary to allow the user to “feel” the bottom of the well. Care should be taken to ensure the use of only inert and chemical-free weighted devices such as stainless steel are used. If the monitoring well top is not flush with the ground surface,

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the distance between the bottom of the well and the top of the riser pipe should be measured; the height of the riser pipe above ground surface should then be subtracted from the first measurement to determine the depth from ground surface to the bottom of the well. The well number, measurement date and time, and individual readings should be recorded in a field logbook.

2.3 IMMISCIBLE LAYER DETECTION AND MEASUREMENT

A LNAPL immiscible layer in a monitoring well can be detected by slowly lowering an interface probe to the surface of the water in the well. When the audible alarm sounds, the depth of the probe should be recorded. If the alarm is continuous, a light immiscible layer has been detected. To measure the thickness of this layer, the probe should then be slowly lowered until the alarm changes to an oscillating signal. The oscillating alarm indicates that the probe has reached a water layer. The probe depth at the time the alarm begins oscillating should be recorded as the depth to water. The thickness of the light immiscible layer should then be determined by subtracting the depth at which a continuous alarm occurred from the depth at which the alarm began to oscillate. The well number, measurement date and time, individual readings for depth and thickness, and average values for depth and thickness should be recorded in a field logbook.

To determine whether a DNAPL immiscible layer is present, the interface probe is lowered into the monitoring well and allowed to slowly drop below the water causing an oscillating alarm. If the alarm changes from an oscillating to a continuous signal, a heavier immiscible layer has been detected, and the probe depth should be recorded at that point. Total well depth obtained in Section 2.2 should be used for calculating the thickness of the DNAPL layer within the well casing. The DNAPL layer is then calculated by subtracting the depth at which the alarm became continuous from the total well depth. This procedure provides an estimate of the thickness of the DNAPL layer in the monitoring well. The well number, measurement date and time, and individual readings for depth and thickness should be recorded in a field logbook.

SOP APPROVAL FORM

TETRA TECH EM INC.

ENVIRONMENTAL STANDARD OPERATING PROCEDURE

RECORDING OF NOTES IN FIELD LOGBOOK

SOP NO. 024

REVISION NO. 1
May 18, 1993

Last Reviewed: December 2008



Quality Assurance Approved

December 5, 2008

Date

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Title: Recording of Notes in Field Logbook	Revision No. 1, May 18, 1993 Last Reviewed: December 2008

1.0 BACKGROUND

The field logbook should contain detailed records of all the field activities, interviews of people, and observations of conditions at a site. Entries should be described in as much detail as possible so that personnel can accurately reconstruct, after the fact, activities and events during their performance of field assignments. Field logbooks are considered accountable documents in enforcement proceedings and may be subject to review. Therefore, the entries in the logbook must be accurate and detailed; and they must reflect the importance of the field events.

1.1 PURPOSE

The purpose of this standard operating procedure (SOP) is to provide guidance to ensure that logbook documentation for any field activity is correct, complete, and adequate. Logbooks are used for identifying, locating, labeling, and tracking samples. A logbook should document any deviations from the project approach, work plans, quality assurance project plans, health and safety plans, sampling plans, and any changes in project personnel. They also serve as documentation of any photographs taken during the course of the project. In addition, the data recorded in the logbook may assist in the interpretation of analytical results. A complete and accurate logbook also aids in maintaining good quality control. Quality control is enhanced by proper documentation of all observations, activities, and decisions.

1.2 SCOPE

This SOP establishes the general requirements and procedures for recording notes in the field logbook.

1.3 DEFINITIONS

None

1.4 REFERENCES

Compton, R.R. 1985. *Geology in the Field*. John Wiley and Sons. New York, N.Y.

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1.5 REQUIREMENTS AND RESOURCES

The following items are required for field notation:

- Field logbooks
- Ballpoint pens with permanent ink
- 6-inch ruler (optional)

Field logbooks should be bound (sewn) with water-resistant and acid-proof covers; they should have preprinted lines and wide columns. They should be approximately 7 1/2 by 4 1/2 inches or 8 1/2 by 11 inches in size. Loose-leaf sheets are not acceptable for field notes. If notes are written on loose paper, they must be transcribed as soon as possible into a regular field logbook by the same person who recorded the notes.

Logbooks can be obtained from an individual's office supply room or directly from outside suppliers. Logbooks must meet the requirements specified in this SOP and should include preprinted pages that are consecutively numbered. If the numbers must be written by hand, the numbers should be circled so that they are not confused with data.

2.0 PROCEDURES

The following subsections provide general guidelines and formatting requirements for field logbooks, and detailed procedures for completing field logbooks.

2.1 GENERAL GUIDELINES

- A separate field logbook must be maintained for each project. If a site consists of multiple subsites, designate a separate logbook for each subsite. For special tasks, such as periodic well water-level measurements, data from multiple subsites may be entered into one logbook that contains only one type of information.
- All logbooks must be bound and contain consecutively numbered pages.
- No pages can be removed from the logbook for any purpose.

