QUALITY ASSURANCE PROJECT PLAN
FOR SAN GABRIEL VALLEY NPL AREA 3
REMEDIAL INVESTIGATION
FIELD ACTIVITIES

SAN GABRIEL BASIN
LOS ANGELES COUNTY, CALIFORNIA

EPA CONTRACT NO. 68-W-98-225
EPA WORK ASSIGNMENT NO. 141-RICO-09ES
CH2M HILL PROJECT NO. 175859.FI.01

Prepared for
U.S. Environmental Protection Agency
Region IX
75 Hawthorne Street
San Francisco, California 94105

Prepared by
CH2M HILL
Southern California Regional Office
3 Hutton Centre Drive
Suite 200
Santa Ana, California 92707

February 2003

QUALITY ASSURANCE PROJECT PLAN
FOR SAN GABRIEL VALLEY NPL AREA 3
REMEDIAL INVESTIGATION
FIELD ACTIVITIES

SAN GABRIEL BASIN
LOS ANGELES COUNTY, CALIFORNIA

EPA CONTRACT NO. 68-W-98-225
EPA WORK ASSIGNMENT NO. 141-RICO-09ES
CH2M HILL PROJECT NO. 175859.FI.01

February 2003

NONDISCLOSURE STATEMENT

This document has been prepared for the U.S. Environmental Protection Agency under Contract No. 68-W-98-225. The material contained herein is not to be disclosed to, discussed with, or made available to any persons for any reason without the prior expressed approval of a responsible official of the U.S. Environmental Protection Agency.

U.S. ENVIRONMENTAL PROTECTION AGENCY REGION IX

Plan Title:	Draft Quality Assurance Project Plan for San Gabriel Valley NPL Area 3 Remedial Investigation Field Activities
Site Name:	NPL Area 3
Site Location:	San Gabriel Valley
City/State/Zip:	Los Angeles County, California
Site EPA ID#:	CAD980818579
Anticipated Sampling Dates:	October 2002 to January 2005
Prepared By:	Michelle Goddard — February 2003 (Date)
Agency or Firm:	CH2M HILL, Inc.
Address:	3 Hutton Centre Drive
City/State/Zip:	Santa Ana, California 92707
Telephone:	714/429-2000
EPA Site Manager:	Lisa Hanusiak — Section: SFD-7-3 — 415/972-3089 (Phone No.)
QAPP Approval Date:	______________________

* *

Approved: Robert Collar ______________________ Date: ______________
CH2M HILL Site Manager

Approved: Artemis Antipas ______________________ Date: ______________
CH2M HILL Quality Assurance Officer

Approved: ______________________ Date: ______________
EPA Remedial Site Manager

Approved: ______________________ Date: ______________
EPA Quality Assurance Officer

Approved: ______________________ Date: ______________
EPA Region IX Quality Assurance Reviewer

* *

Distribution List

Lisa Hanusiak	EPA Region IX Work Assignment Manager
Robert Collar/SCO	CH2M HILL Site Manager
Vikas Mathur/SCO	CH2M HILL Task Manager
Maura Kennelly/SCO	CH2M HILL Field Team Leader
Artemis Antipas/SEA	CH2M HILL QA Manager

Tables

A-1 Selected Concentrations of Contaminants of Concern A-19
A-2a Data Needs and Uses – Regulatory Limits for Organic Parameters A-23
A-2b Data Needs and Uses – Regulatory Limits for Inorganic Parameters A-27
A-3 Measurement Performance Criteria A-31
B-1 Proposed Screen Intervals for the Cluster and MP Monitoring Wells B-2

Figures

A-1 Area 3 Project Organization A-9
A-2 Data Users/Recipients A-11
A-3 Area 3 RI/FS Location A-13
A-4 Hydrogeological Map A-15
A-5 Proposed Sampling Locations A-17

Contents

Section **Page**

Acronyms v

Section A Project Management/Data Quality Objectives **A-1**
A.1 Project Organization A-1
A.2 Problem Definition/Background A-1
A.2.1 Purpose A-1
A.2.2 Problem Statement A-2
A.2.3 Background A-2
A.2.4 Data Needs and Uses A-5
A.3 Project Description and Schedule A-6
A.3.1 Description of Work to be Performed A-6
A.3.2 Schedule of Activities A-7
A.4 Data Quality Objectives A-7
A.4.1 Project Quality Objectives A-7
A.4.2 Measurement Performance Criteria A-7
A.5 Special Training Requirements/Certification (A8) A-8
A.6 Documentation and Records A-8

Section B Measurement Data Acquisition **B-1**
B.1 Sampling Process Design B-1
B.1.1 Background B-1
B.1.2 Schedule of Analyses B-1
B.1.3 Rationale for Sampling Design B-2
B.2 Sampling Methods Requirements B-5
B.3 Sample Handling and Custody Requirements B-6
B.3.1 Chain-of-Custody B-6
B.3.2 Custody Seals B-8
B.3.3 Field Notebooks B-8
B.3.4 Corrections to Documentation B-8
B.4 Analytical Methods Requirements B-8
B.5 Quality Control Requirements B-9
B.5.1 Field QC Procedures B-9
B.5.2 Laboratory Procedures B-9
B.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements B-10
B.7 Instrument Calibration and Frequency B-10
B.7.1 Field Calibration Procedures B-10
B.7.2 Laboratory Calibration Procedures B-11
B.8 Data Acquisition Requirements (Nondirect Measurements) B-11
B.9 Data Management B-11

Section C Assessment/Oversight **C-1**
C.1 Assessment and Response Actions C-1
C.1.1 Reporting and Resolution of Issues C-1
C.2 Reports to Management C-2

Section D Data Validation and Usability **D-1**
D.1 Data Review, Validation, and Verification Requirements D-1
D.2 Validation and Verification Methods D-1
D.3 Reconciliation with Data Quality Objectives D-2

References **R-1**

Appendixes

A Data Quality Objectives

A-1 Drill Cuttings and Drilling Mud
A-2 Well Development Water
A-3 Groundwater Monitoring

B Analytical Technical Specifications

B-1 TCL Volatile Organic Compounds (VOCs) plus MTBE
B-2 1,4-Dioxane
B-3 N-Nitrosodimethylamine (NDMA)
B-4 Perchlorate
B-5 Hexavalent Chromium
B-6 TAL Metals (field filtered)
B-7 Anions: Nitrate-N
B-8 1,2,3-Trichloropropane
B-9 Semivolatile Organic Compounds
B-10 Flashpoint
B-11 pH
B-12 8260 VOCs
B-13 Total Petroleum Hydrocarbons-CA LUFT
B-14 TTLC Metals

C U.S. EPA Region IX Instructions for Sample Shipping and Documentation

Tables

A-1 Selected Concentrations of Contaminants of Concern A-19
A-2a Data Needs and Uses – Regulatory Limits for Organic Parameters A-23
A-2b Data Needs and Uses – Regulatory Limits for Inorganic Parameters A-27
A-3 Measurement Performance Criteria A-31
B-1 Proposed Screen Intervals for the Cluster and MP Monitoring Wells B-2

Figures

A-1 Area 3 Project Organization A-9
A-2 Data Users/Recipients A-11
A-3 Area 3 RI/FS Location A-13
A-4 Hydrogeological Map A-15
A-5 Proposed Sampling Locations A-17

This page intentionally left blank.

Acronyms

amsl	above mean sea level
bgs	below ground surface
°C	degrees Celsius
CLP	Contract Laboratory Program
COC	chain-of-custody
CRDL	contract required detection levels
DHS	Department of Health Services
DQO	data quality objectives
EC	electrical conductivity
EPA	Environmental Protection Agency
FAR	Federal Acquisition Regulations
FSP	field sampling plan
FTL	field team leader
ft/day	feet per day
GC	gas chromatography
GIS	geographic information system
HSP	health and safety plan
MCL	maximum containment level
MDL	method detection limits
MP	multiport
MS	matrix spike; mass spectroscopy
MS/MSD	matrix spike/matrix spike duplicate
MSD	matrix spike duplicate
NDMA	n-nitrosodimethylamine
NPL	National Priorities List
OU	operable unit
PCE	perchloroethylene (tetrachloroethylene)

PE	performance evaluation
PID	photoionization detector
PRP	potentially responsible party
QA	quality assurance
QAO	quality assurance officer
QAPP	quality assurance project plan
QA/QC	quality assurance/quality control
QC	quality control
RAC	response action contract
RPM	remedial project manager
RPD	relative percent difference
RI/FS	remedial investigation/feasibility study
RSCC	Regional Sample Control Center
RSD	relative standard deviation
RWQCB	Regional Water Quality Control Board
SM	site manager
SOW	statement of work
SRM	standard reference material
SSC	site safety coordinator
SVOC	semivolatile organic compound
TCE	trichloroethylene (trichloroethene)
TPH	total petroleum hydrocarbons
TPHd	total petroleum hydrocarbons - diesel
TPHg	total petroleum hydrocarbons - gas
TTLC	total threshold limit concentration
VOC	volatile organic compound
WA	work assignment
WAM	work assignment manager

Section A
Project Management/Data Quality Objectives

A.1 Project Organization

This work assignment issued under the United States Environmental Protection Agency (EPA) Response Action Contract (RAC) Assignment No. 141-RICO-09ES has a site manager (SM) who works directly with the EPA work assignment manager (WAM). The SM will manage the financial, schedule, and technical status of the work assignment. The key people involved in interfacing with the SM are the WAM, quality assurance officer (QAO), review team leader (RTL), and individual task managers for field sampling (field team leader, or FTL).

The primary responsibility for project quality rests with the SM, independent quality control is provided by the RTL and QAO. The RTL/review team and QAO will review project planning documents, data evaluation, and deliverables.

The sampling team will implement the quality assurance project plan (QAPP)/field sampling plan (FSP)/health safety plan (HSP). The site safety coordinator (SSC) is responsible for adherence to the HSP and field decontamination procedures. The entire field effort is directed by the FTL.

The subcontract administrator is responsible for procuring subcontracts for EPA's RAC projects under Federal Acquisition Regulations (FAR), and provides the interface with subcontractors. Subcontractors may be utilized on this work assignment for laboratory analysis depending on EPA regional laboratory availability.

Where quality assurance problems or deficiencies requiring special action are uncovered, the SM, RTL, and QAO will identify the appropriate corrective action to be initiated by the FTL or the laboratory.

Project organization and the line of authority for CH2M HILL efforts are illustrated in Figure A-1. Data users and recipients are shown in Figure A-2. Both EPA and CH2M HILL technical personnel and quality assurance personnel are shown.

The organizational functions noted above are consistent with the overall RAC IX Program Plan, and these functions are further detailed in the program plan.

A.2 Problem Definition/Background

A.2.1 Purpose

This QAPP presents the policies, organizations, objectives, and functional activities/procedures associated with the remedial investigation sampling and analysis activities at the San Gabriel Valley National Priorities List (NPL) Area 3 (Area 3) by EPA and accompanies the data quality objectives (DQOs, [EPA, 1994]), which can be found in Appendix A.

This QAPP follows EPA guidelines contained in *EPA Guidance for Quality Assurance Project Plans* (EPA, 1998), *EPA Requirements for Quality Assurance Project Plans* (EPA, 1999). Thus, the following section headings correlate with the subtitles found in the EPA guidelines (EPA, 1998).

A.2.2 Problem Statement

The San Gabriel Basin is located in the San Gabriel Valley in eastern Los Angeles County, California, and Area 3 is located in the western portion of the San Gabriel Basin (Figure A-3). Groundwater containing volatile organic compounds (VOCs) has been detected in approximately 30 wells throughout Area 3 study area. VOCs at concentrations that exceed state or federal maximum contaminant levels (MCLs) for drinking water have impacted approximately one-half of the production wells in that area (Table A-1).

Based on available production well data, the extent of VOC contamination has not changed for more than a decade. This is apparently due to the fact that Area 3 is within a regional depression of groundwater levels induced by groundwater pumping in the area. However, the sources of contamination, and the long-term effects of contamination on potable water supply wells are poorly understood. Furthermore, groundwater quality data for Area 3 is primarily from samples collected from production wells with long or multiple-screened intervals (i.e., depth-discrete water quality data are not available).

Site assessment investigations of potentially responsible party (PRP) facilities within Area 3 have just been started, and additional data are needed to determine the relationship between the contaminants identified at these sites and those impacting production wells within Area 3.

A.2.3 Background

A.2.3.1 Physical Setting

NPL Area 3 is located along the western boundary of the San Gabriel Valley (Figure A-3), approximately 25 miles from the Pacific Coast, in eastern Los Angeles County. The San Gabriel Basin, a broad piedmont plain that slopes gradually to the southwest at a gradient of approximately 65 feet per mile, is located within the San Gabriel Valley (CDWR, 1934). This structural basin is a natural groundwater reservoir that collects rainfall on the valley floor and runoff from the surrounding highlands, recharging the groundwater aquifer.

The Raymond Fault forms the northern boundary of Area 3, separating the Main San Gabriel Basin from the Raymond Basin located to the northwest. The Repetto Hills abut the western edge of the area, and Rosemead Avenue and the Interstate 10 Freeway have been selected as the eastern and southern geographic boundaries, respectively. Topographic elevation ranges from approximately 550 feet above mean sea level (amsl) in the northern and northwestern portions of Area 3, to approximately 300 feet amsl in the southern portion of Area 3.

The Rio Hondo and San Gabriel River systems drain the San Gabriel Mountains, and carry runoff into the San Gabriel and Central Basins. The Rio Hondo and San Gabriel River systems eventually flow through Whittier Narrows, a structural depression located between

the Montebello and Puente Hills. Groundwater movement through most of the San Gabriel Basin is generally from the perimeter of the basin toward Whittier Narrows, which is the only area through which substantial subsurface outflow from the basin occurs. However, groundwater pumping in the western portion of the basin (including Area 3) has reversed natural groundwater flow directions.

The hydrogeology of Area 3 can be grouped into three regions: west, central, and east. The western portion of Area 3 is characterized by complexly fauled and folded sedimentary bedrock, trending northwest, with folds plunging to the southeast (Figure A-4). In addition, many bedrock outcrops form the series of low-lying hills, comprising parts of the Repetto Hills in the western portion of Area 3. The alluvial sediments of this area are predominantly fine-grained, contributed from the marine sedimentary rocks of the Repetto Hills. Groundwater in this area is relatively shallow, averaging approximately 50 feet below ground surface (bgs) near the exposed bedrock to 160 feet bgs or more along Mission Road (Figure A-4). The depth to water of 160 feet bgs appears to be anomalous and may be related to perched groundwater conditions. The top of the unconfined aquifer is thought to be around 275 feet bgs.

The central portion of Area 3, which corresponds roughly to Alhambra and San Pascual Washes, is a transition zone between the western and eastern areas of the study area. In this area, the complex faulting and folding seen in the western portion are not visible and the depth to groundwater increases, in part due to the increasing ground surface elevation, increasing depth to bedrock, proximity to active production wells, and the absence of fine-grained alluvium impeding downward groundwater flow.

The eastern portion of Area 3 is characterized by coarse-grained alluvial sediments likely derived from the crystalline rocks of the San Gabriel Mountains. Depth to groundwater in the eastern portion of Area 3 is generally between 280 and 380 feet bgs. Stream channel deposits overlie the alluvium and consist of interfingering lenses of cobbles, gravel, sand, and silt that occur in channels developed (scoured) by active or historic surface water bodies.

Groundwater flow conditions throughout the San Gabriel Basin are largely controlled by the volume of water flowing into and out of the Basin, and the hydrogeologic properties of the alluvial aquifer. Historically, and before the invention of the deep turbine well pump, the alluvial aquifer was in a state of approximate dynamic equilibrium, with recharge equaling discharge over the course of hundreds of years. Under predevelopment conditions, virtually all subsurface outflow occurred at Whittier Narrows (EPA, 1992) and groundwater flow patterns throughout the Basin likely paralleled the topography. In Area 3, groundwater likely flowed toward the southeast under predevelopment conditions.

With the advent of the deep turbine well pump in 1909, groundwater pumping increased dramatically in the San Gabriel Basin. Groundwater pumping, which is by far the greatest source of outflow from the Basin, greatly influences groundwater flow conditions, on both a regional and local scale. Locally, concentrated pumping can produce cones of depression that are controlled in size by the pumping rate of a well and the hydraulic conductivity of the surrounding aquifer. This is the case in Area 3.

Hydraulic conductivity is a measure of how easily fluids can flow through porous media. Hydraulic conductivity estimates range from 44 feet per day (ft/day) at Well 01900515,

located adjacent to the southern boundary of Area 3, to 380 ft/day at Well 01900927, located adjacent to the eastern boundary of the study area. The average of hydraulic conductivity estimates available from aquifer tests of wells in Area 3 and nearby vicinity is approximately 200 ft/day.

A.2.3.2 Past Studies/Activities in the Area

The San Gabriel Valley has been the focus of environmental investigations since 1979, when groundwater contaminated with VOCs was first identified. In May 1984, four broad areas of contamination within the basin were listed as San Gabriel Areas 1 through 4 on the EPA NPL. EPA subsequently divided the basin into eight operable units (OUs) to provide a means of describing hydrogeology and contaminant distribution, and to develop and plan remedial activities in the basin.

EPA began conducting RI activities in the San Gabriel Basin in the mid-1980s. RI activities included numerous field investigations to generate hydrogeologic and groundwater quality data; collecting and reviewing hydrogeologic data; database development; development of conceptual models of basin hydrogeology, including groundwater flow and contaminant transport; and construction and calibration of a three-dimensional groundwater flow model.

Available groundwater quality data for Area 3 are primarily from wellhead sampling of production wells. Based on wellhead data, the extent of contamination has apparently not changed for more than a decade. This is likely due to the fact that Area 3 is located within a regional depression of groundwater levels induced by groundwater pumping in the area. However, because of the long or multiple screened or perforated intervals, some as great as 500 feet, in the production wells, the vertical extent of VOC contamination throughout Area 3 is not known. Additionally, because of the limited number of monitoring wells in Area 3, groundwater gradients, flow directions, and the horizontal extent of contamination are not well understood.

To date, little PRP site assessment work has been conducted in Area 3. However, at EPA's request, the Los Angeles Regional Water Quality Control Board (LARWQCB) has stepped up efforts to identify the potential sources of VOC contamination detected in groundwater in Area 3. Currently, groundwater monitoring data are available at two sites within Area 3: the Temple City Sheriff's Station, located in the eastern portion of Area 3, and Charter Communications, located in the southwest portion of Area 3.

Area 3 is in the initial stage of the remedial investigation/feasibility study (RI/FS) process. In January 2001, the Alhambra Operable Unit Draft Data Evaluation Report was completed (EPA, 2001). The report identified data gaps within Area 3 and recommended appropriate field activities to be conducted to meet the technical goals and objectives of the RI.

A.2.3.3 Water Quality

Table A-1 summarizes water quality data for wells located within Area 3 based on information in EPA's San Gabriel database. Wells are organized in Table A-1 by the water purveyor who owns and operates each well. The following text describes the types of contaminants present in groundwater in Area 3, the lateral and vertical extent, and potential sources for the contamination observed in groundwater.

The predominant contaminants detected in groundwater in Area 3 are tetrachloroethylene (PCE) and trichloroethylene (TCE). Figure A-5 illustrates the distribution of PCE and TCE detected in shallow and deep groundwater wells throughout Area 3. Shallow groundwater quality data and soil vapor data collected at several PRP facilities are shown, and the areas of VOC contamination are differentiated on the basis of the predominant contaminant (PCE, TCE, or both).

A relatively large area of PCE contamination is present in groundwater in the eastern portion of Area 3, with a smaller area present in the north-central portion of the study area. Groundwater contamination between these plumes appears to be dominated by TCE. There is a small area of groundwater contamination in the southeastern portion of Area 3 that includes both PCE and TCE. The somewhat distinct characteristics of the areas of VOC contamination in Area 3 suggest there are multiple sources for this contamination. There are no production wells where the alluvial aquifer thickness decreases significantly against the Repetto Hills. Consequently, the current understanding of the lateral extent of contamination in the western portion of Area 3 is poorly understood.

Additionally, the vertical extent of VOC contamination throughout the OU is not well known. Wellhead concentrations from production wells that produce water from long or multiple-screen intervals may not yield accurate information about the occurrence and concentration of contamination present in the groundwater aquifer. For example, a discrete hydrogeologic zone containing elevated contaminant concentrations may be masked in a well having a long screened interval due to dilution from clean, or less-contaminated, zones also providing water to the well.

The distribution of VOCs in groundwater indicates that multiple source areas are likely present in localized commercial and industrial areas throughout Area 3. Although little PRP site assessment work has been conducted to date, the LARWQCB has stepped up efforts to identify potential sources to the VOC contamination detected in groundwater in Area 3.

As discussed previously, available data for Area 3 are mostly from production wells with extensive perforated intervals that potentially dilute concentrations detected at the well head. These data do not provide important information regarding the vertical distribution of contamination with depth in the aquifer. No hydrogeologic or water quality data are available in the western portion of the study area where no groundwater wells are present.

A.2.4 Data Needs and Uses

Data needs and uses for the objectives described in this section have been identified through the DQO process presented in Appendix A. The data needs and uses are summarized in Tables A-2A (organics) and A-2B (inorganics). These tables list the analytes of concern and present regulatory detection limit requirements and rationale for VOCs, SVOCs, and inorganics. The rationale for sampling for each group of analytes is listed below:

- VOCs and 1,2,3-trichloropropane – These compounds have been detected in production wells within Area 3.

- 1,4-Dioxane, NDMA, perchlorate, metals, and hexavalent chromium – These compounds have been found in other operable units within the San Gabriel Basin where industrial practices similar to those in Area 3 occur.
- SVOCs – Industries that are known to use SVOCs are located within Area 3; therefore, SVOCs may be found in groundwater.

Additionally, groundwater samples will be analyzed for dissolved metals so that the samples will most closely represent the conditions of production wells and drinking water. Dissolved metals analytical results represent the concentrations of metals in groundwater, without taking into effect the metals that are bound to suspended solids. Total metals concentrations are typically much higher than dissolved metals concentrations because they do include metals bound to suspended solids. Because production wells typically have very low suspended solid concentrations, and drinking water is often filtered prior to distribution, dissolved metals analysis would give the most representative results.

The tables present a comprehensive listing of regulations reviewed and identify the applicable regulation(s). These regulatory limits were taken into consideration in selecting appropriate methods and reporting levels as described in Section A.4.2. Some of the selected methods (Table A-3) may have higher reporting limits due to current technical limitations, as further described in Section A.4.2. For each of the methods and analytes, the laboratory will provide laboratory-specific method detection limits (MDL) obtained in accordance with 40CFR Part 136 Appendix B. Laboratory-specific MDLs are lower than practicable reporting limits identified in the QAPP. These limits (MDLs) are provided to the project team with the individual data packages, as they are instrument/time specific. Data users (regulatory specialists, risk assessors, treatment engineers) will use these MDLs when comparing site data to project specific regulatory limits/action levels identified in Table A 2.

Analytes with regulatory limits lower than reporting levels have been noted in Tables A2-A and A-2B. For these analytes, laboratory-specific detection levels (i.e., MDLs) are expected to be significantly lower than the identified reporting limits and thus, the laboratory-specific levels will be taken into account in project decisions. Project decisions are not expected to be significantly affected by the higher detection levels. For hexavalent chromium, the required limits as noted on Table A-2B are lower than the applicable regulatory limits to maintain comparability to other historic data collected and analyzed at a lower detection level when the California Department of Health Services (DHS) had an established regulatory level for this compound.

A.3 Project Description and Schedule

A.3.1 Description of Work to be Performed

Groundwater samples will be collected during the RI field activities from cluster and multiport monitoring wells that will be installed as part of the RI activities. Multiple rounds of groundwater samples will be obtained. In addition, samples of investigation-derived wastes will be collected, including drill cuttings and drilling mud, and well development and purge water.

A.3.2 Schedule of Activities

Sampling of investigation-derived wastes is expected to begin in November 2002, will occur periodically, and will last through March 2003. Groundwater sampling is expected to start in December 2002, will occur quarterly, and will last through January 2005.

A.4 Data Quality Objectives

The following subsections cover the data quality objectives.

A.4.1 Project Quality Objectives

The specific needs for data that will be collected during each activity were examined to evaluate whether project objectives for the RI are optimally achieved. Specific data quality objectives were considered independently through the DQO process (EPA Q4/G4, 1994b) to meet the data user's needs for each activity. Appendix A presents the DQO decision-making process for the RI field activities.

The objectives of the field activities are listed below:

- Characterize the three-dimensional nature and extent of VOC contamination in Area 3
- Evaluate whether contaminants such as 1,4-dioxane, perchlorate, and n-nitrosodimethylamine (NDMA), discovered in other parts of the San Gabriel Basin, are present in Area 3
- Collect groundwater data that would assist in identifying contaminant source areas within Area 3

A.4.2 Measurement Performance Criteria

The quality assurance (QA) objective of this plan is to develop implementation procedures that will provide data of known and appropriate quality for the needs identified in previous sections. Data quality is assessed by representativeness, comparability, accuracy, precision, and completeness. These terms, the applicable procedures, and level of effort are described below.

The applicable quality control (QC) procedures, quantitative target limits, and level of effort for assessing data quality are dictated by the intended use of the data and the nature of the analytical methods. Analytical parameters and applicable detection levels, analytical precision, accuracy, and completeness in alignment with needs identified in Section A-2.4 are presented in Table A-3.

Reporting detection levels/target detection limits listed in Table A-3 are based on method reporting limits, which are equivalent to contract required detection levels (CRDLs). Target implies that final sample detection levels may be higher because of sample matrix effects. Detection levels for the individual samples will be reported in the final data. Also, some of the reporting levels may be higher than regulatory limits identified in Table A-2A and Table A-2B, as no practicable methodology for lower detection is available. Analytes with regulatory limits lower than reporting levels have been noted in Tables A2-A and A-2B. Laboratory-specific MDLs are significantly below reporting levels. Where reporting limits

are higher than regulatory limits, the project team will use MDLs as needed for project decisions.

Representativeness is a measure of how closely the results reflect the actual concentration or distribution of the chemical compounds in the matrix samples. Sampling plan design, sampling techniques, and sample-handing protocols (e.g., for storage, preservation, and transportation) have been developed, and are discussed in subsequent sections of this document. The proposed documentation will establish that protocols have been followed and sample identification and integrity ensured.

Comparability expresses the confidence with which one data set can be compared to another. Data comparability will be maintained using defined procedures and the use of consistent methods and consistent units. Actual detection limits will depend on the sample matrix and will be reported as defined for the specific samples.

Accuracy is an assessment of the closeness of the measured value to the true value. For samples, accuracy of chemical test results is assessed by spiking samples with known standards and establishing the average recovery. For a matrix spike, known amounts of a standard compound identical to the compounds being measured are added to the sample. A quantitative definition of average recovery accuracy is given in Section D.3. Accuracy measurement will be carried out with a minimum frequency of 1 in 20 samples analyzed.

Precision of the data is a measure of the data spread, when more than one measurement has been taken on the same sample. Precision can be expressed as the relative percent difference; a quantitative definition is given in Section D.3. The level of effort for precision measurements will be a minimum of 1 in 20 samples.

Completeness is a measure of the amount of valid data obtained from the analytical measurement system and the complete implementation of defined field procedures. The quantitative definition of completeness is given in Section D.3. The target completeness objective will be 90 percent; the actual completeness may vary depending on the intrinsic nature of the samples. The completeness of the data will be assessed during QC reviews.

A.5 Special Training Requirements/Certification (A8)

All project staff working on the site must be health and safety trained, and must follow requirements specified in the HSP of the project, which can be found in the companion FSP (EPA, 2002). The HSP describes the specialized training required for personnel on this project and the documentation and tracking of this training.

A.6 Documentation and Records

Field documentation and records will be as described in Section B and the FSP (EPA, 2002). Laboratory documentation will be per: (1) methods and quality assurance protocols listed in Section B, and (2) EPA Regional Laboratory specific standard operating procedures. Overall project documentation will be per EPA's Region IX RAC Program Plan.

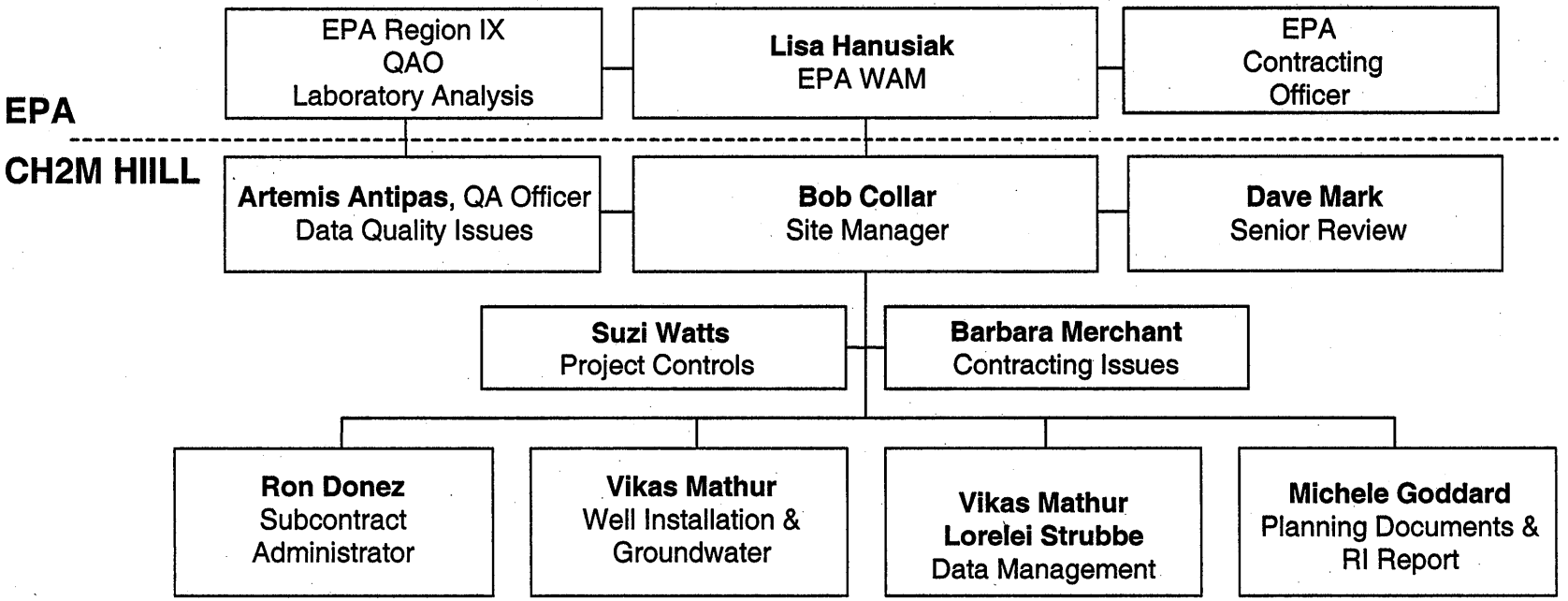


Figure A-1
San Gabriel Valley NPL Area 3
Project Organization
RI Field Activities

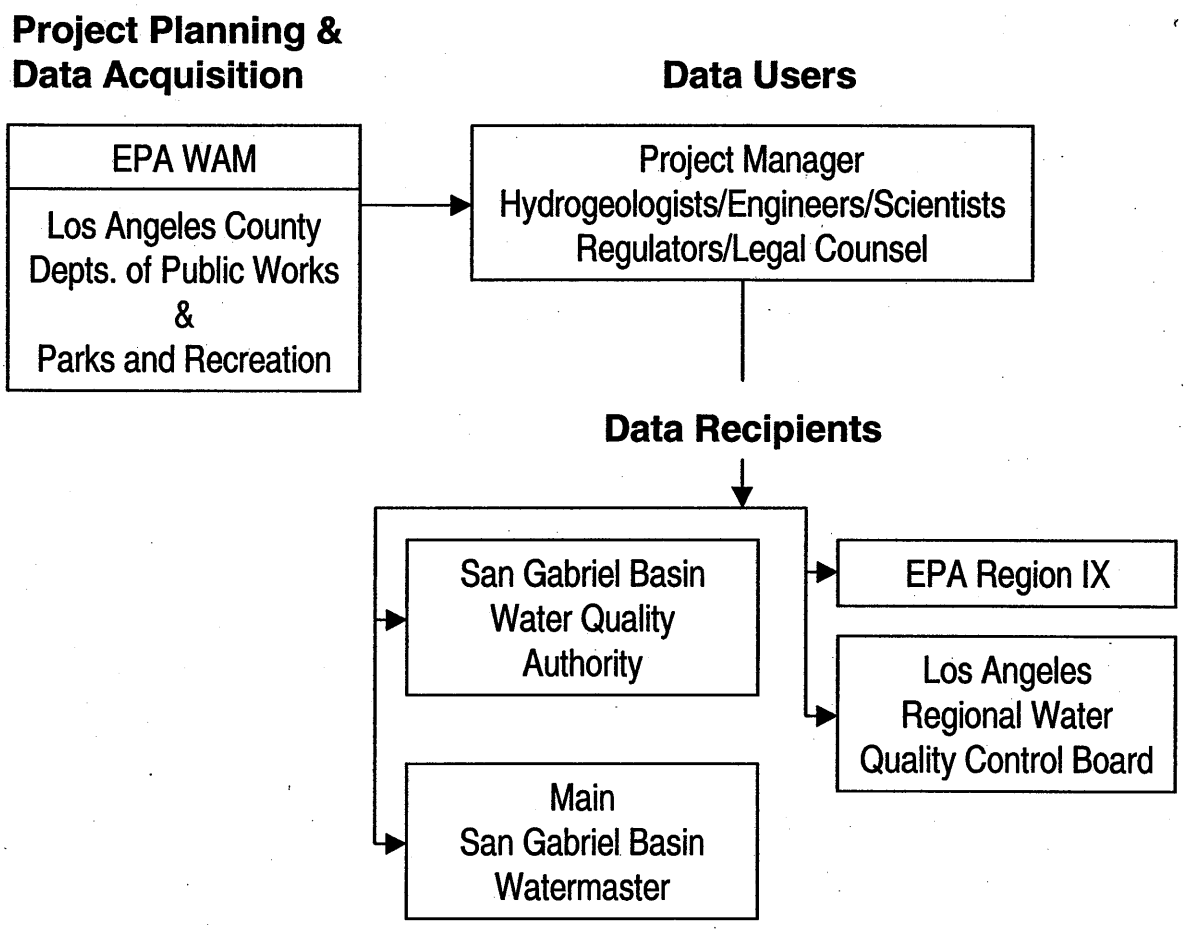


Figure A-2
Data Users/Recipients
RI Field Activities

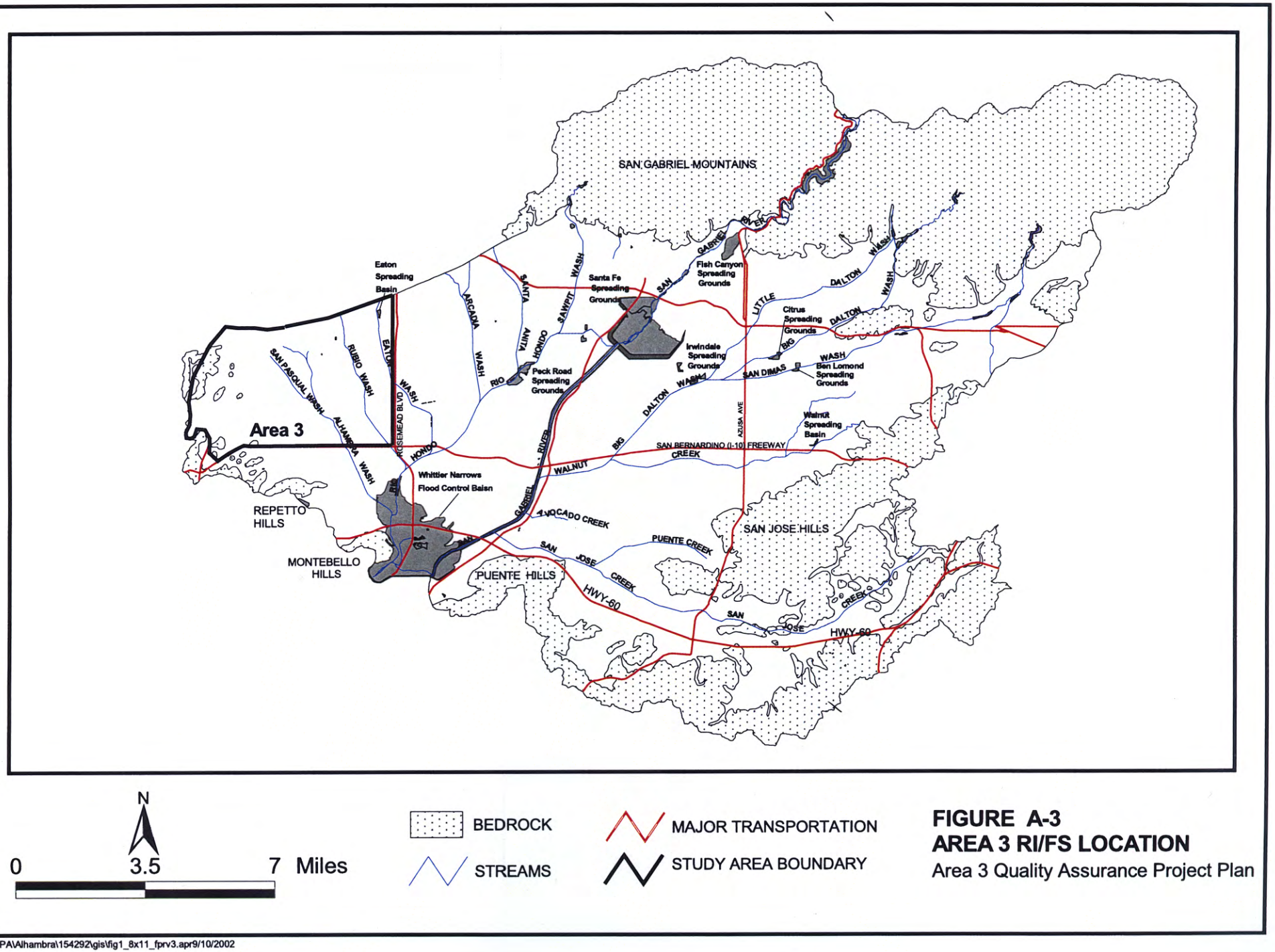
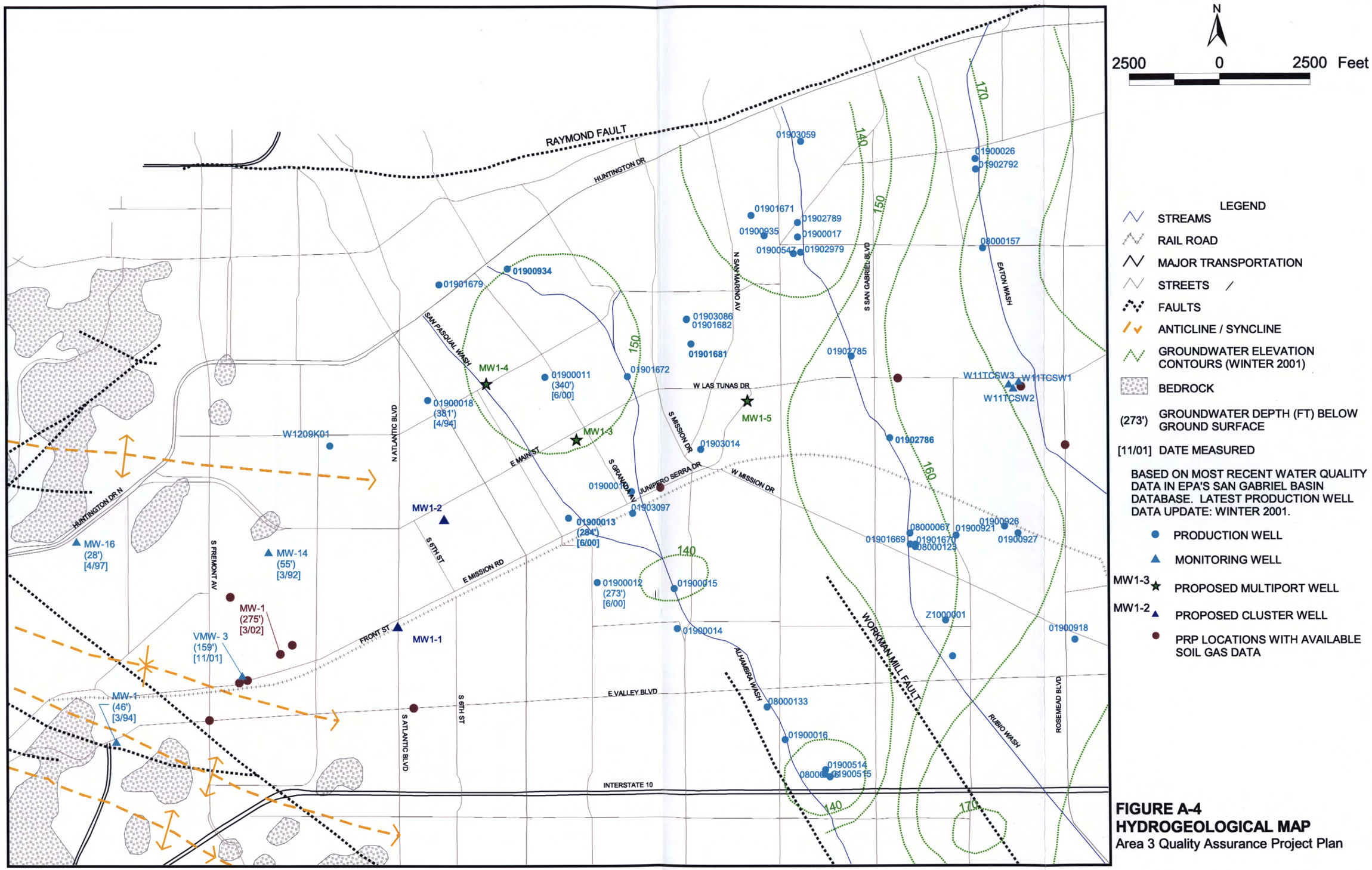


FIGURE A-3
AREA 3 RI/FS LOCATION
Area 3 Quality Assurance Project Plan

H:\EPA\Alhambra\154292\gis\fig1_8x11_fprv3.apr9/10/2002



LEGEND

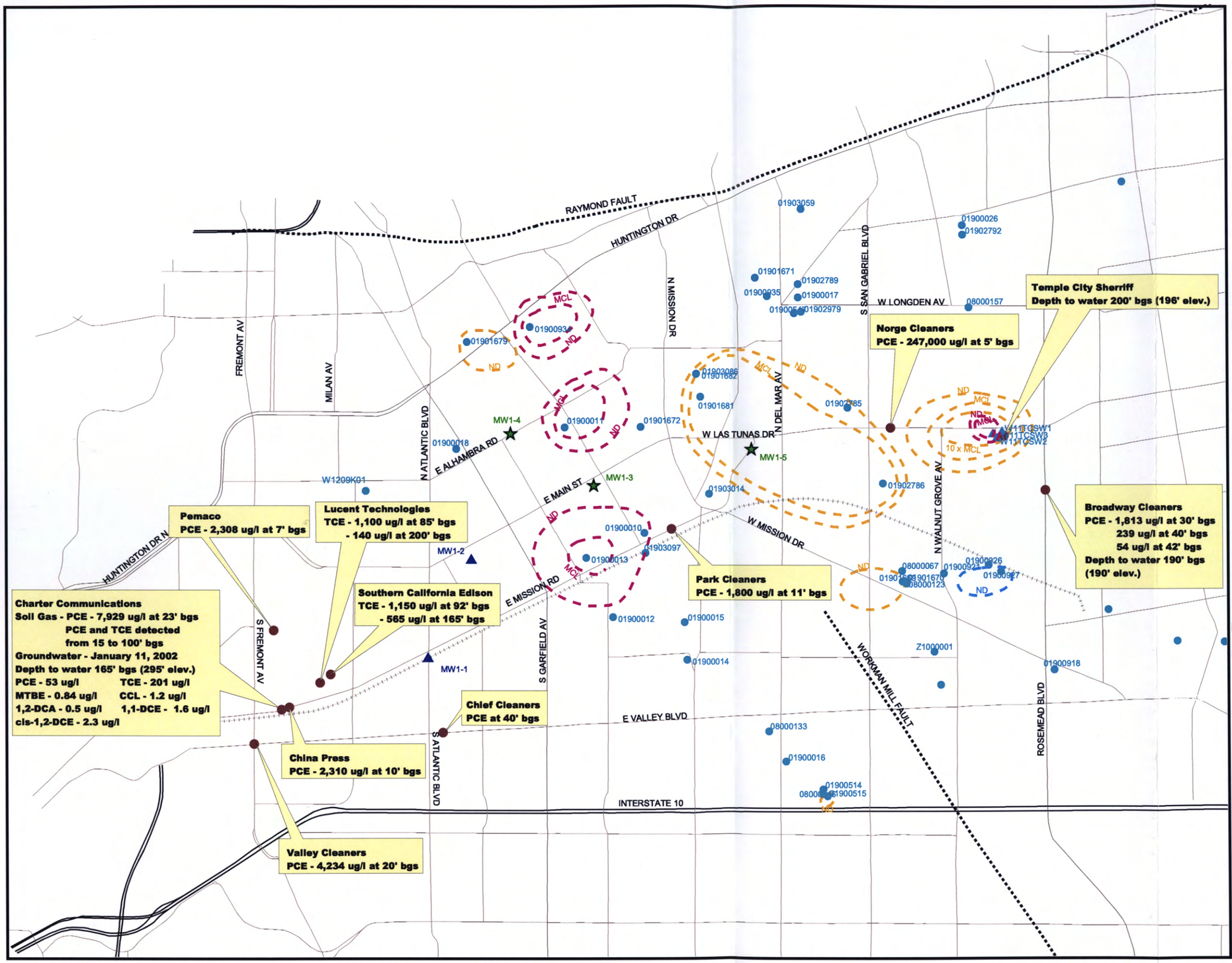
- STREAMS
- RAIL ROAD
- MAJOR TRANSPORTATION
- STREETS
- FAULTS
- ANTICLINE / SYNCLINE
- GROUNDWATER ELEVATION CONTOURS (WINTER 2001)
- BEDROCK
- (273') GROUNDWATER DEPTH (FT) BELOW GROUND SURFACE
- [11/01] DATE MEASURED

BASED ON MOST RECENT WATER QUALITY DATA IN EPA'S SAN GABRIEL BASIN DATABASE. LATEST PRODUCTION WELL DATA UPDATE: WINTER 2001.

- PRODUCTION WELL
- MONITORING WELL
- MW1-3 PROPOSED MULTIPORT WELL
- MW1-2 PROPOSED CLUSTER WELL
- PRP LOCATIONS WITH AVAILABLE SOIL GAS DATA

FIGURE A-4
HYDROGEOLOGICAL MAP
Area 3 Quality Assurance Project Plan

H:\EPA\Alhambra\154292\gis\contour_qapp_rv1.apr 9/16/2002



N

3000 0 3000 Feet

LEGEND

- RAIL ROAD
- MAJOR TRANSPORTATION
- STREETS
- APPROXIMATE EXTENT OF PCE IMPACTED GROUNDWATER
- APPROXIMATE EXTENT OF TCE IMPACTED GROUNDWATER
- APPROXIMATE EXTENT OF PCE & TCE IMPACTED GROUNDWATER

LINES ARE DASHED TO INDICATE UNCERTAINTY IN EXTENT OF VOC DISTRIBUTION SHOWN

MCL = MAXIMUM CONTAMINANT LEVEL
PCE, TCE MCL = 5 MICROGRAMS/LITER

ND - NOT DETECTED (INFERRED)

BASED ON MOST RECENT WATER QUALITY DATA IN EPA'S SAN GABRIEL BASIN DATABASE. LATEST PRODUCTION WELL DATA UPDATE: JUNE 2000.

- PRODUCTION WELL
- MONITORING WELL
- MW1-3 ★ PROPOSED MULTIPORT WELL
- MW1-2 ▲ PROPOSED CLUSTER WELL
- PRP LOCATIONS WITH AVAILABLE SOIL GAS DATA

FIGURE A-5
PROPOSED SAMPLING LOCATIONS
Area 3 Quality Assurance Project Plan

H:\EPA\Alhambra\154292\gis\pwell_11x17_qaprv1.apr 9/16/2002

Table A-1 - Selected Concentrations of Contaminants of Concern
NPL Area 3, San Gabriel Valley

Well Information			Contaminant of Potential Concern Concentration				
				Historic High		Recent	
Name	Recordation Number	Status	Contaminant	Value	Date	Value	Date
Adams Ranch Mutual Water Company							
01	01902106	Not in service - reason unknown	Nitrate	44	02/05/1997	44	02/05/1997
			TCE	1.5	06/26/1989	0.5U	02/05/1997
02	01902689	Not in service - reason unknown	PCE	2.2	05/12/1988	2.2	05/12/1988
			TCE	4.1	01/11/1980	0.5U	05/12/1988
California American Water Company - San Marino System							
GUESS	01900918	Producing	Carbon Tetrachloride	1	05/01/1985	0.5U	08/10/99
			Methylene Chloride	12	05/19/1987	0.5U	08/10/99
			Nitrate	26	02/16/1987	12	11/07/1994
			PCE	3	06/10/1999	2.8	06/15/00
			TCE	4.3	09/18/1998	3.8	06/15/00
			TDS	292	04/28/1986	260	11/07/1994
1954 (Mission View)	01900920	Producing	Chloroform	20.5	08/11/1997	0.5U	08/10/99
			Nitrate	20	02/16/1987	12	11/07/1994
			PCE	0.15	08/03/1982	0.5U	08/10/99
			TDS	356	05/15/1989	248	11/07/1994
1948 GRAND	01900926	Producing	Nitrate	20	07/21/1986	4.8	11/07/1994
			TCE	4	10/07/1998	0.5U	06/15/00
			TDS	244	10/09/1990	232	11/07/1994
1957 ROSEMEAD	01900927	Producing	Chloroform	0.8	03/06/1990	0.5U	08/10/99
			Methylene Chloride	6	05/19/1987	0.5U	08/10/99
			Nitrate	26	02/16/1987	13.9	11/07/1994
			PCE	0.8	06/30/1999	0.6	06/15/00
			TCE	3.3	06/30/1999	2.8	06/15/00
			TDS	256	11/07/1994	256	11/07/1994
1947 (Roanoke)	01900934	Producing	Chloroform	1.1	03/06/1990	0.5U	08/10/99
			Nitrate	39	12/18/1989	20.2	05/25/1994
			PCE	1.2	04/26/1990	0.5U	08/10/99
			TCE	4.8	03/11/1998	5	06/15/00
			TDS	412	10/09/1990	320	12/13/1993
1925 (Longden)	01900935	Not in service - nitrate contamination	Nitrate	106	12/18/1989	61.1	11/07/1994
			PCE	0.19	08/03/1982	0.5U	08/10/99
			TCE	0.17	08/03/1982	0.5U	08/10/99
			TDS	416	11/07/1994	416	11/07/1994
1968 (Del Mar)	01903059	Producing	Nitrate	21	01/23/1989	7.69	11/07/1994
			TDS	228	10/09/1990	220	11/07/1994
RICHARDSON-1	01900921	Not in service - reason unknown	Nitrate	29	01/15/1990	3.9	10/09/1990
			TCE	0.25	09/10/1981	0.5U	10/11/1994
			TDS	272	10/09/1990	272	10/09/1990
City of South Pasadena							
GRAVES 2	01901679	Producing	1,1,1-TCA	1.8	05/11/1988	0.5U	12/23/99
			Carbon Tetrachloride	1	09/06/1995	0.5U	06/19/00
			Methylene Chloride	4.8	06/13/1989	0.5U	12/23/99
			Nitrate	48.4	04/25/1995	48.4	04/25/1995
			PCE	5.5	05/15/1998	3.5	06/19/00
			TDS	410	04/19/1988	370	04/25/1995
WILSON 2	01901681	Producing	1,1,1-TCA	0.5	03/04/1988	0.5U	08/25/99
			Chloroform	0.95	01/19/1987	0.5U	08/25/99
			Nitrate	83.6	04/20/1994	83.6	04/20/1994
			PCE	23	01/07/1988	9.8	06/19/00
			TCE	4.1	03/04/1999	3.4	06/19/00
			TDS	400	04/09/1986	360	04/20/1994
WILSON 3	01901682	Producing	Chloroform	5.8	09/04/1998	0.5U	08/25/99
			Nitrate	10.8	09/18/1992	10.12	04/06/1993
			PCE	19	05/31/1989	4	06/19/00
			TDS	250	04/06/1993	250	04/06/1993
WILSON 4	01903086	Producing	Nitrate	10.8	09/26/1989	9.2	09/08/1993
			PCE	8.1	06/19/00	8.1	06/19/00
			TDS	200	04/24/1990	170	04/06/1993

Table A-1 - Selected Concentrations of Contaminants of Concern
NPL Area 3, San Gabriel Valley

Well Information			Contaminant of Potential Concern Concentration				
				Historic High		Recent	
Name	Recordation Number	Status	Contaminant	Value	Date	Value	Date
City of Alhambra							
8 MOELLER	01900010	Inactive	Nitrate	30.8	08/25/1989	27.5	06/08/1994
			TCE	5.3	06/16/1999	4.76	03/16/00
			TDS	275	05/21/1985	268.5	06/07/1994
09	01900011	Inactive	Nitrate	57.3	06/22/1993	48.2	06/08/1994
			TCE	5.41	03/16/00	5.41	03/16/00
			TDS	352.6	06/22/1993	352.6	06/22/1993
10	01900012	Producing - Irrigation	Nitrate	23.6	07/19/1988	23.6	07/19/1988
			TCE	13.1	08/24/1982	1U	11/23/1987
			TDS	346.9	07/19/1988	346.9	07/19/1988
12	01900013	Not in service - VOC contamination	1,1-DCE	1.2	02/21/1985	0.5U	02/03/1995
			Carbon Tetrachloride	0.13	04/01/1981	0.5U	02/03/1995
			Chloroform	0.5	02/03/1995	0.5	02/03/1995
			Cis-1,2-DCE	6.3	02/03/1995	6.3	02/03/1995
			Nitrate	34.1	08/25/1989	33.5	06/09/1994
			PCE	1.8	08/04/1987	0.5U	02/03/1995
			TCE	18.4	02/03/1995	18.4	02/03/1995
			TDS	319	04/03/1990	306.3	04/13/1993
13	01900014	Producing	Methylene Chloride	7.6	05/20/1987	0.5U	08/27/1998
			Nitrate	39	08/24/1989	31.6	05/04/1995
			TDS	353.8	04/25/1989	287	05/04/1995
14	01900015	Producing	Nitrate	35.7	08/24/1989	23.8	05/05/1995
			TCE	2.3	11/20/1990	0.5U	09/22/99
			TDS	292.8	04/11/1989	226	05/05/1995
15	01900016	Producing	Methylene Chloride	3.1	05/20/1987	0.5U	09/22/99
			Nitrate	11.9	08/24/1989	10.5	05/04/1995
			TDS	224.2	04/11/1989	197	05/04/1995
LONGDEN 2	01900017	Producing	Methylene Chloride	4.3	05/20/1987	0.5U	09/22/99
			Nitrate	50.4	04/15/1986	28.8	05/04/1994
			TDS	291	04/15/1986	249.1	05/04/1994
GARFIELD	01900018	Not in service - reason unknown	1,1,2,2-TCA	0.97	11/23/1987	0.5U	09/17/1993
			1,2-DCE	0.85	08/24/1982	0.85	08/24/1982
			Carbon Tetrachloride	0.14	04/01/1981	0.5U	09/17/1993
			Nitrate	648	08/22/1983	48.8	08/19/1992
			PCE	0.48	11/23/1987	0.5U	09/17/1993
			TCE	16	09/24/1980	0.5U	09/17/1993
			TDS	468	05/21/1985	389.7	06/04/1991
LONGDEN-1	01902789	Producing	Nitrate	14.3	07/24/1990	9.8	08/10/1993
			PCE	0.3	07/08/1981	0.5U	08/27/1998
			TCE	1.5	01/10/1980	0.5U	08/27/1998
			TDS	230	07/31/1984	199	08/10/1993
11	01903014	Producing	Nitrate	41.3	07/30/1990	33.3	06/09/1994
			PCE	1.8	10/23/1996	0.9	06/16/1999
			TCE	4.2	05/15/1989	0.5U	06/16/1999
			TDS	247.8	04/03/1990	241.3	08/10/1993
07 - INACTIVE	01903097	Not in service - VOC contamination	Carbon Tetrachloride	0.6	02/21/1985	0.5U	01/16/1997
			Chloroform	0.8	01/26/1995	0.5U	01/16/1997
			Cis-1,2-DCE	0.8	05/16/1989	0.5U	01/16/1997
			Nitrate	51.6	08/25/1989	36.1	06/08/1994
			TCE	13.4	08/13/1991	0.5U	02/26/1999
			TDS	366	04/11/1989	346	07/13/1993
San Gabriel Country Club							
01	01900547	Not in Service, Reason Unknown	na				
02	01902979	Producing	Methylene Chloride	3.8	05/05/1987	1U	08/18/87
			Toluene	0.6	05/05/1987	0.6J	05/05/1987

Table A-1 - Selected Concentrations of Contaminants of Concern
NPL Area 3, San Gabriel Valley

Well Information			Contaminant of Potential Concern Concentration				
Name	Recordation Number	Status	Contaminant	Historic High		Recent	
				Value	Date	Value	Date
San Gabriel County Water District							
BRA 5	01901669	Producing	Chloroform	0.2	01/10/1985	0.5U	09/23/99
			Nitrate	79	06/29/1993	55.8	06/28/1994
			PCE	1.9	02/08/1999	0.9	06/13/00
			TCE	0.88	01/13/1997	0.5U	06/13/00
			TDS	369	08/20/1990	335.9	06/29/1993
07	01901671	Producing	Chloroform	0.5	06/21/1989	0.5U	09/23/99
			Nitrate	35	04/19/1994	34.5	08/24/1994
			TCE	0.01	01/12/1980	0.5U	09/23/99
			TDS	260	06/26/1991	244.9	06/23/1994
08	01901672	Not in service - reason unknown	Nitrate	19	06/13/1978	1.4	08/24/1993
			PCE	0.26	08/31/1981	0.5U	03/28/1991
			TCE	0.3	08/31/1981	0.5U	03/28/1991
			TDS	700	11/21/1990	670.8	08/24/1993
09	01902785	Producing	Chloroform	0.9	12/16/1996	0.5U	09/23/99
			Nitrate	38	12/29/1983	16.7	11/17/1994
			PCE	0.7	02/08/1999	0.5U	06/13/00
			TDS	280	11/02/1988	198	11/17/1994
10	01902786	Not in service - reason unknown	1,1-DCE	3.95	02/02/1987	0.2U	08/13/1993
			Nitrate	38.6	08/13/1993	36.1/38.6	08/13/1993
			PCE	15	08/13/1993	15	08/13/1993
			TCE	0.09	01/12/1980	0.25U	08/13/1993
			TDS	260	06/06/1984	252/237.1	08/13/1993
11	08000067	Producing	Chloroform	0.5	06/21/1989	0.5U	09/23/99
			Methylene Chloride	4.5	05/02/1985	0.5U	09/23/99
			Nitrate	19.6	06/29/1993	9.8	06/28/1994
			PCE	1	09/15/1989	0.5U	09/23/99
			TCE	0.03	01/12/1980	0.5U	09/23/99
			TDS	217.8	06/29/1993	217.8	06/29/1993
#12	08000123	Producing	Chloroform	0.4	12/17/1990	0.5U	09/23/99
			Nitrate	2.3	12/29/1993	1.5	06/08/1994
			TCE	0.8	06/24/1999	0.5U	06/13/00
			TDS	180	12/17/1990	147.4	12/15/1993
14	08000133	Producing	Nitrate	2.8	06/14/1991	1.5	06/23/1994
			TDS	168.6	06/23/1994	168.6	06/23/1994
Southern California Edison Company							
1EB86	01900342	Not is Service - Reason Unknown					
Southern California Water Company							
SAXON 3	01900514	Producing	Nitrate	12.4	08/15/1994	12.4	08/15/1994
			PCE	0.77	08/08/1996	0.5U	08/13/99
			TCE	0.03	01/14/1980	0.5U	08/13/99
			TDS	207.1	09/19/1989	204	08/15/1994
SAXON 1	01900515	Producing	Methylene Chloride	2.2	04/25/1989	0.5U	08/26/1997
			Nitrate	26.4	01/09/1990	3	08/15/1994
			PCE	1.4	04/18/1997	0.9	12/03/1997
			TDS	249.4	01/09/1990	228	08/15/1994
ENCINITAS 1	01902024	Standby	Nitrate	25.6	08/12/1994	25.6	08/12/1994
			PCE	1.7	06/02/1999	1.6	05/24/00
			TCE	10.2	06/02/1999	9.9	05/24/00
			TDS	248	08/12/1994	248	08/12/1994
ENCINITAS 2	01902035	Standby	Methylene Chloride	3.2	04/25/1989	0.5U	08/31/99
			Nitrate	9.8	08/12/1994	9.8	08/12/1994
			PCE	1.6	06/02/1999	1.4	05/24/00
			TCE	6.7	02/24/1997	4.6	05/24/00
			TDS	243.6.	01/09/1990	224	08/12/1994
ENCINITAS 3	08000073	Producing	2-Butanone	9.6	09/09/1998	5U	08/31/99
			Chloroform	2.9	09/09/1998	0.5U	08/31/99
			Methylene Chloride	4.3	04/25/1989	0.5U	08/31/99
			Nitrate	43.2	07/23/1993	15	08/12/1994
			PCE	2.2	05/31/00	2.2	05/31/00
			TCE	7.7	04/07/1998	6.3	05/31/00
			TDS	276.9	12/15/1987	230	08/12/1994

Table A-1 - Selected Concentrations of Contaminants of Concern
NPL Area 3, San Gabriel Valley

Well Information			Contaminant of Potential Concern Concentration				
Name	Recordation Number	Status	Contaminant	Historic High		Recent	
				Value	Date	Value	Date
SAXON 4	08000146	Producing	Nitrate	7.6	08/15/1994	7.6	08/15/1994
			TDS	194	08/15/1994	194	08/15/1994
Sunny Slope Water Company							
8	01900026	Producing	4-Methyl-2-Pentanone	1	04/03/1987	5U	08/26/99
			Nitrate	23	05/06/1985	12.1	03/27/1995
			TCE	0.03	01/11/1980	0.5U	08/26/99
			TDS	270	06/08/1989	176	03/27/1995
9	01902792	Producing	Nitrate	20.7	09/05/1989	10.5	09/26/1994
			TDS	275	08/16/1990	204	09/26/1994
10	08000048	Not in service - reason unknown	Nitrate	44.1	03/11/1994	29.7	06/28/1994
			TDS	300	06/14/1984	270.7	03/11/1994
13	08000157	Producing	VOCs	ND	03/13/1997	ND	05/30/00
Temple City Sheriff Station Monitoring Wells							
MW-1	W11TCSW1	Observation	1,2-DCA	0.5	06/23/1993	0.5U	04/14/94
			Benzene	8.8	06/23/1993	0.5U	04/14/94
			Total Xylenes	2.5	06/23/1993	1.0U	04/14/94
			PCE	480	04/14/1994	480	04/14/94
			TCE	4.6	02/24/1993	0.5U	04/14/94
MW-2	W11TCSW2	Observation	1,2-DCA	64	10/12/1993	15	04/14/94
			Benzene	440	10/12/1993	11	04/14/94
			PCE	150	10/12/1993	120	04/14/94
			TCE	2.3	01/31/1994	1.6	04/14/94
			Toluene	140	10/12/1993	0.5U	04/14/94
			Total Xylenes	176	10/12/1993	1.0U	04/14/94
MW-3	W11TCSW3	Observation	1,2-DCA	30	04/14/1994	30	04/14/94
			Benzene	100	04/14/1994	100	04/14/94
			PCE	470	04/14/1994	470	04/14/94
			TCE	6.8	04/14/1994	6.8	04/14/94
			Toluene	10	10/12/1993	2.8	04/14/94
			Total Xylenes	32.2	06/23/1993	1.7	04/14/94

Acronyms:

PCE: Tetrachloroethylene
TCE: Trichloroethylene
DCE: Dichloroethylene
DCA: Dichloroethane
TCA: Trichloroethane
TDS: Total Dissolved Solids (mg/L)
na: data are not available

Flags:
U: undetected
J: estimated

Maximum Contaminant Levels (MCLs):

PCE, TCE	5 micrograms per liter (ug/L)
1,1,1-TCA	200 ug/L
1,1-DCE	6 ug/L
1,2-DCE	none
Cis-1,2-DCE	6 ug/L
Trans-1,2-DCE	10 ug/L
1,1,2,2-TCA	1 ug/L
2-Butanone	none
4-Methyl-2-Pentanone	none
Benzene	1 ug/L
Carbon Tetrachloride	0.5 ug/L
Chloroform	100 ug/L
Methylene Chloride	5 ug/L
Toluene	150 ug/L
Total Xylenes	1,750 ug/L
Nitrate	45 milligrams per liter (mg/L)

TABLE A-2A
Data Needs and Uses – Regulatory Limits for Organic Parameters

Organic Compound	Uses/Decisions	Applicable Regulatory Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [2]	Additional Regulatory Limits (µg/L)
Groundwater and Well Development Water					
***Volatile Organic Compouds*:**					
Benzene	Define nature and extent of contamination	1	CA Primary MCL [A]	0.5[4]	0.15 [E]
Bromodichloromethane		100	USEPA Primary MCL [C]	0.5[4]	2.5 [I] ; 100-proposed [A]
Bromoform	Compare data to Federal and State drinking water standards	100	USEPA Primary MCL [C]	0.5[4]	45 [I] ; 100-proposed [A]
Bromomethane		500	CA Proposition 65 Regulatory Level [I]	0.5[4]	--
Carbon disulfide	Assess source of contaminants	160	CA DHS State Action Level [F]	--	--
Carbon tetrachloride		0.5	CA Primary MCL [A]	0.5	0.1 [E]
Chlorobenzene	Assess need for monitoring or treatment	70	CA Primary MCL [A]	--	50 [H]
Chloroethane		16	Other Taste and Odor [H]	0.5[4]	100 [I]
Chloroform		100	CA/USEPA Primary MCL [A,C]	0.5[4]	10 [I]
Dibromochloromethane		100	CA/USEPA Primary MCL [A,C]	0.5[4]	3.5 [I]
Dibromochloropropane (DBCP)[4]	Compare to Federal and State limits for proper disposal	0.2[4]	CA/USEPA Primary MCL [A,C]	0.01	0.05 [I]; 0.0017 [E]
1,2-Dibromoethane [4]		0.05[4]	CA/USEPA Primary MCL [A]	--	0.05 [C]; 0.1 [I]
1,2-Dichlorobenzene		10	CA DHS State Action Level [G]	0.5[4]	10-proposed [D]
1,3-Dichlorobenzene		10	CA DHS State Action Level [G]	0.5[4]	600 [F]
1,4-Dichlorobenzene		5	CA Primary MCL [A]	0.5[4]	5-proposed [D]
Dichlorodifluoromethane		1,000	CA DHS State Action Level [F]	0.5[4]	--
1,1-Dichloroethane		5	CA Primary MCL [A]	0.5[4]	50 [I]
1,2-Dichloroethane		0.5	CA Primary MCL [A]	0.5	0.4 [E]
1,1-Dichloroethylene		6	CA Primary MCL [A]	0.5[4]	7 [C]
cis-1,2-Dichloroethylene		6	CA Primary MCL [A]	0.5[4]	70 [C]
trans-1,2-Dichloroethylene		10	CA Primary MCL [A]	0.5[4]	100 [C]
Dichloromethane		5	CA/USEPA Primary MCL [A]	0.5[4]	4 [E]
1,2-Dichloropropane		5	CA/USEPA Primary MCL [A]	0.5[4]	0.5 [E]
cis-1,3-Dichloropropene		0.5	CA Primary MCL [A]	0.5	0.2 [E]
trans-1,3-Dichloropropene		0.5	CA Primary MCL [A]	0.5	0.2 [E]
Ethylbenzene		30	USEPA Secondary MCL – proposed [D]	0.5[4]	29 [H]

TABLE A-2A
Data Needs and Uses – Regulatory Limits for Organic Parameters (Continued)

Organic Compound	Uses/Decisions	Applicable Regulatory Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [2]	Additional Regulatory Limits (µg/L)
Isopropylbenzene		260	CA DHS State Action Level [F]	0.5[4]	--
Methyl ethyl ketone		8,400	Other Taste and Odor [H]	5	--
Methyl isobutyl ketone (MIBK)		120	CA DHS State Action Level [F]	5	1300 [H]
Styrene		10	USEPA Secondary MCL – proposed [D]	0.5[4]	11 [H]; 100 [A] [C]
1,1,2,2-Tetrachloroethane		1	CA Primary MCL [A]	0.5[4]	1.5 [I]
Tetrachloroethylene (PCE)		5	CA/USEPA Primary MCL [A]	0.5[4]	0.06 [E]
Toluene		40	USEPA Secondary MCL – proposed [D]	0.5[4]	42 [H]; 150 [A] [E]
1,2,4-Trichlorobenzene		5	CA PHG [E]	0.5[4]	70 [A,C]
1,1,1-Trichloroethane		200	CA Primary MCL [A]	0.5[4]	200 [C]
1,1,2-Trichloroethane		5	CA Primary MCL [A]	0.5[4]	5 [C] [I]
Trichloroethylene (TCE)		5	CA/USEPA Primary MCL [A]	0.5[4]	0.8 [E]
Trichlorofluoromethane		150	CA Primary MCL [A]	5	700 [E]
1,1,2-Trichloro-1,2,2-trifluoroethane		1,200	CA Primary MCL [A]	10	4,000 [E]
Vinyl chloride		0.5	CA Primary MCL [A]	0.5	0.05 [E]
Xylene(s)		20	USEPA Secondary MCL – proposed [D]	0.5[4]	17 [H]
Additional Volatile Organic Compounds:					
Methyl tert-butyl ether (MTBE)		5	CA Secondary MCL [B]	3	13 [A] [E]
Formaldehyde		100	CA DHS State Action Level[F]	--	--
Dichlorodifluoromethane (Freon 12)		1,000	CA DHS State Action Level[F]	--	--
Tertiary Butyl Alcohol (TBA)		12	CA DHS State Action Level[F]	--	--
1,2,3-Trichloropropane		0.005[4]	CA DHS State Action Level[F]	--	--
Semivolatile Organic Compounds:					
Benzo(a)pyrene		0.2[4]	CA/USEPA Primary MCL[A,C]	0.1[4]	0.004[E]
Bis(2-ethylhexyl)phthalate		4[4]	CA Primary MCL[A]	3.0	6[C]; 12[E]

TABLE A-2A
Data Needs and Uses – Regulatory Limits for Organic Parameters (Continued)

Organic Compound	Uses/Decisions	Applicable Regulatory Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [2]	Additional Regulatory Limits (µg/L)
2,4-Dimethylphenol		100	CA DHS State Action Level[F]	--	--
Hexachlorobenzene		1[4]	CA Primary MCL[A]	0.5[4]	--
Hexachlorocyclopentadiene		50	CA/USEPA Primary MCL[A,C]	1[4]	50[E]
Pentachlorophenol		1[4]	CA/USEPA Primary MCL[A,C]	0.2[4]	0.4[E]
Phenol		4,200	CA DHS State Action Level[F]	--	--
Bis(2-ethylhexyl)adipate		400	CA/USEPA Primary MCL[A,C]	5[4]	--
Endothall		100	CA/USEPA Primary MCL[A,C]	45	580[E]
Glyphosate		700	CA/USEPA Primary MCL[A,C]	25	1,000[E]
Additional Compounds:					
1,4-Dioxane		3	CA DHS State Action Level [F]	3	15 [I]
N-Nitrosodimethylamine (NDMA)		0.02/10[5]	CA DHS State Action Level [F]	10[5]	0.02 [I]
Investigation-Derived Waste					
Drill Cuttings and Drilling Mud:					
VOCs	Compare to Federal (TCLP), State and TSDF specific limits for proper disposal.				
Benzene		500 µg/L	TCLP limit µg/L		
Carbon tetrachloride		500 µg/L	TCLP limit µg/L		
Chlorobenzene		100,000 µg/L	TCLP limit µg/L		
Chloroform		6,000 µg/L	TCLP limit µg/L		
1,2-dichloroethane		500 µg/L	TCLP limit µg/L		
1,1-dichloroethylene		700 µg/L	TCLP limit µg/L		
Methyl ethyl ketone		200,000 µg/L	TCLP limit µg/L		
Tetrachloroethylene		700 µg/L	TCLP limit µg/L		
Trichloroethylene		500 µg/L	TCLP limit µg/L		
		2,040 mg/kg	California TCLP limit mg/kg		
Vinyl chloride		200 µg/L	TCLP limit µg/L		

TABLE A-2A
Data Needs and Uses – Regulatory Limits for Organic Parameters (Continued)

Organic Compound	Uses/Decisions	Applicable Regulatory Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [2]	Additional Regulatory Limits (µg/L)
TPH-gasoline		Not applicable	Landfill-specific		
TPH-diesel		Not applicable	Landfill-specific		

NOTES:
(1) ARARs from August 2000 California EPA Compilation of Water Quality Goals and Updates through November 2001.
(2) California Department of Health Services required Detection Limit for Purposes of Reporting (DLR).
(3) Calculated ARAR based on hardness = 120 mg/L as $CaCO_3$.
(4) Applicable limit is lower than reporting limit for method proposed as stated in EPA laboratory SOPs (Appendix B).
(5) Newly proposed DHS limit
(A) CA Department of Health Services Primary MCL for Drinking Water.
(B) CA Department of Health Services Secondary MCL for Drinking Water.
(C) USEPA Primary MCL for Drinking Water.
(D) USEPA Secondary MCL for Drinking Water.
(E) CA Office of Environmental Health Hazard Assessment Public Health Goal for Drinking Water.
(F) CA Department of Health Services State Action Level for Toxicity.
(G) CA Department of Health Services State Action Level for Taste and Odor.
(H) Other Taste and Odor Thresholds.
(I) CA Proposition 65 Regulatory Level for Drinking Water.

TABLE A-2B
Data Needs and Uses – Regulatory Limits for Inorganic Parameters

Inorganic Parameter	Uses/Decisions	Applicable Regulatory Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [3]	Additional ARARs (µg/L)
Groundwater and Well Development Water					
Perchlorate	Define nature and extent of contamination Compare data to Federal and State drinking water standards Assess source of contaminants Assess need for monitoring or treatment	4[5]	CA DHS State Action Level [F]	4 (preliminary)	1[6]
Nitrate	Compare to Federal and State limits for proper disposal.	45,000	CA/USEPA Primary MCL [A,C]		
Aluminum[5]		50[5]	USEPA Secondary MCL [D]	50[5]	200 [B]; 600 [E]
Antimony		6[5]	CA/USEPA Primary MCL [A,C]	6[5]	
Arsenic		10[5]	USEPA Primary MCL [C]	2[5]	50 [A]
Barium		1,000	CA Primary MCL [A]	100	2,000 [C] [D]
Beryllium		4	CA/USEPA Primary MCL [A,C]	1	
Cadmium		5	CA/USEPA Primary MCL [A,C]	1[5]	0.7[©]; 2.6 [2] [H]
Calcium			No Applicable ARAR		
Chromium (total)		50	CA Primary MCL [A]	10	
Hexavalent Chromium		11 (0.2) [4]	California Toxics Rule for Aquatic Life Protection [H]	1	
Cobalt			No Applicable ARAR		
Copper[5]		11 [2, 5]	California Toxics Rule for Aquatic Life Protection [H]	50	170 [E]; 1300 [F]
Iron		300	CA/USEPA Secondary MCL [B,D]	100	
Lead		3.1[5]	California Toxics Rule for Aquatic Life Protection [H]	5[5]	15 [F]; 2 [E]; 0.25 [G]

TABLE A-2B
Data Needs and Uses – Regulatory Limits for Inorganic Parameters (Continued)

Inorganic Parameter	Uses/Decisions	Applicable Regulatory Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [3]	Additional ARARs (µg/L)
Magnesium			No Applicable ARAR		
Manganese		50	CA/USEPA Secondary MCL [B,D]	20	
Mercury		2	CA/USEPA Primary MCL [A,C]	1	1.2 [E]
Nickel		61	California Toxics Rule for Aquatic Life Protection [H]	10[5]	12 [E]
Potassium			No Applicable ARAR		
Selenium[5]		5[5]	California Toxics Rule for Aquatic Life Protection [H]	5[5]	50 [A] [C]
Silver		4.7 [2, 5]	California Toxics Rule for Aquatic Life Protection [I]	10	100 [B] [D]
Sodium			No Applicable ARAR		
Thallium		2.0[5]	CA/USEPA Primary MCL [A,C]	1[5]	0.1 [E]
Vanadium		50	CA DHS State Action Level [F]	3 (preliminary)[5]	
Zinc		140 [2]	California Toxics Rule for Aquatic Life Protection [H]	50	5,000 [B] [D]
Investigation-Derived Waste					
Drill Cuttings and Drilling Mud:					
TTLC Metals	Compare to Federal(TCLP), State and TSDF-specific limits for proper disposal.				
Antimony		500 mg/kg	TTLC limit mg/kg		
Arsenic		500 mg/kg	TTLC limit mg/kg		
		5000 µg/L	TCLP limit µg/L		
Barium		10,000 mg/kg	TTLC limit mg/kg		
		100,000 µg/L	TCLP limit µg/L		
Beryllium		75 mg/kg	TTLC limit mg/kg		
Cadmium		100 mg/kg	TTLC limit mg/kg		
		1,000 µg/L	TCLP limit µg/L		
Chromium		2,500 mg/kg	TTLC limit mg/kg		
		5,000 µg/L	TCLP limit µg/L		
Cobalt		8,000 mg/kg	TTLC limit mg/kg		

TABLE A-2B
Data Needs and Uses – Regulatory Limits for Inorganic Parameters (Continued)

Inorganic Parameter	Uses/Decisions	Applicable Regulatory Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [3]	Additional ARARs (µg/L)
Copper		2,500 mg/kg	TTLC limit mg/kg		
Lead		1,000 mg/kg	TTLC limit mg/kg		
		5,000 µg/L	TCLP limit µg/L		
Mercury		20 mg/kg	TTLC limit mg/kg		
		200 µg/L	TCLP limit µg/L		
Molybdenum		3,500 mg/kg	TTLC limit mg/kg		
Nickel		2,000 mg/kg	TTLC limit mg/kg		
Selenium		100 mg/kg	TTLC limit mg/kg		
		1,000 µg/L	TCLP limit µg/L		
Silver		500 mg/kg	TTLC limit mg/kg		
		5,000 µg/L	TCLP limit µg/L		
Thallium		700 mg/kg	TTLC limit mg/kg		
Vanadium		2,400 mg/kg	TTLC limit mg/kg		
zinc		5,000 mg/kg	TTLC limit mg/kg		
pH		Not applicable	Landfill-specific		
Flashpoint		Not applicable	Landfill-specific		

NOTES:
(1) ARARs from August 2000 California EPA Compilation of Water Quality Goals and Updates through November 2001
(2) Calculated ARAR based on hardness = 120 mg/L as $CaCO_3$.
(3) California Department of Health Services required Detection Limit for Purposes of Reporting (DLR).
(4) 0.2 µg/L detection level is needed for comparability to other databases in the region per previous DHS limit.
(5) Applicable limit is lower than reporting limit for method proposed as stated in EPA laboratory SOPs (Appendix B).
(6) Per EPA revised draft toxicity assessment
(A) CA Department of Health Services Primary MCL for Drinking Water.
(B) CA Department of Health Services Secondary MCL for Drinking Water.
(C) USEPA Primary MCL for Drinking Water.
(D) USEPA Secondary MCL for Drinking Water.
(E) CA Office of Environmental Health Hazard Assessment Public Health Goal for Drinking Water.
(F) CA Department of Health Services State Action Level for toxicity.
(G) CA Proposition 65 Regulatory Level for Drinking Water.
(H) California Toxics Rule for Freshwater Aquatic Life Protection - Continuous (4-day average) Concentration.
(I) California Toxics Rule for Freshwater Aquatic Life Protection - Maximum (1-hr average) Concentration.
(J) Other Taste and Odor Thresholds.

TABLE A-3
Measurement Performance Criteria
Quality Assurance Project Plan for Alhambra Operable Unit

Parameter	Method	Reporting Limit/Target Detection Limit[h]	Analytical Accuracy (% Recovery)	Analytical Precision (Relative % Deviation)	Overall Completeness (%)
Groundwater and Well Development Water					
Volatile Organic Compounds (VOCs) [a]	EPA 524.2 (SOP 354)[b]	(c)	70-130	±30	90
1,2,3-Trichloropropane	Cal-DHS[b]	0.005	40-130	±30	90
Semivolatile Organic Compounds	EPA 8270[b,d]	(i)	(j)	(j)	90
1,4-Dioxane	EPA 8270/SIM[b,d]	1 µg/L	40-130	±30	90
NDMA	Modified EPA Method 1625	0.002 µg/L	50-125	±30	90
Nitrate	EPA 300.0[b]	0.1 mg/L	50-125	±25	90
Perchlorate	EPA 314[b,d]	2 µg/L	50-150	±50	90
Hexavalent Chromium	EPA 218.6[d]	0.2 µg/L	70-140	±30	90
Metals [a]	EPA 200.7[b,d] EPA 200.8[b,d] EPA 200.9[b,d] EPA 245.1[b,d]	(g)	70-130	±30	90
Investigation-Derived Waste					
Drill Cuttings and Drilling Mud:					
Volatile Organics	EPA 5035/8260 (SOP 305)[b]	(j)	(j)	(j)	90
Total Petroleum Hydrocarbons (Ca LUFT)	EPA 8015M (Ca LUFT)	0.5 mg/l	70-130	±30	90
TTLC Metals (Ca Title 22)	EPA 6010/7471 (SOPs 405, 503, and 517)	(j)	70-130	±30	90
Flashpoint	EPA 1010	5° F	NA	NA	90
pH	EPA 9045 (SOP 582)[b]	NA	NA	0.1 units	90

Notes:
[a] Compound List as shown in Table A-2a.
[b] EPA Region IX SOP provided in Appendix B. For other analytes a project DQI or CRF is provided in Appendix B as these may be analyzed by laboratories other than the regional laboratory.
[c] Detection limits will be at 1 ug/L for all, except 0.5 ug/L for vinyl chloride, carbon tetrachloride, 1,2 dichloroethane, cis and trans-1,3-dichloropropene.
[d] U.S. Environmental Protection Agency, 1979. *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, revised March 1983; U.S. Environmental Protection Agency, *Test Methods for Evaluating Solid Waste*, SW846.
[e] *Standard Methods for the Examination of Water and Wastewater*, 17th Edition (1989).
[f] State of California Department of Health Services (DHS) Method Determination of Perchlorate by Ion Chromatography, as detailed in EPA Region IX SOP in Appendix B.
[g] Detection limits provided in Appendix B along with methods for the specific metals.
[h] Target detection level is reporting level; see text for explanation.
[i] Detection limits will be 10 ug/L.
[J] Detection levels and quality control criteria are per standard operating procedures presented in Appendix B.

Section B
Measurement Data Acquisition

This section presents sampling process design and requirements for sampling methods, sampling handling and custody, analytical methods, quality control, and instrumentation for the sampling activities that will be conducted as a part of a remedial investigation in Area 3. Data acquisition requirements and data management for these sampling events are also addressed in this section.

B.1 Sampling Process Design

The sampling process design is detailed below.

B.1.1 Background

Area 3 is in the initial stages of the RI/FS process. In January 2001, the Data Evaluation Report was completed. The report identified data gaps within Area 3 and recommended appropriate field activities to be conducted to meet the technical goals and objectives of the RI.

Available groundwater quality data for the Area 3 are primarily from wellhead sampling of production wells. However, because of the long (some as great as 500 feet) and/or multiple-screen intervals in the production wells, the vertical extent of VOC contamination throughout Area 3 is unknown. Additionally, because of the limited number of monitoring wells in Area 3, groundwater gradients, flow directions, and the horizontal extent of contamination are not well understood.

Little assessment of PRP sites has been conducted in Area 3, and groundwater monitoring data are available at only two PRP sites within Area 3. Because of the limited groundwater data from PRPs, the source(s) of VOC contamination in Area 3 has/have not been identified.

Two cluster groundwater monitoring wells and three multiport (MP) monitoring wells will be installed during this phase of the RI activities. Quarterly groundwater monitoring data from each of these wells will be collected to characterize the three-dimensional nature and extent of contamination at the site and to assist in identifying source areas within Area 3.

The sampling process design for investigation-derived wastes and quarterly monitoring in Area 3 includes the schedule of analyses and rationale for sampling design, as described in detail below.

B.1.2 Schedule of Analyses

The analytes scheduled for the RI field program are presented in Table A-3. Analytical services for all samples collected from the cluster and MP monitoring wells will be

submitted for analysis to EPA's Region IX Analytical Program and to private laboratories under subcontract to CH2M HILL as described in Section B.4.

Sampling of investigation-derived wastes is expected to begin in November 2002, will occur periodically, and will last through March 2003.

An initial groundwater sampling event for VOCs and dissolved metals will be conducted within approximately 2 weeks completion of each monitoring well. It is anticipated the initial sampling event will occur in two phases: one for wells MW1-1, MW1-2, and MW1-3 during December 2002 and one for wells MW1-4 and MW1-5 during February 2003. Ongoing groundwater sampling events will be conducted on a quarterly basis for VOCs for 2 years, for a total of eight sampling events, with the last event occurring in January 2005.

During the third sampling event, anticipated to take place in the summer of 2003, additional groundwater sampling will be conducted at each well for SVOCs, NDMA, perchlorate, nitrate, 1,4-dioxane, hexavalent chromium, and 1,2,3-trichloropropane. Additional or continued sampling for these analytes will depend on the results of the third sampling event. For example, one additional confirmation sample will be collected if an analyte is detected in a well.

B.1.3 Rationale for Sampling Design

The rationale for sampling design is detailed in the subsections below.