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- All field activities, meetings, photographs, and names of personnel must be recorded in the site logbook.
- Each logbook pertaining to a site or subsite should be assigned a serial number based on the date the logbook is issued to the project manager. The first issued logbook should be assigned number 1, the next issued logbook assigned number 2, and so on. The project manager is to maintain a record of all logbooks issued under the project.
- All information must be entered with a ballpoint pen with waterproof ink. Do not use pens with “wet ink,” because the ink may wash out if the paper gets wet. Pencils are not permissible for field notes because information can be erased. The entries should be written dark enough so that the logbook can be easily photocopied.
- Do not enter information in the logbook that is not related to the project. The language used in the logbook should be factual and objective.
- Begin a new page for each day’s notes.
- Write notes on every line of the logbook. If a subject changes and an additional blank space is necessary to make the new subject title stand out, skip one line before beginning the new subject. Do not skip any pages or parts of pages unless a day’s activity ends in the middle of a page.
- Draw a diagonal line on any blank spaces of four lines or more to prevent unauthorized entries.

2.2 LOGBOOK FORMAT

The layout and organization of each field logbook should be consistent with other field logbooks. Guidelines for the cover, spine, and internal pagination are discussed below.

2.2.1 FORMAT OF FIELD LOGBOOK COVER AND SPINE

Write the following information in clear capital letters on the front cover of each logbook using a Sharpie® or similar type permanent ink marker:

- Logbook identification number
- The serial number of the logbook (assigned by the project manager)
- Name of the site, city, and state
- Name of subsite if applicable
- Type of activity

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- Beginning and ending dates of activities entered into the logbook
- “Tetra Tech EM Inc.” City and State
- “REWARD IF FOUND”

Some of the information listed above, such as the list of activities and ending dates, should be entered after the entire logbook has been filled or after decision that the remaining blank pages in the logbook will not be filled.

The spine of the logbook should contain an abbreviated version of the information on the cover: for example, “1, Col. Ave., Hastings, 5/88 - 8/88.”

2.2.2 First Page of the Field Logbook

Spaces are usually provided on the inside front cover (or the opening page in some logbooks), for the company name (“Tetra Tech EM Inc.”), address, contact name, and telephone number. If preprinted spaces for this information are not provided in the logbook, write the information on the first available page.

2.3 ENTERING INFORMATION IN THE LOGBOOK

Enter the following information at the beginning of each day or whenever warranted during the course of a day:

- Date
- Starting time
- Specific location
- General weather conditions and approximate temperature
- Names of personnel present at the site. Note the affiliation(s) and designation(s) of all personnel
- Equipment calibration and equipment models used.
- Changes in instructions or activities at the site
- Levels of personal protective clothing and equipment

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- A general title of the first task undertaken (for example, well installation at MW-11, decon at borehole BH-11, groundwater sampling at MW-11)
- Approximate scale for all diagrams. If this can't be done, write "not to scale" on the diagram. Indicate the north direction on all maps and cross-sections. Label features on each diagram.
- Corrections, if necessary, necessarily including a single line through the entry being corrected. Initial and date any corrections made in the logbook.
- After last entry on each page, initials of the person recording notes. No information is to be entered in the area following these initials.
- At the end of the day, signature of the person recording notes and date at the bottom of the last page. Indicate the end of the work day by writing "Left site at (time)." A diagonal line must be drawn across any remaining blank space at the bottom of this last page.

The following information should be recorded in the logbook after taking a photograph:

- Time, date, location, direction, and, if appropriate, weather conditions
- Description of the subject photographed and the reason for taking the picture
- Sequential number of the photograph and the film roll number or disposable camera used (if applicable)
- Name of the photographer.

The following information should be entered into the logbook when collecting samples:

- Location description
- Name(s) of sampler(s)
- Collection time
- Designation of sample as a grab or composite sample
- Type of sample (water, sediment, soil gas, etc.)
- On-site measurement data (pH, temperature, specific conductivity)
- Field observations (odors, colors, weather, etc.)
- Preliminary sample description
- Type of preservative used
- Instrument readings.

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If pre-printed field data forms are available (forms such as the micropurge field data collection form), data should be entered on these pre-printed forms rather than into field logbooks. Note in the logbook that the field data are recorded on separate forms.

2.4 PRECAUTIONS

Custody of field logbooks must be maintained at all times. Field personnel must keep the logbooks in a secure place (locked car, trailer, or field office) when the logbook is not in personal possession.

Logbooks are official project documents and must be treated as such.

SOP APPROVAL FORM

TETRA TECH EM INC.