B.1.3.1 Groundwater Monitoring

Sampling Locations

Figure A-5 shows the locations of the cluster and MP monitoring wells in Area 3. Because there are several screen intervals at each location of the cluster and MP monitoring wells, the number of wells and screen intervals is greater than the number of sampling locations shown in Figure A-5.

The cluster wells (MW1-1 and MW1-2) are located in the western portion of Area 3 to collect groundwater data between existing production wells with VOC contamination and suspected upgradient PRP facilities. The proposed screen depths for these wells are based on depths to groundwater in production wells in the central part of Area 3, east of the proposed cluster well locations (Figure A-5). The cluster well screen depths are relatively shallow compared to the proposed MP wells. The purpose for this is to target the shallower portion of the alluvial aquifer where VOC concentrations intermediate between those observed in production wells and shallow PRP facility monitoring wells may occur (Table B-1).

TABLE B-1
Proposed Screen Intervals for the Cluster and MP Monitoring Wells

Well Name	MW1-1	MW1-2	MW1-3	MW1-4	MW1-5
Well Type	Cluster	Cluster	MP	MP	MP
Screen Intervals (feet below ground surface)	320 to 340 390 to 410	335 to 355 405 to 425	360 to 370 440 to 450 520 to 530 600 to 610 680 to 690 770 to 780	380 to 390 460 to 470 540 to 550 620 to 630 700 to 710 770 to 780	350 to 360 440 to 450 520 to 530 600 to 610 680 to 690 770 to 780

The proposed MP wells are generally located in areas of VOC contamination in deep production wells with long and/or multiple-screen intervals and will be constructed with six depth discrete groundwater sampling intervals. Groundwater data collected from the depth discrete intervals will be used to assess the vertical nature and extent of contamination in Area 3. The depth of these wells generally is consistent with the deepest production wells in Area 3.

Number of Samples

An initial groundwater sampling event for VOCs and dissolved metals will be conducted roughly 2 weeks after the completion of each monitoring well. Ongoing groundwater sampling events will be conducted on a quarterly basis for VOCs for the remainder of a 2-year period, for a total of eight sampling events. These sampling events will be used to evaluate temporal changes in the nature and extent of VOC contamination in Area 3 that might be related to groundwater production, to evaluate any VOC exceedances of regulatory limits, and assist in identifying contaminant source areas. It is anticipated that 2 years data will be sufficient to establish trends in water quality changes. During the third sampling event, additional groundwater samples will be collected at each well for semivolatile organic compounds (SVOCs), NDMA, perchlorate, nitrate, 1,4-dioxane, hexavalent chromium, and 1,2,3-trichloropropane. These samples will be collected to evaluate regulatory level exceedances and to assess the need for continued monitoring or future treatment for those analytes. Future sampling for these analytes will depend on the results of the third sampling event. At least one additional confirmation sample will be collected if the analyte is detected.

In addition to groundwater samples, field QA samples will be collected in the form of duplicates, blanks, and matrix spike/matrix spike duplicate (MS/MSD) samples. At a minimum, one field duplicate will be collected for each analysis for every 10 wells/screens sampled or a one per week, whichever is larger. An attempt will be made to collect duplicate samples from a well that is expected, or known to be, moderately contaminated.

One blank will collected for every analyte every day that a sample is taken. Field blank samples will be collected to check for possible cross-contamination of groundwater samples from the point of sample collection to the analysis of the samples by the laboratory. Equipment (blank) samples will be collected to check for possible cross-contamination of groundwater samples after decontamination of common equipment used to collect samples from a number of different wells or screens in a given day.

Temperature blanks will be used to determine the samples have been maintained at the appropriate temperature of 4 degrees Celsius (°C). Temperature blanks will be prepared each day samples are collected and will be included with each cooler of samples sent to the lab. Laboratory QC samples (MS/MSDs) will be identified for all analyses during each sampling event. One MS/MSD sample per analyte will be identified for each 20 samples collected.

Laboratory Analyses

Analysis of VOCs with low-detection limits will be used to assess the magnitude of groundwater contamination in the new monitoring wells and to determine whether any of the VOCs detected exceed regulatory limits. The rationale for the VOC analyses is that

VOCs are the most prevalent contaminants in production wells in Area 3. Sampling for VOCs will be included in each of the eight sampling events. In addition, sampling for dissolved metals, SVOCs, NDMA, perchlorate, nitrate, 1,4-dioxane, hexavalent chromium, and 1,2,3-trichloropropane will be conducted during one sampling event to evaluate exceedances of regulatory limits and to assess the need for continued monitoring or future treatment for these analytes. The rationale for these analyses is that many of the analytes have maximum contaminant levels, action levels, or other regulatory limits, have been detected in other areas of the San Gabriel Basin where VOCs are present, and require significantly different treatment methods for removal from groundwater compared to VOCs.

B.1.3.2 Investigation-Derived Wastes

Liquid and solid investigation-derived wastes will be generated during drilling, development, and sampling of the proposed monitoring wells. Each of these wastes may potentially be contaminated with VOCs. Samples of the drill cuttings, drilling fluids and development water will be collected from these storage units prior to removal from the site to evaluate the proper storage, disposal, or discharge of the waste materials. The following subsections describe each of the wastes and the sampling procedures that will be used to characterize the wastes.

Drill Cuttings and Fluids

Drill cuttings and fluids will be generated during drilling of the monitoring wells,. The drill cuttings will be contained in roll-off bins stored at each well site. Two grab samples will be collected for every 50 cubic yards of drill cuttings. Samples will be collected from coarse-grained materials, which are likely to be the pathways for contamination migration in the subsurface, or will be collected from bins which contain cuttings representative of the dominant soil material encountered during drilling. In addition, one laboratory QC sample and one duplicate will be analyzed for the drill cuttings. In addition, the number of field blank samples collected will be equal to 10 percent of the drill cutting and drilling fluid samples collected or one per week, whichever is greater. In the past, attempts have been made to use photoionization detector (PID) organic vapor reading to select cuttings for analysis. However, based on previous experience in the Whittier Narrows OU, no organic vapors have been detected during monitoring of drill cuttings during drilling and logging of the cuttings. Thus PID organic vapor monitoring or readings are unlikely to be useful for screening of cuttings for sample collection.

Drilling fluids (water and bentonite) will be containerized in Baker tanks or equivalent and stored on site at each well location. One sample of drilling fluid will be collected per tank. It is likely that the drilling fluid in each tank will be fairly homogeneous as a result of recirculation, mixing, and agitation during the drilling process. Thus, one sample per tank should be sufficient in characterizing the fluids in the tank. Because drilling fluid tends to separate into the heavier mud at depth and lighter water near the top of the tank, the sampling bailer will be lowered near the bottom of the Baker tank to collect a fluid sample with a high solids content.

The drill cuttings and fluids will be analyzed for the following, according to local landfill requirements:

- pH

- Flashpoint
- Total Petroleum Hydrocarbons – gasoline (TPHg)
- Total Petroleum Hydrocarbons – diesel (TPHd)
- VOCs
- Total Threshold Limit Concentration (TTLC) Metals

The analyses listed above have been performed on wastes generated previously during well installation activities associated with VOC contamination in the Whittier Narrows and South El Monte OUs and none of the wastes have been classified as hazardous. A quick turn-around time (7 days) will be necessary for characterization and disposal of the drill cuttings and fluids to avoid costs associated with long-term storage of the wastes.

Development and Purge Water

During development and sampling of the wells, water will be generated that has the potential to be contaminated. Water generated from well development activities will be contained in Baker, or equivalent, tanks, stored temporarily on site. One groundwater sample per tank will be collected. It is likely that the water in each tank will be fairly homogeneous as a result of mixing and agitation during the well development and sampling processes. Thus, one sample per Baker tank should be sufficient in characterizing the fluids in the baker tank. In addition, one laboratory QC sample and one duplicate will be analyzed for well development water from the wells to be drilled. The number of field blank samples collected will be equal to 10 percent of the development and purge water samples collected or one per week, whichever is greater. When collecting the sample from a tank, the sampling bailer will be lowered to the middle of the to avoid any water that may have been affected by evaporation at the top of the water column.

Well development and purge water samples will be analyzed for the following:

- VOCs
- SVOCs
- 1,2,3-Trichloropropane
- NDMA
- Perchlorate
- Nitrate
- 1,4-Dioxane
- Hexavalent Chromium
- Dissolved Metals

The rationale for the chemical analyses listed above is based on review of regulatory levels, as described in the companion QAPP (EPA, 2002). A quick turn-around time (3 days) will be necessary for characterization and disposal of the development and purge water to avoid costs associated with long-term storage of the wastes.

B.2 Sampling Methods Requirements

Sampling method requirements have been detailed in the associated FSP (EPA, 2002), in Section 6.

B.3 Sample Handling and Custody Requirements

A sample is physical evidence collected from a hazardous waste site, from the immediate environment, or from another source. Because of the potential evidentiary nature of samples, the possession of samples must be traceable from the time the samples are collected until they are introduced as evidence. In addition to field notebooks, there are a number of documents for tracking sample custody.

Field documents including sample custody seals, chain-of-custody (COC) records, and packing lists will be obtained from the Regional Sample Control Center (RSCC) in EPA's Quality Assurance Office. Chain-of-custody procedures will be used to maintain and document sample collection and possession. After sample packaging, the following one or more of the COC paperwork forms will be completed, as necessary, for the appropriate samples:

- Organic traffic report & chain of custody record
- Inorganic traffic report & chain-of-custody record
- EPA Region IX Chain-of-Custody Record
- Overnight shipping courier air bill

Copies of the above forms will be filled out and distributed per instructions for sample shipping and documentation in Appendix C. Completed field quality assurance/quality control summary forms will be sent to the RSCC at EPA's Region IX Quality Assurance Office at the conclusion of each sampling event.

B.3.1 Chain-of-Custody

Because samples collected during any investigation could be used as evidence, their possession must be traceable from the time the samples are collected until they are introduced as evidence in legal proceedings. Chain-of-custody procedures are followed to document sample possession.

B.3.1.1 Definition of Custody

A sample is under custody, if one or more of the following criteria are met:

- It is in your possession
- It is in your view, after being in your possession
- It was in your possession and then you locked it up to prevent tampering
- It is in a designated secure area

B.3.1.2 Field Custody

In collecting samples for evidence, only enough to provide a good representation of the media being sampled will be collected. To the extent possible, the quantity and types of samples and sample locations are determined before the actual fieldwork. As few people as possible should handle samples.

The field sampler is personally responsible for the care and custody of the samples collected until they are transferred or dispatched properly.

The SM determines whether proper custody procedures were followed during the fieldwork, and decides if additional samples are required.

B.3.1.3 Transfer of Custody and Shipment

Samples are accompanied by a COC record. When transferring samples, the individuals relinquishing and receiving sign, date, and note the time on the record. This record documents custody transfer from the sampler, often through another person, to the analyst at the laboratory.

Samples are packaged properly for shipment and dispatched to the appropriate laboratory for analysis, with a separate COC record accompanying each shipping container (one for each field laboratory and one for samples driven to the laboratory). Shipping containers will be sealed with custody seals for shipment to the laboratory. Courier names, and other pertinent information, are entered in the "Received by," section of the COC record.

Whenever samples are split with a facility owner or agency, it is noted in the remarks section of the COC record. The note indicates with whom the samples are being split, and is signed by both the sampler and recipient. If the split is refused, this will be noted and signed by both parties. If a representative is unavailable or refuses to sign, this is noted in the remarks section of the COC record. When appropriate, as in the case where the representative is unavailable, the COC record should contain a statement that the samples were delivered to the designated location at the designated time.

All shipments are accompanied by the COC record identifying its contents. The original record and yellow copy accompanies the shipment to the laboratory, and the pink copy is sent to be retained by the SM. A copy of the COC form is included in Appendix C.

If sent by mail, the package is registered with return requested. If sent by common carrier, a bill of lading is used. Freight bills, postal service receipts, and bills of lading are retained as part of the permanent documentation.

B.3.1.4 Laboratory Custody Procedures

A designated sample custodian accepts custody of the shipped samples, and verifies that the packing list sample numbers match those on the COC records. Pertinent information as to shipment, pickup, and courier is entered in the "Remarks" section. The custodian then enters the sample numbers into a bound notebook, which is arranged by project code and station number.

The laboratory custodian uses the sample identification number or assigns a unique laboratory number to each sample, and is responsible for seeing that all samples are transferred to the proper analyst or stored in the appropriate secure area.

The custodian distributes samples to the appropriate analysts. Laboratory personnel are responsible for the care and custody of samples from the time they are received, until the sample is exhausted or returned to the custodian. The data from sample analyses are recorded on the laboratory report form.

When sample analyses and necessary QA checks have been completed in the laboratory, the unused portion of the sample will be disposed of properly. All identifying stickers, data sheets, and laboratory records are retained as part of the documentation. Sample containers

and remaining samples are disposed of in compliance with all federal, state, and local regulatory requirements.

B.3.2 Custody Seals

When samples are shipped to the laboratory, they must be placed in containers sealed with custody seals. One or more custody seals must be placed on each side of the shipping container (cooler).

B.3.3 Field Notebooks

Typical field information to be entered in the field notebook is included in the companion FSP (EPA, 2002; Section 6.8). In addition to COC records, a bound field notebook must be maintained by each sampling team leader to provide a daily record of significant events, observations, and measurements during field investigations. All entries should be signed and dated. It should be kept as a permanent record.

These notebooks are intended to provide sufficient data and observations to enable participants to reconstruct events that occurred during the project, and to refresh the memory of the field personnel if called upon to give testimony during legal proceedings. In a legal proceeding, notes, if referred to, are subject to cross-examination and are admissible as evidence.

B.3.4 Corrections to Documentation

All original data recorded in field notebooks, sample identification tags, COC records, and receipts-for-sample forms will be written with waterproof ink, unless prohibited by weather conditions. None of these accountable serialized documents are to be destroyed or thrown away, even if they are illegible or contain inaccuracies that require a replacement document.

If an error is made on an accountable document assigned to one team, the team leader may make corrections simply by drawing a single line through the error and entering the correct information. The erroneous information should not be obliterated. Any subsequent error discovered on an accountable document should be corrected by the person who made the entry. All subsequent corrections must be initialed and dated.

B.4 Analytical Methods Requirements

Project analytes and methods have been listed in Table A-3. Method standard operating procedures or data quality indicators are provided in Appendix B. For parameters that will be analyzed by the EPA Regional Laboratory, regional standard operating procedures have been included. For analyses outside the regional laboratory (NDMA; hexavalent chromium) project specific data quality indicators have been provided. For VOCs (carbon disulfide, tertiary butyl alcohol, methyl isobutyl ketone, methyl ethyl ketone) not included on the list shown in Appendix B, the regional laboratory will include additional standards to cover these compounds during the analyses. The laboratory will be provided the additional compounds on the chain of custody accompanying the samples, has reviewed these compounds, and agreed to carry out the additional analyses.

As soon as project schedules are known the EPA Quality Assurance Office will be provided with an analytical request form prior to analyses. This form details project specific needs, including detection limit and analyte requirements, as described in Sections A.2.4 and A.4 above.

B.5 Quality Control Requirements

Quality control requirements are detailed in the subsections below.

B.5.1 Field QC Procedures

QC requirements related to the sample process (i.e., design, methods, and handling and custody) requirements have been discussed in the previous sections of this document.

QC samples consisting of field duplicates, field blanks, and laboratory QC samples (for matrix spike [MS] and matrix spike duplicates [MSDs]). QC samples will be collected immediately following collection of target samples, and using the same procedures as the collection of the target sample. These procedures are presented in Section 6.6 of the FSP (EPA, 2002).

Background samples will not be collected as part of the Field QC procedures. Background samples are needed when the project goals include distinguishing native chemical concentrations from concentrations resulting from contamination such as distinguishing background metals concentrations from site metal concentrations. However, as seen in the project DQOs, these types of samples are not required for this site. Because much of the groundwater flow is radially inward to the central portion of Area 3 (see Figure A-4), surrounding production wells in Area 3 and other, adjacent operable units will essentially serve as the upgradient, "background" samples for sources of VOC contamination that may be located in the outer portions of, or outside Area 3.

B.5.2 Laboratory Procedures

Laboratory QC procedures will include the following:

- Analytical methodology according to specific methods listed in Table A-3 and Appendix B
- Instrument calibrations and standards as defined in specific methods in Table A-3 and Appendix B
- Laboratory blank measurements at a minimum 5 percent or 1-per-batch frequency
- Accuracy and precision measurements at a minimum of 1 in 20, 1 per set
- Data reduction and reporting according to specific methods listed in Table A-3
- Laboratory documentation equivalent to contract laboratory program (CLP) statement of work (SOW) or specifications in Appendix B

B.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

Instrument maintenance logbooks are maintained in laboratories at all times. The logbooks, in general, contain a schedule of maintenance, as well as a complete history of past maintenance, both routine and nonroutine.

Preventive maintenance is performed according to the procedures delineated in the manufacturer's instrument manuals, including lubrication, source cleaning, detector cleaning, and the frequency of such maintenance. Chromatographic carrier gas-purification traps, injector liners, and injector septa are cleaned or replaced on a regular basis. Precision and accuracy data are examined for trends and excursions beyond control limits to determine evidence of instrument malfunction. Maintenance will be performed when an instrument begins to degrade as evidenced by the degradation of peak resolution, shift in calibration curves, decrease in sensitivity, or failure to meet one or another of the QC criteria.

Instrument downtime is minimized by keeping adequate supplies of all expendable items, where expendable means an expected lifetime of less than 1 year. These items include gas tanks, gasoline filters, syringes, septa, gas chromatography (GC) columns and packing, ferrules, printer paper and ribbons, pump oil, jet separators, open-split interfaces, and mass spectroscopy filaments.

Preventive maintenance for field equipment (e.g., pH meter), will be carried out in accordance with procedures and schedules outlined in the operation and maintenance handbook of the particular model. Extra probes will accompany the field equipment to minimize downtime.

B.7 Instrument Calibration and Frequency

The following subsections review instrument calibration and frequency information.

B.7.1 Field Calibration Procedures

For water analyses, field equipment requiring calibration includes: (1) pH, (2) turbidity, and (3) electrical conductivity (EC) meters. These meters will be calibrated before the start of work, and at the end of the sampling day. Any instrument "drift" from prior calibration should be recorded in a field notebook. Calibration will be in accordance with procedures and schedules outlined in the particular instrument's operations and maintenance manual. The calibration standards to be used for the pH meter are pH 4, 7, and 10 buffers. Water-temperature measurements will be made using the temperature mode of the digital readout pH meter.

Calibrated equipment will be uniquely identified by using either the manufacturer's serial number or other means. A label with the identification number and the date when the next calibration is due will be physically attached to the equipment. If this is not possible, records traceable to the equipment will be readily available for reference. In addition, the results of calibrations and records of repairs will be recorded in a logbook.

Scheduled periodic calibration of testing equipment does not relieve field personnel of the responsibility of employing properly functioning equipment. If an individual suspects an equipment malfunction, the device must be removed from service, tagged so that it is not inadvertently used, and the appropriate personnel notified so that a recalibration can be performed, or a substitute piece of equipment can be obtained.

Equipment that fails calibration or becomes inoperable during use will be removed from service and either segregated to prevent inadvertent use or tagged to indicate it is out of calibration. Such equipment will be repaired and satisfactorily recalibrated. Equipment that cannot be repaired will be replaced.

Results of activities performed using equipment that has failed recalibration will be evaluated. If the activity results are adversely affected, the results of the evaluation will be documented and the task manager and quality assurance/quality control (QA/QC) reviewer will be notified.

B.7.2 Laboratory Calibration Procedures

Laboratory calibration procedures are specified in the referenced methods (Table A-3) or in Appendix B for all parameters listed in Table A-3. The calibration procedures at a minimum are at the following level of effort:

- Initial calibration for all methods will include a three-point calibration before a run
- Continuing calibration for all methods will include a midrange calibration standard after every tenth sample

B.8 Data Acquisition Requirements (Nondirect Measurements)

Previously collected data and other information will be used to assist decision-making at activities during the RI field activities. Previous groundwater sampling at EPA and non-EPA monitoring and water-supply wells have allowed a substantial database of water-quality data for the San Gabriel Valley. These water-quality data will assist in the planning and design of additional phases of RI activities.

B.9 Data Management

All data for all parameters will undergo two levels of review and validation: (1) at the laboratory and (2) outside the laboratory as described in Section D. Following receipt of validated data, it will be input into the San Gabriel Basin Oracle and geographic information system (GIS) databases to facilitate database inquires and report preparation. The data will be stored in the databases with all laboratory qualifiers included. Established data queries and formats developed during the previous work assignment (WA) will be adapted for incorporation of laboratory data from ASCII files provided by EPA's QAO, to files compatible with the project database. The database will be maintained in a manner that is compatible with, and provided to, EPA, Regional Water Quality Control Board (RWQCB), or others, at EPA's request. All available data from sources in the San Gabriel Basin will be integrated into the Oracle database, and uploaded into the GIS database. Major components for complete data management will be as follows:

- **Data Conversion/Manipulation/Review.** Reports of water-quality data from sampling of monitoring wells are received from QAO in hardcopy or electronic format. These data must be converted, input, reviewed, and QC checked.

  In addition, available data from other sources may be incorporated into the database. These data will need to be manually input, output, reviewed, QC checked, then uploaded into GIS database.

- **Preparation of Tables.** Data tables will be prepared following receipt of validated data from QAO following each sample event of the WA. Queries will be created for the database, to generate updated tables. These tables will be used by the SM to assess changes in contaminant concentrations within the study area and evaluate sampling frequencies at each well in EPA's monitoring network each quarter.

- **Database Documentation.** An update of the database and complete documentation will be performed on a quarterly basis. The commands, file names, and general operating procedures for all the data queries and graphics will be documented as part of the systematic GIS records as directed by the EPA WAM. This documentation will be provided to EPA and transferred to others (at EPA's request).

Section C
Assessment/Oversight

C.1 Assessment and Response Actions

The review team and the SM will monitor the performance of the QA procedures. If problems arise and the WAM directs the SM, the review team will conduct field audits, currently not scheduled or included in the scope of work. Audits may be scheduled to evaluate (1) the execution of sample identification, COC procedures, field notebooks, sampling procedures, and field measurements; (2) whether trained personnel staffed the sample event; (3) whether equipment was in proper working order (i.e., calibration); (4) availability of proper sampling equipment; (5) whether appropriate sample containers, sample preservatives, and techniques were used; (6) whether sample packaging and shipment were appropriate; and (7) whether QC samples were properly collected.

The analyses will be carried out by the EPA Regional Laboratory or laboratories subcontracted to EPA or to CH2M HILL. The analyses that are expected to be carried outside the Regional Laboratory have been identified in Section B.4 and Appendix B. The distribution of analyses may change at the time of analyses depending on implementation of additional procedures at the Regional Laboratory as well as capacity. The quality assurance of the Regional Laboratory is managed by the QAO. Laboratories subcontracted to CH2M HILL will be selected based on prior performance on Regional Superfund Projects. Additionally, Blind performance evaluation (PE) samples will be sent to all laboratories for all the methods (as available) in the initial phase of the field work. Single blind samples will be submitted prior to sending actual groundwater samples to the laboratory. Double blind samples will be sent together with actual groundwater samples collected in the field. Currently, the availability of PE samples for NDMA, 1,2,3-trichloropropane, and 1,4-dioxane is not known. The individual results of the PE samples will be compared to the results/ranges from the supplier (tentatively identified as the EPA QATS laboratory in Las Vegas, Nevada); the findings will be detailed in a memorandum; and corrective actions requested from the laboratory, as applicable.

Audits will be followed up with an audit report prepared by the reviewer. The auditor will also debrief the laboratory or the field team at the end of the audit and request that the laboratory or field team comply with the corrective action request.

C.1.1 Reporting and Resolution of Issues

If QC audits result in detection of unacceptable conditions or data, the SM will be responsible for developing and initiating corrective action. The WAM will be notified if nonconformance is of program significance or requires special expertise not normally available to the project team. In such cases, the remedial project manager (RPM) will decide whether any corrective action should be pursued. Corrective action may include the following:

- Reanalyzing samples if holding time criteria permit
- Resampling and analyzing
- Evaluating and amending sampling and analytical procedures
- Accepting data acknowledging a level of uncertainty

C.2 Reports to Management

The SM or WAM may request that a QA report be made to the WAM on the performance of sample collection and data quality. The report will include the following:

- Assessment of measurement data accuracy, precision, and completeness
- Results of performance audits
- Results of systems audits
- Significant QA problems and recommended solutions

Monthly progress reports will summarize overall project activities and any problems encountered. QA reports generated on sample collection and data quality will focus on specific problems encountered and solutions implemented. Alternatively, in lieu of a separate QA report, sampling and field measurement data quality information may be summarized and included in the final reports summarizing field activities (e.g., well installation or aquifer testing technical memoranda). The objectives, activities performed, overall results, sampling, and field measurement data quality information of the project will be summarized and included in the final field activities reports along with any QA reports.

Section D
Data Validation and Usability

D.1 Data Review, Validation, and Verification Requirements

All data for all parameters will undergo two levels of review and validation: (1) at the laboratory and (2) outside the laboratory by the EPA Quality Assurance Management Section or their designee. Data will be reviewed outside the laboratory at the following level of effort:

> Ninety-percent of the groundwater sample analytical batches will be reviewed for all the analytical parameters, detections and nondetections, at Tier 2, as defined by the regional EPA QAO guidance. Also, 10 percent of the analytical batches selected for Tier 3 for all parameters, detections and nondetections. The analytical batches selected for Tier 3 review will be selected at random, unless a new laboratory is performing the analyses. In this instance, the first analytical batch should undergo the Tier 3 review as a proactive measure.
>
> Tier 2 review has been selected to provide for review of all the QA/QC summary forms in accordance with EPA CLP National Functional Guidelines for Inorganic/Organic Data review (to include all calibrations and internal standards) and flagging of the individual results, as opposed to review of a subset of the QC data as is the case for Tier 1 review. Tier 2 economizes the lab data review compared to Tier 3, by limiting the review to QC summary data, as opposed to raw data checks. Review of QC summary data that includes all QC parameters provides for the needed comprehensive coverage and this scope is covered under the current Regional Tier 2 review.

The above level of effort is based on that the objectives of this project deal with quantitative evaluation of groundwater samples at trace levels for all analytes. The full database needs consistent flags for comparable and reproducible data. The above level of effort should accomplish that. These levels of effort are appropriate, because data are compared quantitatively to past data to establish quantitative trends, as well as compared to regulatory limits. Quantitative trends apply to all analytes, not just a subset of the target analytes. All analytes are contaminants of concern, even though, for example, PCE and TCE are detected more often than the other analytes. As establishing the validity of nondetect results is as important as the detected results for monitoring, both detections and nondetect results will be reviewed.

D.2 Validation and Verification Methods

Initial data reduction, validation, and reporting at the laboratory will be carried out as described in the laboratory standard operating procedures.

Independent data validation by EPA or their designee will follow EPA *Contract Laboratory Program National Functional Guidelines for Inorganic/Organic Data Review* (EPA, February 1994 and 1999) as described above.

D.3 Reconciliation with Data Quality Objectives

Results obtained from the project will be reconciled with the requirements specified in Table A-3 of this QAPP. Assessment of data for precision, accuracy, and completeness will be per the following quantitative definitions.

Precision

If calculated from duplicate measurements:

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

RPD = relative percent difference
C_1 = larger of the two observed values
C_2 = larger of the two observed values

If calculated from three or more replicates, use relative standard (RSD) rather than relative percent difference (RPD):

$$RSD = (s / \bar{y}) \times 100\%$$

RSD = relative standard deviation
s = standard deviation
$\bar{y}$ = mean of replicate analyses

Standard deviation, s, is defined as follows:

$$S = \sqrt{\sum_{i=1}^{n} \frac{(yi/y)^{-2}}{n-1}}$$

s = standard deviation
y_i = measured value of the ith replicate
$\bar{y}$ = mean of replicate analyses
n = number of replicates

Accuracy

For measurements where matrix spikes are used:

$$\%R = 100\% \times \left[\frac{S - U}{C_{sa}}\right]$$

%R = percent recovery
S = measured concentration in spiked aliquot
U = measured concentration in unspiked aliquot
C_{sa} = actual concentration of spike added

For situations where a standard reference material (SRM) is used instead of or in addition to matrix spikes:

$$\%R = 100\% \times \left[\frac{C_m}{C_{sm}}\right]$$

%R = percent recovery
C_m = measured concentration of SRM
C_{sm} = actual concentration of SRM

Completeness (Statistical)

Defined as follows for all measurements:

$$\%C = 100\% \times \left[\frac{V}{T}\right]$$

%C = percent completeness
V = number of measurements judged valid
T = total number of measurements

References

California Department of Water Resources. Bulletin 45. South Coastal Basin Investigation. Eckis, Rollin. 1934.

U.S. Environmental Protection Agency. *Interim San Gabriel Basin Remedial Investigation Report, Los Angeles County, California.* Prepared by CH2M HILL. June 15, 1992.

———. *Guidance for the Data Quality Objectives Process.* EPA QA/G4. September 1994b.

———. *EPA Guidance for Quality Assurance Project Plans.* EPA QA/G5, EPA/600/R-98/018. February 1998.

———. *Contract Laboratory Program National Functional Guidelines for Inorganic/ Organic Data Review,* February 1994 and 1999.

———. *Requirements for Quality Assurance Project Plans.* 1999.

———. *Alhambra Operable Unit, Draft Data Evaluation Report.* Prepared by CH2M HILL. January 2001.

———. *Draft Field Sampling Project Plan for San Gabriel Valley NPL Area 3 Remedial Investigation Field Activities.* Prepared by CH2M HILL. September 2002.

Appendix A
Data Quality Objectives

Appendix A-1
Drill Cuttings and Drilling Mud

A-1 Data Quality Objectives
Drill Cuttings and Drilling Mud
Remedial Investigation Field Activities
San Gabriel Valley NPL Area 3

Step 1. State the Problem

(1) *Identify members of the planning team* – The members of the planning team are the EPA Work Assignment Manager, CH2M HILL Site Manager, CH2M HILL hydrogeologist, and CH2M HILL Quality Assurance Officer.

(2) *Identify the primary decision maker* – There will not be a primary decision maker. Decisions will be made by consensus.

(3) *Develop a concise description of the problem* – The problem is that drill cuttings and drilling mud generated during installation of the RI monitoring wells need to be characterized for proper disposal.

(4) *Specify available resources and relevant deadlines for the study* – Drilling is expected to start in October 2002 and take approximately 20 weeks. Samples will be collected periodically during this time. Project resources are described in work plan and include hydrogeologists, chemists, regulatory specialists, risk assessors, remedial engineers, laboratories, and the well drilling subcontractor.

Step 2. Identify the Decision

(1) *Identify the principal study question* – Are the drill cuttings and/or drilling mud classified as hazardous (i.e., toxic, flammable, corrosive, or reactive)?

(2) *Define alternate actions that could result from resolution of the principal study question* –

a) The drill cuttings and/or drilling mud will be disposed of in a local Class III landfill or a recycling facility.

(b) The drill cuttings and/or drilling mud will be disposed of at a hazardous waste facility approved to receive Comprehensive Environmental Response, Compensation and Liability (CERCLA) wastes.

(3) *Combine the principal study question and the alternative actions into a decision statement* – Decide if the drill cuttings and/or drilling mud are considered hazardous waste and determine the appropriate disposal method.

(4) *Organize multiple decisions* –

(a) The drill cuttings and/or drilling mud are classified as nonhazardous and will be disposed of at a local Class III landfill or a recycling facility.

(b) The drill cutting and/or drilling mud is classified as hazardous and will be disposed of at a hazardous waste facility approved to receive CERCLA wastes.

Step 3. Identify Inputs to the Decision

(1) *Identify the information that will be required to resolve the decision statement* – To resolve the decision statement, the planning team needs to compare observed concentrations of VOCs (analyzed by direct analyses of samples) with VOC limits on the toxic characteristics (TC) list (Attachment A of this DQO) or limits set by the state of California (see Attachment B). For direct analyses of samples, measured concentrations are multiplied by factors to obtain the equivalency for comparison to limits shown in Attachment A. In addition, the planning team will compare state of California total threshold limit concentration (TTLC) metals (see Attachment B), pH, flashpoint, and total petroleum hydrocarbon (TPH) concentrations with those acceptable as nonhazardous at California Class III landfills.

(2) *Determine the sources for each item of information identified* – The drill cuttings and drilling mud samples need to be analyzed to determine if they meet regulatory and landfill standards.

(3) *Identify the information that is needed to establish the action level* – The action level will be based on the toxic characteristics for site specific compounds of concern: VOCs, TTLC metals, TPH, pH, and flashpoint.

(4) *Confirm that appropriate measurement methods exist to provide the necessary data* – Methods consistent with the above needs are identified in Table A-3 in the QAPP. VOCs, TTLC metals, pH, and flashpoint can be measured by the standard EPA methods and TPH by standard EPA and State methods. The detection limits are below the regulatory levels of the TC list shown in Attachment A. As noted above, VOC concentrations measured directly are multiplied by a factor (20) to obtain the TCLP equivalent value for comparison. This approach, as prescribed in the regulation, is a more conservative approach than using the actual TCLP analysis. Standard EPA methods for pH and flashpoint are available to assess whether the wastes are corrosive or flammable. TPH will be measured by the CA LUFT method.

Step 4. Define the Boundaries for the Study

(1) *Specify the characteristics that define the population of interest* – Drill cuttings in a roll-off bins and drilling mud in Baker™ tanks constitute the population of interest.

(2) *Define the spatial boundary of the decision statement* –

(a) Define the geographical area to which the decision statement applies – Decisions will apply to the collective group of roll-off bins full of drill cuttings

from each well location and the individual Baker™ tank of drilling mud from each well installed during the RI field activities.

(b) Divide the population into strata that have relatively homogeneous characteristics –The drill cuttings and drilling mud are expected to be relatively homogeneous in their respective containers and thus can be considered as one stratum.

(3) *Define the temporal boundary of the decision statement* –

(a) Determine the time frame to which the decision statement applies – The decision regarding the disposal of the drill cuttings and drill mud for disposal applies indefinitely.

(b) Determine when to collect data – Following the completion of each monitoring well.

(4) *Define the scale of decision making* – The scale of the decision making will be the drill cuttings and drilling mud for each well installed during RI field activities.

(5) *Identify practical constraints on data collection* – The needed fast turnaround for analytical results to reduce onsite storage costs may not be practicable for all parameters. Although open access exists for the roll-off bins and Baker™ tanks, sampling procedures will have to be implemented for the samples to be representative of the entire roll-off bin (for drill cuttings) and Baker tank (for drilling mud). A consideration is the ability to obtain samples of drilling mud containing enough solids, as the drilling mud in tanks tends to stratify. The use of weighted bailers has proved to eliminate this concern in previous activities and will be used during these operations.

Step 5. Develop a Decision Rule

(1) *Specify the statistical parameter that characterizes the population of interest* – The actual individual sample concentrations of VOCs, metals, pH, flashpoint, and TPH from the drill cuttings and drilling mud at each well location is the parameter of interest.

(2) *Specify the action level for the study* – The action level for the decision will be the regulatory standard for the VOCs and metals listed on the TC and state of California lists (Attachments A and B) and the acceptable value for TPH at CA Class III landfills (e.g., less than 100 milligrams per kilogram [mg/kg]).

(3) *Develop a decision rule (an "if...then..." statement)* – If, for each container of drill cuttings or drilling mud sampled (i.e., for any individual sample), the concentration of TPH or any of the volatiles and metals on the TC or state of California lists (using direct analysis and multiplying by 20 and then reanalyzing with TCLP methods if the concentrations exceed regulatory levels) exceeds the regulatory levels, then the wastes at that well location will be considered hazardous and hauled to a hazardous waste disposal facility approved to receive

CERCLA wastes. If, for each container of drill cuttings or drilling mud sampled (i.e., for any individual sample) the concentration of TPH and the volatiles and metals on the TC or state of California lists are less than the regulatory levels (using direct analysis and multiplying by 20), then the waste at that well location will be considered nonhazardous, and the drill cuttings will be transported to a local Class III landfill and the drilling mud may be sent to a recycler.

Step 6. Specify Tolerable Limits on Decision Errors

(1) *Identify the decision errors and choose a null hypothesis* – The DQO guidance prescribes the identification of the null hypothesis and associated decision errors for determining the number of statistical random samples and the locations to attain a given level of confidence with the spatial distribution. As sampling will be judgmental rather than statistical, project error tolerances are defined in terms of precision, accuracy, representativeness, comparability, and completeness (PARCC) in Section A.4 of the QAPP. Analyte-specific accuracy and precision ranges are shown in Table A-3 of the QAPP. The project completeness goal is set at 90 percent.

(2) *Specify a range of possible values of the parameter of interest where the consequences of decision error are relatively minor* – Because the error for precision and accuracy is on average about 30 percent, the consequences of decision errors based on sample results less than half the regulatory levels or greater than twice the regulatory levels, are expected to be relatively small.

(3) *Assign probability values to points above and below the action level that reflect the tolerable probability for the occurrence of decision errors* – As judgmental, rather than statistical, design is being implemented, error tolerances will be weighed as described in (2) and (3) above.

Step 7. Optimize the Design

(1) *Review the DQO outputs and existing data* – There are sufficient existing data relevant to this problem to allow the disposal alternative to be based on a judgmental approach. Drill cuttings and drilling mud from each of the extraction and monitoring wells previously installed by EPA in the San Gabriel Valley were characterized following TPH procedures in CA LUFT, EPA methods for pH and flashpoint, direct analysis of VOCs by EPA method 8260, metals by the TTLC procedure, and the TCLP procedure as specified in method 1311/SW-846. Based on these data, it has been observed that each container of drill cuttings or drilling mud is fairly homogeneous, and the concentrations of the measured constituents have been below the regulatory levels specified by the state of California and on the TC list.

(2) *Develop general data collection design alternatives* – Data collection for the drill cuttings and drilling mud will be consistent with procedures used during previous well installation activities at neighboring sites (Whittier Narrows and South

El Monte). Based on past data, it has been observed that each container of drill cuttings or drilling mud is fairly homogeneous, and historically the concentrations have been below the regulatory levels specified by the state of California and on the TC list. Thus, one drilling mud sample per Baker™ tank will be collected using a new, disposable polyethylene bailer to fill the appropriate sample containers. Grab drill cuttings samples will be collected and placed directly into a brass sleeve or Encore sample container, allowing no headspace. Per discussion with local landfills, the sample analyses will be limited to site-specific compounds of concern (e.g., volatiles and metals) rather than the full TC list.

(3) *For each data collection design alternative, select the optimal sample size that satisfies the DQOs* –As described above under (2), the collection design will be per past data and judgement. Thus, one drilling mud sample per container/bin (each bin represents a different well) will be collected. For drill cuttings, samples representative of the materials from the borehole(s) at each well site will be collected. This design is consistent with project cost constrains.

(4) *Select the most resource-effective data collection design that satisfies the DQOs* – See (3) above.

(5) *Document the operational details and theoretical assumptions of the selected design in sampling and analysis plan* – Section B.1.3 of this QAPP provides the operational details and theoretical assumptions/rationale of the selected design as described in the companion FSP (EPA, 2002), prepared in conjunction with this document.

Attachment A
Data Quality Objectives – Drill Cuttings and Drilling Mud
Remedial Investigation Activities
Toxicity Characteristics Constituents and Regulatory Levels

Substance	Regulatory Level (mg/L)	Substance	Regulatory Level (mg/L)
Benzene	0.5	Arsenic	5.0
Carbon tetrachloride	0.5	Barium	100.0
Chlordane	0.03	Cadmium	1.0
Chlorobenzene	100.0	Chromium	5.0
Chloroform	6.0	Lead	5.0
m-Cresol	200.0[a]	Mercury	0.2
o-Cresol	200.0	Selenium	1.0
p-Cresol	200.0	Silver	5.0
1,4-Dichlorobenzene	7.5	Endrin	0.02
1,2-Dichloroethane	0.5	Lindane	0.4
1,1-Dichloroethylene	0.7	Methoxychlor	10.0
2,4-Dinitrotoluene	0.13	Toxaphene	0.5
Heptachlor (and its hydroxide)	0.008	2,4 D	10.0
Hexachloro-1,3-Butadiene	0.5	2,4,5 T-Silvex	1.0
Hexachlorobenzene	0.13[b]	Pyridine	5.0[b]
Hexachloroethane	3.0	Tetrachloroethylene	0.7
Methyl ethyl ketone	200.0	Trichloroethylene	0.5
Nitrobenzene	2.0	2,4,5-Trichlorophenol	400.0
Pentachlorophenol	100.0	2,4,6-Trichlorophenol	2.0
		Vinyl Chloride	0.2

[a]If o-, m-, and p-Cresol concentrations cannot be differentiated, the total cresol concentration is used. The regulatory level for total cresol is 200.0 mg/L.
[b]Quantitation limit is greater than the calculated regulatory level. The quantitation limit, therefore, becomes the regulatory level.

Attachment B
Data Quality Objectives – Drill Cuttings and Drilling Mud
Remedial Investigation Activities
California Title 22 Regulatory Levels

Substance	Regulatory Level (mg/kg)	Substance	Regulatory Level (mg/kg)
Antimony	500	Mercury	20
Arsenic	500	Molybdenum	3,500
Barium	10,000	Nickel	2,000
Beryllium	75	Selenium	100
Cadmium	100	Silver	500
Chromium	2,500	Thallium	700
Cobalt	8,000	Vanadium	2,400
Copper	2,500	Zinc	5,000
Lead	1,000	Trichloroethylene	2,040

Appendix A-2
Well Development Water

A-2 Data Quality Objectives
Well Development Water
Remedial Investigation Field Activities
San Gabriel Valley NPL Area 3

Step 1. State the Problem

(1) *Identify members of the planning team* – The members of the planning team are the EPA Work Assignment Manager, CH2M HILL Site Manager, CH2M HILL hydrogeologist, and CH2M HILL Quality Assurance Officer.

(2) *Identify the primary decisionmaker* – There will not be a primary decisionmaker. Decisions will be made by consensus.

(3) *Develop a concise description of the problem* – The problem is that well development water resulting from developing monitoring wells during the RI field activities needs to be characterized for proper disposal.

(4) *Specify available resources and relevant deadlines for the study* – The work is expected to be started in October 2002 and will take approximately 20 weeks. Samples will be collected periodically during this time. Data are needed within 72 hours of collection of well development water to minimize storage/disposal costs. Project resources are described in work plan and include hydrogeologists, chemists, regulatory specialists, risk assessors, remedial engineers, laboratories, and the well drilling subcontractor.

Step 2. Identify the Decision

(1) *Identify the principal study question* – Are the contaminant levels in the well development water above state and/or federal maximum contaminant levels (MCLs) or action levels (ALs)?

(2) *Define alternate actions that could result from resolution of the principal study question* –

(a) The water will be disposed of in a local flood control channel or storm drain.

(b) The water will be treated onsite.

(c) The water will be hauled to a disposal facility approved to receive CERCLA wastes.

(3) *Combine the principal study question and the alternative actions into a decision statement* – Decide if the contaminant levels of the well development water are above state and/or federal MCLs or ALs and determine the correct disposal method.

(4) *Organize multiple decisions* –

- The contaminant levels of the well development water are below state and federal MCLs or ALs and the water will be disposed of in a local flood control channel or storm drain.
- The contaminant levels of the well development water are above state and/or federal MCLs or ALs and the water will be either treated onsite or hauled to a disposal facility approved to receive CERCLA wastes.

Step 3. Identify Inputs to the Decision

(1) *Identify the information that will be required to resolve the decision statement* – Well development water chemical concentration data are needed for the same analytes as the list for RI groundwater samples (shown in Table A-3 of QAPP).

(2) *Determine the sources for each item of information identified* – Laboratory analysis of well development water samples.

(3) *Identify the information that is needed to establish the action level* – The action level will be based on the state and federal MCLs or ALs for RI groundwater analytes.

(4) *Confirm the appropriate measurement methods exist to provide the necessary data* – Methods consistent with the above needs are identified in Table A-3 in the QAPP.

Step 4. Define the Boundaries for the Study

(1) *Specify the characteristics that define the population of interest* – The population of interest is the well development water that is collected in containers (Baker™ tanks) onsite.

(2) *Define the spatial boundary of the decision statement* –

(a) Define the geographical area to which the decision statement applies – Decisions will apply to the well development water in the individual containers (Baker™ tanks) from each monitoring well installed during the RI field activities.

(b) Divide the population into strata that have relatively homogeneous characteristics – Stratification is not applicable because the well development water is relatively homogeneous.

(3) *Define the temporal boundary of the decision statement* –

(a) Determine the time frame to which the decision statement applies – The decision regarding the well development water in containers to be disposed of will apply indefinitely.

(b) Determine when to collect data – Following the completion and development of each monitoring well during the RI field activities.

(4) *Define the scale of decision making* – The scale of the decision making will be well development water in each container (Baker™ tank) from each monitoring well installed during the RI field activities.

(5) *Identify practical constraints on data collection* – To avoid storage costs associated with long-term containment, fast turnaround (72 hours) of analytical results is needed. Given the extensive analyte list, this may not be practicable for all analytes. For example, NDMA analyses may need a longer turnaround time.

Step 5. Develop a Decision Rule

(1) *Specify the statistical parameter that characterizes the population of interest* - the individual concentration of each analyte from each well development water sample.

(2) *Specify the action level for the study* – The action level for the decision will be California or federal MCLs or ALs whichever is lower. The applicable level for the individual analytes is listed in Table A-2 of the QAPP.

(3) *Develop a decision rule (an "if...then..." statement)* – If, for each container of well development water, the concentrations of analytes are below State and Federal MCLs or ALs, then the water in that container will be disposed of in a local flood control channel or storm drain. If, for each container of well development water, the concentrations of analytes exceed State and/or Federal MCLs or ALs, then the water in that container will be considered hazardous and will be either treated onsite or hauled to a disposal facility approved to receive CERCLA wastes.

Step 6. Specify Tolerable Limits on Decision Errors

(4) *Determine the range of the parameters of interest* – From records of analyses conducted on well development water at previously-installed monitoring wells in the area of interest, contaminant concentrations were generally below state and federal MCLs or ALs. At some sites, closer to contaminant source areas, contaminant concentrations were above MCLs or ALs.

(5) *Identify the decision errors and choose a null hypothesis* – The DQO guidance prescribes the identification of the null hypothesis and associated decision errors for determining the number of statistical random samples and the locations to attain a given level of confidence with the spatial distribution. As sampling will be judgmental rather than statistical, project error tolerances are defined in terms of precision, accuracy, representativeness, comparability, and completeness (PARCC) in Section A.4 of the QAPP. Analyte-specific accuracy and precision ranges are shown in Table A-3 of the QAPP. The project completeness goal is set at 90 percent.

(6) *Specify a range of possible values of the parameter of interest where the consequences of decision error are relatively minor* – Because the error for precision and accuracy is on

average about 30 percent, the consequences of decision errors based on sample results less than half the regulatory levels or greater than twice the regulatory level are expected to be relatively small.

(7) *Assign probability values to points above and below the action level that reflect the tolerable probability for the occurrence of decision errors* – As judgmental rather than statistical design is being implemented error tolerances will be weighed as described in (2) and (3) above.

Step 7. Optimize the Design

(1) *Review the DQO outputs and existing data* – There are sufficient existing data relevant to this problem to allow the study to be based on a judgmental approach. Well development water from each of the previously-installed monitoring wells in neighboring areas (South El Monte and Whittier Narrows OUs) was characterized using the judgmental data proposed here. Based on these data, it has been observed that each container of well development water is fairly homogeneous and results for well development water are similar for the different tanks and generally below the regulatory thresholds.

(2) *Develop general data collection design alternatives* – Data for the well development water will be collected consistent with procedures used during previous well installation activities in neighboring areas (South El Monte and Whittier Narrows OUs). The well development water from different depths will be mixed and then stored in individual containers (20,000 gallon Baker™ tank). One sample from each tank will be collected. Well development water samples will be collected using a new, disposable polyethylene bailer to fill the appropriate sample containers, allowing no headspace where necessary.

(3) *For each data collection design alternative, select the optimal sample size that satisfies the DQOs* – Mixing of well development water from different depths and storage in individual containers is expected to provide a homogenous representative medium of the waste. One sample from each container is expected to be sufficient for waste characterization of the homogenous medium. In this case, one container per 20,000 gallons of well development water or less will be used and thus one sample will be collected from each container to characterize the water.

(4) *Select the most resource-effective data collection design that satisfies the DQOs* – See item (3), above. This design is also consistent with project cost constraints.

(5) *Document the operational details and theoretical assumptions of the selected design in sampling and analysis plan* – Section B.1.3 of this QAPP provides the operational details and theoretical assumptions/rationale of the selected design as described in the companion FSP (EPA, 2002), prepared in conjunction with this document.

Appendix A-3
Groundwater Monitoring

A-3 Data Quality Objectives
Groundwater Monitoring
Remedial Investigation Field Activities
San Gabriel Valley NPL Area 3

Step 1. State the Problem

(1) *Identify members of the planning team* – The members of the planning team are the EPA Work Assignment Manager, CH2M HILL Site Manager, CH2M HILL hydrogeologist, and CH2M HILL Quality Assurance Officer.

(2) *Identify the primary decisionmaker* – There will not be a primary decisionmaker. Decisions will be made by consensus.

(3) *Develop a concise description of the problem* – Given that contamination of drinking water with VOCs has been observed in the area, data are needed to establish nature and extent of contamination, sources of contamination, and assess remedial alternatives.

(4) *Specify available resources and relevant deadlines for the study* – The work is expected to be started in October 2002 and last through January 2005. An initial groundwater sampling event for VOCs and dissolved metals will be conducted within approximately 2 weeks completion of each monitoring well. During the third sampling event, anticipated to take place in the summer of 2003, additional groundwater sampling will be conducted at each well for SVOCs, NDMA, perchlorate, nitrate, 1,4-dioxane, hexavalent chromium, and 1,2,3-trichloropropane. Ongoing groundwater sampling events will be conducted on a quarterly basis for VOCs for two years, for a total of eight sampling events, with the last event occurring in January 2005. Project resources are described in work plan and include hydrogeologists, chemists, regulatory specialists, risk assessors, remedial engineers, laboratories, and the drilling subcontractor.

Step 2. Identify the Decision

(1) *Identify the principal study question* – What is the nature and extent of contamination in the groundwater, what are potential sources, and what are feasible remedial alternatives for cleaning up the groundwater contamination.

(2) *Define alternate actions that could result from resolution of the principal study question* –

(a) No action.

(b) Additional groundwater data (e.g., new monitoring wells) are needed.

(c) The ground water will be monitored.

(d) Remedial alternatives are developed.

(3) *Combine the principal study question and the alternative actions into a decision statement* – Measure the contaminant levels in groundwater water, compare to state and/or federal MCLs or ALs and determine the appropriate action: no action, additional data collection, monitoring or remedial alternatives development.

(4) *Organize multiple decisions* –

- If contaminant levels of groundwater samples are below detection limits, then no further action may be taken or additional data collection may be necessary.
- If contaminant levels of any of the groundwater samples are above detection limits, but below state and/or federal MCLs or ALs, then future monitoring will be planned and implemented and additional data collection may be necessary.
- If contaminant levels of any of the groundwater samples are above detection limits and above state and/or federal MCLs or ALs, then future monitoring will be planned and implemented, additional data may be collected, and remedial alternatives will be evaluated.

Step 3. Identify Inputs to the Decision

(1) *Identify the information that will be required to resolve the decision statement* – Groundwater chemical concentration data are needed for the analytes listed in Table A-2 of the QAPP.

(2) *Determine the sources for each item of information identified* – Laboratory analysis of groundwater samples.

(3) *Identify the information that is needed to establish the action level* – The action level will be based on the state and federal MCLs or ALs for RI groundwater analytes identified under (1) above.

(4) *Confirm the appropriate measurement methods exist to provide the necessary data* – Methods consistent with the above needs are identified in Table A-3 of the QAPP.

Step 4. Define the Boundaries for the Study

(1) *Specify the characteristics that define the population of interest* – The population of interest is all groundwater within the boundary of NPL Area 3 shown in Figure A-1.

(2) *Define the spatial boundary of the decision statement* –

(a) Define the geographical area to which the decision statement applies – Decisions will apply to groundwater within the Area 3 boundaries shown in Figure A-3 in the QAPP.

(b) Divide the population into strata that have relatively homogeneous characteristics –All groundwater in Area 3 is currently considered as one stratum and, based on available is expected to be homogeneous.

(3) *Define the temporal boundary of the decision statement* –

(a) Determine the time frame to which the decision statement applies – The decision regarding groundwater contaminants in Area 3 will apply until the last set of monitoring data are collected at the end of this study.

(b) Determine when to collect data – As soon as practicable, subsequent to development of the monitoring wells.

Define the scale of decision making – The scale of the decision making will be groundwater within the Area 3 boundaries shown in Figure A-3 in the QAPP.

(4) *Identify practical constraints on data collection* – Current budget constraints may not allow collection of sufficient data points for representativeness.

Step 5. Develop a Decision Rule

(1) *Specify the statistical parameter that characterizes the population of interest* - The individual concentration of each analyte from groundwater sampling.

(2) *Specify the action level for the study* – The action level for the decision will be California or federal MCLs or ALs, whichever is lower, as well as the method detection limits. The applicable level for the individual analytes is listed in Table A-2 of the QAPP

(3) *Develop a decision rule (an "if...then..." statement)* – If contaminant levels of groundwater samples are below detection limits, then no further action may be taken or additional data collection may be necessary. If contaminant levels of any of the groundwater samples are above detection limits, but below state and/or federal MCLs or ALs, then future monitoring will be planned and implemented and additional data collection may be necessary. If contaminant levels of any of the groundwater samples are above detection limits and above state and/or federal MCLs or ALs, then future monitoring will be planned and implemented, additional data may be collected, and remedial alternatives will be evaluated.

Step 6. Specify Tolerable Limits on Decision Errors

(1) *Determine the range of the parameters of interest* – From records of analyses conducted on groundwater samples collected at previously-installed monitoring wells in the San Gabriel Valley, contaminant concentrations were generally below state and federal MCLs or ALs. At some sites, closer to contaminant source areas, contaminant concentrations were above MCLs or ALs. MCLs or ALs are listed in Table A-2 in the QAPP.

(2) *Identify the decision errors and choose a null hypothesis* – The DQO guidance prescribes the identification of the null hypothesis and associated decision errors for determining the number of statistical random samples and the locations to attain a given level of confidence with the spatial distribution. Sample/well locations are

determined per hydrogeologic characteristics of the area and the available resources. Thus sampling will be judgmental rather than statistical and project error tolerances are defined in terms of precision, accuracy, representativeness, comparability, and completeness (PARCC) in Section A.4 of the QAPP. Analyte-specific accuracy and precision ranges are shown in Table A-3 of the QAPP. The project completeness goal is set at 90 percent.

(3) *Specify a range of possible values of the parameter of interest where the consequences of decision error are relatively minor* – Because the error for precision and accuracy is on average about 30 percent, the consequences of decision errors based on sample results less than half the regulatory levels or greater than twice the regulatory levels, are expected to be relatively small.

(4) *Assign probability values to points above and below the action level that reflect the tolerable probability for the occurrence of decision errors* – As judgmental, rather than statistical, design is being implemented, error tolerances will be weighed as described in (2) and (3) above.

Step 7. Optimize the Design

(1) *Review the DQO outputs and existing data* – Existing data available for Area 3 do not allow evaluation of >MCL contamination within specific depth intervals and do not allow evaluation of potential source areas within the Area 3 boundary.

(2) *Develop general data collection design alternatives* – Data collected from the proposed monitoring wells will enable evaluation of whether contaminant >MCLs are present in groundwater at specific depth intervals and will allow evaluation of sources areas.

(3) *For each data collection design alternative, select the optimal sample size that satisfies the DQOs* – Sample locations are predetermined by the location of the wells. The new wells have been located based on interpretation of distribution of contamination, geographic constraints, property ownership constraints, and equipment access constraints. The rationale for the individual locations is detailed below in item (5).

(4) *Select the most resource-effective data collection design that satisfies the DQOs* – See item (3), above. This design is also consistent with project cost constraints.

(5) *Document the operational details and theoretical assumptions of the selected design in sampling and analysis plan* – Section B.1.3 of this QAPP provides the operational details and theoretical assumptions/rationale of the selected design as described in the companion FSP (EPA, 2002), prepared in conjunction with this document.

Appendix B
Analytical Program
Technical Specifications

Appendix B
Analytical Program Technical Specifications

Contents

B-1	TCL Volatile Organic Compounds (VOCs) plus MTBE
B-2	1,4-Dioxane
B-3	N-Nitrosodimethylamine (NDMA)
B-4	Perchlorate
B-5	Hexavalent Chromium
B-6	TAL Metals (field filtered)
B-7	Anions: Nitrate-N
B-8	1,2,3-Trichloropropane
B-9	Semivolatile Organic Compounds
B-10	Flashpoint
B-11	pH
B-12	8260 VOCs
B-13	Total Petroleum Hydrocarbons-CA LUFT
B-14	TTLC Metals

Appendix B-1
TCL Volatile Organic Compounds (VOCs) plus MTBE

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE #354

VOLATILE ORGANICS ANALYSIS
(524.2 Reference Method)

Signature & Title

Prepared by: _____ _____
Li-Pin Lee, ESAT Region 9, ICF Consulting Date

Reviewed by: _____ _____
Richard Bauer, Chemistry Team Leader Date

Approved by: _____ _____
Brenda Bettencourt, Laboratory Director Date

Periodic Review:

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

STANDARD OPERATING PROCEDURE #305

VOLATILE ORGANICS ANALYSIS

This SOP was prepared by ICF Consulting for the United States Environmental Protection Agency (USEPA) under the Environmental Services Assistance Team (ESAT) contract (EPA contract No. 68-W-01-028).

APPROVED BY:

Nicholas Kish, Organic Group Leader	Date
Surender Kaushik, QA Task Manager	Date
Jerry Vail, ESAT Program Manager	Date

ESAT Document Control Number: B0101029-0498

TABLE OF CONTENTS

1 SCOPE AND APPLICATION 4

2 METHOD SUMMARY 4

3 DEFINITIONS 4

4 HEALTH & SAFETY 6

5 SAMPLE HANDLING AND PRESERVATION 7

6 INTERFERENCES 8

7 APPARATUS AND MATERIALS 9

8 QUALITY CONTROL 10

9 ANALYTICAL PROCEDURES 26

10 DOCUMENTATION 37

11 REFERENCES 43

APPENDIX A - SOP Deviations from reference method
APPENDIX B - Analyte List
APPENDIX C - Calibration and Quality Control Criteria
APPENDIX D - Purge and Trap Concentrator Parameters
APPENDIX E - GC and MSD Parameters
APPENDIX F - Data File Naming Convention

1 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the procedures used for the analysis of volatile organic compounds (VOC's) in the USEPA Region 9 Laboratory in Richmond, California. The procedures reference EPA method 524.2, Revision 4.1, 1995. The compounds which may be determined using this SOP are listed in Appendix B.

This SOP is applicable to the analysis of surface water, ground water, and drinking water for VOC's in support of the EPA's Superfund, RCRA, WQM, NPDES, UIC, and SDWA programs. The applicability of these procedures to specific project data quality objectives (DOQ's) must be assessed on a case by case basis. The quality control (QC) criteria specified in this SOP meet compliance criteria for drinking water and NPDES monitoring projects.

2 METHOD SUMMARY

VOC's are purged from a 25mL water sample in a fritted sparge cell. An inert gas (helium) is bubbled through the sample in the sparge cell, which causes the purgeable VOC's to be transferred from the aqueous sample to the vapor phase. The vapor phase is swept through a trap, containing an adsorbent material at ambient temperature, where the VOC's are trapped. After the purging of the sample is completed, the adsorbent trap is heated and back flushed with helium which desorbs the VOC's onto a capillary column in a gas chromatograph (GC). The VOC's are separated in the GC column and detected by a mass spectrometer (MS).

The samples are fortified with internal standards (IS) and surrogate compounds (SUR) before they are purged. The target VOC's and surrogate compounds are identified in the sample by analyzing standards under the exact same conditions employed for samples, and comparing the resulting mass spectra and GC retention times. A response factor is established for each target and surrogate compound during the initial and continuing calibrations by comparing the MS response of the primary ion produced by the target and surrogate compounds to the MS response for the primary ion produced by the associated internal standard. Each target and surrogate compound is quantitated by comparing the responses of the target and surrogate compound responses to the internal standard responses, using the average response factors from the most recent initial calibration.

Non-target compounds are identified by comparing the resulting mass spectra of the non-target compound to the mass spectra contained in the National Institute of Standards and Technology (NIST) Library in the MS database. An estimated quantitation is performed for the non-target compounds by comparing the total MS response to the nearest internal standard total MS response, assuming a relative response factor of 1.0.

3 DEFINITIONS

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

3.2 Laboratory Fortified Blank (LFB) - Referred to as a Laboratory Control Sample (LCS) in this SOP. An aliquot of reagent water 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. For this SOP, the LCS is prepared using a second source standard, and thus also acts as an independent quality control sample (QCS).

3.3 Laboratory Fortified Sample Matrix (LFM) and Laboratory Fortified Sample Matrix Duplicate (LFMD) - Commonly referred to as 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 a sample. The MS and MSD are used to determine whether the sample matrix contributes bias to sample results and to indicate the precision associated with laboratory procedures. The MS samples are fortified to the midpoint of the calibration curve with a subset of the target compounds.

3.4 QL Standard - An aliquot of reagent water containing method analytes at a concentration of 0.5 g/L. The QL standard is used to demonstrate the ability to analyze low level samples for the State of California.

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

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

3.7 Calibration Standard (CAL) A solution prepared from the primary dilution standard solution and/or the stock standard solutions containing the method analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentrations.

3.8	GC/MS	Gas Chromatograph / Mass Spectrometer
3.9	BFB	Bromofluorobenzene, the compound used as the system performance check for the GC/MS. Also used as a surrogate.
3.10	IS	Internal Standard
3.11	SUR	Surrogate Compound, also known as System Monitoring Compound in other methods
3.12	FC43	Perfluorotributylamine. Compound used to tune the MS.
3.13	QL	Quantitation Limit (see Appendix B).
3.14	RIC	Reconstructed Ion Chromatogram
3.15	NIST	National Institute of Standards and Technology

4 HEALTH & SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals should be minimized through the use of personal protective equipment and laboratory engineering and design. A reference file of material safety data sheets (MSDS) is available to all personnel involved in the chemical analysis and can be found in the library (Room 118) or Room 413.

4.2 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, methylene chloride and vinyl chloride. Primary standards of these toxic compounds must be prepared in a hood. Routine procedures in this SOP do not require contact with concentrated or neat solutions of these materials. All standard preparation procedures associated with this SOP should be performed in a hood.

4.3 Methanol is the primary solvent used for the preparation of standards in this procedure. 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 fumehood. The analyst must wear appropriate personal protective equipment (laboratory coat, nitrile gloves and safety glasses). Store methanol in a flammables storage cabinet away from oxidizers and sources of ignition.

4.4 Due to the unknown and potentially hazardous characteristics of samples all sample handling and preparation must be performed in a laboratory fumehood.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Sample receipt at the Region 9 Laboratory is performed under strict chain-of-custody procedures.

5.2 Samples for 504 analysis are delivered by the Sample Custodian to room 201, logged into the Internal Chain of Custody log, and transferred to the sample refrigerator. Maintain the refrigerator at 4 C ± 2 C. Record the refrigerator temperatures daily in the temperature logbook as described in SOP 805. Do not store samples and standards in the same refrigerator.

5.3 Check the following information to ensure that the information on the sample containers corresponds to the information on the tracking sheets and the chain-of-custody record.

5.3.1 EPA sample number.

5.3.2 Region 9 Laboratory number.

5.3.3 Case number.

5.3.4 Sample Delivery Group number.

5.4 Confirm that the integrity of the samples has not been compromised by checking the samples for the following items. Note any problems in the injection logbook and in the case narrative.

5.4.1 Broken chain-of-custody seals on the sample containers.

5.4.2 Leaking or broken sample containers.

5.4.3 Altered sample information on the sample containers.

5.4.4 The presence of headspace or air bubbles.

5.5 Sort samples according to date sampled, so that samples can be analyzed in order of date sampled to prevent missed holding times.

5.6 Samples must be analyzed in an efficient and timely manner such that no analytical holding times are exceeded. Generally, samples should be analyzed on the GC/MS system which is set up to analyze samples for SOP 354 (other analyses are performed in the Region 9 VOA Laboratory). Samples should be analyzed in the order of their sampling date, if possible.

5.7 Analyze water samples which are preserved with acid within 14 days of the time of sampling. Analyze unpreserved samples within 7 days of the time of sampling.

Note: Drinking water compliance samples must be dechlorinated and preserved with acid to pH < 2 at the time of sampling. These samples have a maximum holding time of 14 days from 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 EPA Chemistry Team Leader immediately so that the proper notifications can be made.

5.8 Store excess samples at 4 C ± 2 C in the sample refrigerators in rooms 201or 209. Thirty (30) days after the close date for an SDG remove the excess samples for the entire SDG from refrigerated storage and place on the shelves in Room 211, for a period of 60 days after the submission of the data deliverables associated with the sample delivery group (SDG). After 60 days, the samples may be disposed of in the appropriate manner as specified in SOP 125, unless otherwise directed by the EPA Chemistry Team Leader.

6 INTERFERENCES

6.1 Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and 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 9. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

6.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during storage and handling.

6.3 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 a detergent solution between analyses, rinse it with distilled water, and then dry it in an oven at 105 C. 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.

6.4 Solvents and other compounds which are target analytes must never be introduced into the laboratory where volatiles analysis is performed. Methylene chloride, 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 (acetone is used to remove writing from glassware).

7 APPARATUS AND MATERIALS

7.1 The volatiles laboratory has three GC/MS instruments for the analysis of volatile organic compounds. The components of each system are summarized in the table below. All three systems may be used to analyze samples following this SOP.

Region 9 GC/MS Volatiles Analytical Systems

System Name	HP5973J	HP5973H	HP5973K
Purge and Trap Concentrator	Hewlett Packard (Tekmar 3000)	Hewlett Packard (Tekmar 3000)	Tekmar LSC 2000
Autosampler	Varian Archon	Varian Archon	Tekmar ALS 2016
Gas Chromatograph	HP 6890 plus	HP6890 plus	Agilent 6890 Plus
Mass Spectrometer	HP 5973	HP5973	Agilent 5973 Network
Data System	HP Chemstation	HP Chemstation	HP Chemstation
Analytical Column	RestekRTX-VMS 30M x 0.25 mm, 1.40 micron film	HP-624 25M x 0.20 mm, 1.12 micron film	HP-624 25M x 0.20 mm, 1.12 micron film

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 Standard solutions (Region 9 Laboratory SOP 255).

7.2.1 4-Bromofluorobenzene Tuning Solution (BFB Solution, 50 ng/μL).

7.2.2 Drinking water surrogate & IS solution (DWIS mix, 50 ng/μL) for Tekmar ALS 2016 Autosampler and (DWISA mix, 125 ng/μL) for Varian Archon Autosampler.

7.2.3 Drinking water calibration mix (DW mix, 25 ng/μL)

7.2.4 LCS (Laboratory Fortified Blank) Solution (DWLF solution, 25 ng/μL)

7.2.5 Matrix Spike solution (DWMS solution, 50 ng/uL)

7.3 Organic-free method blank water (Region 9 Laboratory SOP 205).

7.4 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).

7.5 25-mL fritted sparge vessels

7.6 25-mL Fritless sparge vessels.

7.7 Stainless steel spatulas.

7.8 Disposable Pasteur pipettes.

7.9 Methanol (Purge & Trap grade).

7.10 pH paper (pH 0-14 range).

7.11 Trap K (VOCARB 3000, or equivalent)

7.12 40-mL VOC vials for standards with screw-hollow cap lined with 22 mm PTFE-faced silicone septa.

8 QUALITY CONTROL

This section describes the QA/QC criteria which must be followed in the analysis of samples for volatile organic compounds.

8.1 Drinking Water Compliance samples. If samples are to be analyzed for compliance with Safe Drinking Water Act, all regulated analytes listed in Appendix B must meet the QC criteria listed in Appendix C. Analyses for other programs may use shortened analyte lists.

8.2 Initial Demonstration of Performance

8.2.1 For each instrument and analyst, the performance of the analytical system must be demonstrated. This demonstration consists of the successful analysis of a method blank (LRB), a demonstration of precision and accuracy, and an acceptable Method Detection Limit (MDL) study. Perform the demonstration of analyst proficiency and instrument capability in accordance with EPA Region 9 Laboratory SOP #880, *Initial and Continuing Demonstration of Capabilities and Performance*

8.2.2 The method blank analyzed for the initial demonstration must meet the requirements of Section 8.8.

8.2.3 Calculate the MDL in accordance with 40 CFR Part 136, Appendix B or in Section 13 of method 524.2, Revision 4.1, 1995. For seven replicates the formula is: MDL(g/L) = SD x 3.143. Where SD is the sample standard deviation of the concentration obtained from the seven replicate runs for the analyte and 3.143 is Student's t value for seven replicates.

8.2.4 Acceptance criteria: The MDL must be less than or equal to one-half the method QL and analyte recoveries must be between 80% to 120%.

8.3 Mass calibration.

8.3.1 Calibrate the mass axis of the mass spectrometer whenever the mass spectrometer is shut down, or whenever there is a mass misassignment. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer. Perfluorotributylamine (FC43) is used to perform the mass calibration of the instrument. The FC43 spectrum must meet the following criteria:

Mass	Target % of Mass 69
69	100
131	25.0-75.0
219	25.0-60.0
414	1.4-4.0
502	0.8-4.0

Isotope Ratio

Mass Ratio	Target %
70/69	0.8-1.3
132/131	2.0-3.4
220/219	3.5-5.2
415/414	7.2-10.8
503/502	8.1-12.1

8.3.2 If the FC43 spectrum does not meet the criteria listed above, corrective action must be taken; this 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.

8.4 GC/MS System Performance Check (BFB analysis.)

8.4.1 Prior to the analysis of any calibration standards, blanks, and samples (including LFM/LFMDs), 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.

8.4.2 Frequency of GC/MS Performance Check.

8.4.1.1 Inject BFB once at the beginning of each 12-hour period during which standards, blanks and samples are to be analyzed. The twelve-hour time period begins at the moment of injection of the BFB and ends after twelve hours have elapsed. Samples analyzed after the 12-hour time period have elapsed must be re-analyzed.

8.4.3 Analyze the BFB according to Section 9 of this SOP.

8.4.4 The ion abundance ratios must meet the following criteria.

Mass (m/z)	Relative Ion Abundance Criteria
50	15 - 40 percent of mass 95
75	30 - 80 percent of mass 95
95	Base peak, 100 percent relative abundance
96	5 - 9 percent of mass 95
173	< 2 percent of mass 174
174	>50 percent of mass 95(Mass 95 must be base peak)
175	5 - 9 percent of mass 174
176	95 - 101 percent of mass 174
177	5 - 9 percent of mass 176

8.4.4.1 If the ion abundances fail to meet the 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 also be necessary to clean the ion source or take other corrective action to achieve the ion abundance criteria.

8.5 Initial calibration (ICAL).

8.5.1 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 can not be met.

8.5.2 The initial and continuing calibration criteria are listed in Appendix C.

8.5.3 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 more than one standard fails, corrective action is required.

8.5.4 Analyze the ICAL standards according to Section 9 of this SOP.

8.5.5 No quantitation ion may saturate the detector.

8.5.6 The data system calculates the relative response factor (RRF) for each target compound and surrogate compound for all five calibration standards using equation 1. The quantitation ions and internal standard assignments are listed in Appendix B.

Eq. 1

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

Where
Ax = Area of quantitation ion of compound x
Ais = Area of quantitation ion for associated internal standard
Cx = Concentration of compound x
Cis = Concentration of the associated internal standard

8.5.7 Calculate the average RRF for all analytes

8.5.8 Calculate the percent relative standard deviation (%RSD) of the RRF values for each compound using equation 2.

EQ. 2

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

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

8.5.9 Process and check the data files immediately after the initial calibration is completed to ensure that the calibration QC criteria have been satisfied (see Appendix C). If a sample is for drinking water compliance, all regulated compounds must meet QC criteria. If any of the criteria have not been met because of a single concentration point in the curve, then that single point can be reanalyzed once, and the data checked against the criteria. 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 repairs are made to the system, then a new initial calibration must be performed. 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.

8.5.10 If the initial calibration meets all the specified criteria, the remainder of the 12-hour analytical period may be used for the analysis of blanks and samples, using the average RRF from the ICAL to quantitate the QC and field sample data.

8.5.11 Manual integration. There will be instances when the data system will not produce accurate integrations. Examples of this are misidentification of a peak, inaccurate dropping of a perpendicular between peaks, or failure to integrate the entire tail of a peak. When necessary, chromatograms can be manually integrated if the following steps are taken (see USEPA Region 9 Laboratory SOP # 835, *Chromatographic Integration Procedures*):

8.5.11.1 Print a view of the chromatogram to be reintegrated using QEDIT. Include the background subtracted spectrum of the apex of the peak and the reference spectrum. Indicate the reasons for manually integrating the chromatographic results on the chromatogram and initial and date the statement.

8.5.11.2 Reintegrate the peak and print the new view. Save the reintegrated value(s). Print the peak and reference spectra. Document the manual integration on the reintegrated chromatogram and initial and date the statement.

8.5.11.3 Print the new quant report and chromatogram after all manual integrations have been completed. Indicate each manual integration on the new quant report. Document the fact that there was manual integration in the instrument run log.

8.5.11.4 Show the chromatograms, quant reports and log book to a group leader, QA/QC Task Manager, or Program Manager for review and acceptance.

8.6 Continuing Calibration

8.6.1 A continuing calibration standard must be analyzed at the beginning of each 12-hour analytical period (see Section 8.4.2 for definition of 12-hour time period). If the continuing calibration meets acceptance criteria listed in Appendix C, the average response factor from the initial calibration is used to quantitate analytical results during the associated 12-hour time period.

8.6.2 The initial and continuing calibrations must meet the criteria listed in Appendix C.

8.6.3 Analyze the continuing calibration standard according to Section 9 of this SOP.

8.6.4 Calculate the relative response factor (RRF) for each target compound and surrogate compound using equation 1. The quantitation ions and internal standard assignments are listed in Appendix B.

8.6.5 Calculate the percent difference (%D) between the continuing calibration RRF and the most recent initial calibration average RRF for each target compound and surrogate using equation 3.

EQ 3.

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

8.6.6 Compare the %Ds with the maximum %D criteria listed in Appendix C. Up to 10 % of the compounds may fail to meet the criteria, but if the samples are for drinking water compliance, all regulated compounds must meet the criteria. If the criteria are not satisfied a second continuing calibration may be analyzed. Repeated failure requires the analysis of a new initial calibration. 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 relative response, loss of classes of compounds, etc. which may signal the need for instrument maintenance.

Check the continuing calibrations for mis-identified peaks due to retention time shifts. The most commonly mis-assigned compounds are the 1,3- and 1,4-dichlorobenzenes.

8.7 Quantitation Limit (QL) Standard

8.7.1 Analyze a low level quantitation standard at 0.5 μg/L immediately after the initial or continuing calibration for each 12-hour analytical period. This analysis demonstrates the ability to analyze samples at levels specified by the State of California.

8.7.2 Analyze the low level quantitation standard according to Section 9 of this SOP.

8.7.3 The observed concentration of the five compounds -- vinyl chloride, 1,2-dichloroethane, carbon tetrachloride, cis-1,3-dichloropropene, and trans-1,3-dichloropropene -- must be greater than or equal to 0.25 μg/L and less than or equal to 0.75 μg/L (50 -150 % recovery).

8.7.4 If the requirements of 8.7.3 are not met corrective action must be taken. The standard can be reanalyzed once. Repeated failure indicates that maintenance is required to improve instrument response.

8.8 Laboratory Control Sample (LCS)

Analyze an LCS daily to demonstrate that the calibration standards used to calibrate the instrument are appropriate. Specifically the LCS verifies that the standards include the appropriate compounds at the correct concentration. Prepare the LCS spiking mixture from a source (or sources) entirely separate from those used to calibrate the instrument. The LCS must be analyzed once per 12 hour tune period.

8.8.1 Prepare the LCS as a method blank except also add the volume of the LCS STD which results in a concentration equal to the concentration of the mid-level calibration standard.

8.8.2 Analyze the LCS exactly as a sample is analyzed.

8.8.3 All analytes must be recovered at the percent accuracy specified in Appendix C. The source of any discrepancy should be determined prior to reporting any sample data. This may require preparing fresh standards (either the calibration standard, the LCS, or both) which may require a new initial calibration analysis.

8.9 Method Blank (LRB) analysis.

8.9.1 Analyze a method blank immediately after the calibration standards and the QL verification standard -- before the samples are analyzed -- in order to demonstrate that the instrument is free of contamination.

8.9.2 Analyze the method blank according to Section 9 of this SOP.

8.9.3 Check the method blank RIC and quantitation report immediately after it is analyzed, or as soon as possible, to determine that the following criteria have been met:

The method blank is acceptable if it contains less than 2.5 times the QL of methylene chloride and less than ½ the QL of any other volatile target compound. The total area of any non-target compound detected must be less than 50 percent of the total area of the nearest internal standard. If the blank does not meet these requirements, prepare and reanalyze a new blank before analyzing any samples. If the second blank fails to meet the above criteria corrective action must be initiated and documented.

Note: For drinking water compliance samples, methylene chloride in the method blanks must be less than 0.5 µg/L.

8.9.4 The method blank internal standards must meet the criteria listed in Section 8.12.

8.9.5 The method blank surrogate recoveries must meet the criteria listed in Section 8.13.

8.9.6 All volatile analyses associated with a blank that does not meet the above requirements must be reanalyzed.

8.10 Storage Blank analysis.

8.10.1 Analyze a storage blank once every week. A storage blank is a blank sample which has been preserved with HCl and stored in the same storage area as other samples for VOC analysis at the laboratory. The storage blank indicates whether contamination may have occurred during sample storage.

8.10.2 Every Monday morning, or the first work day of the week, two acidified 40-mL screw-cap volatile vials with PTFE-faced silicone septa must be filled with reagent water and stored with the samples, in the sample storage refrigerator in room 201.

8.10.3 Analyze the storage blank the following Monday, or on the first work day of that week, and new storage blanks placed in the refrigerator.

8.10.4 Analyze the storage blank according to Section 9 of this SOP.

8.10.5 The storage blank internal standards must meet the criteria listed in Section 8.12; if not, reanalysis is required.

8.10.6 The storage blank surrogate recoveries must meet the criteria listed in Section 8.13 or reanalysis is required.

8.10.7 Compare the results of the storage blank analysis to the criteria listed in Section 8.9.3. If the storage blank does not meet these requirements, report the variances in the report narrative and flag the affected analytes with a "J" flag and a "B" qualifier summary of analytical results spreadsheet.

8.11 Instrument Blanks

8.11.1 In the event that a sample is analyzed which exceeds the calibration range of the instrument, an instrument blank must be analyzed on the same autosampler port to demonstrate that the system is free of carryover contamination prior to the analysis of another sample using that autosampler port. Instrument blanks are prepared in the same manner as method blank samples.

8.11.2 Analyze the instrument blanks according to Section 9 of this SOP.

8.11.3 The instrument blank is acceptable if it contains less than or equal to the QL of methylene chloride and less than or equal to ½ the QL of any other volatile target compound. The total area of any non-target compounds detected must be less than 50 percent of the total area of the nearest internal standard. If the instrument blank does not meet these requirements, the autosampler port must be cleaned and a new instrument blank must be analyzed on that autosampler port to demonstrate the absence of contamination before any samples can be analyzed on the autosampler port. This is an iterative process which must be repeated until the port has been demonstrated to be free of contamination.

8.11.4 The instrument blanks can be analyzed beyond the twelve-hour tune time period.

8.11.5 Instrument blanks do not need to meet the surrogate recovery criteria listed in Section 8.13.

8.11.6 Instrument blanks must meet the internal standard criteria listed in Section 8.12.

8.12 Internal standard recovery.

8.12.1 Check the internal standard recovery, determined by total quantitation ion area, for all standards, blanks, samples, and spikes immediately after analysis in order to determine if all applicable criteria have been met.

8.12.2 If the quantitation ion area of any internal standard in any blank, sample, or spike analysis changes by more than (50 -200%) from the average response of the corresponding internal standard from the initial calibration, the system must be checked for malfunctions and the necessary corrections must be made. After the corrections are made, the analyses performed while the system was malfunctioning must be repeated. Keep in mind that many "corrections" to the system will require that the initial calibration be performed prior to reanalysis of the samples.

8.12.3 If after reanalysis, the area for all internal standards are within the criteria, then the problem is considered to have been within the laboratory's control. Report the data from the reanalysis, and submit data from both analyses.

8.12.4 If reanalysis of the sample does not solve the problem, submit the data for both analyses. Distinguish between the analysis and reanalysis by adding an "RE" suffix to the EPA sample number on the reanalysis. The problem must be documented in the report narrative (see Section 11.1.1.1.9).

8.12.5 The internal standard retention times in all samples must be checked immediately after data acquisition. If the retention time for any internal standard changes by more than 15 seconds from the latest daily calibration standard, the system must be inspected for malfunctions, and the necessary corrections made. Compare blanks, samples, and spikes analyzed within the 12-hour analytical period of the initial calibration to the 5 ug/L standard for low detection limit waters.

8.13 Surrogate compound recovery.

8.13.1 The surrogate compound (SUR) recovery in all blanks, samples, and spike must be calculated and checked immediately after analysis and compared to the limits listed in Appendix C. In addition the following should be monitored:

Monitor the integrated areas of the quantitation ions of the surrogates in all samples, continuing calibration checks, and blanks. These should remain relatively constant over time. An abrupt change may indicate a matrix effect or an instrument problem. Low areas also may indicate an inefficient transfer from the trap to the column. A gradual drift of more than 50% from the average response of the corresponding internal standard from the initial calibration, is indicative of a change in sensitivity.

8.13.2 If the recovery of one or more of the surrogate compounds is not within the limits listed in Appendix C, the following steps must be taken.

8.13.2.1 Check to ensure that there are no calculation errors, and check the system performance.

8.13.2.2 Reanalyze the sample if a system performance problem or calculation error is not evident.

8.13.2.3 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 runlog and report narrative.

8.13.2.4 Do not reanalyze the MS or MSD samples, even if the surrogate recoveries are outside the limits.

8.13.2.5 If the sample associated with the MS and MSD analyses does not meet the surrogate recovery criteria, it should be reanalyzed only if the MS and MSD 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 reanalysis. The similarity in surrogate recoveries in the sample and spike analyses must be discussed in the report narrative (See Section 11.1.1.1.9.).

8.13.3 If the surrogate recoveries of the reanalysis are within limits, then the problem was within the laboratory's control. Therefore, the analysis with the surrogate recoveries within limits shall be considered the initial analysis, and should be the one reported. Provide raw data for both the initial (failing) analysis and the reanlysis.

8.13.4 If the reanalysis does not solve the problem, then submit the data from both analyses. Distinguish between the original analysis and the reanalysis by adding the "RE" suffix to the EPA sample number in the reanalysis.

8.14 Matrix Spike and Matrix Spike Duplicate analysis.

8.14.1 In order to determine the matrix effect upon the analytical methodology, a MS and MS duplicate analysis must be performed according to the following scheme, whichever is most frequent:

One MS/MSD for each case of samples received.

One MS/MSD for each SDG of twenty samples within a case.

Matrix QC samples are usually designated in the field. In the event that a sample was not designated as the QC sample and adequate sample volume exists, the analyst will choose one representative sample from the SDG for QC analysis. Do not designate any obvious field blanks as the QC sample.

8.14.2 Analyze MS and MSD samples immediately following the analysis of the sample designated as the QC sample.

8.14.3 Analyze the MS and MSD according to Section 9 of this SOP.

8.14.4 The recovery and RPD criteria for MS and MS duplicate are found in Appendix C.

8.14.5 Calculate the recovery of each compound as follows:

$$\% \text{ Rec} = ((SSR - SR)/SA)*100$$

where,

SSR = Spiked sample result
SR = Sample result
SA = Spike added

8.14.6 Calculate the relative percent differences (RPD) of the recoveries of each compound in the MS and MS duplicate as follows:

$$RPD = \frac{MSR - MSDR}{(½)\,(MSR + MSDR)} \times (100)$$

where,

MSR = MS recovery
MSDR = MS duplicate recovery

8.14.7 The limits for MS and MS duplicate recovery are advisory limits only. If the limits are not met, then no further action is required since the purpose of these analyses is to determine matrix effects on compound recovery. A comment regarding the MS recoveries must be included in the report narrative. 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 check the MS solution by spiking a method blank sample and checking the recoveries of the spike compounds. A new solution should be prepared if the recoveries are outside the limits.

8.15 Sample dilution.

8.15.1 If the on-column concentration of any target compound in any sample exceeds the initial calibration range, a new aliquot of that sample must be diluted and purged. The following criteria shall be used in performing dilutions.

8.15.1.1 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

8.15.1.2 Choose a dilution factor to keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

8.15.1.3 Do not dilute MS or 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.

8.15.1.4 In the case of extremely contaminated samples several dilutions may be required.

8.15.2 After a sample is analyzed that contains one or more target compounds at a level exceeding the initial calibration range of the system, it must be demonstrated that there is no carryover to subsequent analyses.

8.15.2.1 If analyzing one sample at a time, analyze an instrument blank immediately after the contaminated sample. If the Tekmar type autosampler was used, the instrument blank must be analyzed using the same sparge cell as the contaminated sample. The instrument blank must meet the acceptance criteria in Section 8.10.

8.15.2.2 If analyzing samples in automated run mode, monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the limits above. The maximum contamination criteria are as follows: the sample must not contain a

concentration above the QL for the target compounds that exceeded the limits in the contaminated sample. The next sample analyzed using the same sparge cell that was used for the contaminated sample must be an instrument blank analyzed as specified in Section 8.10.1.

8.16 Review of Target Analytes

Each reported value must be reviewed for both qualitative and quantitative validity. This process, in particular the qualitative review of mass spectra, relies upon the technical judgement of the analyst.

8.16.1 Qualitative Review

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.

8.16.1.1 The peak must elute within ±0.03 minutes of the retention time of the analyte in the continuing calibration standard. The retention time difference will be shown as Delta R.T. in each analyte's detailed profile quantitation report.