ENVIRONMENTAL STANDARD OPERATING PROCEDURE

PACKAGING AND SHIPPING SAMPLES

SOP NO. 019

REVISION NO. 6

December 2008



Quality Assurance Approved

December 18, 2008

Date

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Title: Packaging and Shipping Samples	Revision No. 6, December 18, 2008 Last Reviewed: December 2008

1.0 BACKGROUND

In any sampling program, the integrity of a sample must be ensured from its point of collection to its final disposition. Procedures for classifying, packaging, and shipping samples are described below. Steps in the procedures should be followed to ensure sample integrity and to protect the welfare of persons involved in shipping and receiving samples. When hazardous substances and dangerous goods are sent by common carrier, their packaging, labeling, and shipping are regulated by four primary agencies that have regulatory or advisory guidelines: (1) the U.S. Department of Transportation (DOT) Hazardous Materials Regulations (HMR, *Code of Federal Regulations*, Title 49 [49 CFR] Parts 106 through 180); (2) the International Air Transportation Association (IATA) Dangerous Goods Regulations (DGR); (3) International Civil Aviation Organization (ICAO), which provides technical instructions for safe transportation of hazardous materials (dangerous goods) by air; and (4) United Nations (UN) “Recommendations of the Committee of Experts on Transport of Dangerous Goods.”

1.1 PURPOSE

This standard operating procedure (SOP) establishes the requirements and procedures for packaging and shipping samples. It has been prepared in accordance with the U.S. Environmental Protection Agency (EPA) “Sampler’s Guide to the Contract Laboratory Program (CLP),” the DGR, the HMR, ICAO, and UN. Sample packaging and shipping procedures described in this SOP should be followed for all sample packaging and shipping. Deviations from the procedures in this SOP must be documented in a field logbook. This SOP assumes that samples are already collected in the appropriate sample jars and that the sample jars are labeled and tagged appropriately.

1.2 SCOPE

This SOP applies to sample classification, packaging, and shipping.

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1.3 DEFINITIONS

Custody seal: A custody seal is a tape-like seal. Placement of the custody seal is part of the chain-of-custody process and is used to prevent tampering with samples after they have been packaged for shipping.

Dangerous goods: Dangerous goods are articles or substances that can pose a significant risk to health, safety, or property when transported by air; they are classified as defined in Section 3 of the DGR (IATA 2008).

Environmental samples: Environmental samples include drinking water, most groundwater and ambient surface water, soil, sediment, treated municipal and industrial wastewater effluent, and biological specimens. Environmental samples typically contain low concentrations of contaminants and when handled require only limited precautionary procedures.

Hazardous Materials Regulations: The HMR are DOT regulations for the shipment of hazardous materials by air, water, and land; they are located in 49 CFR 106 through 180.

Hazardous samples: Hazardous samples include dangerous goods and hazardous substances. Hazardous samples shipped by air should be packaged and labeled in accordance with procedures specified by the DGR; ground shipments should be packaged and labeled in accordance with the HMR.

Hazardous substance: A hazardous substance is any material, including its mixtures and solutions, that is listed in Appendix A of 49 CFR 172.101 and its quantity, in one package, equals or exceeds the reportable quantity (RQ) listed in the appendix.

IATA Dangerous Goods Regulations: The DGR are regulations that govern the international transport of dangerous goods by air. The DGR are based on the International Civil Aviation Organization (ICAO) Technical Instructions. The DGR contain all of the requirements of the ICAO Technical Instructions and are more restrictive in some instances.

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Nonhazardous samples: Nonhazardous samples are those samples that do not meet the definition of a hazardous sample and **do not** need to be packaged and shipped in accordance with the DGR or HMR.

Overpack: An enclosure used by a single shipper to contain one or more packages and to form one handling unit (IATA 2008). For example, a cardboard box may be used to contain three fiberboard boxes to make handling easier and to save on shipping costs.

1.4 REFERENCES

U.S. Department of Transportation (DOT). 2007. Code of Federal Regulations, Title 49, Parts 171 through 180, especially Parts 171 (general), 172 (table, emergency response, and so on), and 173 (for shippers). Available from <http://www.access.gpo.gov/nara/cfr/cfr-table-search.html#page1>. Updated annually, late in the year or early in the following year.

DOT. 2008. "Hazardous Materials Table". (49 CFR 172.101 Table) Available on-line from <http://phmsa.dot.gov/hazmat/library>. Updated irregularly.

DOT. 2008. "Emergency Response Guidebook". Available on-line at <http://phmsa.dot.gov/hazmat/library/erg>. Updated annually.

Federal Express. 2008. "Dangerous Goods Shipping". Available on-line from <http://www.fedex.com/us/services/options/dangerousgoods/index.html>. Note especially "Declaration Forms", which can be filled out on-line or downloaded for future use, and "Resources", which includes the "Dangerous Goods Job Aid" on how to fill out the form, mark the package, and so on, the "Shipping Checklists" and the 1-800 numbers for assistance.

International Air Transport Association (IATA). 2008. "Dangerous Goods Regulations. 2009". For sale at <http://www.iata.org/ps/publications/dgr.htm>. Updated annually, with new edition available late in year.

U.S. Environmental Protection Agency. 2007. "Contract Laboratory Program Guidance for Field Samplers". EPA 540-R-07-06. Available on-line at http://www.epa.gov/superfund/programs/clp/download/sampler/clp_sampler_guidance.pdf. July.

The following additional in-house resources are also available:

Email: Contact either the TtEMI Health & Safety Director and the Regional Safety Officers at EMI.HASPAprovers or your Office Health and Safety Representative (all are included at EMI.HealthSafety).

On-line: TtEMI Intranet Page "Dangerous Goods Shipping" at <http://home.ttemi.com/C14/Dangerous%20Goods%20Shipping/default.aspx>. Includes the "Dangerous Goods Shipping Manual", various "Emergency Response Guide" excerpts, and other information, updated regularly.

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1.5 REQUIREMENTS AND RESOURCES

The procedures for packaging and shipping **nonhazardous** samples require the following:

- Coolers
- Ice
- Vermiculite, bubble wrap, or similar cushioning material
- Chain-of-custody forms and seals
- Airbills
- Resealable plastic bags for sample jars and ice
- Tape (strapping and clear)

The procedures for packaging and shipping **hazardous** samples require the following:

- Ice
- Vermiculite or other non-combustible, absorbent packing material
- Chain-of-custody forms and seals
- Appropriate dangerous goods airbills and emergency response information to attach to the airbill
- Resealable plastic bags for sample jars and ice
- Tape (strapping and clear)
- Appropriate shipping containers as specified in the DGR
- Labels that apply to the shipment such as hazard labels, address labels, “Cargo Aircraft Only” labels, and package orientation labels (up arrows)

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2.0 PROCEDURES

The following procedures apply to packaging and shipping nonhazardous and hazardous samples.

2.1 SAMPLE CLASSIFICATION

Prior to sample shipment, it must be determined whether the sample is subject to the DGR. Samples subject to these regulations shall be referred to as hazardous samples. If the hazardous sample is to be shipped by air, then the DGR should be followed. Any airline, including FedEx, belonging to IATA must follow the DGR. As a result, FedEx **may not** accept a shipment that is packaged and labeled in accordance with the HMR (although in most cases, the packaging and labeling would be the same for either set of regulations). The HMR states that a hazardous material may be transported by aircraft in accordance with the ICAO Technical Instruction (49 CFR 171.11) upon which the DGR is based. Therefore, the use of the DGR for samples to be shipped by air complies with the HMR, but not vice versa.

Most environmental samples are not hazardous samples and do not need to be packaged in accordance with any regulations. Hazardous samples are those samples that can be classified as specified in Section 3 of the DGR, can be found in the List of Dangerous Goods in the DGR in bold type, are considered a hazardous substance (see definition), or are mentioned in “Section 2 - Limitations” of the DGR for countries of transport or airlines (such as FedEx). The hazard classifications specified in the DGR (and the HMR) are as follows:

Class 1 - Explosives

- Division 1.1 - Articles and substances having a mass explosion hazard
- Division 1.2 - Articles and substances having a projection hazard but not a mass explosion hazard
- Division 1.3 - Articles and substances having a fire hazard, a minor blast hazard and/or a minor projection hazard but not a mass explosion hazard
- Division 1.4 - Articles and substances presenting no significant hazard
- Division 1.5 - Very sensitive substances mass explosion hazard
- Division 1.6 - Extremely insensitive articles which do not have a mass explosion hazard

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Class 2 - Gases

- Division 2.1 - Flammable gas
- Division 2.2 - Non-flammable, non-toxic gas
- Division 2.3 - Toxic gas

Class 3 - Flammable Liquids

Class 4 - Flammable Solids; Substances Liable to Spontaneous Combustion; Substances, which, in Contact with Water, Emit Flammable Gases

- Division 4.1 - Flammable solids
- Division 4.2 - Substances liable to spontaneous combustion
- Division 4.3 - Substances, which, in contact with water, emit flammable gases

Class 5 - Oxidizing Substances and Organic Peroxides

- Division 5.1 - Oxidizers
- Division 5.2 - Organic peroxides

Class 6 - Toxic and Infectious Substances

- Division 6.1 - Toxic substances
- Division 6.2 - Infectious substances

Class 7 - Radioactive Materials

Class 8 - Corrosives

Class 9 - Miscellaneous Dangerous Goods

The criteria for each of the first eight classes are very specific and are outlined in Section 3 of the DGR and 49 CFR 173 of the HMR. Some classes and divisions are further divided into packing groups based on their level of danger. Packing group I indicates a great danger, packing group II indicates a medium danger, and packing group III indicates a minor danger.

Class 1, explosives, includes any chemical compound, mixture, or device that by itself is capable of chemical chain reaction sufficient to produce a substantial, instantaneous release of gas, heat, and/or pressure. Tetra Tech does not ship substances that fall under this class.

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Class 2, gases, includes any compressed gas being shipped and any noncompressed gas that is either flammable or toxic. A compressed gas is defined as having a pressure over 40 pounds per square inch (psi) absolute (25 psi gauge). Most air samples and empty cylinders that did not contain a flammable or toxic gas are exempt from the regulations. An empty hydrogen cylinder, as in a flame ionization detector (FID), is considered a dangerous good unless it is properly purged with nitrogen in accordance with the HMR. A landfill gas sample is usually considered a flammable gas because it may contain a high percentage of methane.