8.16.1.2 The mass spectra used for qualitative identification must be obtained using the GC/MS system used to analyze the samples.

8.16.1.2.1 All ions present in the standard mass spectra at a relative intensity of 10 percent of the most abundant ion must be present in the sample spectra.

8.16.1.2.2 The relative intensities of the ions must agree within ±20 % between the standard and sample spectra.

8.16.1.2.4 Ions present in the sample at greater than 10 percent abundance but not present in the standard spectra must be reviewed and accounted for by the analyst making the comparison.

8.16.1.3 If a compound cannot be verified by these criteria but, in the technical judgement of the analyst, is present the supporting evidence must be indicated on the raw data and the analyte reported.

8.16.2 Quantitative Review

Reported values must be reviewed to determine that the correct calculations were used to generate the results, that the average RRFs from the associated initial calibration were used, and that all other numbers are accurate.

8.16.2.1 Review of data system integrations

The analyst must review the data system integration to verify that the internal standards, surrogates and target compounds are integrated properly. All automated and manual integrations must comply with Region 9 Laboratory SOP 835, *Chromatographic Integration Procedures*.

8.16.2.2 Calculations

Results for target analytes are calculated using the following equation:

$$\text{Conc. (}\ \mu\text{g/L)} = A_x * AMT_{IS} * DF / (A_{IS} * RRF)$$

where:

A_x	= area of the characteristic ion of the compound
AMT_{IS}	= amount of internal standard in μg/L (5 μg/L)
DF	= dilution factor
A_{IS}	= area of the characteristic ion of the associated internal standard
RRF	= analyte's average relative response factor from the initial calibration

8.17 Review the Tentatively Identified Compound search results for the following:

8.17.1 Verify that all unknown peaks in the RIC greater than 10 percent of the area of the nearest internal standard are accounted for in the summary.

8.17.2 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.

8.17.3 The relative intensities of the major ions should agree within 20 percent.

8.17.4 Molecular ions present in the reference spectrum should be present in the sample spectrum.

8.17.5 Review ions present in the sample spectrum but not in the reference spectrum for possible background contamination or the presence of co-eluting compounds.

8.17.6 Ions present in the reference spectrum but not within the scan range (35 to 300 amu) of the method should not be considered when making a tentative identification.

8.17.7 If, in the technical judgement 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.). The probable molecular weight should be included, if distinguishable.

8.18 If any of the data reports have been edited, or if manual integration or quantitation has been performed, the analyst shall identify them and show the chromatograms, quant reports and log book to a group leader, QA/QC Task Manager, or Program Manager for review and acceptance.

9 ANALYTICAL PROCEDURES

9.1 Analytical system preparation.

Perform mass calibration of the analytical system according to the schedule prescribed in Section 8.3. Mass calibration is done to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer. Perfluorotributylamine (FC43) is used to perform the mass calibration of the instrument.

9.1.1 Open the HP 5973 MSD Instrument Control window and choose the Instrument menu. Select Perform MS Autotune.

9.1.2 The autotune software will adjust the mass ratio, abundance, peak shape, width, isotope peak resolution and mass assignment.

9.1.3 An autotune report will be generated and the parameters will be saved in ATUNE.U.

9.1.4 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. Save the manual tune file in the format of month-date-year-sequential letter. For example: 082301A.U.

9.1.5 Check the mass spectrum/peak ratios with the specifications listed in Section 8.3. If the specifications are not met the instrument must be retuned and recalibrated.

9.2 Leak Checking

Check the mass spectrometer for leaks on a daily basis, prior to the analysis of 4-bromofluorobenzene (BFB) tuning compound.

9.2.1 Check that the MSD analyzer temperatures displayed as MS zones are set to the following values:

9.2.1.1 MS Quad @ 150°C.

9.2.1.2 MS Source@ 230°C.

9.2.1.3 If the display indicates that the analyzer temperatures are not at the desired set points, perform corrective action according to the operator's manual.

9.2.2 Check the source analyzer pressure.

9.2.2.1 The analyzer pressure should be less than 10^{-5} torr as indicated by the ion gauge controller.

9.2.2.2 Values higher than indicated above are indicative of large leaks and must be corrected.

9.2.3 Check the nitrogen (m/z 28) to water (m/z 18) ratio.

9.2.3.1 From View menu in Instrument Control panel of the HP 5973 MSD Instrument, select Perform Diagnostic/Vacuum and then run the Air / Water program from Diagnostics menu. The Air and Water Check report will be printed out. Alternatively, set the mass spectrometer to scan over a range of 10 to 50 m/z. Observe the ratio of the water peak (m/z 18) to the nitrogen peak (m/z 28). If a leak is present in the mass spectrometer the nitrogen peak will be greater than the water peak. Corrective action must be taken if a leak is detected.

9.3 GC/MS Performance Check

9.3.1 Prior to the analysis of any calibration standards, blanks, or samples (including MS/MSDs), the GC/MS system must meet the mass spectral ion abundance criteria for bromofluorobenzene (BFB) prescribed in Section 8.4. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target and non-target compounds.

9.3.2 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Appendix E.

9.3.3 Set up a data acquisition for the direct injection of BFB. See Appendix F for data file naming convention.

9.3.4 Inject 0.5 μL of BFB Solution (50 ng/μL) into injection port and press the start button on the GC.

9.3.5 After the data acquisition is complete, execute the BFB evaluation procedure. 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.

9.3.6 The ion abundance ratios must meet the criteria listed in Section 8.4.

9.4 Analysis of samples

The 12-hour analytical time period for this method begins with the injection of BFB and ends 12 hours after the injection time. Standards, blanks, and samples must be analyzed within this 12-hour analytical time period.

9.4.1 Five-point initial calibration

Perform a five-point initial calibration to demonstrate that the GC/MS system provides a linear response over the desired concentration range. Set up the purge and trap concentrator for analysis using 25-mL sparge cells. The five concentration points are listed in the table 1 below.

Table 1 25-mL Calibration Standard Amounts

Calibration Point	Tekmar 2016 Autosampler		Varian Archon Autosampler	
	DWIS Mix 50 µg/mL	DW Calibration Mix 25 µg/mL	DWISA Mix 125 µg/mL	DW Calibration Mix 25 µg/mL
25 µg/L	2.5 µL	25 µL	1 µL	50 µL
10 µg/L	2.5 µL	10 µL	1 µL	20 µL
5 µg/L	2.5 µL	5 µL	1 µL	10 µL
2 µg/L	2.5 µL	2 µL	1 µL	4 µL
1 µg/L	2.5 µL	1 µL	1 µL	2 µL

9.4.1.1 Fill a 25-mL (For Tekmar ALS2016 Autosampler) or 50-mL (For Varian Archon Autosampler) syringe with method blank water. Invert the syringe, remove any air bubbles, and bring the level to 25 mL or 50 mL by displacement with the plunger.

9.4.1.2 Lay the 25 mL syringe on the lab bench and spike the water with 2.5 µL of DWIS Solution for Tekmar 2016 Autosampler. For Varian Archon autosampler, this step is omitted since 1 µL of DWISA Solution will be automatically spiked in the later step. The amount used results in the analytical equivalent of 5 µg/L.

9.4.1.3 Spike the water with the appropriate amount of DW mix solution for the specific point being analyzed

9.4.1.4 For Tekmar ALS2016 Autosampler, 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. Remove the syringe from the mount. Continue with Section 9.4.1.9.

9.4.1.5 For Varian Archon Autosampler, cap the end of the 50 mL syringe containing the DW mix solution. Rotate and invert the closed syringe to mix. Let the standard solution equilibrate in the syringe for about 1 minute. While the standard solution is equilibrating, label the 40-mL vial with information about the standard.

9.4.1.6 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.

9.4.1.7 Gently place the vial in the appropriate autosampler position. Avoid causing any hairline cracks in the vial, as this may result in the vial disintegrating in the autosampler.

9.4.1.8 The Archon autosampler will analyze a 25 mL aliquot and add 1 μL of the 125 ng/μL DWISA solution.

9.4.1.9 Analyze the standards. Press the start button on the concentrator to begin purging the standard. See Appendix D for purge and trap parameters.

9.4.1.10 Set up an acquisition on the GC/MS system with the appropriate GC/MS conditions. See Appendix E. Name the data files according to the data file naming convention in Appendix F.

9.4.1.11 Acquire the GC/MS data.

9.4.1.12 Analyze the four other initial calibration standards following the procedures outlined above.

9.4.1.13 Update the initial calibration response factors for the method by associating the current data file with each calibration level. Save the method.

9.4.1.14 Generate the initial calibration summary report. Samples must not be analyzed if the initial calibration does not meet the criteria specified in Appendix C.

9.4.1.15 If the initial calibration meets all the criteria specified in Section 8.5 of this SOP, the remainder of the 12-hour analytical period may be used for the analysis of QL standard (0.5 µg/L), LFB, blanks and samples, using the average response factor of the initial calibration to quantitate the blank and sample data files.

9.4.2 Continuing calibration.

Analyze a continuing calibration standard in every 12-hour analytical time period, after BFB tuning and prior to a method blank analysis. The continuing calibration check is performed in order to determine if the percent difference criteria meet the appropriate QC criteria specified in Section 8.6. The continuing calibration is analyzed at a level of 5 µg/L.

9.4.2.1 Prepare the mid-level standard as described for procedures in Sections 9.4.1 using the 5 µg/L calibration level in Table 1. The amounts used result in a final concentration of 5 µg/L.

9.4.2.2 Press the start button on the concentrator to begin purging the standard. See Appendix D for purge and trap parameters.

9.4.2.3 Set up an acquisition on the GC/MS system with the appropriate GC/MS conditions. See Appendix E. Name the data files according to the data file naming convention in Appendix F.

9.4.2.4 Analyze the standard and acquire the data.

9.4.2.5 Quantitate the data and print out a quantitation report and chromatogram. Quantitate the data using the average relative response factor from the initial calibration.

9.4.2.6 Examine the areas of the quantitation ions of the internal standard and surrogate compounds. These should not have decreased by more than 30% from the areas measured during the most recent previous continuing calibration or by more than 50% from the average of the areas measured during the initial calibration. If the areas have

decreased by more than these amounts, the necessary maintenance, source cleaning, and/or recalibration must be performed to restore system sensitivity. Generate a continuing calibration response report. Check that the relative response factor values meet the criteria specificed in Section 8.6 of this SOP.

9.4.2.7 If the continuing calibration response factors meet all of the criteria specified in Appendix C of this SOP, the remainder of the 12-hour analytical period may be used for the analysis of QL standard (0.5 μg/L), LCS, blanks and samples, using the average response factor of the initial calibration to quantitate the blank and sample data files.

9.4.3 Quantitation Limit Standard

Analyze a QL standard at a concentration of 0.5 μg/L to verify that the low detection limits for vinyl chloride, 1,2-dichloroethane, carbon tetrachloride, cis-1,3-dichloropropene, and trans-1,3-dichloropropene can be achieved. Prepare and analyze the QL standard in a manner analogous to the continuing calibration standard except use 0.5 μL of the DW calibration mix solution for Tekmar ALS 2016 Autosampler and 1 μL of the DW calibration mix solution for Varian Archon Autosampler.

9.4.3.1 Prepare the quantitation limit standard as described in Sections 9.4.1 using 0.5 μL of the DW calibration mix and 1 μL of the DW calibration mix for different Autosamplers as stated above. The amounts used result in a final concentration of 0.5 μg/L.

9.4.3.3 Press the start button on the concentrator to begin purging the standard. See Appendix D for purge and trap parameters.

9.4.3.4 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Appendix E. Name the data files according to the data file naming convention in Appendix F.

9.4.3.5 Analyze the standard and acquire the data.

9.4.3.6 Quantitate the data and print out a quantitation report and chromatogram. Use the average relative response factor from the initial calibration for quantitation.

9.4.3.7 Evaluate the calculated concentrations against the criteria listed in Section 8.7. Do not analyze samples if the QL standard does not meet the criteria specified in Section 8.7.

9.4.3.8 If the QL standard meets all the criteria specified in Section 8.7, the remainder of the 12-hour analytical period may be used for the analysis of blanks and samples.

9.4.4 Laboratory Control Sample (LCS)

Analyze an LCS once in every 12-hour analytical time period, immediately after the initial or continuing calibration. An LCS is analyzed to demonstrate that the calibration standards used to calibrate the instrument are appropriate. Specifically the LCS verifies that the standards include the appropriate compounds at the correct concentration. This is done by preparing the LCS spiking mixture from a source (or sources) entirely separate from those used to calibrate the instrument. The LCS is analyzed at a level of 5 μg/L.

9.4.4.1 Prepare the LCS as described in Sections 9.4.2 for the mid-point (5 μg/L) continuing calibration level, but using the LCS standard (DWLF at 25 μg/mL) rather than the DW calibration standard. The amounts used result in a final concentration of 5 μg/L.

9.4.4.2 Press the start button on the concentrator to begin purging the standard. See Appendix D for purge and trap parameters.

9.4.4.3 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Appendix E. Name the data files according to the data file naming convention in Appendix F.

9.4.4.4 Analyze the standard and acquire the data.

9.4.4.5 Quantitate the data and print out a quantitation report and chromatogram. Use the average relative response factor from the initial calibration for quantitation.

9.4.4.6 Evaluate the calculated concentrations against the criteria listed in Section 8.8. Do not analyze samples if the LCS does not meet the criteria specified in Appendix C.

9.4.4.7 If the LCS meets all the criteria specified in Appendix C, the remainder of the 12-hour analytical period may be used for the analysis of blanks and samples.

9.4.5 Laboratory Reagent Blank analysis. (Method Blank)

Analyze a method blank after the initial or continuing calibration is performed and before samples are analyzed.

9.4.5.1 Prepare the method blank as described in Sections 9.4.1.1 to 9.4.1.7 except do not add DW calibration mix.

9.4.5.2 Press the start button on the concentrator to begin purging the standard. See Appendix D for purge and trap parameters.

9.4.5.3 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Appendix E. Name the data files according to the data file naming convention in Appendix F.

9.4.5.4 Analyze the standard and acquire the data.

9.4.5.5 Quantitate the data and print out a quantitation report and chromatogram. Use the average relative response factor from the initial calibration for quantitation.

9.4.5.6 Evaluate the calculated concentrations against the criteria listed in Section 8.8. Do not analyze samples if the method blank does not meet these criteria. If the method blank meets all the criteria, the remainder of the 12-hour analytical period may be used for the analysis of blanks and samples.

9.4.6 Sample analysis.

Analyze samples only after the BFB tune, initial calibration, continuing calibration, LCS, QL standard, and method blank analysis meet all of the appropriate criteria specified in the QA/QC section of this SOP.

9.4.6.1 Allow the sample to reach ambient temperature before analysis.

9.4.6.2 Check that the numbers on the vials coincide with the numbers on the routing forms to ensure that the correct sample is being analyzed.

9.4.6.3 Break the chain of custody seal on the vial with a scalpel or other appropriate implement, again making note if the seal is missing or compromised in any way.

9.4.6.4 Take note if the sample has an unusual color or other physical characteristic such as more than one phase, presence of a precipitate or unusual viscosity. If any physical signs of contamination are present a screening analysis to protect the analytical system from damage or contamination, and to determine the appropriate subsequent dilution is required. If an initial screening is necessary dilute the sample 1:50, unless the group leader, program manager, or EPA Chemistry TOPO decides otherwise.

9.4.6.5 Note in the runlog if there is head space present in the sealed sample vial.

9.4.6.6 For the Tekmar ALS 2016 Autosampler system, fill a 25-mL syringe with the sample. Invert the syringe, remove any air bubbles, and bring the level to 25-mL by displacement with the plunger. Any excess sample displaced from the syringe should be either place back into the sample vial or placed in the aqueous waste containers.

Spike the water with 2.5 μL of DWIS solution. The amounts used result in a final concentrations of 5 μg/L.

Attach the syringe to the Luer-lock mount on the appropriate autosampler position sparge apparatus. Open the mount valve and inject the contents of the syringe into the sparge cell and close the valve. Remove the syringe from the mount.

9.4.6.7 For the Varian Archon Autosampler systems, gently place the vial in the appropriate autosampler position. The autosampler will analyze a 25 mL aliquot and add 1 μL of the IS solution.

9.4.6.8 Press the start button on the concentrator to begin purging the sample. See Appendix D for purge and trap parameters.

9.4.6.9 Set up the GC/MS system with the appropriate GC and MS conditions. See Appendix E. Include the EPA sample number and the laboratory sample number, as well as the dilution level, if any in the sample description. Name the data files according to the data file naming convention in Appendix F.

9.4.6.10 Check the pH of the sample using pH 0-14 range pH paper. Record the pH in the injection logbook. If any samples have a pH greater than 2, note the samples in the report narrative.

9.4.6.11 Quantitate the data and print out a quantitation report and chromatogram. Use the average relative response factor from the initial calibration for quantitation.

9.4.6.12 Review the results as discussed in Section 8.16 for qualitative identification of target analytes. Cross out all reported hits which do not meet the qualitative criteria. Review all target compounds that are detected to verify they are integrated properly. Review the chromatogram for possible false negatives.

9.4.6.13 Check the sample's surrogate and internal standard recoveries with the criteria in Sections 8.11 and 8.12 in this SOP.

9.4.6.14 If any manual integrations are performed to integrations performed by the software, they must be performed in accordance with USEPA Region 9 Laboratory SOP#835, *Chromatographic Integration Procedures.*

9.4.6.16 In addition to undiluted analysis, the sample must be diluted and reanalyzed if any of the target analytes exceed the calibration range of the instrument. The sample should be diluted so that the target compound(s) which was originally outside of the calibration range will fall within the initial calibration range of the instrument.

9.4.6.17 If dilutions are performed due to compound(s) being over calibration range, refer to Section 8.10 to ensure no carryover has occurred.

9.4.7 Analysis of matrix spike (MS) and matrix spike duplicate (MSD) samples.

9.4.7.1 Analyze matrix spike and matrix spike duplicate analyses according to the schedule prescribed in Section 8.13 of this SOP.

9.4.7.2 For the Tekmar ALS 2016 Autosampler system, analyze matrix spike and matrix spike duplicate samples according to the instructions for sample analysis (Section 9.4.6), except spike the sample with 2.5 uL of 50 μg/mL Matrix Spike Solution, after spiking the sample with the IS/SMC Solution.

9.4.7.3 For the Varian Archon Autosampler systems, analyze MS/MSD samples according to the instructions for sample analysis (Section 9.4.6), except spike the sample with 4 μL of the 50 ng/μL MS solution. Using a microliter syringe, inject the MS solution directly into the sample, through the Teflon-lined septum of the 40-mL screw cap vial. Assuming the vial contains 40 mL of sample, the final spike concentration is 5 μg/L.

Since spiking of each vial for MS/MSD analysis occurs, the MS/MSD analysis will proceed only if a sufficient number of sample vials have been submitted to the laboratory.

9.4.7.4 Press the start button on the concentrator to begin purging the samples. See Appendix D for purge and trap parameters.

9.4.7.5 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Appendix E. Name the data files according to the data file naming convention in Appendix F.

9.4.7.6 Analyze the sample and acquire the data.

9.4.5.5 Quantitate the data and print out a quantitation report and chromatogram. Use the average relative response factor from the initial calibration for quantitation.

9.4.5.6 Evaluate the calculated concentrations against the criteria listed in Section 8.13.

9.4.8 Analysis of storage blanks.

9.4.8.1 A storage blank analysis must be performed according to the schedule specified in Section 8.9 of this SOP.

9.4.8.2 Analyze storage blank samples according to the instructions for laboratory reagent blank analysis in Section 9.4.5 of this SOP; except that the storage blanks shall be analyzed, rather than laboratory reagent water. Compare the storage blank results to the criteria listed in Section 8.9 of this SOP.

9.5.1 Tekmar ALS 2016 Autosampler operation.

The Tekmar ALS2016 Autosampler along with LSC2000 Concentrator may be employed in any of the methods described in Sections 9.4.1 through 9.4.8. The operating parameters of the autosamplers are found in Appendix D at the end of this SOP.

9.5.1.1 Outfit the autosampler with the 25-mL fritted sparge cells.

9.5.1.2 Prepare and deliver each standard, blank, or sample into a separate sparge cell according to the instructions set forth in the analysis sections of this SOP.

9.5.1.3 Display the ALS function on the purge and trap concentrator and select the purge positions which are to be used in the autosampler sequence (total possible are 1 through 16).

9.5.1.4 Position the concentrator to the first cell to be used in the sequence.

9.5.1.5 The analytical sequence file must be created using the data acquisition software. Complete the header information for each sample and save the file. Load and run the sequence.

9.5.1.6 Press the start button on the concentrator to start the sequence.

9.5.1.7 The concentrator will automatically start the GC/MSD analytical run. The acquisition sequence must be entered in the GC software for this to occur. Each data file will be automatically quantitated. The files should be processed in accordance with the instructions found in the sample analysis section relevant to the type of analysis being conducted.

9.5.2 Varian Archon autosampler operation

The Varian Archon autosamplers may be employed in any of the methods described in Sections 9.4.1 through 9.4.8. The operating parameters of the autosamplers are found in Appendix D at the end of this SOP.

9.5.2.1 Prepare the standard, blank or sample as described in Sections 9.4.1 to 9.4.8.

9.5.2.2 Place the vials in the autosampler tray.

9.5.2.3 Establish a method on the keypad on the autosampler. The method will establish the volume of sample to use, dilutions, addition of internal standard, and which vials to analyze.

9.5.2.4 Once the method has been established, begin the method by pressing the autostart method on the keypad.

9.5.2.5 The concentrator will automatically start the GC/MSD analytical run. The acquisition sequence must be entered in the GC software for this to occur. Each data file will be automatically quantitated. The files should be processed in accordance with the instructions found in the sample analysis section relevant to the type of analysis being conducted.

10 DOCUMENTATION

10.1 Data from the Region 9 Laboratory is presented to the client in one of two general reporting formats: a complete, validatable data package or a summary report. For the former the laboratory prepares calibration and quality control summary forms and a summary of analytical results spreadsheet and provides this information along with the raw data, a report narrative, and an analytical report spreadsheet to the client. If a summary report is all that is required the laboratory prepares a report narrative and the summary of analytical results spreadsheet for delivery to the client and collects the raw data which will be filed at the laboratory. Section 10.2 details the requirements of a complete data package and Section 10.3 lists the summary report requirements.

10.2 Complete Data package assembly.

Assemble a discrete data package for each SDG in each case requiring the delivery of a data package for validation according to the following instructions, and in the following order. Each section of the data package shall have a cover sheet titled with the appropriate section name. The data package is sequentially numbered using a hand operated numerator.

10.2.1 Report Narrative section.

10.2.1.1 The Report Narrative is a text narrative in WordPerfect 8 format describing, but not limited to, the following.

10.2.1.1.1 Site name.

10.2.1.1.2 Case number.

10.2.1.1.3 SDG number.

10.2.1.1.4 Date(s) the samples were received.

10.2.1.1.5 EPA sample number.

10.2.1.1.6 Region 9 Laboratory sample number.

10.2.1.1.8 Summary of the analyses performed.

10.2.1.1.9 Description of data qualifiers used in results spreadsheet.

10.2.1.1.10 Problems with the analyses.

10.2.1.1.11 Summary of the QA/QC results.

10.2.1.1.12 Glossary

10.2.1.1.13 Analytical comments including example calculations for an analyte and a surrogate.

10.2.2 Summary of Analytical Results spreadsheet

10.2.2.1 Include a spreadsheet (Lotus 123, Version 5) containing a summary of the results for all target analytes for all samples and blanks in the data package.

10.2.2.2 The header information for each sample contains the station location, client sample ID, Region 9 Laboratory sample ID, date of sample collection, and reporting units (usually g/L).

10.2.2.3 The results section contains the results for each target analyte as follows:

If an analyte is not detected then report the quantitation limit and enter a "U" in the column to the right.

If an analyte is detected then report the value reported on the quantitation report. Enter any associated qualifier in the "Q" column, and a letter identifying a comment, if applicable, in the "Com" column. Define the letter in the Report Narrative.

If an analyte requires a dilution then report the value from the sample dilution.

10.2.3 Tracking Forms section.

The Tracking Form section contains the following forms.

10.2.3.1 A copy of the applicable technical direction form (TDF).

10.2.3.2 A copy of the chain of custody record received with each sample shipment.

10.2.3.3 A copy of the shipper's airbill, or bill of lading.

10.2.4 QA/QC Summary section.

The QA/QC section contains all of the QA/QC summary forms for the specific sample delivery group. Forms are generated using EnviroQuant software. All of the forms are checked by the analyst to ensure that all of the filenames are

correct, and that all of the appropriate standards, blanks, samples, spikes, and tune files have been included.

10.2.4.1 Surrogate and internal standard compound recovery data summary.

10.2.4.2 MS and MS duplicate recovery data summary.

10.2.4.3 Detailed quantitation and library search compound (LSC) report for applicable storage blanks.

10.2.5 Initial Calibration section

10.2.5.1 Copy of peer reviewed instrument run log page(s)

10.2.5.2 DFTPP tuning report including pass/fail table, bar spectrum and tabulated mass listing.

10.2.5.3 Initial calibration summary form containing response factors for each file, the average response factor and %RSD for each compound in the initial calibration.

10.2.5.4 Quantitation reports and reconstructed ion chromatograms (RIC).

10.2.5.5 Documentation of any manual integrations as described in Section 8.5.11 and USEPA Region 9 Laboratory SOP #835, *Chromatographic Integration Procedures.*

10.2.6 Sample section(s).

The sample section(s) contain data for each sample in the sample delivery group analyzed during a 12-hour analytical period, organized in chronological order, with associated QC data. Make a separate sample section for samples analyzed during different 12-hour analytical periods. Each daily sample section contains:

10.2.6.1 QC standard information consisting of the following:

10.2.6.1.1 Copy of peer reviewed run log page.

10.2.6.1.2 BFB tune data; including the background subtracted spectra, the mass listing, and the RIC labeled so as to indicate the BFB peak.

10.2.6.1.3 Continuing calibration file, including the RIC, quantitation report, and the continuing calibration report file. (This can be generated using the "evaluate data file as continuing calibration" command in the software.)

10.2.6.1.4 LCS data file, including the RIC and the quantitation report.

10.2.6.1.5 QL data file, including the RIC and the quantitation report.

10.2.6.1.6 Method blank, including the RIC and the detailed quantitation report, as well as detailed LSC report.

10.6.2 Sample data arranged chronologically. Data for all analyses must be included, even data not used.

10.2.6.2.1 The raw data quantitation report of the data file. Enter appropriate qualifiers on this report:

B This analyte was detected in an associated blank.

E The amount detected exceeds the linear calibration range.

10.2.6.2.2 The reconstructed ion chromatogram (RIC) of the data file.

10.2.6.2.3 The raw spectra and enhanced spectra of the target compounds detected in the sample, as well as the enhanced spectra of the corresponding target compound in the calibration file, in order of elution.

10.2.6.2.4 Selected ion chromatograms of any manual integrations performed. The ion chromatograms showing integration before and after the manual integration shall

be included. See SOP 835 for manual integration procedures.

10.2.6.2.5 TIC report, non-target compound report form detailing the compound names, retention times, the estimated concentrations, and the CAS number of up to twenty tentatively identified compounds.

10.2.6.2.6 Enhanced spectra of non-target compounds detected in the sample. Library search listing the three best fits of a forward library search of the non-target compounds.

10.2.7 Logbooks and Miscellaneous Data.

10.2.7.1 Copies of all applicable standards preparation logbook pages.

10.3 Summary Report and Raw Data

When the client requirements stipulate a summary report the laboratory prepares the case narrative, analytical results spreadsheet, and organizes the raw data associated with each SDG for filing in the event that future data review or validation is required. The summary report is prepared in a manner identical to the full data package with the following exceptions:

1.) The raw data is not paginated
2.) Copies of the standards logs are not included

10.4 Notification of exceedance of MCL

If samples are for drinking water compliance, examine the quantitated results, corrected for any dilution. If the results exceed the MCL for any regulated compound (see Appendix B), report the exceedance in accordance with EPA Region 9 Laboratory SOP 830.

10.5 Peer review

Assign the data package an ESAT document control number after assembly. The completed data package is reviewed by a chemist, other than the chemist who performed the analyses or assembled the data package. All reviews are documented using a document review form.

10.6 Technical review.

The GC/MS Group Leader or a senior level chemist, other than the chemist who performed the analyses reviewed the data package. Following the technical review, a final review is be performed by the group leader, QA/QC task manager, program manager or their designee. Once the final review is completed, a cover letter is prepared and signed by the group leader and the entire data package is paginated and turned in to the TOPO.

10.7 Injection logbook.

Maintain a logbook for each instrument in accordance with the instructions in EPA Region 9 Laboratory SOP #840 *Notebook documentation and control.*

10.8 Refrigerator temperature log.

Maintain a refrigerator temperature log for each refrigerator or freezer according to EPA Region 9 Laboratory SOP #805, *Refrigerator Temperature Monitoring*. Record the temperatures on a daily basis whenever the refrigerator is in use.

11 REFERENCES

11.1 USEPA Region 9 Laboratory SOP 110, *Sample Receiving and Login*

11.2 USEPA Region 9 Laboratory SOP 125. *Sample Disposal*

11.3 USEPA Region 9 Laboratory SOP 205. *Preparation of Organic Free Method Blank Water.*

11.4 USEPA Region 9 Laboratory SOP 255. *Standard Preparation for Volatile Organics Laboratory.*

11.5 USEPA Region 9 Laboratory SOP 805, *Refrigerator Temperature Monitoring*.

11.6 USEPA Region 9 Laboratory SOP 830, *Notification Procedure for Results Exceeding the Safe Drinking Water Act Maximum Contaminant Level.*

11.7 USEPA Region 9 Laboratory SOP 835, *Chromatographic Integration Procedures.*

11.8 USEPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control.*

11.9 USEPA Region 9 Laboratory SOP #880, *Initial and Continuing Demonstration of Capabilities and Performance*

11.10 Tekmar LSC2000 and ALS2016 Operator's Manuals.

11.11 Varian Archon Autosampler and HP 3000 Concentrator Operator's Manuals.

11.12 EPA Method 524.2 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry; Revision 4.1, 1995.

Appendix A

SOP Deviations from Reference Method, EPA Method 524.2, Rev. 4.1

1. Final analytical standards are prepared directly into 25 mL or 50 mL of organic-free water in a syringe rather than into volumetric flasks. Because the entire volume of standard is used, this avoids losses of analytes during mixing and standard transfer.

2. The Region 9 Laboratory routinely examines data for the presence of non-target compounds (Tentatively Identified Compounds or TICs).

3. Method 524.2 recommends using Fluorobenzene as the internal standard and 4-Bromofluorobenzene and 1,2-Dichlorobenzene-d4 as the surrogate compounds. The Region 9 Laboratory uses Dichloromethane-d2, Fluorobenzene, and Chlorobenzene-d5 as the internal standards, and 1,2-Dichloromethane-d4, Toluene-d8, 4-Bromofluorobenzene, and 1,2-Dichlorobenzene-d4 as the surrogate compounds.

4. Method 524.2 recommends using m/z ion 95 as the quantitation ion for 4-Bromofluorobenzene, and m/z ion 91 for the three xylenes. The Region 9 Laboratory uses m/z ion 174 for quantitation of 4-Bromofluorobenzene, and m/z 106 for the quantitation of the xylenes.

5. Method 524.2 does not require analysis of a laboratory fortified matrix (matrix spike). The Region 9 Lab performs MS/MS duplicate analysis with every sample delivery group (SDG) of 20 samples.

6. The calibration range for 1,2-dibromo-3-chloropropane is 2 to 25 μg/L. There are no %RSD requirements for this compound.

Appendix B

Analyte List

The following is the Target Compound list for volatile organics, as well as the associated internal standard and surrogate compounds, for analysis by EPA Drinking Water method 524.2. Included are the quantitation limits and the internal standard reference for each target compound, as well as the quantitation mass for each analyte.

Internal Standards

Compound Name	ISTD #	Quant m/z
Dichloromethane-d2	1	53
Fluorobenzene	2	96
Chlorobenzene-d5	3	117

Surrogate Compounds

Compound Name	ISTD REF	Quant m/z
1,2-Dichloroethane-d4	2	65
Toluene-d8	3	98
4-Bromofluorobenzene	3	174
1,2-Dichlorobenzene-d4	3	152

Target Compounds

Compound Name	QL (µg/L)	MCL (µg/L)	ISTD REF	Quant m/z	R	MDL (µg/L)
Dichlorodifluoromethane	1	—	1	85		
Chloromethane	1	—	1	50		
Vinyl chloride	0.5	2	1	62	#	0.4
Bromomethane	1	—	1	94		
Chloroethane	1	—	1	64		
Trichlorofluoromethane	1	—	1	101		
1,1-Dichloroethene	1	7	1	96	#	0.5
Methylene chloride	1	5	1	84	#	0.5
trans-1,2-Dichloroethene	1	100	1	96	#	0.5
1,1-Dichloroethane	1	—	1	63		
Methyl t-butyl ether (MTBE)	1	—	1	73		
2,2-Dichloropropane	1	—	1	77		
cis-1,2-Dichloroethene	1	70	1	96	#	0.5
Chloroform	1	100*	1	83	#	
Bromochloromethane	1	—	1	128		
1,1,1-Trichloroethane	1	200	2	97	#	0.5
1,1-Dichloropropene	1	—	2	75		
Carbon tetrachloride	0.5	5	2	117	#	0.5

Benzene	1	5	2	78	#	0.5
1,2-Dichloroethane	0.5	5	2	62	#	0.5
Trichloroethene	1	5	2	95	#	0.5
1,2-Dichloropropane	1	5	2	63	#	0.5
Bromodichloromethane	1	100*	2	83	#	
Dibromomethane	1	—	2	93		

Compound Name	QL (µg/L)	MCL (µg/L)	ISTD REF	Quant m/z	R	MDL (µg/L)
cis-1,3-Dichloropropene	0.5	—	2	75		
Toluene	1	1,000	3	92	#	0.5
trans-1,3-Dichloropropene	0.5	—	2	75		
1,1,2-Trichloroethane	1	5	2	83	#	0.5
Tetrachloroethene	1	5	3	166	#	0.5
1,3-Dichloropropane	1	—	3	76		
Dibromochloromethane	1	100*	3	129	#	
Dibromoethane	1	—	3	107		
Chlorobenzene	1	100	3	112	#	0.5
1,1,1,2-Tetrachloroethane	1	—	3	131		
Ethylbenzene	1	700	3	91	#	0.5
m & p-Xylene	1	10,000**	3	91	#	0.5
o-Xylene	1	10,000**	3	91	#	0.5
Styrene	1	100	3	104	#	0.5
Bromoform	1	100*	3	173	#	
Isopropylbenzene	1	—	3	105		
1,1,2,2-Tetrachloroethane	1	—	3	83		
Bromobenzene	1	—	3	156		
1,2,3-Trichloropropane	1	—	3	75		
n-Propylbenzene	1	—	3	91		
2-Chlorotoluene	1	—	3	91		
1,3,5-Trimethylbenzene	1	—	3	105		
4-Chlorotoluene	1	—	3	91		
tert-Butylbenzene	1	—	3	119		
1,2,4-Trimethylbenzene	1	—	3	105		
sec-Butylbenzene	1	—	3	105		
p-Isopropyltoluene	1	—	3	119		
1,3-Dichlorobenzene	1	—	3	146		
1,4-Dichlorobenzene	1	75	3	146	#	0.5
n-Butylbenzene	1	—	3	91		
1,2-Dichlorobenzene	1	600	3	146	#	0.5
1,2-Dibromo-3-chloropropane	2	—	3	75		

1,2,4-Trichlorobenzene	1	70	3	180	#	0.5
Hexachlorobutadiene	1	—	3	225		
Naphthalene	1	—	3	128		
1,2,3-Trichlorobenzene	1	—	3	180		

MCL = Maximum contaminant level from SDWA.
R- # = Regulated Compound
MDL=Regulated compound maximum MDL
*= MCL for total trihalomethanes is 100 μg/L
**= MCL for total xylenes is 10,000 μg/L

Appendix C

Calibration Levels and Quality Control Criteria

Calibration Standards for Incos 50 A/Incos XL			Calibration Standards for Archon Autosamplers		
Calibration Point	**DWIS Mix 50 µg/mL**	**DW Calibration Mix 25 µg/mL**	**Calibration Point**	**DWIS Mix 125 µg/mL**	**DW Calibration Mix 25 µg/mL**
25 µg/L	2.5 µL	25 µL	25 µg/L	1 µL	50 µL
10 µg/L	2.5 µL	10 µL	10 µg/L	1 µL	20 µL
5 µg/L	2.5 µL	5 µL	5 µg/L	1 µL	10 µL
2 µg/L	2.5 µL	2 µL	2 µg/L	1 µL	4 µL
1 µg/L	2.5 µL	1 µL	1 µg/L	1 µL	2 µL

Quality Control Criteria

Initial demonstration accuracy must be greater than or equal to 80% and less than or equal to 120 % recovery. Initial demonstration precision must result in a RSD of less or equal to 20% The MDL achieved must meet that specified for the regulated compounds, and be less than the Quantitation Limit (QL) for the unregulated compounds.

Initial Calibration RSD must be less than or equal to 20% for all regulated analytes. The %RSD of the non-regulated analytes must be less than or equal to 30%. 1,2-dibromo-3-chloropropane has no %RSD requirement as the recommended method for analysis of this compound is 504.1

The internal standard areas of the continuing calibration standard must be ±50% of the average of the internal standard areas of the initial calibration.

Continuing Calibration %D must be less than or equal to ± 30% of the initial calibration average response factor for all regulated analytes. Up to ten percent of analytes in any one continuing calibration curve may be greater than the 30% D value, provided those analytes are not regulated, and the %D is 40.

LCS recoveries must be greater than or equal to 70% and less than or equal to 130% for all regulated analytes. For all non-regulated analytes, the recoveries must be greater than or equal to 60% and less than or equal to 140%. Past experience at the Region 9 Laboratory demonstrates that dichlorodifluoromethane exhibits poor recovery values for the LCS, and thus is exempt from this criteria.

Laboratory Fortified Matrix recoveries should be greater than or equal to 70% and less than or equal to 130%. The RPD between the MS and MSD should be less than or equal to 20%.
Surrogate (system monitoring compounds) recoveries should be greater than or equal to 70% and less than or equal to 130%.

Appendix D

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.

PARAMETER	SETTING	
	Tekmar LSC2000	HP (Tekmar) 3000
Standby temperature	38 C	38 C
Preheat temperature	N/A	N/A
Prepurge time	N/A	N/A
Sample temperature	Ambient	Ambient
Purge Time	11 minutes	11 minutes
Dry purge	3 minute	1 minute
Purge Flow	35 - 40 mL/min	35-40 mL/min
Desorb preheat temperature	245 C	240 C
Desorb	6.00 minutes @ 250 C	4.00 minutes @ 250 C
Bake	4 minutes @ 260 C	6 minutes @ 260 C
Auto drain	On	Off (controlled by Archon)
Bake gas bypass	Off	Off
Valve temperature	120 C	120 C
Mount temperature	40 C	40 C
Line temperature	120 C	120 C

Tekmar ALS2016 Autosampler

The operating method for the ALS2016 autosampler which is interfaced with the Tekmar LSC2000 and an Agilent 6890GC/Agilent 5973 MSD Network is as follows.

PARAMETER	SETTING
Valve temperature	120 C
Line temperature	120 C
Sample temperature	Ambient
Auto drain	On

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), and number of vials to be analyzed.

Appendix E

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	220 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:	Splitless for 0.1 min
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	35-300 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 115 C for 12 minutes; 20 C/minute to 200 C for 4.25 minutes *10 C/minute to 120 C for 10.5 minutes; *30 C/minute to 200 C for 2.67 minutes
Final Oven Temp	200 C
Final Hold Time	2.0/* 5.0 minutes
Inlet mode:	Split
Split ratio:	20
Column Flow rate	0.8/* 1.2 mL/min at constant flow mode.
Electron Energy	70 volts (nominal)
MS Scan Range	35-300 amu

* for Restek RTX-VMS 30m x 0.25mm, 1.4 micro film column

Appendix F

Data File Naming Convention

Sub directory naming convention
A subdirectory must be made daily where the data for that day will be stored.

MMDDYY

25 mL waters analyzed on HP5973K on 08/12/01

X:\HPCHEM\1\data\081201DW where x: is the drive.

Instrument Identifiers

Instrument ID	HP5973H	HP5973J	HP5973K
File Identifier	H	J	K

All matrix identifiers will be W, for waters.

BFB
(No Matrix Identifier Required)

BF?MMDD?
The first BFB analyzed on HP5973H on 03/05/01 = BFH0305
The second BFB analyzed onHP5973H on 03/05/01 = BFH0305A

Initial Calibrations
I??MMDD?
25 mL water initial calibration analyzed on HP5973J on 01/10/01

Concentration	Calibration ID	Filename
25 µg/L	VSTD025	IWJ0110A
10 µg/L	VSTD010	IWJ0110B
5 µg/L	VSTD005	IWJ0110C
2 µg/L	VSTD002	IWJ0110D
1 µg/L	VSTD001	IWJ0110E

In the event that a CCAL that fails a previous ICAL is used as part of a new ICAL the CCAL final naming convention below is used for that CCAL

Continuing Calibrations

C??MMDD?
First 25 mL water continuing calibration analyzed on HP5973K on 04/21/01

CWK0421

Laboratory Fortified Blank (LCS)
LW?MMDD?

First LCS of the day =void
Second LCS of the day = A.....

Instrument	File ID
HP5973J	LWJ0101
HP5973H	LWH0530A

QL Standard

QW?MMDD?
First QL standard analyzed on HP5973H on 01/12/01

QWH0112

Method Blank (Laboratory Reagent Blanks) (LRB)

MW?MMDD?

First blank of the day = void
Second blank of the day = A.....

Instrument	File ID/Blank ID
HP5973H	MWH0530
HP5973J	MWJ0401A

Storage Blanks

LAB ID = VHBLKm1m1d1d1 - SBXm2m2d2d2
where m1m1d1d1 is the day the storage blank was placed in the sample refrigerator and m2m2d2d2 is the day the storage was analyzed. X= instrument Identifier

Instrument	File ID	LAB ID
HP5973K	VHBLK0610	SBK0617
HP5973J	VHBLK0321	SBJ0328

Samples including MS/MSD, Instrument Blanks, etc...

YY?####

YY = Federal Fiscal year (Begins October 1st)
? = Instrument Identifier
= sequential number (first sample analysis in the fiscal year = 0001)

The 100th sample analysis on HP5973J

01J0100

Appendix B-2
1,4-Dioxane

Amendment to Region 9 SOP #315

The Region 9 SOP # 315 "*SEMIVOLATILE ORGANICS ANALYSIS*" is amended to allow for the addition of 1,4-dioxane as an analyte as follow:

Initial Calibration:

The SVOC initial calibration mix was modified to include 1,4-dioxane as follow:

Level	1	2	3	4	5
SVOC IS (ng/μL)	20	20	20	20	20
SVOC Targets (ng/μL)	10	25	40	60	80
1,4-dioxane-d8 (ng/μL)	5	5	5	5	5
1,4-dioxane (ng/μL)	1	2	5	10	20

Initial results indicate that 1,4-dioxane response is linear over the above calibration range; thus, it would be reasonable to assign the normal SVOC %RSD limit of ± 20%.