Class 3, flammable liquids, are based on the boiling point and flash point of a substance. DOT defines flammable liquids as substances with a flash point less than 140 °F. Most class 3 samples include solvents, oil, gas, or paint-related material collected from drums, tanks, or pits.

Class 4 are flammable solids; substances liable to spontaneous combustion; and substances which, in contact with water, emit flammable gasses. Tetra Tech does not ship substances that fall under this class.

Class 5, oxidizers and organic peroxides, include substances that readily yields oxygen, which may result in the ignition of combustible materials. Organic peroxide is combustible and reacts as an oxidizer in contact with other combustible materials. By itself, an organic peroxide can be flammable or explosive. Tetra Tech does not ship substances that fall under this class.

Division 6, toxic and infectious substances, is based on oral toxicity (LD₅₀ [lethal dose that kills 50 percent of the test animals]), dermal toxicity (LD₅₀ values), and inhalation toxicity (LC₅₀ [lethal concentration that kills 50 percent of the test animals] values). Division 6.1 substances include pesticides and cyanide. Tetra Tech does not ship substances that fall under this class.

Class 7, radioactive material, is defined as any article or substance with a specific activity greater than 70 kiloBecquerels (kBq/kg) (0.002 [microCuries per gram [: Ci/g]). If the specific activity exceeds this level, the sample should be shipped in accordance with Section 10 of the DGR.

Class 8, corrosives, are based on the rate at which a substance destroys skin tissue or corrodes steel; they are not based on pH. Class 8 materials include the concentrated acids used to preserve water samples. Preserved water samples are not considered Class 8 substances and should be packaged as nonhazardous samples.

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Class 9, miscellaneous dangerous goods, are substances that present a danger but are not covered by any other hazard class. Examples of Class 9 substances include asbestos, polychlorinated biphenyls (PCB), and dry ice.

Unlike the DGR, the HMR includes combustible liquids in hazard class 3. The definition of a combustible liquid is specified in 49 CFR 173.120 of the HMR. The HMR has an additional class, ORM-D, that is not specified in the DGR. “ORM-D material” refers to a material such as a consumer commodity that, although otherwise subject to the HMR, presents a limited hazard during transport due to its form, quantity, and packaging. It must be a material for which exceptions are provided in the table of 49 CFR 172.101. The DGR lists consumer commodities as a Class 9 material.

In most instances, the hazard of a material sampled is unknown because no laboratory testing has been conducted. A determination as to the suspected hazard of the sample must be made using knowledge of the site, field observations, field tests, and other available information.

According to 40 CFR 261.4(d) and (e), samples transported to a laboratory for testing or treatability studies, including samples of hazardous wastes, are **not** hazardous wastes. FedEx will not accept a shipment of hazardous waste.

2.2 PACKAGING NONHAZARDOUS SAMPLES

Nonhazardous samples, after being appropriately containerized, labeled, and tagged, should be packaged in the following manner. Note that these are general instructions; samplers should be aware of any client-specific requirements concerning the placement of custody seals or other packaging provisions.

1. Place the sample in a resealable plastic bag.
2. Place the bagged sample in a cooler and pack it to prevent breakage.
3. Prevent breakage of bottles during shipment by either wrapping the sample container in bubble wrap, or lining the cooler (bottom and sides) with a noncombustible material such as vermiculite. Vermiculite is especially recommended because it will absorb any free liquids inside the cooler. It is recommended that the cooler be lined with a large plastic garbage bag before samples, ice, and absorbent packing material are placed in the cooler.

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4. Add a sufficient quantity of ice to the cooler to cool samples to 4 °C. Ice should be double bagged in resealable plastic bags to prevent the melted ice from leaking out. As an option, a temperature blank (a sample bottle filled with distilled water) can be included with the cooler.
5. Seal the completed chain-of-custody forms in a plastic bag and tape the plastic bag to the inside of the cooler lid.
6. Tape any instructions for returning the cooler to the inside of the lid.
7. Close the lid of the cooler and tape it shut by wrapping strapping tape around both ends and hinges of the cooler at least once. Tape shut any drain plugs on the cooler.
8. Place two signed custody seals on the cooler, ensuring that each one covers the cooler lid and side of the cooler. Place clear plastic tape over the custody seals.
9. Place address labels on the outside top of the cooler.
10. Ship samples overnight by a commercial carrier such as FedEx.

2.3 PACKAGING HAZARDOUS SAMPLES

The procedures for packaging hazardous samples are summarized below. Note that according to the DGR, all spellings must be exactly as they appear in the List of Dangerous Goods, and only approved abbreviations are acceptable. The corresponding HMR regulations are provided in parentheses following any DGR referrals. The HMR must be followed only if shipping hazardous samples by ground transport.

1. Determine the proper shipping name for the material to be shipped. All proper shipping names are listed in column B of the List of Dangerous Goods table in Section 4 of the DGR (or column 2 of the Hazardous Materials Table in 49 CFR 172.101). In most instances, a generic name based on the hazard class of the material is appropriate. For example, a sample of an oily liquid collected from a drum with a high photoionization detector (PID) reading should be packaged as a flammable liquid. The proper shipping name chosen for this sample would be “flammable liquid, n.o.s.” The abbreviation “n.o.s.” stands for “not otherwise specified” and is used for generic shipping names. Typically, a specific name, such as acetone, should be inserted in parentheses after most n.o.s. descriptions. However, a technical name is not required when shipping a sample for testing purposes and the components are not known. If shipping a hazardous substance (see definition), then the letters “RQ” must appear in front of the proper shipping name.
2. Determine the United Nations (UN) identification number, class or division, subsidiary risk if any, required hazard labels, packing group, and either passenger aircraft or cargo aircraft packing instructions based on the quantity of material being shipped in one

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package. This information is provided in the List of Dangerous Goods (or Hazardous Materials Table in 49 CFR 172.101) under the appropriate proper shipping name. A “Y” in front of a packing instruction indicates a limited quantity packing instruction. If shipping dry ice or a limited quantity of a material, then UN specification shipping containers do not need to be used.

3. Determine the proper packaging required for shipping the samples. Except for limited quantity shipments and dry ice, these are UN specification packages that have been tested to meet the packing group of the material being shipped. Specific testing requirements of the packages is listed in Section 6 of the DGR (or 49 CFR 178 of the HMR). All UN packages are stamped with the appropriate UN specification marking. Prior planning is required to have the appropriate packages on hand during a sampling event where hazardous samples are anticipated. Most samples can be shipped in either a 4G fiberboard box, a 1A2 steel drum, or a 1H2 plastic drum. Drums can be purchased in 5- and 20-gallon sizes and are ideal for shipping multiple hazardous samples. When FedEx is used to ship samples containing PCBs, the samples must be shipped in an inner metal packaging (paint can) inside a 1A2 outer steel drum. This method of packaging PCB samples is in accordance with FedEx variation FX-06, listed in Section 2 of the DGR.
4. Place each sample jar in a separate resealable plastic bag. Some UN specification packagings contain the sample jar and plastic bag to be used when shipping the sample.
5. Place each sealed bag inside the approved UN specification container (or other appropriate container if a limited quantity or dry ice) and pack with enough noncombustible, absorbent, cushioning material (such as vermiculite) to prevent breakage and to absorb liquid.
6. Place chain-of-custody forms in a resealable plastic bag and either attach it to the inside lid of the container or place it on top inside the container. Place instructions for returning the container to the shipper on the inside lid of the container as appropriate. Close and seal the shipping container in the manner appropriate for the type of container being used.
7. Label and mark each package appropriately. All irrelevant markings and labels need to be removed or obliterated. All outer packagings must be marked with proper shipping name; identification number; and name, address, and phone numbers of the shipper and the recipient. For carbon dioxide, solid (dry ice), the net weight of the dry ice within the package needs to be marked on the outer package. For limited quantity shipments, the words “limited quantity” or “LTD. QTY.” must be marked on the outer package. Affix the appropriate hazard label to the outer package. If the material being shipped contains a subsidiary hazard, then a subsidiary hazard label must also be affixed to the outer package. The subsidiary hazard label is identical to the primary hazard label except that the class or division number is not present. It is acceptable to obliterate the class or division marking on a primary hazard label and use it as the subsidiary hazard label. If using cargo aircraft only packing instructions, then the “Cargo Aircraft Only” label must be used. Package orientation labels (up arrows) must be placed on opposite sides of the outer package. Figure 1 depicts a properly marked and labeled package.

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8. If using an overpack (see definition), mark and label the overpack and each outer packaging within the overpack as described in step 7. In addition, the statement “INNER PACKAGES COMPLY WITH PRESCRIBED SPECIFICATIONS” must be marked on the overpack.
9. Attach custody seals, and fill out the appropriate shipping papers as described in Section 2.4.

2.4 SHIPPING PAPERS FOR HAZARDOUS SAMPLES

A “Shippers Declaration for Dangerous Goods” and “Air Waybill” must be completed for each shipment of hazardous samples. Four copies of the Shipper’s Declaration are required and it must be typed. FedEx supplies a Dangerous Goods Airbill to its customers; the airbill combines both the declaration and the waybill. An example of a completed Dangerous Goods Airbill is depicted in Figure 2. A shipper’s declaration must contain the following:

- Name and address of shipper and recipient
- Air waybill number (not applicable to the HMR)
- Page ____ of ____
- Shipper’s reference number (project number)
- Deletion of either “Passenger and Cargo Aircraft” or “Cargo Aircraft Only,” whichever does not apply
- Airport or city of departure
- Airport or city of destination
- Deletion of either “Non-Radioactive” or “Radioactive,” which ever does not apply
- The nature and quantity of dangerous goods. This includes the following information in the following order (obtained from the List of Dangerous Goods in the DGR): proper shipping name, class or division number, UN identification number, packing group number, subsidiary risk, quantity in liters or kilograms (kg), type of packaging used, packing instructions, authorizations, and additional handling information. Authorizations include the words “limited quantity” or “LTD. QTY.” if shipping a limited quantity, any special provision numbers listed in the List of Dangerous Goods in the DGR, and the variation “USG-14” when a technical name is required after the proper shipping name but not entered because it is unknown.