1,4-Dioxane-d8 is utilized as an internal standard and as a surrogate as follow:

> 1,4-dioxane-d8 (internal standard): 1,4-dioxane-d8 is treated as a normal SVOC standard with the exception that it is spiked at the 5 ng/μL. Native 1,4-dioxane concentration is calculated based on 1,4-dioxane-d8.
>
> 1,4-Dioxane-d8 (surrogate): 1,4-dioxane-d8 concentration is calculated based on 1,4-dichlorobenzene-d4 (SVOC IS1).

Two entries for 1,4-dioxane-d8 will appear in the raw data. The above method allows us to determine the actual recovery of 1,4-dioxane-d8 (as a surrogate) and to correct for the extraction efficiency of native 1,4-dioxane.

Continuing Calibration:

The continuing calibration will be analyzed at level two (2 ng/μL). 1,4-Dioxane response appears to be linear; thus, it would be reasonable to assign the normal SVOC %D limit of ± 25%.

Quantitation Level Standard:

The QLS is analyzed at the 1 ng/μL level with a recovery limit of 50-150%.

Surrogate:

1,4-Dioxane-d8 is added to the SVOC surrogate mix at the 5 ng/μL level. The method blanks, blank spikes, and field samples are spiked with the surrogate during extraction. The SVOC surrogate recovery limits vary depending on the specific SVOC surrogate. Initial analysis results indicate that 1,4-dioxane-d8 was recovered in the 76-124% range in the MDL and P&A standards. For field samples, an initial surrogate recovery limit of 50-130% is therefore recommended.

Matrix Spike:

The SVOC matrix spike mix is modified to include 1,4-dioxane at the 5 μg/L level. Initial analysis results indicate that 1,4-dioxane was recovered in the 72-97% range in the MDL and P&A standards. For field samples, initial MS/MSD recovery limits of 50-130% is therefore recommended.

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE #315

SEMIVOLATILE ORGANICS ANALYSIS

Signature & Title

Prepared by: _____ _____
Li-Pin Lee, ESAT Region 9, ICF Consulting Date

Reviewed by: _____ _____
Richard Bauer, Chemistry Team Leader Date

Approved by: _____ _____
Brenda Bettencourt, Lab. Director Date

Periodic Review:

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

STANDARD OPERATING PROCEDURE #315

SEMIVOLATILE ORGANICS ANALYSIS

This SOP was prepared by ICF Consulting for the United States Environmental Protection Agency (USEPA) under the Environmental Services Assistance Team (ESAT) contract (EPA contract No. 68D60005).

APPROVED BY:

Ziyad Rajabi, Organic Group Leader	Date
Surender Kaushik, QA/QC Task Manager	Date
Jerry Vail, ESAT Program Manager	Date

ESAT Document Control Number: B0101063-1371

TABLE OF CONTENTS

1 SCOPE AND APPLICATION 4

2 METHOD SUMMARY 4

3 DEFINITIONS 4

4 HEALTH & SAFETY 6

5 SAMPLE HANDLING AND PRESERVATION 7

6 INTERFERENCES 7

7 APPARATUS AND MATERIALS 7

8 QUALITY CONTROL 9

9 ANALYTICAL PROCEDURES 27

10 DOCUMENTATION 31

11 REFERENCES 37

APPENDIX A 38

APPENDIX B 40

APPENDIX C 42

APPENDIX D 44

APPENDIX E 46

ATTACHMENT A - Semivolatile Organics Run Log example page

ATTACHMENT B - GC/MS Semivolatile Standards Log example page

ATTACHMENT C - Maintenance Logbook example page

1 SCOPE AND APPLICATION

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 analytes of interest. This SOP is based on procedures contained in EPA Method SW-846 8270.

The applicability of these procedures to specific project data quality objectives must be assessed on a case by case basis. The QC criteria specified in the procedures do not meet compliance criteria for either drinking water or NPDES monitoring projects.

2 METHOD SUMMARY

Sample extracts, which have been fortified with surrogate analytes and internal standards, are injected into a gas chromatograph with a Mass Spectrometer (MS). Analytes are separated in the narrow-bore fused-silica capillary gas chromatographic column during temperature programming, then detected by the MS.

Target semivolatile organic compounds are identified in the sample extract by comparing the mass spectra and GC retention times of the target analytes to the mass spectra and retention times of standards analyzed under the same conditions as samples. A response factor is established for each target and surrogate compound during the initial calibration by comparing the MS response of the quantitation ion produced by the target and surrogate compounds to the MS response for the quantitation ion produced by the associated internal standard. Each target analyte and surrogate are quantitated using an internal standard method of calculation using the average response factors from the initial calibration.

Non-target compounds are identified by comparing the resulting mass spectra of the non-target compound to the mass spectra contained in the National Institute of Standards and Technology (NIST) Library in the MS database. An estimated quantitation is performed for the non-target compounds by comparing the total MS response to the nearest internal standard total MS response, assuming a 1:1 response factor.

3 DEFINITIONS

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

3.2 Surrogate Analyte (SA) - A pure analyte, which is extremely unlikely to be found in any sample, 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.

3.3 Laboratory Reagent Blank (LRB) - 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 LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the solvents, or the equipment.

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

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

3.6 GC/MS Performance Check Solution (decafluorotriphenylphosphine (DFTPP) - A solution of 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.

3.7 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.

3.8 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.

3.9 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

3.10 Quality Control Sample (QCS) – Equivalent to the mid-point initial calibration solution but prepared from a source different from the source of calibration standards. The QCS is used to check the accuracy of the initial calibration solutions.

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

3.12 System Performance Check Compounds (SPCC) - analytes that typically have low response factors. These compounds are used as indicators of deteriorating system performance.

3.13 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.

4 HEALTH & SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals should be minimized through the use of personal protective equipment and laboratory engineering and design. A reference file of material safety data sheets (MSDS) is available to all personnel involved in the chemical analysis and can be found in the library (Room 118) or Room 413.

4.2 Methylene chloride 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. Methylene chloride 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.

4.3 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.

5 SAMPLE HANDLING AND PRESERVATION

5.1 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 in the extraction logbook. Copies of tracking sheets, chain-of-custody records, extraction logbook pages, and percent solids determination records should accompany the sample extracts.

5.2 The extracts are marked with the Region 9 Laboratory number, which can be checked against the tracking sheets and chain-of-custody record to determine the Client sample number, Case number, and Sample Delivery Group (SDG) number.

5.3 Store extracts in the refrigerator in Room 406 at 4 $\pm$ 2°C. Extracts must be analyzed within 40 days of extraction.

5.4 Store extracts in the refrigerator in Room 406 at 4 $\pm$ 2°C following analysis and submission of the data deliverables for an SDG an additional 90 days before segregating for disposal.

6 INTERFERENCES

6.1 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 laboratory reagent blank as described in Section 9. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components should be avoided.

6.2 Contamination by carryover can occur whenever high level and low level samples are sequentially analyzed. Splitless injection port liners must be cleaned carefully or replaced as needed. After analysis of a sample containing high concentrations of compounds, a laboratory instrument blank should be analyzed to ensure that accurate values are obtained for the next sample.

6.3 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 sample may be affected.

7 APPARATUS AND MATERIALS

7.1 GCMS System

7.1.1 Gas Chromatograph (GC): Hewlett Packard 5890 Series 2 or equivalent 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).

7.1.2 GC column: 30 m, 0.25 mm ID, 0.25 μm df, DB-5MS or equivalent. A fused silica capillary column with a bonded phase coating of 5% phenyl-95% methyl silicone such as DB-5, DB-5MS, Rtx-5, XTI-5, or HP-5. 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.

7.1.3 Mass spectrometer: Hewlett Packard 5972 or equivalent. Capable of scanning from 35 to 500 amu every one second or less using 70 volts (nominal) electron energy in the electron impact ionization mode. Must be able to produce a mass spectrum that meets acceptance criteria when 50 ng of DFTPP is injected through the GC inlet.

7.1.4 Data system: HP EnviroQuant ChemStation G1701BA Version B.01.00 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 data base, 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 response factors and concentrations of analytes in samples.

7.2 Standard solutions

Document the preparation of all standards in the Semivolatile Standards logbook following EPA Region 9 Laboratory SOP # 840, Notebook Documentation and Control.

7.2.1 Internal Standard Solution (IS) - A solution of acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, 1,4-dichlorobenzene-d_4, perylene-d_{12}, and naphthalene-d_8 at 2,000 μg/mL each in dichloromethane. Restek catalog # 31206 or equivalent.

7.2.2 Surrogate solution (SA) - A solution of 2-fluorobiphenyl, nitrobenzene-d_5, p-terphenyl-d_{14}, and 1,2-dichlorobenzene-d_4 (B/N surrogates) at 100 μg/mL each and 2-fluorophenol, phenol-d_5, 2,4,6-tribromophenol, and 2-chlorophenol-d_4 (Acid surrogates) at 150 μg/mL each in dichloromethane. Prepare by diluting purchased

solutions - B/N surrogates: Restek catalog# 31002 or equivalent. Acid surrogates: Restek catalog# 31003 or equivalent.

7.2.3 Calibration Stock Standard. A solution of target analytes listed in Appendix B at a concentration of 2,000 µg/mL in dichloromethane. Restek SV calibration mix #2 (cat# 31008), #3 (cat# 31009), #4 (cat# 31010), #5 (cat# 31011), #7 (cat# 31013), and #8 (cat# 31026) or equivalent.

7.2.4 Calibration standards - A solution of target analytes listed in Appendix B at concentrations of 10, 25, 40, 60, and 80 µg/mL. Prepare by diluting from the calibration stock standard. Add 10 µL of the IS solution per 1.0 mL of standard.

7.2.5 GC/MS Performance Check Solution (DFTPP+). A solution of decafluorotriphenylphosphine (DFTPP), 4,4'-DDT, pentachlorophenol, and benzidine at 50 ng/µL each in methylene chloride. Prepare from a purchased solution - ULTRA Scientific cat# GCM-150 or equivalent.

7.2.6 Matrix Fortification Solution - A solution of 1,2,4-Trichlorobenzene, Acenaphthene, 2,4-Dinitrotoluene, Pyrene, n-Nitroso-di-n-propylamine, and 1,4-Dichlorobenzene (B/N spike mix) at 100 µg/mL each and Pentachlorophenol, Phenol, 2-Chlorophenol, 4-Chloro-3-methylphenol, and 4-Nitrophenol (Acid spike mix) at 150 µg/mL each in methanol. Prepare from purchased solutions - B/N spike mix: Restek catalog# 31004 or equivalent. Acid spike mix: Restek catalog# 31005 or equivalent.

7.2.7 Storage of Standard Solutions - Store the unopened ampulated stock standard solutions at 4°C (± 2°C). Store all other working standard solutions in glass bottles or vials with Teflon lined screw caps at ≤-10°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 quality control check samples indicates a problem. CAUTION: Analysts must allow all standard solutions to equilibrate to room temperature before use.

7.2.8 Methylene chloride -- High purity pesticide quality or equivalent.

7.2.9 Helium carrier gas - as contaminant free as possible.

7.3 Syringes (10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, 1-mL).

8 QUALITY CONTROL

8.1 Quality control requirements include the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified matrix samples.

8.2 The laboratory must perform an initial demonstration of capability with each sample preparation technique used in analyzing analytes of interest with this SOP before analyzing any samples. See EPA Region 9 SOP #880, *Initial and Continuing Demonstration of Capabilities and Proficiency* for requirements and procedures.

8.2.1 Analyze Laboratory Fortified Blanks (LFBs) containing all the analytes of interest at a concentration of 40 µg/L in aqueous samples and 1320 µg/Kg in solid samples, equivalent to 40 µg/mL in the extract, to demonstrate initial laboratory capability.

8.2.2 Analyze LFBs which have been fortified with all analytes of interest at 10 µg/L in water samples and 330 µg/Kg in soil samples, corresponding to 10 µg/mL in the extract for MDL determination.

8.3 Mass calibration.

8.3.1 Calibrate the mass axis of the mass spectrometer daily. You must also calibrate the mass axis whenever the mass spectrometer is shut down, or whenever there is a mass mis-assignment. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer. Perfluorotributylamine (FC43) is used to perform calibration of the mass axis. The FC43 spectrum with the following criteria are recommended:

Mass	Target % of Mass 69
69	100
131	25.0 - 40.0
219	25.0 - 40.0
414	1.4 - 4.0
502	0.5 - 2.0

8.3.2 Take corrective action if the FC43 spectrum does not meet the criteria listed above as DFTPP will probably not pass criteria. The corrective action may be as simple as

adjusting the mass gain and peak width or manually retuning the MS. Alternatively, retuning the MS by selecting target tune with mass ratio(s) set based on the failure on criteria in Section 8.4.4. If retuning the MS does not produce adequate FC43 spectra or repeated failure to meet DFTPP criteria, further maintenance such as cleaning the ion source may be required. See Section 9.4.

8.4 GC/MS System Performance Check

8.4.1 Prior to the analysis of any calibration standards, blanks, and samples (including LFM/LFMDs), the GC/MS system must meet the mass spectral ion abundance criteria for DFTPP. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target and non-target compounds.

8.4.2 Frequency of GC/MS Performance Check.

8.4.2.1 Analyze the DFTPP solution once at the beginning of each 12-hour period during which standards, blanks and samples are to be analyzed. The twelve-hour time period begins at the moment of injection of the DFTPP solution. The time period ends after twelve hours have elapsed. If a sample is injected after the 12-hour time period has elapsed it must be re-analyzed.

8.4.3 Analyze the DFTPP solution according to Section 9 of this SOP.

8.4.4 The ion abundance ratios must meet the following criteria:

Mass (m/z)	Relative Ion Abundance Criteria
51	30 - 60% of the base peak
68	less than 2% of mass 69
70	less than 2% of mass 69
127	40 -60% of the base peak
197	less than 1% of mass 198
198	Base peak (100% relative abundance)
199	5 - 9% of mass 198
275	10 - 30% of the base peak
365	Greater than 1% of the base peak
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17 - 23% of mass 442

8.4.4.1 If the ion abundances fail to meet the criteria listed above the DFTPP 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 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. See Section 9.4.

8.4.4.2 Evaluate the breakdown of DDT using Equation 1. Locate the degradation products of 4,4'-DDT (4,4'-DDD and 4,4'-DDE). If the percent breakdown calculated using peak areas based on each Quantitation ion (Qion) exceeds 20%, corrective maintenance must be taken

Equation 1:

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

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

8.4.4.3 Benzidine and pentachlorophenol responses should be at their expected levels in the DFTPP solution and peak tailing should be minimal. Replacing the inlet liner and /or the inlet seal and breaking off a portion of the column from the injector end should restore instrument performance.

8.5 Initial calibration.

8.5.1 Calibrate the GC/MS system whenever corrective action which may change instrument response (e.g., ion source cleaning, column replacement, etc.) is performed or if the continuing calibration acceptance criteria have not been met.

8.5.2 Analyze the 10 or 25 μg/mL calibration standard according to Section 9.

8.5.2.1 Evaluate the separations of anthracene /phenanthrene and benzo(a)anthracene/chrysene. Anthracene /phenanthrene should have baseline separation. Benzo(a)anthracene/chrysene should be separated by a valley whose height is less than 25% of the average height of the two peaks. If not, the GC column requires maintenance.

8.5.2.2 If any target analytes, surrogates or internal standards are mis-identified or not found, corrective action or system maintenance is required.

8.5.3 If all performance criteria are met, analyze the remaining initial calibration standards according to Section 9 of this SOP.

8.5.4 The data system calculates the relative response factor (RRF) for each target compound and surrogate for all five calibration standards using Equation 2. The quantitation ions and internal standard assignments are listed in Appendix C.

Equation 2:

$$RRF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

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 in μg/mL
C_{is} = Concentration of the associated internal standard in μg/mL

8.5.5 Calculate the average RRF for all analytes

8.5.6 Calculate the percent relative standard deviation (%RSD) of the RRF values for each compound using Equation 3.

Equation 3

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

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

8.5.7 Check the initial calibration for misidentified peaks due to retention time shifts. The most commonly mis-assigned compounds are the 1,3- and 1,4-dichlorobenzenes and the benzo(b) and benzo(k) fluoranthenes.

8.5.8 Verify that the minimum average RRF's in the initial calibration for the following system performance check compounds (SPCC's) is 0.050:

N-nitroso-di-n-propylamine
hexachlorocyclopentadiene
2,4-dinitrophenol
4-nitrophenol

Corrective action must be taken before sample analysis can begin if any SPCC fails the minimum RRF criterion.

8.5.9 All other analytes must meet the minimum RRF criteria in Appendix C.

8.5.10 Verify that the maximum %RSD for the following calibration check compounds (CCC's) in the initial calibration is ≤ 20:

acenaphthene	4-chloro-3-methylphenol
1,4-dichlorobenzene	2,4-dichlorophenol
hexachlorobutadiene	2-nitrophenol
di-n-octyl phthalate	phenol
fluoranthene	pentachlorophenol
benzo(a)pyrene	2,4,6-trichlorophenol

Corrective action must be taken before sample analysis can begin if any CCC fails the maximum %RSD criterion.

8.5.11 All other analytes should meet the maximum %RSD of 20. Any project specific analyte of interest must meet the maximum %RSD criterion. If one or more analytes exceed the RSD limit, the initial calibration may still be acceptable if the following conditions are met:

8.5.11.1 The %RSD of the analytes that exceed the limit is ≤ 30.

8.5.11.2 The mean of the RSD values for all analytes is less than or equal to 20%.

8.5.11.3 If an analyte that exceeds the %RSD limit is found in a sample extract, that extract must be re-analyzed using an initial calibration that meets QC limits for that analyte.

8.5.12 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 before sample analysis begins.

8.5.13 If the five point calibration fails the minimum RRF or maximum %RSD criteria for target analytes with on column quantitation limits of 25 ng listed in Appendix D, then a four-point calibration, excluding the 10 μg/mL standard, may be used if it meets the initial calibration criteria.

8.5.14 Remember that the lowest concentration standard defines the reporting limit for each compound. If appropriate reporting limits cannot be obtained by this procedure, the system must be repaired so that the criteria are satisfied before any samples are analyzed. If repairs are made to the system, then a new initial calibration must be performed.

8.5.15 No quantitation ion may saturate the detector.

8.5.16 Analyze a QCS sample immediately after each initial calibration. The RRF for each analyte in the QCS must be within 30% of the mean RRF in the initial calibration. If the QCS sample fails, the cause must be determined and corrected before analysis of samples can proceed.

8.5.17 If the initial calibration and the QCS meet the specified criteria, the remainder of the 12-hour analytical period may be used for the analysis of field and QC samples, using the average RRF from the initial calibration to quantitate the sample data.

8.5.18 Manual integration. There will be instances when the data system will not produce accurate integrations. Examples of this are misidentification of a peak, inaccurate dropping of a perpendicular between peaks, or failure to integrate the entire tail of a peak. When necessary, chromatograms can be manually integrated if the following steps are taken (see SOP 835, *Chromatographic Integration Procedures*):

8.5.18.1 Print a view of the chromatogram to be reintegrated using QEDIT. Include the background-subtracted spectrum of the apex of the peak and the reference spectrum. Indicate the reasons for manually integrating the chromatographic results on the chromatogram and initial and date the statement.

8.5.18.2 Reintegrate the peak and print the new view. Save the reintegrated value(s). Print the peak and reference spectra. Document the manual integration on the reintegrated chromatogram and initial and date the statement.

8.5.18.3 Print the new quant report and chromatogram after all manual integrations have been completed. Indicate each manual integration on the new quant report. Document the fact that there was manual integration in the instrument's run log and initial and date the statement.

8.5.18.4 Show the chromatograms, quant reports and log book to a supervisor, QA/QC coordinator or team leader for review and acceptance. The QA/QC coordinator or team leader will initial and date the integrations.

8.6 Calibration Verification

8.6.1 Verify the MS tune and initial calibration at the beginning of each 12-hour period (see Section 8.4.2.1 for definition of 12-hour time period) when analyses of field and QC samples are performed using the following procedure.

8.6.2 Analyze a DFTPP+ solution according to Section 9

8.6.2.1 Check that the DFTPP ion abundances meet the criteria in Section 8.4.4

8.6.2.2 Evaluate the DDT breakdown using the Equation 1 and the acceptance criteria in Section 8.4.4.2.

8.6.2.3 Evaluate the benzidine and pentachlorophenol responses according to the criteria in section 8.4.4.3.

8.6.3 Analyze the calibration verification standard (25 μg/mL) according to Section 9 of this SOP.

8.6.4 The responses of the internal standards in the calibration verification standard must meet the criteria in Section 8.11.2.

8.6.5 Check the calibration verification for misidentified peaks due to retention time shifts. The most commonly mis-assigned compounds are closely eluting pairs such as the benzo(b) and benzo(k)fluoranthenes. If any are found, corrective action must be taken and the chromatogram re-quantitated to ensure the corrective action was successful.

8.6.6 Calculate the relative response factor (RRF) for each target compound and surrogate using Equation 1. The quantitation ions and internal standard assignments are listed in Appendix C.

8.6.7 Calculate the percent difference (%D) between the continuing calibration RRF's and the average RRF's from the most recent initial calibration for each target compound and surrogate using Equation 4.

Equation 4

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

Where :

RRFc = relative response in the continuing calibration
Avg RRFi = average relative response in the initial calibration

8.6.8 Verify that the minimum RRF for the SPCC's listed in section 8.5.8 is 0.050.

8.6.9 All other analytes must meet the minimum RRF's listed in Appendix B.

8.6.10 Verify that the maximum %D for the CCC's listed in section 8.5.10 is ≤ 25.

8.6.11 All other analytes must meet the maximum %D criteria listed in Appendix B.

8.6.12 All project specific analytes of interest must meet the minimum RRF and maximum %D criteria in Appendix B. If one or more analytes exceed the minimum RRF and maximum %D limit, the calibration verification may still be acceptable if the following conditions are met:

8.6.12.1 The %D of the analytes that exceed the limit is ≤ 40.

8.6.12.2 The minimum RRF of the analytes that exceed the limit is 0.050.

8.6.12.3 The mean of the %D values for all analytes is less than or equal to 25.

8.6.12.4 If an analyte that exceeds the QC limits is found in a sample extract, that extract must be re-analyzed using a calibration verification that meets QC limits for that analyte.

8.6.13 If any of the criteria are not satisfied a second continuing calibration may be analyzed. Repeated failure requires the analysis of a new initial calibration before analysis of samples can begin. If repairs to the system are required then a new initial calibration must be performed.

8.6.14 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. See Section 9.4.

8.7 Quantitation Limit Standard analysis

8.7.1 Analyze a quantitation limit standard (QLS) in each 12-hour period (see Section 8.4.2.1 for definition of 12-hour time period) when analyses of field or QC samples are performed. The QLS is used to verify analytical system response at the quantitation limit.

8.7.2 Analyze the 10 µg/mL calibration standard according to Section 9 of this SOP

8.7.3 Calculate the percent of true value for each target compound using Equation 5.

Equation 5

$$\% \text{ True Value} = (Cd / Tv) \times 100$$

Where:

Cd = Concentration determined by analysis
Tv = True value

8.7.4 The accuracy for each analyte, expressed as a percentage of true value must be between 50 - 150%. If the QLS sample fails, the cause must be determined and corrected before analysis of samples can begin.

8.7.5 If the 10 µg/mL QLS standard fails for target analytes with on column quantitation limits of 25 ng listed in Appendix B, then analyze a 25 µg/mL standard. Calculate the % True Value using Equation 6. The %True Value must be between 50 - 150%. If the QLS sample fails, the cause must be determined and corrected before analysis of samples can begin.

8.7.6 If the QLS standard fails, a fresh QLS solution of that standard may be analyzed.

8.8 Laboratory Reagent Blank (LRB) analysis.

8.8.1 An LRB is extracted with each extraction batch in order to demonstrate that the entire analytical system - from extraction through GC/MS analysis - is free of contamination.

8.8.2 Analyze the LRB according to Section 9 of this SOP.

8.8.3 Evaluate the LRB as soon as possible after it has been analyzed to determine if the following criteria have been met:

The LRB is acceptable if it contains less than the quantitation limit (QL) of any single target compound. Exceptions are the target phthalate esters, each of which may be present at up to five times the QL.

8.8.4 The LRB internal standards must meet the criteria listed in Section 8.11.2

8.8.5 The LRB surrogate recoveries must meet the criteria listed in Section 8.12.1

8.8.6 Corrective action - If the LRB 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.

8.8.7 If surrogate or internal standard recoveries do not meet acceptance criteria, re-analyze the extract. If the surrogate recoveries still do not meet acceptance criteria, document failure in the report narrative.

8.9 Laboratory fortified matrix and duplicate analysis.

8.9.1 A laboratory fortified matrix and a duplicate sample are extracted and analyzed for each batch of twenty or fewer samples extracted as a group.

8.9.2 LFM and LFMD extracts should be analyzed as soon as possible following the analysis of the sample designated as the laboratory fortified matrix sample.

8.9.3 Analyze the LFM and LFMD according to Section 9 of this SOP.

8.9.4 The recovery and RPD criteria for the LFM and LFMD analyses are as follows:

	% Recovery		RPD	
Compound	**Water**	**Soil**	**Water**	**Soil**
Phenol	12 - 110	26 - 100	21	35
2-Chlorophenol	27 - 123	25 - 102	16	50
1,4-Dichlorobenzene	36 - 100	28 - 104	22	27

	% Recovery		RPD	
Compound	**Water**	**Soil**	**Water**	**Soil**
n-Nitroso-di-n-propylamine	41 - 116	41 - 126	38	38
1,2,4-Trichlorobenzene	39 - 100	38 - 107	28	23
4-Chloro-3-methylphenol	23 - 100	26 - 103	42	33
Acenaphthene	46 -118	31 - 137	31	19
2,4-Dinitrotoluene	24 - 100	28 - 100	38	50
4-Nitrophenol	10 - 100	11 - 114	50	47
Pentachlorophenol	9 - 103	17 - 109	50	107
Pyrene	26 - 127	35 - 142	31	36

8.9.5 Calculate the recovery of each compound using Equation 6.

Equation 6

$$\% \text{ Rec} = ((SSR - SR)/SA) \times 100$$

where,

SSR = Spiked sample result (volume/weight corrected)
SR = Sample result (volume/weight corrected)
SA = Spike added

8.9.6 Calculate the relative percent differences (RPD) of the recoveries of each compound in the matrix spike and matrix spike duplicate using Equation 7.

Equation 7

$$RPD = \frac{(LFMC - LFMDC)}{(LFMC + LFMDC)/2} \times 100$$

where:

LFMC = Measured concentration of analyte in LFM
LFMDC = Measured concentration of analyte in LFMD

8.9.7 The limits for LFM/LFMD recovery are advisory limits only. If the limits are not met, then no further action is required, as long as the LFB 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 30% of the expected values.

8.10 Laboratory Fortified Blank (LFB) An LFB is analyzed to demonstrate that the analytical system is in control. The LFB is extracted and analyzed once per batch or every 20 samples, whichever is more frequent. The LFB is an LRB spiked with laboratory fortified matrix solution.

8.10.1 All analytes and surrogates must be recovered within the QC limits listed in section 8.9.4. If not, the source of the problem must be determined prior to reporting any sample data. It usually indicates either a discrepancy between the spiking solution and the calibration standard, or a problem in the extraction laboratory.

8.10.2 The table below lists the action to be taken based on the LFB and LFM/LFMD results.

QC ACCEPTANCE MATRIX

+ = PASS − = FAIL

CASE	1	2	3	4	5	6	7	8
LFB - % REC	+	+	+	+	−	−	−	−
LFM/LFMD -% REC	+	−	+	−	+	−	+	−
LFM/LFMD - RPD	+	+	−	−	+	+	−	−

Case 1: Extraction batch is acceptable.

Case 2: Extraction batch is acceptable; matrix effect confirmed.

Cases 3 & 4: Extraction batch is unsatisfactory. Investigate LFM/LFMD problem and document findings in report narrative.

Case 5: Extraction batch is rejected. The batch may have to be re-extracted unless LFB problem is determined and documented.

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

8.11 Internal standard recovery.

8.11.1 Check the internal standard recovery, determined by total area, for all standards, blanks, samples, and spikes immediately after analysis in order to determine if all applicable criteria have been met.

8.12.3.1 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 an "RE" suffix to the client sample ID on the re-analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.12.3.2 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 "DL" suffix to the client sample ID on the diluted analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.12.4 If the sample was re-extracted and 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" suffix to the client sample ID in the re-analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.12.5 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 "RX" suffix to the client sample ID in the re-analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.13 Sample dilution.

8.13.1 Dilute and inject a new aliquot of the extract if the on-column concentration of any target compound in any sample exceeds the initial calibration range. Add more internal standard solution to the diluted extract to maintain the initial internal standard concentration. Use the following criteria in performing dilutions:

8.13.1.1 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

8.13.1.2 Keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument by choosing an appropriate dilution factor.

8.13.1.3 Do not dilute LFM/LFMD 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.

8.13.1.4 In the case of extremely contaminated samples several dilutions may be required.

8.13.1.5 Distinguish between the undiluted and diluted analysis by adding a "DL" suffix to the client sample ID on the diluted analysis.

8.13.2 Demonstrate that there is no carryover to subsequent analyses after a sample is analyzed that contains one or more target compounds at a level exceeding the initial calibration range of the system. This can be done by analyzing an instrument blank.

8.13.2.1 Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the limits above. The maximum contamination criteria are as follows:

8.13.2.2 The sample should not contain a concentration above the QL for the target compounds that exceeded the limits in the contaminated sample, unless other analytes present in the sample indicate that the presence of these compounds is likely. The most common scenario for this is when PNAs are found in both samples, and the pattern in the second sample does not follow the pattern in the first.

8.13.3 The most common cause of a carryover is hydrocarbon in the oil/asphalt range. This may require cleaning the injection port and analyzing an instrument blank.

8.14 Review of Target Analytes

Review each reported value for both qualitative and quantitative validity. This process, in particular the qualitative review of mass spectra, relies upon the technical judgement of the analyst.

8.14.1 Qualitative Review

Both the relative retention time and the mass spectra must match those of the standard's in order for a target compound to be identified as present in a sample.

8.14.1.1 Target analytes must elute within 0.06 relative retention time units of the analyte in the continuing calibration standard. The relative retention time is the retention time of the target divided by the retention time of the associated internal standard. If the relative retention time for the target analyte in the CCAL is 0.82 then the peak in the sample must have a relative retention time of 0.76 to 0.88.

8.14.1.2 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other.

8.14.1.3 The mass spectra used for qualitative identification must be obtained using the GCMS system used to analyze the samples.

8.14.1.3.1 All ions present in the standard mass spectra at a relative intensity of 10 percent of the most abundant ion must be present in the sample spectra.

8.14.1.3.2 The relative intensities of the ions must agree within ±30 % (absolute) between the standard and sample spectra.

8.14.1.3.3 Ions present in the sample at greater than 10 percent abundance but not present in the standard spectra must be reviewed and accounted for by the analyst making the comparison.

8.14.1.3.4 If a compound cannot be verified by these criteria but, in the technical judgement of the analyst, is present the supporting evidence must be indicated on the raw data and the analyte reported.

8.14.2 Quantitative Review

Review reported values to determine that the correct calculations were used to generate the results, that the RRFs from the associated continuing calibration standard were used, and that all other numbers are accurate.

8.14.2.1 Review of data system integrations

The analyst must review the data system integration to verify that the internal standards, surrogates and target compounds are integrated properly. In the

event that the analyst observes an incorrect integration, the analyst must manually correct the integration and document the correction following Section 8.5.11 of this SOP and EPA Region 9 SOP #835, *Chromatographic Integration Procedures.*

8.14.2.2 Water calculations

Calculate results for target analytes using Equation 9:

Equation 9:

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

where:

A_x = area of the quantitation ion of the compound
C_{IS} = concentration of internal standard in μg/mL (normally 20)
DF = dilution factor
A_is = area of the quantitation ion of the associated internal standard
RRF = analyte's mean relative response factor from the initial calibration
V_o = volume of water extracted in mL
V_i = volume of extract injected in μL
V_t = volume of concentrated extract in μL

8.14.2.3 Soil calculations

Calculate results for target analytes using Equation 10:

Equation 10:

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

where:

A_x = area of the quantitation ion of the compound
C_{IS} = concentration of Internal Standard in μg/mL (normally 20)
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's 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

8.15 Review the Tentatively Identified Compound search results for the following:

8.15.1 Verify that all unknown peaks in the chromatogram greater than10 percent of the area of the nearest internal standard are accounted for in the summary.

8.15.2 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.

8.15.3 The relative intensities of the major ions should agree within 20 percent.

8.15.4 Molecular ions present in the reference spectrum should be present in the sample spectrum.

8.15.5 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.

8.15.6 Ions present in the reference spectrum but not within the scan range (35 to 500 amu) of the method should not be considered when making a tentative identification.

8.15.7 If, in the technical judgement 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.

8.16 If any of the data reports have been edited, or if manual integration or quantitation has been performed, the analyst must identify the changes. A supervisor, QA/QC coordinator, or team leader must review both the original and the changed data and indicate acceptance by initialing and dating the report. See SOP#835, *Chromatographic Integration Procedures*.

9 ANALYTICAL PROCEDURES

9.1 Analytical system preparation.

9.1.1 Calibrate the mass axis and optimize the peak width of the mass spectrometer using FC43 at the beginning of each 12-hour period during which standards or QC or field samples are to be analyzed.

9.1.2 Check the GC/MS system for leaks prior to the analysis of the DFTPP tuning compound. The system must also be checked for leaks after any disconnection and re-connection in the entire system, from the carrier gas source to the MS.

9.1.2.1 Acquire a scan of m/z's 18, 28, and 69. Observe the ratio of the water peak (m/z 18) to the nitrogen peak (m/z 28). If a leak is present in the mass spectrometer, the nitrogen peak will be greater than the water peak. Corrective action must be taken if a leak is detected. The ratios of these ions to the m/z 69 ion should be no more than 10%. Ratios between 10 and 20% indicate a problem that should be repaired as soon as practical, and ratios greater than 20% indicate problems that should be repaired immediately.

9.1.3 The GC/MS system must meet the mass spectral ion abundance criteria for DFTPP and the maximum breakdown criteria for DDT prescribed in Section 8.4 prior to the analysis of any calibration standards, blanks, or samples

9.1.3.1 Analyze the DFTPP+ solution using the system conditions in Appendix E. Obtain ion abundance ratios from a background subtracted average of three scans around the apex of the DFTPP peak or from any one or two of these scans with or without background subtraction. The ion abundance ratios must meet the criteria listed in Section 8.4.4. If not, appropriate corrective action must be taken before calibrations or extracts are analyzed. See Section 9.4.

9.1.3.2 Evaluate the percentage of DDT breakdown as described in Section 8.4.4.2. If it is greater than 20%, take corrective action.

9.2 Calibration - The target compounds for this method are listed in Appendix B.

9.2.1 Five-point initial calibration

Perform a five-point initial calibration in order to demonstrate that the GC/MS system provides a linear response over the desired concentration range.

9.2.1.1 Create a method (if not present already) to operate the GC and collect data as described in Appendix E. Create a sequence to use this method to analyze the standard solutions - 80, 60, 40, 25 and 10 μg/mL.

9.2.1.2 Analyze the 10 or 25 µg/mL standard. Verify that all of the peaks have been properly identified. Update the retention times in the method. Save the method and re-quantitate the chromatogram. Make sure that all of the standards are quantitated using the updated retention times.

9.2.1.3 Update the initial calibration response factors in the method by associating the correct data file with each calibration level. Save the method.

9.2.1.4 Generate the initial calibration summary report. Samples shall not be analyzed if the initial calibration does not meet the criteria specified in Appendix B of this SOP.

9.2.1.5 Analyze a QCS sample immediately after each initial calibration. The RRF for each analyte in the QCS must be within 30% of the mean RRF in the initial calibration. If the QCS sample fails, the cause must be determined and corrected before analysis of samples can proceed.

9.2.1.6 If the initial calibration and the QCS meet all the criteria specified in Section 8.5 of this SOP, the remainder of the 12-hour analytical period may be used for the analysis of blanks, spikes and samples, using the average RRF from the initial calibration to quantitate these data files.

9.2.2 Calibration Verification

Analyze a calibration verification standard once in every 12-hour analytical time period, after DFTPP tuning and prior to continuing with extract analysis. The calibration verification is performed in order to determine if the GC/MS system is operating within the acceptable range as demonstrated by the percent difference and the minimum response factor criteria meeting the appropriate QA/QC criteria. The continuing calibration is analyzed at a level of 25 µg/mL.

9.2.2.1 Analyze the 25 µg/mL standard. Verify that all compounds have been properly identified. Update the retention times in the method. Save the method. Re-quantitate the chromatogram, again verify that all compounds have been properly identified. Select Report Continuing Calibration to Printer. Examine the RRFs and %Ds for method compliance following sections 8.6.4 through 8.6.12 of this SOP. If the continuing calibration meets QC criteria, analysis of extracts can begin.

9.2.2.2 If any of the criteria are not satisfied a second continuing calibration may be analyzed. Repeated failure requires the analysis of a new initial calibration before analysis of samples can begin. If repairs to the system are required then a new initial calibration must be performed.

9.2.2.3 Take corrective action if the continuing calibration fails. This may consist of re-analyzing the standard, clipping the column and replacing the injection port seal, or creating a new five point calibration.

9.2.3 Sample analysis.

Samples can be analyzed only after the DFTPP tune and initial calibration or continuing a calibration meet all of the appropriate criteria specified in Section 8 of this SOP.

9.2.3.1 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Appendix E.

9.2.3.2 Set up a data acquisition sequence. The sample description shall include the client sample ID and the laboratory sample ID. Additional header information shall include the dilution factor, instrument ID, and the analyst's initials.

9.2.3.3 Add 10 μL of the IS solution to each 1 mL of field and QC sample extract.

9.2.3.4 Include all QC sample extracts. It is highly recommended that the LRB, LFB and LFM/LFMD extracts be analyzed as early as possible in the analysis of a batch.

9.2.3.5 After completion of analysis, quantitate the data using the appropriate initial calibration mean RRF's and print out quantitation reports and chromatograms for each field and QC sample.

9.2.3.6 Review the results as discussed in Section 8.14 for identification of target analytes. Manually cross out all reported hits which do not meet the qualitative criteria and document the reason on the quant report. Review all target compounds that are detected to verify they are integrated properly. Review the chromatogram for possible false negatives.

9.2.3.7 Document any required manual integrations as described in Section 8.5.11 and Region 9 SOP #835. Print out the updated quantitation report.

10.2.1.1.7 LRB results

10.2.1.1.8 Surrogate recoveries

10.2.1.1.9 Internal standard recoveries.

10.2.1.1.10 LFM/LFMD results.

10.2.1.1.11 LFB results.

10.2.1.1.12 Analytical comments section to include:

10.2.1.1.12.1 Problems with analysis

10.2.1.1.12.2 Examples of calculations

10.2.2 Summary of Analytical Results spreadsheet

10.2.2.1 Include a spreadsheet containing a summary of the results for all target analytes for all samples and LRB's in the data package.

10.2.2.2 The header information for each sample contains the station location, Sample ID, and date sampled.

10.2.2.3 The results section contains the results for each target analyte as follows:

If an analyte is not detected then the quantitation limit with a "U" qualifier will be reported

If an analyte is detected then the value reported on the quant report and the associated qualifier (Section 10.2.5.1) will be reported.

If an analyte requires a dilution then value from the sample dilution will be reported.

10.2.3 Tracking Forms section.

The Tracking Form section contains the following forms.

10.2.3.1 A technical direction form

10.2.3.2 A copy of the chain of custody records received with each sample shipment.

10.2.3.3 A copy of the shipper's air bill, or bill of lading.

10.2.4 QA/QC Summary section.

The QA/QC section contains all of the QA/QC summary forms for the specific sample delivery group. All of the forms are checked by the analyst to ensure that all of the filenames are correct, and that all of the appropriate standards, blanks, samples and spikes have been included.

10.2.4.1 Data analysis of sample SDG matrix summary report

10.2.4.2 Surrogate recovery and internal standard area count data. In a chronological order by instrument.

10.2.4.3 LFB recovery data.

10.2.4.4 LFM and LFMD recovery data.

10.2.5 Initial Calibration section:

10.2.5.1 Copy of the peer reviewed instrument run log page(s).

10.2.5.2 DFTPP tuning report, which includes the pass/fail table, bar spectrum and tabulated mass listing.

10.2.5.3 Initial calibration summary form containing the response factors for each file, the average response factor for each compound, and the percent RSD for each compound in the initial calibration.

10.2.5.4 Quantitation reports and RICs.

10.2.5.5 Documentation of any required manual integrations as described in Section 8.5.11 and Region 9 SOP #835.

10.2.6 Daily Sample Package section.

The daily sample package section contains the following forms and raw data for each sample including QC samples of LFM/LFMD, LFB, and LRB in the data package, assembled in data file alphanumeric order. Each daily package is arranged in chronological order.

10.2.6.1 Quantitation report, data report form listing all detected target compounds, surrogates and internal standards and the levels detected in the sample. All analyses must be included, even those not used. The analyst shall check to be sure that the appropriate qualifier is added to the form as indicated below.

B This analyte was detected in the associated method blank as well as in the sample.

E The amount detected exceeds the calibration range of the instrument.

J The analyte was positively identified . The amount is less than QL but greater than or equal to ½ of QL and/or the associated numerical value is approximate. It is an estimated value.

10.2.6.2 The reconstructed ion chromatogram (RIC) of the data file.

10.2.6.3 The raw spectra and enhanced spectra of the target compounds, internal standards and surrogates detected in the sample, as well as the corresponding reference spectra in order of elution.

10.2.6.4 Documentation of any required manual integrations as described in Section 8.5.11 and Region 9 SOP #835.

10.2.6.5 Non-target compound report form detailing the compound names, retention times, the estimated concentrations, and the CAS number of up to twenty tentatively identified compounds. The exceptions are QC samples of LFB, LFM/LFMD.

10.2.6.6 Enhanced spectra of non-target compounds detected in the sample. Library search listing the three best fits of a forward library search of the non-target compounds.

10.2.6.7 Area summary showing results of integrating the RIC.

10.2.7 Logbooks and Miscellaneous Data.

All logbooks must be peer reviewed and complete in compliance with USEPA Region 9 Laboratory SOP #840, Notebook Documentation and Control.

10.2.7.1 Copies of all applicable standards preparation logbook pages.

10.2.7.2 Copies of extraction log pages.

10.2.7.3 Copies of Percent Solids logbook pages, if applicable.

10.2.7.4 Copies of GPC run log logbook pages, if applicable

10.2.7.5 Copies of applicable Semivolatile Organics Run Log pages

10.3 Summary Report and Raw Data

When the clients' requirements stipulate a summary data package, the laboratory prepares the report narrative, analytical results spreadsheet, and sample specific raw data and organizes other data associated with the package for filing in the event that future data review or validation is required.

10.3.1 Prepare the report narrative according to the requirements listed in Section 10.2.1.

10.3.2 Prepare the analytical results spreadsheet according to the specifications provided in Section 10.2.2.

10.3.3 Organize the raw data associated with the analysis of all the samples in the package for filing and present it for review along with the report narrative and the spreadsheet. No summary forms need be generated with the raw data but any forms which would normally be generated as part of the analysis must be included in the package. For example, the calibration summary reports generated by the data system and used by the analyst to assess the acceptability of the calibration should be filed with the raw data.