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- Signature for the certification statement
- Name and title of signatory
- Place and date of signing certification
- A 24-hour emergency response telephone number for use in the event of an incident involving the dangerous good
- Emergency response information attached to the shipper's declaration. This information can be in the form of a material safety data sheet or the applicable North American Emergency Response Guidebook (NAERG; DOT 1996) pages. Figure 3 depicts the appropriate NAERG emergency response information for "Flammable liquids, n.o.s." as an example.

Note that dry ice does not require an attached shipper's declaration. However, the air waybill must include the following on it: "Dry ice, 9, UN1845, ____ x ____ kg." The blanks must include the number of packages and the quantity in kg in each package. If using FedEx to ship dry ice, the air waybill includes a box specifically for dry ice. Simply check the appropriate box and enter in the number of packages and quantity in each package.

The HMR requirements for shipping papers are located in 49 CFR 172 Subpart C.

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3.0 POTENTIAL PROBLEMS

The following potential problems may occur during sample shipment:

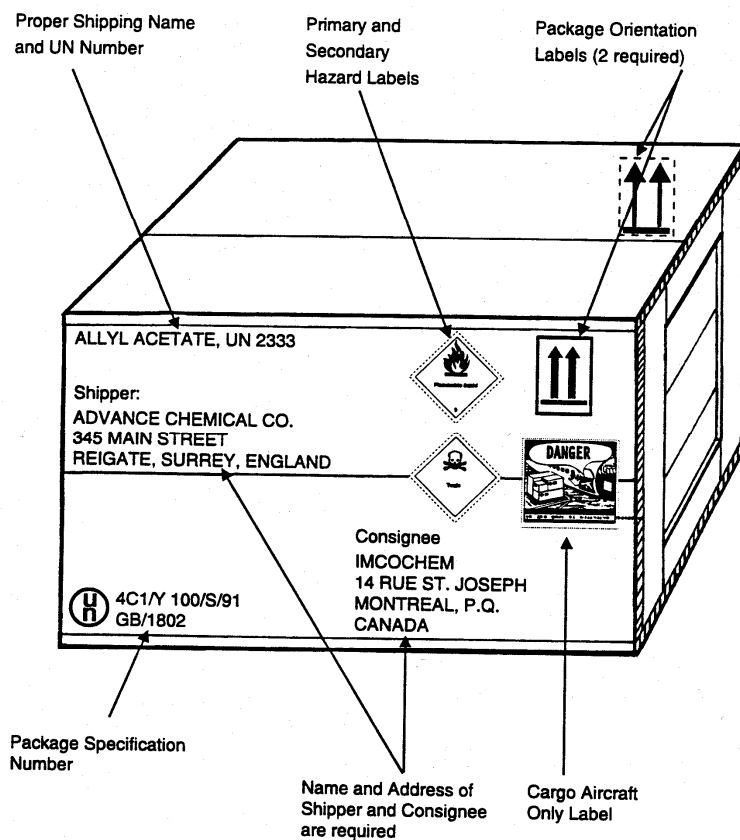
- Leaking package. If a package leaks, the carrier may open the package, return the package, and if a dangerous good, inform the Federal Aviation Administration (FAA), which can result in fines.
- Improper labeling and marking of package. If mistakes are made in labeling and marking the package, the carrier will most likely notice the mistakes and return the package to the shipper, thus delaying sample shipment.
- Improper, misspelled, or missing information on the shipper's declaration. The carrier will most likely notice this as well and return the package to the shipper.

Contact FedEx with questions about dangerous goods shipments by calling 1-800-463-3339 and asking for a dangerous goods expert.

Also contact Tetra Tech health and safety representatives using the website identified on Page 3 of this SOP.

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FIGURE 1
EXAMPLE OF A CORRECTLY MARKED AND LABELED DANGEROUS GOODS PACKAGE



Source: International Air Transport Association (IATA). 1997.

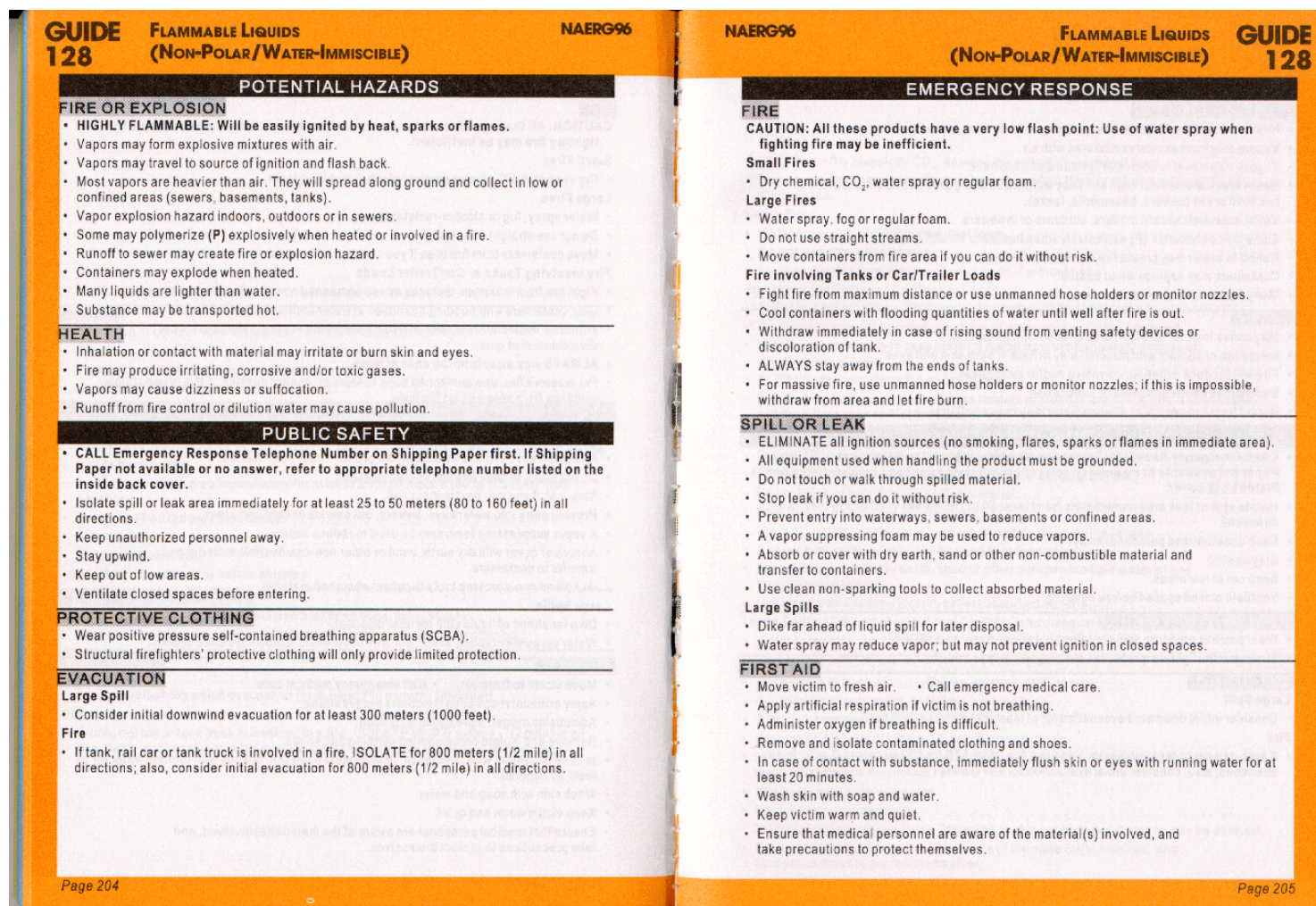
FIGURE 2**EXAMPLE OF A DANGEROUS GOODS AIRBILL****Filling Out the FedEx Dangerous Goods Airbill**

- The Dangerous Goods Airbill has two sections
 - The top section of the page is the airbill portion.
 - The bottom section is the Shipper's Declaration for Dangerous Goods.
- The sender *must complete* the following fields on the pre-printed airbill:
 - Section 1: Date
 - Section 1: Sender's Name
 - Section 7: Total Packages
 - Section 7: Total Weight
- Declaration for Dangerous Goods:
 - Under the section labeled "Proper Shipping Name" fill in the infectious substance (i.e., HIV, HCV, etc.) in the parentheses.
 - Under the "Quantity and Type of Packing" section, fill in the amount of specimen in the box (in mls).
 - List an emergency telephone number in the space provided at the bottom of the airbill.
 - Sign and date the airbill in the bottom right corner.

IMPORTANT: You must follow explicitly all packaging and labeling instructions for shipping infectious substances. Correct spelling and legibility are important. Otherwise, your package will be delayed or may be rejected by FedEx.

The image shows a FedEx Dangerous Goods Airbill form. The form is divided into two main sections: the top section for the airbill and the bottom section for the Shipper's Declaration. Red arrows point to specific fields that need to be completed by the sender. The top section includes fields for 'Section 1: Date', 'Section 1: Sender's Name', 'Section 7: Total Packages', and 'Section 7: Total Weight'. The bottom section includes fields for 'Proper Shipping Name', 'Quantity and Type of Packing', 'Emergency Telephone Number', and 'Sign and Date'. A large orange stamp in the center of the form reads 'FOR SHIPMENTS CONTAINING USA, AK, AND HI ONLY'.

FIGURE 3
NAERG EMERGENCY RESPONSE INFORMATION
FOR FLAMMABLE LIQUIDS, N.O.S.



Source: DOT and others. 1996.