10.3.3.1 Include sample tracking information as detailed in Section 10.2.3 as the analyst has a copy of the information readily available.

10.3.3.2 Sample raw data organized by laboratory sample ID must include: the quantitation report; the RIC; the raw and enhanced spectra of the internal standards, surrogates and any target compounds detected in the sample, as well as the enhanced spectra of the corresponding compounds in the calibration file; and enhanced spectra of non-target compounds detected in the sample along with the library search listing the three best matches for the non-target compounds. (Sections 10.2.5.3 through 10.2.5.6)

10.3.3.3 Calibration data must include any available summary information and the quantitation reports and RICs for all initial calibrations and continuing calibrations associated with the SDG. This information must be organized by instrument and date. Additionally, any manual integration must be demonstrated by including the associated peak integration as described in Section 8.5.11.

10.3.3.4 Include raw data for QC samples. Tuning data and the associated summary used by the analyst to determine acceptability, blanks (quant report, RIC and spectra and TICs), LFM/LFMD data (quant report and RICs) should all be included in this order.

10.3.3.5 Runlogs and standard preparation logbooks need not be included in the raw data as these are already filed in an accessible manner in the laboratory.

10.4 Technical review.

Assign the data package an ESAT document control number after assembly. Each data package is reviewed by the GC Group Leader or a senior level chemist, other than the chemist who performed the analyses. All reviews are documented using the review form. After the peer review is performed, a cover letter is prepared and signed by the Group Leader. Final review of the data package is done by ESAT QA/QC Coordinator or ESAT Team Leader and the package is then paginated and submitted to EPA Region 9.

10.5 Injection logbook.

Maintain an injection logbook listing each field and QC sample injected for each instrument in accordance with ESAT SOP #840, *Notebook Documentation and Control.*

10.6 Standards' logbook

Maintain a logbook documenting the preparation of all standard solutions. Record the standard ID, preparation date, expiration date, solvent and solvent lot number used. Record the identification, supplier, lot number, concentration purity, and expiration date of the stock standard solution used. Record the aliquot weight or volume of the stock standard solution, final volume of the standard solution and the concentration of the analyte(s) in the standard. Document the calculations used in preparing the standard.

10.7 Maintenance logbook

Maintain a logbook for each instrument. Record the date, the problem and resolution, and documentation of return to control. Document all preventive or routine maintenance procedures, as well as repairs or corrective or remedial actions in accordance with ESAT SOP #840, *Notebook Documentation and Control.*

11 REFERENCES

1 EPA Method 8270C, *Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*, Revision 3, December 1996.

2 EPA 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

3 EPA Region 9 SOP #125. *Disposal Procedures for Unused Aqueous Environmental Samples*

4 HP 5972A MSD Hardware Manual

5 HP EnviroQuant Chemstation User's Guide

6 HP Environmental Analysis User's Guide

7 EPA Region 9 SOP #835, *Chromatographic Integration Procedures*

8 EPA Region 9 SOP #840, *Notebook Documentation and Control*

9 EPA Method 8000B, *Determinative Chromatographic Separations*, Revision 2, December 1996.

10 EPA Region 9 SOP #805, *Refrigerator Temperature Monitoring*

11 40 CFR, Part 136, Appendix B.

12 HP 5890 Gas Chromatograph Users Manual

13 HP 6890 Gas Chromatograph Users Manual

APPENDIX A

DEVIATIONS FROM SW-846 METHOD 8270C

1. There is no requirement in the reference method for the analysis of a quality control sample (QCS), or a second source standard.

2. This SOP uses a GC column with a 0.25 μm film instead of a 1 μm film as specified in the reference method.

3 The surrogate solution used in this SOP contains 1,2-dichlorobenzene-d_4 and 2-chlorophenol-d_4, neither of which are specified by method 8270.

4 The reference method recommends a concentration of 40 ng/μL in the sample extract for each internal standard; this SOP specifies 20 ng/μL instead.

5 SW-846 method 3500B referenced by method 8270C specifies a concentration of 200 mg/L for the acid matrix spiking solution; this SOP specifies 150 mg/L.

6 The reference method does not have criteria for the chromatographic separations of anthracene/phenanthrene or benzo(a)anthracene/chrysene.

7. This SOP allows for the re-analysis of certain calibration, QC, and sample solutions if the first analysis fails QC limits. This practice is not addressed in the reference method.

8. This SOP allows for a four-point calibration for certain analytes with on column quantitation limits of 25 ng (see Appendix D). The reference method requires a five-point calibration for all analytes.

9. There is no requirement in the reference method that a quantitation ion not saturate the detector.

10. There is no requirement in the reference method for the analysis of a quantitation limit standard (QLS).

11. This SOP allows the phthalate esters to be present at levels exceeding the QL in the laboratory reagent blank; the reference method does not.

12. The LFB/LFM/LFMD acceptance criteria are predetermined and fixed; they are not updated using laboratory data as in the reference method.

13. The retention times of internal standards must be within 0.2 minute from the latest daily calibration, instead of 0.5 minutes as in the reference method.

14. The acceptance criteria for surrogates are predetermined and fixed; they are not updated using laboratory data as in the reference method.

15. There is no requirement in the reference method that the response of the largest analyte peak in a dilution be kept in the upper half of the initial calibration range.

16. There is no requirement in the reference method that all ions present in the standard mass spectra at a relative intensity of 10 percent of the most abundant ion must be present in the sample spectra.

17. There is no requirement in the reference method that ions present in the sample at greater than 10 percent abundance but not present in the standard spectra must be reviewed and accounted for by the analyst making the comparison.

18. There is no requirement in the reference method that the GC/MS system is to be checked for leaks prior to the analysis of the tuning compound by monitoring m/z's 18, 28, and 69.

19. Diphenylamine is not used as a CCC in this SOP as in the reference method since it is not a target analyte in this SOP.

20. The maximum RSD of target analytes in the initial calibration in this SOP is 20%, not 15% as in the reference method.

21. The maximum RSD for any CCC in this SOP is 20%, not 30% as in the reference method.

22. The maximum %D for any CCC in this SOP is 25, not 20 as in the reference method.

23. The reference method has no %D criteria for analytes in the calibration verification other than the calibration check compounds (CCC's).

APPENDIX B
Calibration Criteria

SEMIVOLATILE COMPOUND	MINIMUM RRF	MAXIMUM %RSD	MAXIMUM %DIFF
Phenol	0.800	20	±25
bis(2-Chloroethyl)ether	0.700	20	±25
2-Chlorophenol	0.800	20	±25
1,3-Dichlorobenzene	0.600	20	±25
1,4-Dichlorobenzene	0.500	20	±25
benzyl alcohol	0.050	20	±25
1,2-Dichlorobenzene	0.400	20	±25
2-Methylphenol	0.700	20	±25
2,2'-oxybis(1-Chloropropane)	0.010	20	±25
4-Methylphenol	0.600	20	±25
N-Nitroso-di-n-propylamine	0.050	20	±25
Hexachloroethane	0.300	20	±25
Nitrobenzene	0.200	20	±25
Isophorone	0.400	20	±25
2-Nitrophenol	0.100	20	±25
2,4-Dimethylphenol	0.200	20	±25
bis(2-Chloroethoxy)methane	0.300	20	±25
2,4-Dichlorophenol	0.200	20	±25
1,2,4-Trichlorobenzene	0.200	20	±25
Naphthalene	0.700	20	±25
4-Chloroaniline	0.010	20	±25
Hexachlorobutadiene	0.010	20	±25
4-Chloro-3-methylphenol	0.200	20	±25
2-Methylnaphthalene	0.400	20	±25
Hexachlorocyclopentadiene	0.050	20	±25
2,4,6-Trichlorophenol	0.200	20	±25
2,4,5-Trichlorophenol	0.200	20	±25
2-Chloronaphthalene	0.800	20	±25
2-Nitroaniline	0.010	20	±25
Dimethylphthalate	0.010	20	±25
Acenaphthylene	0.900	20	±25
3-Nitroaniline	0.010	20	±25
2,6-Dinitrotoluene	0.200	20	±25
Acenaphthene	0.900	20	±25
2,4-Dinitrophenol	0.050	20	±25
4-Nitrophenol	0.050	20	±25
Dibenzofuran	0.800	20	±25
2,4-Dinitrotoluene	0.200	20	±25
Diethylphthalate	0.010	20	±25
4-Chlorophenyl-phenylether	0.400	20	±25
Fluorene	0.900	20	±25
4-Nitroaniline	0.010	20	±25
4,6-Dinitro-2-methylphenol	0.010	20	±25
N-Nitrosodiphenylamine	0.010	20	±25
4-Bromophenyl-phenylether	0.100	20	±25
Hexachlorobenzene	0.100	20	±25

SEMIVOLATILE COMPOUND	MINIMUM RRF	MAXIMUM %RSD	MAXIMUM %DIFF
Pentachlorophenol	0.050	20	±25
Phenanthrene	0.700	20	±25
Anthracene	0.700	20	±25
Carbazole	0.010	20	±25
Di-n-butylphthalate	0.010	20	±25
Fluoranthene	0.600	20	±25
Pyrene	0.600	20	±25
Butylbenzylphthalate	0.010	20	±25
3,3'-Dichlorobenzidine	0.010	20	±25
Benzo(a)anthracene	0.800	20	±25
bis(2-Ethylhexyl)phthalate	0.010	20	±25
Chrysene	0.700	20	±25
Di-n-octylphthalate	0.010	20	±25
Benzo(b)fluoranthene	0.700	20	±25
Benzo(k)fluoranthene	0.700	20	±25
Benzo(a)pyrene	0.700	20	±25
Indeno(1,2,3-cd)pyrene	0.500	20	±25
Dibenzo(a,h)anthracene	0.400	20	±25
Benzo(g,h,i)perylene	0.500	20	±25
SURROGATES			
Nitrobenzene-d5	0.200	20	±25
2-Fluorobiphenyl	0.700	20	±25
Terphenyl-d14	0.500	20	±25
Phenol-d5	0.800	20	±25
2-Fluorophenol	0.600	20	±25
2,4,6-Tribromophenol	0.010	20	±25
2-Chlorophenol-d4	0.800	20	±25
1,2-Dichlorobenzene-d4	0.400	20	±25

APPENDIX C

TARGET COMPOUND LIST FOR SEMIVOLATILE ORGANICS ANALYSIS

The following is the Target Compound List for semivolatile organics, as well as the associated internal standards and surrogates. Included are the internal standard reference for each target compound, as well as the quantitation mass for each analyte.

Compound	Primary Quant Ion	Secondary Ion(s)	Int. Std
Phenol	94	65, 66	1
bis(2-Chloroethyl)ether	93	63, 95	1
2-Chlorophenol	128	64, 130	1
1,3-Dichlorobenzene	146	148, 113	1
1,4-Dichlorobenzene	146	148, 113	1
benzyl alcohol	108	79, 77	1
1,2-Dichlorobenzene	146	148, 113	1
2-Methylphenol	108	107	1
2,2'-oxybis(1-Chloropropane)	45	77, 79	1
4-Methylphenol	108	107	1
N-Nitroso-di-n-propylamine	70	42, 101, 130	1
Hexachloroethane	117	201, 199	1
Nitrobenzene	77	123, 65	2
Isophorone	82	95, 138	2
2-Nitrophenol	139	65, 109	2
2,4-Dimethylphenol	107	121, 122	2
bis(2-Chloroethoxy)methane	93	95, 123	2
2,4-Dichlorophenol	162	164, 98	2
1,2,4-Trichlorobenzene	180	182, 145	2
Naphthalene	128	129, 127	2
4-Chloroaniline	127	129	2
Hexachlorobutadiene	225	223, 227	2
4-Chloro-3-methylphenol	107	144, 142	2
2-Methylnaphthalene	142	141	2
Hexachlorocyclopentadiene	237	235, 272	3
2,4,6-Trichlorophenol	196	198, 200	3
2,4,5-Trichlorophenol	196	198, 200	3
2-Chloronaphthalene	162	164, 127	3
2-Nitroaniline	65	92, 138	3
Dimethyl phthalate	163	194, 164	3
Acenaphthylene	152	151, 153	3
2,6-Dinitrotoluene	165	89, 121	3
3-Nitroaniline	138	108, 92	3
Acenaphthene	153	152, 154	3
2,4-Dinitrophenol	184	63, 154	3
4-Nitrophenol	109	139, 65	3
Dibenzofuran	168	139	3
2,4-Dinitrotoluene	165	63, 182	3
Diethylphthalate	149	177, 150	3
4-Chlorophenyl-phenylether	204	206, 141	3
Fluorene	166	165, 167	3
4-Nitroaniline	138	92, 108	3

Compound	Primary Quant Ion	Secondary Ion(s)	Int. Std
4,6-Dinitro-2-methylphenol	198	182, 77	4
N-Nitrosodiphenylamine	169	168, 167	4
4-Bromophenyl-phenylether	248	250, 141	4
Hexachlorobenzene	284	142, 249	4
Pentachlorophenol	266	264, 268	4
Phenanthrene	178	179, 176	4
Anthracene	178	179, 176	4
Carbazole	167	166, 139	4
Di-n-butylphthalate	149	150, 104	4
Fluoranthene	202	101, 100	4
Pyrene	202	101, 100	5
Butylbenzylphthalate	149	91, 206	5
3,3'-Dichlorobenzidine	252	254, 126	5
Benzo(a)anthracene	228	229, 226	5
bis(2-Ethylhexyl)phthalate	149	167, 279	5
Chrysene	228	226, 229	5
Di-n-Octyl phthalate	149	150, 279	6
Benzo(b)fluoranthene	252	253, 125	6
Benzo(k)fluoranthene	252	253, 125	6
Benzo(a)pyrene	252	253, 125	6
Indeno(1,2,3-cd)pyrene	276	138, 227	6
Dibenzo(a,h)anthracene	278	139, 279	6
Benzo(g,h,i)perylene	276	138, 277	6
SURROGATES			
Phenol-d5	99	42, 71	1
2-Fluorophenol	112	64	1
2,4,6-Tribromophenol	330	332, 141	4
Nitrobenzene-d5	82	128, 54	2
2-Fluorobiphenyl	172	171	3
Terphenyl-d14	244	122, 212	5
2-Chlorophenol-d4	132	68, 134	1
1,2-Dichlorobenzene-d4	152	115, 150	1
INTERNAL STANDARDS			
1,4-Dichlorobenzene-d4	152	115	1
Naphthalene-d8	136	68	2
Acenaphthene-d10	164	162, 160	3
Phenanthrene-d10	188	94, 80	4
Chrysene-d12	240	120, 236	5
Perylene-d12	264	260, 265	6

APPENDIX D

SEMIVOLATILES TARGET COMPOUND LIST AND QUANTITATION LIMITS

Semivolatiles	CAS Number	Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column ng
Phenol	108-95-2	10	330	10000	10
bis-(2-Chloroethyl)ether	111-44-4	10	330	10000	10
2-Chlorophenol	95-57-8	10	330	10000	10
1,3-Dichlorobenzene	541-73-1	10	330	10000	10
1,4-Dichlorobenzene	106-46-7	10	330	10000	10
benzyl alcohol	100-51-6	10	330	10000	10
1,2-Dichlorobenzene	95-50-1	10	330	10000	10
2-Methylphenol	95-48-7	10	330	10000	10
2,2'-oxybis (1-Chloropropane)	108-60-1	10	330	10000	10
4-Methylphenol	106-44-5	10	330	10000	10
N-Nitroso-di-n-propylamine	621-64-7	10	330	10000	10
Hexachloroethane	67-72-1	10	330	10000	10
Nitrobenzene	98-95-3	10	330	10000	10
Isophorone	78-59-1	10	330	10000	10
2-Nitrophenol	88-75-5	10	330	10000	10
2,4-Dimethylphenol	105-67-9	10	330	10000	10
bis(2-Chloroethoxy)methane	111-91-1	10	330	10000	10
2,4-Dichlorophenol	120-83-2	10	330	10000	10
1,2,4-Trichlorobenzene	120-82-1	10	330	10000	10
Naphthalene	91-20-3	10	330	10000	10
4-Chloroaniline	106-47-8	10	330	10000	10
Hexachlorobutadiene	87-68-3	10	330	10000	10
4-Chloro-3-methylphenol	59-50-7	10	330	10000	10
2-Methylnaphthalene	91-57-6	10	330	10000	10
Hexachlorocyclopentadiene	77-47-4	10	330	10000	10
2,4,6-Trichlorophenol	88-06-2	10	330	10000	10
2,4,5-Trichlorophenol	95-95-4	25	830	25000	25
2-Chloronaphthalene	91-58-7	10	330	10000	10
2-Nitroaniline	88-74-4	25	830	25000	25
Dimethylphthalate	131-11-3	10	330	10000	10
Acenaphthylene	208-96-8	10	330	10000	10
2,6-Dinitrotoluene	606-20-2	10	330	10000	10
3-Nitroaniline	99-09-2	25	830	25000	25
Acenaphthene	83-32-9	10	330	10000	10
2,4-Dinitrophenol	51-28-5	25	830	25000	25
4-Nitrophenol	100-02-7	25	830	25000	25
Dibenzofuran	132-64-9	10	330	10000	10
2,4-Dinitrotoluene	121-14-2	10	330	10000	10
Diethylphthalate	84-66-2	10	330	10000	10
4-Chlorophenyl-phenylether	7005-72-3	10	330	10000	10
Fluorene	86-73-7	10	330	10000	10
4-Nitroaniline	100-01-6	25	830	25000	25
4,6-Dinitro-2-methylphenol	534-52-1	25	830	25000	25
N-Nitroso-diphenylamine	86-30-6	10	330	10000	10
4-Bromophenyl-phenylether	101-55-3	10	330	10000	10
Hexachlorobenzene	118-74-1	10	330	10000	10
Pentachlorophenol	87-86-5	25	830	25000	25

Phenanthrene	85-01-8	10	330	10000	10
Anthracene	120-12-7	10	330	10000	10
Carbazole	86-74-8	10	330	10000	10
Di-n-butylphthalate	84-74-2	10	330	10000	10
Fluoranthene	206-44-0	10	330	10000	10
Pyrene	129-00-0	10	330	10000	10
Butylbenzylphthalate	85-68-7	10	330	10000	10
3,3'-Dichlorobenzidine	91-94-1	10	330	10000	10

Semivolatiles	CAS Number	Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column (ng)
Benzo(a)anthracene	56-55-3	10	330	10000	10
Chrysene	218-01-9	10	330	10000	10
bis(2-Ethylhexyl)phthalate	117-81-7	10	330	10000	10
Di-n-octylphthalate	117-84-0	10	330	10000	10
Benzo(b)fluoranthene	205-99-2	10	330	10000	10
Benzo(k)fluoranthene	207-08-9	10	330	10000	10
Benzo(a)pyrene	50-32-8	10	330	10000	10
Indeno(1,2,3-cd)-pyrene	193-39-5	10	330	10000	10
Dibenzo(a,h)-anthracene	53-70-3	10	330	10000	10
Benzo(g,h,i)perylene	191-24-2	10	330	10000	10

APPENDIX E

GC PARAMETERS

HP6890

Typical operating parameters for the gas chromatograph are as follows:

DFTPP analysis

PARAMETER	SETTING
Injector temperature	280°C
Column Stability time	0.5 minutes
MS Source Temp	230°C
MS Quad Temp	150°C
MSD Heater Temp	280°C
EPC split-splitless inlet	Pulsed splitless
Injection pulse pressure	20 psi until 0.55 min
Purge flow to split vent	20 ml/min @ 0.50 min
Initial Oven Temp	100°C
Initial Oven Time	0 minutes
Temperature Ramp	20°C/minute for 10 minutes
Final Oven Temp	300°C
Final Hold Time	2 minutes
Column Flow rate	~ 1 mL/min
Electron Energy	70 volts (nominal)
Injector	Front
Injection Volume	1.0 µL
Pre Injection	
Sample Washes	0
Solvent A Washes	1
Solvent B Washes	0
Post Injection	
Solvent A Washes	3
Solvent B Washes	3
Pumps	3
Syringe Size	10 µL
Viscosity	0
Plunger Speed	Fast Injection

Target Compound Analysis

PARAMETER	SETTING
Injector temperature	280°C
Column Stability time	0.5 minutes
MS Source Temp	230°C

MS Quad Temp	150°C
MSD Heater Temp	280°C
EPC split-splitless inlet	Pulsed splitless
Injection pulse pressure	20 psi until 0.55 min
Purge flow to split vent	20 ml/min @ 0.50 min
Initial Oven Temp	40°C
Initial Oven Time	1 minutes
Temperature Ramp	20°C/minute
Final Oven Temp	130°C
Temperature Ramp A	12°C/minute
Final Oven Temp A	270°C
Temperature Ramp B	4°C/minute
Final Oven Temp B	313°C
Final Hold Time	2 minutes
Column Flow rate	~ 1 mL/min
Electron Energy	70 volts (nominal)
Injection Volume	1.0 µL
Pre Injection	
Sample Washes	0
Solvent A Washes	1
Solvent B Washes	0
Post Injection	
Solvent A Washes	3
Solvent B Washes	3
Pumps	3
Syringe Size	10 µL
Viscosity	0
Plunger Speed	Fast Injection

Appendix B-3
N-Nitrosodimethylamine (NDMA)

Summary of Calibration and QC Procedures for NDMA (GC/MS SIM)

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria*	Corrective Action
GC/MS /SIM	NDMA	5-point initial calibration	Initial calibration prior to sample analysis	RSD <30 %	Correct problem then repeat initial calibration
		Second-source calibration verification	Once per six-point initial calibration	All analytes within ±25% of expected value	Correct problem then repeat initial calibration
		Calibration verification	Daily, before and at the end of sample analysis and every 12 hours of analysis time	RF for NDMA within ±25% of RF for the 1.0 ug/L Initial Calibration Standard	Correct problem then repeat initial calibration

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria*	Corrective Action
GC/MS /SIM	NDMA	Internal Standards	Immediately after or during data acquisition of calibration check standard	Retention time ±30 seconds: EICP area within -50% to +100% of last calibration verification (12 hours) for each	Inspect mass spectrometer and GC for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning
		Method blank	One per analytical batch	No analytes detected ≥ RL	Correct problem then reprep and analyze method blank and all samples processed with the contaminated blank
		LCS	One LCS per analytical batch	QC acceptance criteria is 70 to 120% recovery.	Correct problem then reprep and analyze the LCS and all samples in the affected analytical batch

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria*	Corrective Action
GC/MS /SIM	NDMA	Surrogate spike Results reported between method detection limit and CRQL are flagged as estimate with a "J" qualifier.	Every sample, spiked sample, standard, and method blank none	QC acceptance criteria is 60 to 120% recovery none	Correct problem then reextract and analyze sample None
		MDL study	Once per 12 month period	Detection limits established shall be < 0.002 ug/l	None

* Control limits may be modified prior to start of analyses per laboratory specific data

Appendix B-4
Perchlorate

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 531

ANALYSIS OF PERCHLORATE BY ION CHROMATOGRAPHY

Prepared by:

Osellie Salvador, ESAT Region 9, ICF Consulting — Date

Review by:

Richard Bauer, Chemistry Team Leader — Date

Approved by:

Brenda Bettencourt, Laboratory Director — Date

Periodic Review:

Signature	Title	Date

STANDARD OPERATING PROCEDURE 531

ANALYSIS OF PERCHLORATE BY ION CHROMATOGRAPHY

This SOP was prepared by ICF Consulting for the United States Environmental Protection Agency (USEPA) under the Environmental Services Assistance Team (ESAT) contract (EPA contract No. 68-W-01-028).

APPROVED BY:

Osellie Salvador, Inorganic Group Leader	Date
Surender Kaushik, QA Task Manager	Date
Jerry Vail, ESAT Program Manager	Date

ESAT Document Control Number: B01010000-0073

CONTENTS

1 SCOPE AND APPLICATION 4

2 METHOD SUMMARY 4

3 DEFINITIONS 4

4 HEALTH AND SAFETY 7

5 SAMPLE HANDLING AND PRESERVATION 7

6 INTERFERENCES 7

7 APPARATUS AND MATERIALS 8

8 QUALITY CONTROL PROCEDURES 11

9 ANALYTICAL PROCEDURES 18

10 DOCUMENTATION 22

11 REFERENCES 23

Attachment A - Deviations from Reference Method (EPA 314.0)

Attachment B - Inorganic Standards and Reagents Preparation Log Book

Attachment C - Ion Chromatography Run Log for Dionex 600

Attachment D - Analytical Spreadsheet

Attachment E - QC Summary Report

1 SCOPE AND APPLICATION

1.1 This method covers the determination of perchlorate in reagent water, surface water, ground water, and drinking 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.

1.2 The Region 9 Laboratory quantitation limit (QL) for perchlorate is 5.0 *u*g/L.

2 METHOD SUMMARY

2.1 A 1.0 mL volume of sample is injected onto 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 exchanger where it is converted to the highly conductive acid form. The sodium hydroxide eluent is converted to weakly conductive acid. The separated anion in its acid form is detected by electrical conductivity and is determined on the basis of retention time as compared to the external standards. Quantitation is based on peak areas and a quad calibration curve is used to determine concentrations in environmental samples.

3 DEFINITIONS

3.1 Analytical Sample - Any sample in which perchlorate is being determined, excluding standards and calibration blanks.

3.2 Calibration Blank (CB) - A volume of reagent water analyzed immediately after an IPC to check the stability of the baseline.

3.3 Calibration Standard (CAL) - A solution prepared from the stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.4 Field Duplicates (FD) - Two separate samples collected at the same time and placed 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.

3.5 Field Reagent Blank (FRB) - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical

procedures. The purpose of the FRB is to determine if contamination is occurring in the field environment. Note: Field reagent blanks cannot be used for LD or LFM analyses.

3.6 Instrument Performance Check Solution (IPC) - A solution of perchlorate used to evaluate the performance of the instrument system with respect to a defined set of criteria. For this method, the initial IPC has been combined with the QCS (3.15) and analyzed as a single solution.

3.7 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.

3.8 Laboratory Fortified Blank (LFB) - An aliquot of a characterized matrix with the analytes of interest, or alternatively, an aliquot of blank matrix to which known quantities of the elements of interest are added in the laboratory. The LFB 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.

3.9 Laboratory Fortified Sample Matrix (LFM) - An aliquot of an analytical sample to which known quantities of perchlorate is added in the laboratory. The LFM 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 analyte in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 Laboratory Fortified Matrix Duplicate (LFMD) - A duplicate aliquot of an analytical sample to which known quantities of perchlorate is added in the laboratory. The LFMD 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 concentrations of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.11 Laboratory Reagent Blank (LRB) - An aliquot of reagent water or other blank matrix 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.

3.12 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 (uS/cm) or microMhos/cm (uMhos/cm) which are considered equivalent terms.

3.13 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.

3.14 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.

3.15 Quality Control Sample (QCS) - A solution of perchlorate 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 laboratory performance with externally prepared test materials. For this method, the QCS has been combined with the IPC (3.6) and analyzed as a single solution.

3.16 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. Region 9 laboratory currently has a QL of 5 g/L.

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

3.18 Stock Standard Solution (SSS) - A concentrated solution containing perchlorate prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.19 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

4 HEALTH AND SAFETY

4.1 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 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Specifically, sodium hydroxide is moderately toxic and extremely irritating to skin and mucus membranes. Use this reagent in a fume hood whenever possible and if eye or skin contact occurs, flush with large amounts of water for at least 15 minutes.

Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing when working with these reagents.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis and minimize waste disposal.

5.2 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 Samples must be received and stored at 4 ±2 C. Any deviations from the 4 ±2 C temperature requirements must be noted in the report narrative.

5.4 Holding Time - The recommended sample holding time for perchlorate is 28 days.

6 INTERFERENCES

6.1 Method 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.

6.2 Interferences can be divided into three different categories: direct chromatographic coelution, where an analyte response is observed at very nearly the same retention time as the target anion; concentration dependant coelution, 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, 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's retention times.

6.2.1 A direct chromatographic coelution may be solved by changing columns, eluent strength, modifying the eluent with organic solvents (if compatible with IC columns), changing the detection systems, or selective removal of the interference with pretreatment. Sample dilution will have little or no effect.

6.2.2 Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependant coelution or ionic character displacement, but it must be clarified that sample dilution will alter the reported quantitation limit (QL) by a proportion equivalent to that of the dilution.

6.3 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. These common anion levels can be indirectly assessed by monitoring the conductivity of the matrix. Consequently, all sample matrices must be monitored for conductivity (Section 9.3) prior to analysis. When laboratory determined Matrix Conductivity Threshold (MCT) is exceeded, procedures incorporating sample dilution must be performed as specified in Section 9.3.7.

6.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

7 APPARATUS AND MATERIALS

7.1 Apparatus

7.1.1 Dionex Ion Chromatograph System - Includes the Advance Chromatography Module, Gradient Pump, Eluent Degas Module, an Auto-Regen System that includes a Pump, Anion Cartridge and a Regenerant Reservoir, Conductivity Cell Detector, Dionex Advance Computer Interface and Dionex DX-600 Data Chromatography Software.
7.1.2 Dionex Autosampler.
7.1.3 Anion Guard Column - Dionex IonPac AG16 4-mm (10-32), or equivalent.
7.1.4 Anion Separator Column - Dionex IonPac AS16 4-mm(10-32), or equivalent.
7.1.5 EG40 Eluent Generator using Dionex EluGenCartridge (Potassium Hydroxide), or equivalent.
7.1.6 Analytical Balance - capable of weighing accurately to ±0.0001 g.
7.1.7 Class "S" weights.
7.1.8 Stirrer Plate and stirring bars.
7.1.9 Disposable Syringe Filters, 0.20 micron and 0.45 micron.
7.1.10 10 mL Disposable Syringes with luer-lock fittings.
7.1.11 Dionex Polyvials, 5 mL capacity with filter caps (Dionex P/N 38141).
7.1.12 Drying oven, capable of being controlled at 105 ± 5 C.
7.1.13 Desiccator.
7.1.14 An Eppendorf air-displacement pipetter capable of delivering volumes ranging from 100 to 2500 uL with an assortment of high quality disposable pipet tips, or equivalent.
7.1.15 Conductivity bridge, range 1 to 200,000 umhos per centimeter with automated temperature compensation (VWR Model EC 2052 Catalog No. 23198-013 or equivalent).
7.1.16 Conductivity cell, cell constant 1.0 or micro dipping type cell with 1.0 constant (VWR Catalog No. 23198-020 or equivalent).

7.2 Glassware and Incidentals

7.2.1 Volumetric Class "A" Flasks - 2000 mL, 1000 mL, 500 mL, 250 mL and 100 mL.
7.2.2 Volumetric Class "A" Pipettes - 50 mL, 25 mL, 10 mL and 5 mL.
7.2.3 Plastic or Teflon spray bottle.
7.2.4 Porcelain evaporating dish, 150-mL volume.

7.3 Materials and Reagents

Reagents may contain impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society (ACS) specifications should be used. If the purity of a reagent is in question, analyze for contamination. Record all standard and reagent preparations in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.3.1 Reagent water - All references to reagent water in this method refer to ASTM Type II grade water, ASTM D1193.
7.3.2 Degassed reagent water - Reagent water that has been purged with helium for 2 minutes.
7.3.3 Potassium Perchlorate ($KClO_4$), reagent grade.
7.3.4 Sulfuric Acid (H_2SO_4), concentrated, reagent grade.
7.3.5 Sodium Hydroxide (NaOH, (CASRN) 1310-73-2), reagent grade.
7.3.6 Sodium Chloride (NaCl, CASRN [7647-14-5]), reagent grade.
7.3.7 Sodium Sulfate (Na_2SO_4, CASRN [7757-82-6]), reagent grade.
7.3.8 Sodium Carbonate (Na_2CO_3, CASRN [497-19-8]), reagent grade.
7.3.9 Conductivity Solution - Purchase a 1000 *u*mhos/cm solution from a reputable vendor (VWR Brand Catalog No. 23226-603 or equivalent).
7.3.10 Gases
7.3.10.1 Helium, Ultra high purity (UHP).
7.3.10.2 Nitrogen, Ultra high purity (UHP).

7.4 Preparation of Solutions and Standards

Record all standard and reagent preparations in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.4.1 Eluent Solutions

7.4.1.1 Reagent water (Section 7.3.1).

7.4.2 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 1 month when stored at 4°C.

7.4.2.1 1000 mg/L Perchlorate Stock Standard - Prepare by dissolving 0.1393 g $KClO_4$ in reagent water and dilute to volume in a 100-mL volumetric flask. Alternatively, a 1000 mg/L stock standard solution may be purchased from a reputable supplier such as SPEX, E.R.A. or Inorganic Ventures.

7.4.2.2 10 mg/L Intermediate standard perchlorate solution. Pipet 1.0 mL of the perchlorate stock standard solution (7.4.2.1) into a 100-mLvolumetric flask and dilute to volume with reagent water. Prepare fresh daily.

7.4.2.3 Calibration Standard 5: 100 *ug*/L perchlorate standard - Pipet 1.0 mL of intermediate standard (7.4.2.2) into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily.

7.4.2.4 Calibration Standard 4: 50 *ug*/L perchlorate standard - Pipet 0.5 mL of intermediate standard (7.4.2.2) into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily. This calibration standard will also be analyzed as the continuing IPC.

7.4.2.5 Calibration Standard 3: 25 *ug*/L perchlorate standard - Pipet 0.25 mL of intermediate standard (7.4.2.2) into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily.

7.4.2.6 Calibration Standard 2: 10 *ug*/L perchlorate standard - Pipet 10.0 mL of Calibration Standard 5 (7.4.2.3) into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily.

7.4.2.7 Calibration Standard 1: 5 *ug*/L perchlorate standard - Pipet 5.0 mL of Calibration Standard 5 (7.4.2.3) into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily. This calibration standard will also be analyzed as the QL sample at the beginning of the analytical run (after the IPC/QCS/LFB and initial CB have been analyzed).

7.4.3 IPC/QCS/LFB Standard: The IPC/QCS/LFB is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials. The Region 9 laboratory uses a custom solution from E.R.A. (part #: Perchlorate) containing 1000 *ug*/L perchlorate. A 45 *ug*/L IPC/QCS/LFB standard is prepared by pipetting 4.5 mL of the 1000 *ug*/L IPC/QCS stock standard into a 100-mL volumetric flask and diluting to volume with reagent water. Prepare fresh daily.

7.4.4 Regenerant Solution

7.4.4.1 A regenerant solution of 50 mN H_2SO_4 is prepared by adding 5.6 mL of concentrated H_2SO_4 to approximately 4000 mL of reagent water and bringing to final volume in a 4-L volumetric flask.

7.4.5 Mixed Common Anion 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.

7.4.5.1 Dissolve the following salts in reagent water to a final volume of 25 mL:
1.0 g sodium chloride (Section 7.3.6) = 0.61 g Cl
0.93 g sodium sulfate (Section 7.3.7) = 0.63 g SO4
1.1 g sodium carbonate (Section 7.3.8) = 0.62 g CO3

8 QUALITY CONTROL PROCEDURES

8.1 EPA Region 9 Laboratory operates a formal quality control (QC) program. As it relates to this SOP, the QC program consists of an initial 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.

8.2 Initial Demonstration of Proficiency - Prior to use in routine analysis, each analyst must perform the procedures noted in Region 9 Laboratory SOP 880.

8.2.1 Matrix Conductivity Threshold (MCT)- The MCT is an individual laboratory defined value which must be determined by preparing a series of sequentially increasing, common anion fortified, reagent water samples each contain a constant percholorate concentration. Initially, a reagent water prepared LFB, containing no common anions, must be analyzed which contains perchlorate at a suggested concentration of 25 *ug*/L perchlorate. Next, the series of sequentially increasing anionic solutions are prepared, each containing perchlorate at a suggested concentration of 25 *ug*/L, which also containing 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. A concentration of 25 *ug*/L perchlorate has been suggested assuming the QL has been set at 5.0 *ug*/L. If a laboratory's QL is higher, choose a perchlorate concentration for this exercise at approximately 5 times that QL.

8.2.1.1 Prepare the mixed common anion stock solution (see Section 7.4.5) containing chloride, sulfate and carbonate, each at 25 mg/mL.

8.2.1.2 Prepare the LFB at suggested perchlorate concentration of 25 *ug*/L by diluting 0.625 mL of the 1000 *ug*/L perchlorate standard to a final volume of 25 mL.

8.2.1.3 Next, 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 (Section 7.4.5) into separate 25 mL volumetric flasks. Next, add 0.625 mL of the 1000 *u*g/L perchlorate standard to each 25 mL volumetric flask and dilute to volume with reagent water to yield a final perchlorate concentration of 25 *u*g/L.

8.2.1.4 Measure and record the conductance of each of these prepared solutions on a calibrate conductivity meter (This meter must be calibrated as described in Section 9.3 prior to measuring conductance). To use as a relative reference conductance, the 400 mg/L mixed anion sample, which contains chloride at 400 mg/L, sulfate at 400 mg/L and carbonate at 400 mg/L, should display a conductance of between 3200 uS/cm and 3700 uS/cm.

8.2.1.5 Analyze each solution, recording the peak area to height (A/H) ratio and the quantified concentration of perchlorate. In many data acquisition and instrument control software, the peak area to height ratio is a definable parameter which can be specified for printout on the analysis report.

8.2.1.6 Both the A/H ratio and quantified perchlorate concentration for the LFB and the 200 mg/L mixed common anion solution should be reproducibly consistent but as the common anion levels increase, the A/H ratio will aso begin to increase as the peak height is distorted and reduced. As the peak is distorted, the area will also eventually begin to be distorted and the quantitated concentration will be reduced, but this is typically secondary, with the ratio of peak area to height initially prediction this pending quantitation problem.

8.2.1.7 Calculate the A/H ratio percent difference ($PD_{A/H}$) between the average A/H ratio for the LFB (A/H_{LFB}) and the average A/H ratios for each mixed common anion solutions (A/H_{MA}) using the following equation:

$$PD\ A/H = |(A/H_{LFB} - A/H_{MA})| / A/H_{LFB} * 100$$

8.2.1.8 As the conductivity of the matrices increase, the $PD_{A/H}$ will increase. The MCT is the matrix conductance where the $PD_{A/H}$ exceeds 20%. To derive the MCT, perform a linear regression on these data by plotting $PD_{A/H}$ (as the independent variable, x) versus the matrix conductance (as the dependent variable, y). The resulting regression data should yield an r2 value of > 0.95. Record the "constant" (intercept value) and the "X-coefficient" (slope) and calulate the MCT as follows,

MCT = (20%) x (X-coefficient) + (constant)

NOTE: Be careful to consistently apply percentages as either whole numbers or as fractional values (20%=0.20) for both the regression analysis and MCT calculation.

8.2.1.9 As an alternate to the regression analysis, the laboratory can choose to establish their MCT at the conductance level of the highest mixed anion solution which yielded a $PD_{A/H}$ value below the 20% threshold.

8.2.1.10 As a final procedure, the laboratory should confirm their perchlorate QL in a mixed common anion solution which reflects a conductance near (within +/- 10%) that specified as the MCT. This solution must contain perchlorate, at the laboratory determined 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 +/-10% of the MCT and followin gthe analysis, the recovered perchlorate must be between 70-130% of the QL concentration. If the QL recovery fails this criteria, the MCT should be lowered by 10% and this MRL verification must be repeated.

8.2.1.10 Prior to conducting any field sample analysis, the conductivity of that matrix must be determined. When the conductance of a field sample is above the MCT, sample dilution or pretreatment must be performed.

8.3 Routine Analytical Quality Control

8.3.1 Calibrate the instrument using the standards prepared in Section 7.4.2. Check the correlation coefficient (r); the correlation coefficient of the curve must be $\geq$0.995 or the instrument must be re-calibrated. All five standards must be used when determining the correlation coefficient. The software cannot handle a blank as a standard; analyze a blank immediately after the calibration but before the IPC/QCS/LFB. The blank must be less than ½ the QL or the instrument re-calibrated.

8.3.2 IPC/QCS/LFB and IPC - The accuracy and stability of the calibration shall be verified by the initial analysis of an IPC/QCS/LFB standard and the continued analysis of an IPC standard. The IPC/QCS/LFB (true value of 45 *ug*/L) standard must be from a source external to the calibration standards. It must be analyzed at the beginning of the analytical run. The IPC (true value of 50 *ug*/L) standard must be analyzed after every 10 samples and at the end of the analytical run. The recovery of perchlorate in the IPC/QCS/LFB and IPC is calculated as follows:

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

Where

%R = percent recovery of the standard.

M = measured concentration of perchlorate in the IPC/QCS/LFB or IPC, *u*g/L.
T = true concentration of perchlorate in the IPC/QCS/LFB or IPC, *u*g/L.

If the IPC/QCS/LFB or IPC recoveries exceeds the limits of 90-110%, the analysis shall be terminated. The cause of the poor recovery must be determined and the problem corrected. The instrument must be re-calibrated and all samples not bracketed by acceptable IPC/QCS/LFB and IPC results must be re-analyzed.

8.3.3 CB - The stability of the baseline must be monitored by analyzing a CB immediately after the IPC/QCS/LFB standard and every IPC standard. If the absolute value of the CB result is less than or equal to the QL, the result is acceptable. If the absolute value of the CB result exceeds the QL, the analysis must be terminated. 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. If no preparation steps were required, the initial CB can also be used as the LRB.

8.3.4 Quantitation Limit (QL) - To verify the ability to detect perchlorate near the QL, a QL standard must be analyzed at the QL level (Section 1.2) at the beginning of the analytical run but not before the IPC/QCS/LFB. The QL standard has a true value of 5 *u*g/L. The recovery of perchlorate in the QL is calculated as follows:

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

Where

%R = percent recovery of the standard.
M = measured concentration of perchlorate in the QL, *u*g/L.
T = true concentration of perchlorate in the QL, *u*g/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. The instrument must be re-calibrated and all samples analyzed after the out-of-control QL standard must be re-analyzed. If, after re-calibration, the QL recovery still exceeds the 70-130% limits, the calibration standards must be re-prepared and the instrument re-calibrated.

8.3.5 LRB - The laboratory must analyze at least one LRB daily or with each batch of 20 or fewer samples of the same matrix, whichever is more frequent. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the QL indicate potential

laboratory contamination. If the potential contamination significantly impacts the analytical results, the LRB must be re-prepared along with the affected samples, and re-analyzed. Unless specified otherwise by project DQOs, the following statements describe when samples must be re-prepared and re-analyzed:

1) If the sample concentration is less than or equal to 5 times the QL and the LRB concentration is greater than the QL, the LRB and sample must be re-prepared and re-analyzed.

Note: Most analytical samples will not require any preparation and thus the initial CB can be used as the LRB. An exception to this would be for any samples which are turbid or which contain any solid material which may clog the filter cap on the polyvial. These samples will require filtration through a syringe filter prior to transferring to the polyvial for analysis. A LRB MUST also be filtered through a syringe filter prior to transferring to the polyvial for analysis to determine if there is contamination from the syringe filter.

8.3.6 LFB - Region 9 laboratory uses the QCS (45 *ug*/L perchorate) as the LFB; the QCS and LFB would be the from the same source and are also analyzed as the initial IPC. No preparation step is required.

8.3.7 LD - Sample homogeneity can affect the quality and interpretation of the data. LD results can be used to assess sample homogeneity. Laboratory duplicates are only to be analyzed when the level of perchlorate in the QC sample is greater than 4 times the added 25 *ug*/L LFM/LFMD spike.

One LD must be prepared for every 10 routine samples of the same matrix in a sample batch (e.g., 1 LD for a batch containing 1-10 routine samples, 2 LDs for a batch containing 11-20 routine samples, etc.). Shake 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 perchlorate in the LD, corrected for any dilutions *ug*/L.
C	=	measured perchlorate in the routine sample, corrected for any dilutions, *ug*/L.

The relative percent difference (RPD) for perchlorate must be ≤20% for samples. The absolute difference between the sample and duplicate results must be less than the quantitation limit for samples with perchlorate concentrations less than 5 times the quantitation limit. If the control limits are exceeded, the perchlorate result must be flagged as estimated (J) on the analytical spreadsheet and a comment added on the spreadsheet and report narrative informing the data user that sample imprecision may be present in samples of similar composition.

8.3.8 LFM - Sample homogeneity and the chemical nature of the sample matrix can affect perchlorate recovery and the quality of the data. LFM results can be used to assess these matrix effects and potential impact to data usability. One LFM must be prepared for every 10 routine samples of the same matrix in a sample batch (e.g., 1 LFM for a batch containing 1-10 routine samples, 2 LFMs for a batch containing 11-20 routine samples, etc.). The LFM must be spiked at two levels, 5 *ug*/L and 25 *ug*/L. Calculate the percent recovery for perchlorate using the following equation:

$$\%R = \frac{C_{lfm} - C}{s} \times 100$$

Where

$\%R$	=	percent recovery.
C_{lfm}	=	measured concentration in the LFM corrected for sample preparation and any dilutions, g/L.
C	=	measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions, g/L.
s	=	expected analyte concentration in the LFM, corrected for sample preparation and any dilutions, g/L.

If the value of ***C*** is less than 4 times the value of ***s***, the acceptance window for ***%R*** is 70-130%. If the recovery of analyte falls outside the acceptance window other QC data must be examined to determine if a matrix problem exists. If the laboratory performance is in control (i.e., the IPC, IPC/QCS/LFB and QL results are acceptable), the poor LFM recovery is most likely matrix-related. The affected analyte result must be flagged as estimated (J) on the analytical spreadsheet and a comment added on the spreadsheet and report narrative informing the data user that matrix effects may be present in samples of similar composition.

8.3.9 LFMD - Sample homogeneity can affect the quality and interpretation of the data. LFMD results can be used to assess sample homogeneity. One LFMD must be prepared for every 10 routine samples of the same matrix in a sample batch (e.g., 1 LFMD for a batch containing 1-10 routine samples, 2 LFMDs for a batch containing 11-20 routine samples, etc.). The LFMD must be spiked at two levels, 5 *ug*/L and 25 *ug*/L. Calculate the relative percent difference using the following equation:

$$\%RPD = \frac{|Clfmd - Clfm|}{(Clfmd + Clfm)/2} \times 100$$

Where

$\%RPD$ = relative percent difference.

C_{lfm} = measured concentration in the LFM corrected for sample preparation and any dilutions, g/L.

C_{lfmd} = measured concentration in the LFMD corrected for sample preparation and any dilutions, g/L.

If the recovery of analyte falls outside the acceptance window other QC data must be examined to determine if a matrix problem exists. If the laboratory performance is in control (i.e., the IPC, IPC/QCS/LFB and QL results are acceptable), the poor LFMD recovery is most likely matrix-related. The affected analyte result must be flagged as estimated (J) on the analytical spreadsheet and a comment added on the spreadsheet and report narrative informing the data user that matrix effects may be present in samples of similar composition.
The relative percent difference (RPD) between the LFM and LFMD must be $\leq$20%. If the control limits are exceeded, the affected analyte result must be flagged as estimated (J) on the analytical spreadsheet and a comment added on the spreadsheet and report narrative informing the data user that sample imprecision may be present in samples of similar composition. is suspect due to a matrix effect.

9 ANALYTICAL PROCEDURES

9.1 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.
Typical operating settings for the Dionex DX600 are as follows:

DX600 Detector Parameters

Detector Type: Conductivity
Data Collection time (minutes): 11.50
Data Collection Rate: 1.00
Real time plot scale maximun (uS): 6.000
Real time plot scale minimum (uS): -2.000

DX600 Integration Parameters

Peak detection algorithm: Standard
Starting peak width (seconds):10.00
Peak threshold: 1.00
Peak area reject (area counts): 0.003[Signal]*min

DX600 Smoothing Parameters

Filter Type: No filter

DX600 Integration Data Events

Time	Description
0.00	Inhibit integration On
0.00	Minimum Area 0.003[Signal]*min
7.50	Inhibit integration Off

DX600 Calibration Parameters

External or internal calibration: EXTERNAL
Number of replicates for calibration:1
Rejection: Manual
Level Weighting: Equal
Sample Loop: 740 *u*L
Calibration standard volume: 1.00 mL
Default sample volume: 1.00 mL
Amount units: *u*g/L
Replace retention time: Yes
Update response: Yes
Default dilution factor: 1.00
Default response factor for unknown peaks:0.00
Calculate unknowns by area or height: Area
Flow: 1 mL/min.

9.2 Initial Calibration

9.2.1 An initial calibration is performed by analysis of a blank and five standards of increasing perchlorate concentration (5.0, 10.0, 25.0, 50.0 and 100.0 *u*g/L) with cubic fit. All standards must be used in the calibration. The correlation coefficient for the initial calibration must be $\geq$ 0.995 AND the blank must be less than ½ the QL AND the IPC/QCS/LFB standard analyzed immediately after the calibration must be within 90-110% of the true value for the calibration to be valid. If the calibration does not meet the criteria, the analysis shall be terminated, the problem corrected, and

a new calibration curve performed. In addition, an initial calibration must be performed monthly, when new standards are used, when any instrument parameters have been changed or if any IPC/QCS/LFB is outside the 90-110% method QC limits

9.2.2 The QC samples in Section 8.3 must be analyzed and must be within the appropriate control limits before sample analyses are performed.

9.3 Conductivity Check

9.3.1 Allow samples and standards to reach room temperature. The EC Model 2052 is designed to compensate for temperatures in the 5 to 45°C range but the readings will be most accurate near 25°C. Turn the conductivity meter knob to the "ATC" position. Allow the meter to warm up for 2-3 minutes.

9.3.2 Fill a porcelain dish with standard potassium chloride solution (9.3.9) 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.

9.3.3 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".

9.3.4 Read the displayed conductance. Record the specific conductance in the Ion Chromatography Run Log for Dionex 600. The units are determined by the range switch.

9.3.5 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 continue with section 9.7, but then return to section 9.3 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.

9.3.6 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 rinsings 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.

9.3.7 Determine the specific conductance of all samples using the procedure just described in sections 9.3.1 through 9.3.6, omitting section 9.3.5. Samples which exceed the MCT of 4200 uS/cm must be diluted such that the sample conductivity will be approximately 1000-2000 uS/cm.

9.4 Sample Analysis

9.4.1 Fill a 5mL polyvial with well-mixed sample. Samples which are turbid or which contain solids which may clog the filter cap on the polyvial and damage instrument columns and flow systems require filtration. Dilute samples which exceed the MCT (Section 9.3.7). Attach a 0.45 micron disposable syringe filter to a 10mL disposable syringe; pull out the plunger and pour approximately 10 mL of well-mixed sample into the syringe and reattach the plunger. Apply pressure to the plunger and filter the sample through the syringe filter and into the 5mL polyvial (discard the remaining sample into the waste container and the syringe assembly into a solid waste container). Record any sample filtrations in the comments section of the Ion Chromatography Run Log. (Note - the LRB **must** be filtered if any samples in the batch are filtered.) Attach a filter cap to the 5mL polyvial and push down the filter cap with the supplied tool until it is flush with the top of the polyvial. Label the contents of the polyvial and insert into the autosampler cassette.

9.4.2 Load the autosampler cassettes into the autosampler; the instrument will automatically inject the samples. The sample loop will automatically flushed thoroughly by the instrument program.

9.43 The width of the retention time window used to make identifications is based upon measurements of actual retention time variations of standards over the course of the day.
All chromatograms are reviewed to ensure that the correct peaks are integrated. The retention time windows currently used on the DX600 are listed in the following table:

Parameter	Retention Time (min)	Retention Time Window (min)
Perchlorate	8.67	7.80 - 9.54

9.4.4 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.

An example of a loading list for an analytical run sequence is listed in the table below.

Seq.	Desc.	Seq.	Desc.	Seq.	Desc.	Seq.	Desc.
1	IPC/QCS/ LFB	13	IPC	25	IPC	37	IPC
2	CB/LRB	14	CB	26	CB	38	CB
3	QL	15	S4	27	S14	39	S20
4	IPC	16	S5	28	S14-LFM, 5 *ug*/L	40	IPC
5	CB	17	S6	29	S14-LFMD, 5 *ug*/L	41	CB
6	S1	18	S7	30	S14-LFM, 25 *ug*/L		
7	S1-LFM, 5 *ug*/L	19	S8	31	S14-LFMD, 25 *ug*/L		
8	S1-LFMD, 5 *ug*/L	20	S9	32	S15		
9	S1-LFM, 25 *ug*/L	21	S10	33	S16		
10	S1-LFMD, 25 *ug*/L	22	S11	34	S17		
11	S2	23	S12	35	S18		
12	S3	24	S13	36	S19		

9.5 Data Reduction and Reporting

9.5.1 Data for aqueous samples should be reported in units of *u*g/L using the following calculation:

$$C = M \times D$$

where:

C	=	final reported concentration, in *u*g/L.
M	=	measured concentration reported by software, in *u*g/L.
D	=	sample analysis dilution factor, to account for any dilution.

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 ½ the QL. Values between ½ 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.

9.5.2 The data must be reviewed for correctness and completeness by a chemist other than the analyst. The reviewer must check that the correlation coefficient of the calibration curve is >0.995 and that all sample and standard criteria are within the method QC limits. The reviewer must check the run log for completeness (i.e. standard information present and all sample ID's correct and legible). The reviewer must then sign their name at the bottom of the run log in the space set aside for the reviewer's signature.

9.5.3 There may be occasion where the chromatography software integrates the peak baseline in a manner which may produce an inconsistent value. Manual chromatographic integration is then used to accurately produce a correct baseline. Any manual chromatographic integration must be initialed and dated by the analyst, noted in the Ion Chromatography Run Log for Dionex 600 and approved by the ESAT task leader, ESAT QA/QC director or ESAT team manager the same day the manual integration was performed (Reference 11.7)

10 DOCUMENTATION

10.1 Raw Data

10.1.1 Ion Chromatography Run Log for Dionex 600 - Entries are made for the case number, SDG number, data file name, schedule file name, date of analysis, calibration standard IDs, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any. An entry is made for any sample that required manual integration in the "M" column. The Ion Chromatography Run Log for Dionex 600 is maintained in Room 207. (Attachment C)

10.1.2 Inorganic Standards and Reagents Preparation Log Book - Copies of all standard solution preparation entries (CAL, IPC, QL, LFB, LFM, QCS, etc.) must be submitted with each data package. (Attachment B)

10.1.3 Chromatograms and Quantitation Reports - The chromatograms must be scaled such that the baseline used for measuring the peak is visible.

10.2 Report Narrative and Deliverable

The data package consists of the report narrative, reports, and data, as listed in the table below.

Data Package Contents
Report Narrative: Discusses any problems encountered, both technical and administrative, the corrective action taken, and the resolution. All universal analytical flags should also be discussed in the report narrative.
Tabulated sample results on an analytical spreadsheet, with units, sample collection dates, client sample IDs, laboratory IDs and station locations. (Attachment D)
LRB data included on the analytical spreadsheet. (Attachment D)
Duplicate or LFM/LFMD results on a QC summary report with calculated relative percent difference (RPD). (Attachment E)
QCS/LFB, LFM and LFMD results on a QC summary report with calculated percent recoveries (%R). (Attachment E)
Raw sample, standard and QC data, including run logs and any work sheets, if applicable. (Attachments B & C)

11 REFERENCES

11.1 EPA Method 314.0, Determination of Perchlorate in Drinking Water Using Ion Chromatography, Environmental Monitoring Systems Laboratory, Revision 2.1, August 1993.
11.2 Dionex DX-600 Operation and Maintenance Manual, Dionex Corp., Sunnyvale, California 94086, 1999.
11.3 Record 269, Dionex Chromatography Database 4.2.0, Dionex Corp., Sunnyvale, California 94086.
11.4 Region 9 SOP 110, *Sample Receipt, Log-in and Storage.*
11.5 Region 9 SOP 125, *Sample Disposal.*
11.6 Region 9 SOP 130, *Glassware Cleaning Procedures.*
11.7 Region 9 SOP 835, *Chromatographic Integration Procedures.*
11.8 Region 9 SOP 840, *Notebook Documentation and Control.*
11.9 Region 9 SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency.*

Attachment A
Deviations From Reference Method (EPA 314.0)

A.1 This SOP specifies the use of quadratic regression calibration. Review of instrument response using various calibration protocols demonstrates that instrument response is not linear at low concentrations but that the data fit quad calibration model very well. Using these calibration protocols has resulted in acceptable performance evaluation samples from a variety of sources. Additionally, the SOP requires the analysis of a standard at the QL on a daily basis to verify instrument performance and calibration.

A.2 Sample pretreatment will not be performed.

Appendix B-5
Hexavalent Chromium

- **Method 218.6–Hexavalent Chromium**

This method addresses the determination of hexavalent chromium in water at low levels by use of ion exchange chromatography.

The sample is pumped through three different ion exchange columns and into a conductivity detector. The first two columns, a pre-column (guard) column and a separator column, are packed with a low-capacity, strongly basic anion exchanger. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The last column is a suppressor column that reduces the anions in the sample to their corresponding acids. The separated anions in their acid form are measured using an electrical-conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

RLs are listed in Table--1. The calibration, QC, and corrective action, requirements are given in Tables --2and -3

Table---1. RLs for Method

		Water			
Parameter/Method	**Analyte**	**RL**	**Unit**		
Hexavalent Chromium/218.6	Hexavalent Chromium	0.1	ug/ L		

Table .-2. QC Acceptance Criteria for Method 218.6

Method	**Analyte**	**Accuracy Water (% R)**	**Precision Water (% RPD)**		
218.6	Hexavalent Chromium	70-140	≤30		

Table 3. Summary of Calibration and QC Procedures for Method 218.6

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
218.6	Hexavalent Chromium	Five point	Initial calibration prior to sample analysis	R^2>0.999	Correct problem then continue
		Second source calibration	Once per five point calibration	± 10%	Correct problem then repeat
		Retention time window calculated	Each initial calibration and calibration verification	± 0.5 min.	Correct problem then repeat
		Initial calibration verification	Every 20 samples	Within ± 10% of expected value	Correct problem then repeat
		Calibration verification	After every 20 samples	Within ± 10% of expected value	Correct problem then repeat
		Laboratory control standard	Every 20 samples	70-140%	Correct problem then repeat
		Method Blank	Every 20 samples	No analyte detected ≥ RL	Find problem, repeat
		MS/MSD or Dup/MS	Every 20 samples	70-140%recovery 30%RPD	Find problem, repeat or explain
		MDL Study	Every 12 months	None (0.1ug/l needed)	None

Appendix B-6
TAL Metals (field filtered)

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 505

DETERMINATION OF TRACE ELEMENTS IN WATER BY INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETRY

Prepared by:		
	Stephen Carroll, ESAT Region 9, ICF Consulting	Date
Review by:		
	Richard Bauer, Chemistry Team Leader	Date
Approved by:		
	Brenda Bettencourt, Laboratory Director	Date

Periodic Review:

Signature	Title	Date

STANDARD OPERATING PROCEDURE 505

DETERMINATION OF TRACE ELEMENTS IN WATER BY INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETRY

This SOP was prepared by ICF Consulting for the United States Environmental Protection Agency (USEPA) under the Environmental Services Assistance Team (ESAT) contract (EPA contract No. 68-W-01-028).

APPROVED BY:

Osellie Salvador, Inorganic Group Leader	Date
Surender Kaushik, QA Task Manager	Date
Jerry Vail, ESAT Program Manager	Date

ESAT Document Control Number: B0101029-0484

CONTENTS

1 SCOPE AND APPLICATION 4

2 METHOD SUMMARY 5

3 DEFINITIONS 6

4 HEALTH AND SAFETY 8

5 SAMPLE HANDLING AND PRESERVATION 8

6 INTERFERENCES 9

7 APPARATUS AND MATERIALS 11

8 QUALITY CONTROL PROCEDURES 13

9 ANALYTICAL PROCEDURES 18

10 DOCUMENTATION 21

11 REFERENCES 22

Table 1: Method Analytes and Interfering Elements 23

Table 2: Calibration Standard Concentration 24

Table 3: IPC, QCS, LFB/LFM/LFMD Concentrations 25

Attachment A - Deviations from Reference Method
Attachment B - Inorganic Standards and Reagents Preparation Log Book
Attachment C - MET-1 TJA ICAP 61E Run Log
Attachment D - Analytical Spreadsheet
Attachment E - QC Summary Report

1 SCOPE AND APPLICATION

1.1 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. It is applicable to water and wastewater. This SOP is based on EPA Method 200.7, Rev. 4.4 (May 1994) and is applicable to the determination of the following elements:

Analyte	Chemical Abstract Services Registry Number (CASRN)	Region 9 Laboratory Quantitation Limits (*ug*/L)
Aluminum (Al)	7429-90-5	200
Antimony (Sb)	7440-36-0	100
Arsenic (As)	7440-38-2	250
Barium (Ba)	7440-39-3	50
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	20
Copper (Cu)	7440-50-8	20
Iron (Fe)	7439-89-6	100
Lead (Pb)	7439-92-1	150
Magnesium (Mg)	7439-95-4	500
Manganese (Mn)	7439-96-5	10
Molybdenum (Mo)	7439-98-7	50
Nickel (Ni)	7440-02-0	50
Potassium (K)	7723-14-0	5000
Selenium (Se)	7782-49-2	250
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	500
Tin (Sn)	7440-31-5	100
Titanium (Ti)	7440-32-6	10
Vanadium (V)	7440-62-2	20
Zinc (Zn)	7440-66-6	20

1.2 Dissolved elements are determined after suitable filtration and acid preservation. In order to reduce potential interferences, dissolved solids should not exceed 0.2% (w/v).

1.3 Where this method is approved for the determination of metal and metalloid contaminants in drinking water, samples are analyzed directly by pneumatic nebulization without acid digestion if the samples have been properly acid-preserved and have turbidity of < 1 NTU at the time of analysis. This total recoverable determination procedure is referred to as "direct analysis". Note the exception for silver discussed in Section 1.6.

1.4 For the determination of total recoverable analytes in aqueous samples containing particulate and suspended solids a digestion step is required prior to analysis. Aqueous samples containing suspended or particulate material $\geq$ 1% should be digested as a solid sample (Region 9 Laboratory SOP 405).

1.5 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.

1.6 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, succeeding smaller volume, well mixed sample aliquots must be digested until the analysis solution contains < 0.1 mg/L silver.

1.7 The total recoverable sample digestion procedure given in Region 9 Laboratory 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.

2 METHOD SUMMARY

2.1 An aliquot of a well-mixed, homogeneous aqueous sample is accurately measured for sample processing. For total recoverable analysis of an aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. After cooling, the sample is made up to volume, mixed and allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered aqueous sample aliquot, or for the "direct analysis"

total recoverable determination of analytes in drinking water where sample turbidity is <1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then mixed before analysis.

2.2 The method describes the multi-elemental determination of trace elements in aqueous solutions by ICP-AES using a simultaneous instrument. The instrument measures the characteristic atomic-line emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Photo currents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of the analytes. Background must be measured adjacent to the analyte wavelength during analysis.

3 DEFINITIONS

3.1 Analytical Sample - Any solution introduced into the ICP-AES instrument excluding calibration standards, calibration blanks, or instrument performance check samples.

3.2 Calibration Blank (CB) - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP-AES instrument.

3.3 Calibration Standard (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.4 Dissolved Analyte Concentration - The concentration of analyte in an aqueous sample that is filtered through a 0.45- m membrane filter assembly prior to sample acidification.

3.5 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.

3.6 Field Reagent Blank (FRB) - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purposes of the FRB is to determine if method analytes or other interferences are present in the field environment. Note:Field reagent blanks cannot be used for LFM or LFMD analyses

3.7 Instrument Performance Check Solution (IPC) - A solution containing method analytes used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.8 Laboratory Fortified Blank (LFB) - An aliquot of LRB to which known quantities of the method analytes are added. The LFB 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.

3.9 Laboratory Fortified Sample Matrix (LFM) - An aliquot of an environmental sample to which known quantities of the method analytes are added. The LFM is analyzed exactly like a sample. The LFM results are compared to the results for the un-fortified sample to determine whether the sample matrix contributes bias to the analytical results.

3.10 Laboratory Fortified Matrix Duplicate (LFMD) - A duplicate aliquot of an analytical sample to which known quantities of the method analyte is added in the laboratory. The LFMD 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.

3.11 Laboratory Reagent Blank (LRB) - An aliquot of reagent water or other blank matrix 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.

3.12 Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear.

3.13 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.

3.14 Quality Control Sample (QCS) - A solution containing known concentrations of method analytes. The QCS source must be different than the source of calibration standards. It is used to check laboratory or instrument performance.

3.15 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.

3.16 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 interelement spectral interferences with respect to a defined set of method criteria.

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

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

3.19 Total Recoverable Analyte Concentration - The concentration of analyte in either a solid sample or an unfiltered aqueous sample after preparation by acid digestion. Refer to Region 9 Laboratory SOPs 405 and 403 for the sample preparation procedures.

3.20 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 AND SAFETY

4.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Concentrated nitric and hydrochloric acids present various hazards and according to MSDS may be fatal and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large amounts of water for at least 15 minutes or if inhalation occurs, remove to fresh air. ESAT personnel should contact the Group Leader or Health and Safety and Env. 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.

4.2 Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing when working with these reagents. Refer to the Material Safety Data Sheets located in the library and Room 413 for additional information.

4.3 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

4.4 The ICP-AES emits radio-frequency and intense UV radiation. Personnel should not stand near the plasma while the ICP is in operation.

4.5 Areas of high, lethal voltages exist within the instrument. Never touch parts of the instrument which are not intended for access by the instrument operator.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Samples are received at the Region 9 Laboratory by EPA staff in Room 503. Preservation and pretreatment of samples are verified against the chain-of-custody form and analytical request as follows:

5.1.1 Dissolved Analyte Samples: The samples must be filtered through a 0.45- m 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 to pH<2 with (1+1) nitric acid immediately following filtration (normally, 3 mL of (1+1) nitric acid per liter of sample is sufficient).

5.1.2 Aqueous Total Recoverable Analyte Samples: Samples are preserved by acidifying with (1+1) nitric acid to pH<2 (normally, 3 mL of (1+1) 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 sample pH >2, more acid must be added and the sample held for sixteen hours until verified to be pH<2.

5.1.3 Drinking Water Samples: Samples are preserved by acidifying with (1+1) nitric acid to pH<2 (normally, 3 mL of (1+1) 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 <1 NTU, the sample can be analyzed directly without digestion.

5.2 The holding time for properly preserved samples is six months.

6 INTERFERENCES

6.1 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.

6.1.1 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 (interelement or molecular) or adequately corrected to reflect the same change in background intensity that occurs at the wavelength peak.

6.1.2 Spectral overlaps can be compensated for by equations that correct for the inter-element contributions, which involves measuring the interfering elements. When present and uncorrected, these interferences will produce false-positive results and be reported as analyte concentrations.

6.1.3 When interelement corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions. Interelement 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. Interelement 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. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. It should not be forgotten that some samples may contain uncommon elements that could contribute spectral interferences.

6.1.4 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, 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 interelement 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, 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.

6.1.5 When interelement corrections are **not** used, the on-going SIC solutions (Sect. 7.2.13) 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 may not be available for all matrices. In these circumstances the analyte must be determined using another approved test procedure.

6.2 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.

6.3 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.

6.4 Memory Interference - 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.

7 APPARATUS AND MATERIALS

7.1 Apparatus

Note: All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives and isolated from other laboratory glassware. Please refer to Region 9 Laboratory SOP 130, Glassware Cleaning Procedures, for specific instructions (reference 11.2).

7.1.1 ICP-AES System, comprised of following: Thermo Jarrell Ash Inductively Coupled Plasma-Atomic Emission Spectrometer Thermo Jarrell Ash Autosampler
7.1.2 Argon gas supply (high-purity grade, 99.99%)
7.1.3 Analytical balance, with capability to measure to 0.1 mg.
7.1.4 Class "S" weights.
7.1.5 Hot plate, variable temperature, capable of maintaining a temperature of 85 $\pm$5°C.
7.1.6 Pipetters, capable of delivering volumes ranging from 10 to 1000 L, and associated metal-free disposable pipet tips.
7.1.7 Syringe with 0.45um Whatman disk filters.
7.1.8 Glassware - Class A volumetric flasks, graduated cylinders and funnels (glass and/or metal-free plastic).
7.1.9 Class A volumetric pipettes.
7.1.10 150-mL Teflon beakers, 50-mm Teflon watch glasses.
7.1.11 Narrow-mouth storage bottles, LDPE with screw closure, 125-mL to 1-L capacities.
7.1.12 One-piece stem FEP wash bottle with screw closure, 500-mL capacity.

7.2 Materials and Reagents

Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society (ACS) specifications should be used. If the purity of a reagent is in question, analyze for contamination. Record all standard and reagent preparations in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.2.1 Reagent water - All references to water in this method refer to ASTM Type II grade water.

7.2.2 Hydrochloric acid, (HCl) concentrated (sp.gr. 1.19) - trace metals grade or better.

7.2.3 Hydrochloric acid (1+1) - Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

7.2.4 Nitric acid, (HNO_3) concentrated (sp.gr. 1.41) - trace metals grade or better.

7.2.5 Nitric acid (1+1) - Add 500 mL concentrated HNO_3 to 400 mL reagent water and dilute to 1L.

7.2.6 Standard stock solutions (1000 g/mL) can be purchased from a commercial supplier such as Spex or Inorganic Ventures. The list of elements required for this method is provided in Section 1.1.

7.2.7 Calibration Standards - Calibration stock standard solutions are normally purchased from Inorganic Ventures and the final concentrations are listed in Table 2. Each calibration solution is prepared by an appropriate amount of the calibration stock standard to 200 mL with 2% (v/v) nitric acid/2% (v/v) hydrochloric acid.

7.2.8 Calibration Blank (CB) - Dilute concentrated nitric acid and hydrochloric acid with reagent water to obtain a 2% (v/v) nitric acid/2%(v/v) hydrochloric acid solution.

7.2.9 Laboratory Fortified Blank (LFB) and Laboratory Fortified Matrix (LFM) Spiking Solution - Region 9 Laboratory uses Inorganic Ventures Laboratory Fortifying Stock Solutions WW-LFS-1 (contains Al, As, Ba, Be, B, Cd, Ca, Ce, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Sr, Tl, V and Zn) and WW-LFS-2 (contains Sb, Mo,SiO_2, Sn and Ti). The LFB is prepared by spiking 1.0 mL each of the two spiking solutions into 100 mL reagent water and adding the appropriate acids. The LFM and LFMD are prepared by spiking 1.0 mL each of the two spiking solutions into 100 mL of the designated LFM and LFMD samples and adding the appropriate acids. The final concentrations for the LFB and LFM/LFMD are listed in Table 3.

7.2.10 Rinse Blank - Dilute concentrated nitric acid and hydrochloric acid with reagent water to obtain a 2% (v/v) nitric acid/2% (v/v) hydrochloric acid solution.

7.2.11 Instrument Performance Check (IPC) Solution - The IPC solution is used to verify instrument performance during analysis. The IPC is normally purchased from Inorganic Ventures and consists of solution 1, part# WW-IPC-1 (containing Al, As, Ba, Be, B, Cd, Ca, Ce, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Sr, Tl, V and Zn) and solution 2, part# WW-IPC-2 (containing Sb,

Mo, SiO_2, Sn and Ti). The IPC is prepared by adding 5.0 mL each of the two solutions and diluting to 500 mL with 2% (v/v) nitric acid/2% (v/v) hydrochloric acid. The concentrations of the IPC are listed in Table 3.

7.2.12 Quality Control Sample (QCS) - Analysis of a QCS is required for the initial and periodic verification of the calibration standards and instrument performance. The QCS 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 analytes in the QCS solution should be $\geq$ 1 mg/L, except silver, which must be limited to a concentration of 0.5 mg/L for solution stability. A fresh solution should be prepared quarterly or more frequently as needed. The QCS standard is listed in Table 3.

7.2.13 Spectral Interference Check (SIC) solutions - When interelement corrections are applied, SIC solutions are needed containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors. The SIC solutions required are 200 mg/L Al, 300 mg/L Fe, 50 mg/L Ba, 10 mg/L Be, 50 mg/L Cd, 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 Sn, 50 mg/L SIO_2, 50 mg/L Ti, 50 mg/L Tl, 50 mg/L V. The SIC solutions are prepared by diluting the 1000 g/mL single element stock solutions.

7.2.14 Profile Solution - A solution of 10 mg/L copper and manganese is needed to profile the instrument prior to analysis. The solution is made by diluting 5.0 mL each of 1000 g/mL copper and manganese stock standard to 500 mL with 2% (v/v) nitric acid/2% (v/v) hydrochloric acid.

8 QUALITY CONTROL PROCEDURES

8.1 Method Characterization - Prior to routine use of this method, the LDR, MDL and spectral interferences for each analyte were determined for each operating condition, and the average of triplicate analyses of the QCS yielded acceptable results.

8.2 EPA Region 9 Laboratory operates a formal quality control (QC) program. As it relates to this SOP, the QC program consists of an initial demonstration of laboratory and analyst capability (refer to Region 9 Laboratory SOP 880), and the periodic analysis of laboratory solutions as a continuing check on performance.

8.2.1 LDR - 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 1 to 100 times the highest calibration 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 reanalyzed. The LDR should be verified whenever the analytical conditions are changed.

8.2.2 MDL - A method detection limit must be confirmed annually and must be <½ the QL or corrective action must be initiated.

8.2.3 LFB - Analyze a LFB in quadruplicate and take average results to demonstrate initial acceptable performance. The average percent recovery must be ±15%.

8.2.4 SIC - The laboratory must establish and initially verify an interelemental spectral interference correction routine to be used during sample analysis. Criteria for determining an interelement 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 verified annually, or whenever there is a change in instrument operating conditions. Only a portion of the correction routine must be verified more frequently or daily. The test criteria and the solutions are as follows:

8.2.4.1 For interferences from aluminum and iron, only those correction factors (positive or negative) when multiplied by 100 which exceed ± ½ the QL are tested daily.

8.2.4.2 For all other interfering elements, only those correction factors (positive or negative) when multiplied by 10 which exceed ± ½ the QL are tested daily.

8.2.4.3 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interfering solution should fall within a specific concentration range. The range shall be the greater of either (1) ± ½ the QL or (2) a concentration range that is calculated by multiplying 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 redetermined and updated prior to sample analysis.

8.2.4.4 If the nature of the samples analyzed is such that they do not contain concentrations of the interfering elements at the 10 mg/L level, daily verification is not required; however, all interelement spectral correction factors must be verified annually and updated, if necessary.

8.3 Routine Analytical Quality Control

8.3.1 Instrument performance check (IPC) solution - The laboratory must check instrument performance and verify that the instrument is properly calibrated on a continuing basis. To verify calibration, the IPC and the calibration blank are run as routine samples immediately following calibration, after every 10 analytical samples, and at the end of each run. For each analyte in the IPC, the percent recovery is calculated as follows:

$$\%R = \frac{IPC}{s} \times 100$$

where:

%R	=	percent recovery.
IPC	=	measured concentration of analyte in the IPC, mg/L.
s	=	expected analyte concentration in the IPC, mg/L.

8.3.1.1 The QC criteria for the initial IPC are 95-105% (exception: 90-110% for potassium). If the %R for any analyte in the IPC falls outside of the QC criteria, the instrument must be recalibrated for at least the out-of-control analyte. Samples cannot be analyzed for the unacceptable analyte until an acceptable IPC is analyzed.

8.3.1.2 The QC criteria for continuing IPC samples are 90 -110%. If the %R for any analyte in the IPC falls outside of the QC criteria, analysis must stop. The instrument must be recalibrated for at least the out-of-control analyte. Once an acceptable calibration is obtained, the samples preceding the out-of-control IPC must be reanalyzed for the affected analytes.

8.3.1.3 The results for analytes measured in the CBs analyzed after IPCs are compared to the QL. If the absolute value of the CB result is less than ½ the QL, the result is acceptable. If the absolute value of the CB result equals or exceeds ½ the QL, the analysis must be terminated. 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 reanalyzed.

8.3.2 QL - The accuracy of the calibration 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 run, immediately after the QCS. The recovery of analytes in the QL is calculated as follows:

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

Where

%R	=	percent recovery of the standard.
M	=	measured concentration of the analyte, mg/L.
T	=	true concentration of the analyte in the QL, mg/L.

If the QL recovery exceeds the limits of 50 - 150%, the analysis shall be terminated. The cause of the poor recovery must be determined and the problem corrected. The instrument must be recalibrated and all affected samples must be reanalyzed. If, after re-calibration, the QL recovery still exceeds the 50-150% limits, the calibration standards must be re-prepared and the instrument re-calibrated.

8.3.3 QCS - Analyze a QCS daily to verify the calibration standards and acceptable instrument performance. If the measured concentrations are not within 5% of the true values (exception: 10% for potassium), the method performance is unacceptable. The source of the problem must be identified and corrected before proceeding with analyses.

8.3.4 SIC - Analyze daily SIC solutions to test interelemental spectral correction factors. If the SIC solutions do not meet the test criteria given in section 8.2.4, 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 ½ the QL, daily verification is not required. If the corrected concentration of the analyte due to spectral interference is less than 10% the total analyte concentration, daily verification is not required.

8.3.5 LRB - The laboratory must analyze at least one LRB with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment and sample preparation reagents. LRB values that exceed the QL indicate potential laboratory or reagent contamination. If the potential contamination significantly impacts the analytical results, the LRB must be reprepared along with the affected samples, and the affected analytes reanalyzed. Unless specified otherwise, the following statement describe when samples must be reprepared:

1) If the LRB analyte concentration is ≥ the QL and the sample result is less than 5 times the LRB analyte concentration, the LRB and sample must be reprepared and reanalyzed.

8.3.6 LFB - The laboratory must analyze at least one LFB with each batch of 20 or fewer samples of the same matrix. Calculate the percent recovery for each analyte using the following equation:

$$\%R = \frac{LFB}{s} \times 100$$

Where

$\%R$	=	percent recovery.
LFB	=	measured concentration of analyte in the LFB, mg/L.
s	=	analyte concentration in the LFB, mg/L.

If the recovery falls outside the control limits of 85-115%, reanalyze once. If the recovery still falls outside the control limits of 85-115% upon re-analysis, 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 LFB must be reprepared and reanalyzed.

8.3.7 LFM - Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. LFM results can be used to assess these matrix effects and potential impact to data usability.

One LFM must be prepared for every 10 routine samples of the same matrix in a sample batch (e.g., 1 LFM for batches containing 1-10 routine samples, 2 LFMs for batches containing 11-20 routine samples, etc.). Samples identified as field blanks cannot be used for LFM sample analysis. Homogenize the routine sample selected as the LFM and spike a representative aliquot with the analytes of interest prior to any sample preparation. For aqueous samples, the spiking level is listed in Table 3. Calculate the percent recovery for each analyte using the following equation:

$$\%R = \frac{C_{lfm} - C}{s} \times 100$$

Where

$\%R$	=	percent recovery.
C_{lfm}	=	measured concentration of analyte in the LFM, corrected for sample preparation and any dilutions, mg/L.
C	=	measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions, mg/L.
s	=	analyte concentration in the LFM, corrected for sample preparation and any dilutions, mg/L.

If the value of ***C*** is less than 4 times the value of ***s***, the acceptance window for ***%R*** is 70-130%. If the recovery of any analyte falls outside the acceptance window other QC data must be examined to determine if a matrix problem exists. If the laboratory performance for that analyte is in control (i.e., the IPC, QCS, and LFB results are acceptable), the poor LFM recovery is most likely matrix related. The problem should be discussed in the report narrative and the data user informed that the result for that analyte in the unfortified sample is suspect due either to the heterogeneous nature of the sample or a matrix effect and considered to be an estimated quantity. All affected results should be flagged with a "J" on the analytical spreadsheet.

8.3.8 LFMD - Sample homogeneity can affect the quality and interpretation of the data. LFMD results can be used to assess sample homogeneity. One LFMD must be prepared for every 10 routine samples of the same matrix in a sample batch (e.g., 1 LFMD for a batch containing 1-10 routine

samples, 2 LFMDs for a batch containing 11-20 routine samples, etc.). Samples identified as field blanks cannot be used for LFMD sample analysis. Homogenize the routine sample selected as the LFMD, obtain a representative aliquot, and proceed with sample preparation and analysis, treating the LFMD sample as a routine sample. Calculate the recovery of analyte in the LFMD following the equation in Section 8.3.7 and the relative percent difference using the following equation:

$$RPD = \frac{|C_{lfmd} - C_{lfm}|}{(C_{lfmd} + C_{lfm})/2} \times 100$$

Where

RPD	=	relative percent difference.
C_{lfm}	=	measured concentration in the LFM corrected for sample preparation and any dilutions, mg/L.
C_{lfmd}	=	measured concentration in the LFMD corrected for sample preparation and any dilutions, mg/L.

The relative percent difference (RPD) must be $\leq$20%. If the control limits for an analyte are exceeded, flag the associated result for the analyte as estimated (J flag). Document actions in the report narrative.

9 ANALYTICAL PROCEDURES

9.1 Sample Preparation - The sample preparation procedure for water samples to be analyzed by ICP-AES is found in Region 9 Laboratory SOP 403.

9.1.1 Aqueous Samples, Dissolved Analytes - For the determination of dissolved analytes in ground and surface waters, pipet a 20mL aliquot of the filtered, acid preserved sample into a 50-mL polypropylene centrifuge tube. Add 0.40 mL (1+1) nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis.

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.

9.1.2 Drinking Water Samples, Total Recoverable Analytes, Direct Analysis - Drinking water samples with turbidity <1 NTU may be acidified and analyzed directly without digestion. Pipet a 20mL aliquot of the unfiltered, acid-preserved sample into a 50-mL polypropylene centrifuge tube. Add 0.40 mL (1+1) nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis.

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.

9.2 Calibration and Analysis

9.2.1 Instrument Set-up - Check the condition of the pump tubing for wear. Replace as needed. Tighten the pump tubing on the pump. 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. Check torch for salt build up. Verify that the drain tubing is tight and check the waste container.

9.2.2 Select the appropriate method file and change the data file name to correspond to the correct day (i.e.; 10109151, indicating ICP instrument number (1), present date (year/month/day), and analytical run number(1)). Check the flush times and change to desired time, minimally 60 seconds. Save all changes.

9.2.3 Set up the autosampler table with the desired sample run. Old autosampler files may be written over and resaved. Print the autosampler file and place the standards and samples in the racks as indicated by autosampler file and enter into the Run Log (Attachment C).

9.2.4 The Profile procedure is to align the optical path of the instrument prior to calibration and sample analysis. Profile the instrument using the 10 mg/L Cu/Mn solution. Aspirate the profile solution and run the profile routine as per the manufacturer's procedure. Adjust the profile position with the profile adjustment knob. Repeat the procedure until the profile peak position is $\pm$ 0.05 as indicated by the profile plot observed on the computer monitor. Print the acceptable profile plot.

9.2.5 Calibration - A calibration blank and a calibration standard are used for calibration (the standard is obtained from mixed calibration standard in different solutions). The calibration standards are given in Table 2. The calibration is automatically updated in the method file as they are run.

9.2.6 Sample Analysis - After calibration the autosampler continues with the samples and QC. Load SIC solutions according to the requested analyte list. An example of a loading list for an analytical run sequence is listed in the table below:

Seq.	Desc.	Seq.	Desc.	Seq.	Desc.	Seq.	Desc.
1	IPC	13	IPC	25	IPC	37	IPC
2	CB	14	CB	26	CB	38	CB
3	QCS	15	LRB	27	S7	39	S15
4	QL	16	LFB	28	S8	40	S16
5	Fe SIC	17	S1	29	S9	41	S17
6	Al SIC	18	S1-LFM	30	S10	42	S18
7	V SIC	19	S1-LFMD	31	S11	43	S19
8	Mn SIC	20	S2	32	S12	44	S20
9	Cr SIC	21	S3	33	S12-LFM	45	IPC
10	Co SIC	22	S4	34	S12-LFMD	46	CB
11	Ni SIC	23	S5	35	S13	47	
12	Ce SIC	24	S6	36	S14	48	

9.2.7 Review results for QC compliance and off-scale results. Identify samples which must be re-analyzed in a different analytical run. Samples having analytes at concentrations higher than 90% of the linear dynamic range must be diluted into range and re-analyzed.

9.3 Data Reduction and Reporting - After set-up and calibration the instrument reports results for the analyzed solution in the units of mg/L. The instrument calculations include elemental correction calculations and calibration factors.

9.3.1 Aqueous Samples - Data for aqueous samples should be reported in units of g/L using the following calculation:

$$C = M \times \frac{1000ug}{mg} \times D$$

Where

C	=	final reported concentration, in ug/L.
M	=	measured concentration reported by instrument, in mg/L.
D	=	sample analysis dilution factor, to account for any dilution performed after sample preparation.

9.3.2 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 ½ the QL. Values between ½ the QL and the QL will be flagged as estimated (J flag). For rounding results, adhere to the following rules:

- If the number following those to be retained is less than 5, round down;
- If the number following those to be retained is greater than 5, round up; or
- 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.

10 DOCUMENTATION

10.1 Acid Digestion Log for Metals Preparation - A copy of the acid digestion log for metals digestion must be submitted with the raw data. The digestion log is maintained in Room 302.

10.2 MET-1 TJA ICAP 61E Run Log - Entries are made for the case number, SDG number, date of analysis, site name, file name, analyst initials, lab sample IDs, client sample IDs, and comments, if any. The run log is maintained in Room 303. (Attachment C)

10.3 Inorganic Standards and Reagents Preparation Log Book - Copies of all standard solution preparation entries (CAL, IPC, QL, LFB, LFM, LFMD, QCS, etc.) must be submitted with each data package. (Attachment B)

10.4 Report Narrative and Deliverable

The data package consists of the report narrative, reports, and data, as listed in the table below.

Data Package Contents
Report Narrative: Discusses any problems encountered, both technical and administrative, the corrective action taken, and the resolution. All universal analytical flags should also be discussed in the report narrative.
Tabulated sample results: On an analytical spreadsheet, with units, sample collection dates, client sample IDs, laboratory IDs and station locations. (Attachment D)
LRB data: Included on the analytical spreadsheet. (Attachment D)
LFM and LFMD results: On a QC summary report with calculated relative percent difference (RPD). (Attachment E)
LFM, LFMD and LFB results: On a QC summary report with calculated percent recoveries (%R). (Attachment F)
Raw sample, standard and QC data, including run logs and any work sheets, if applicable. (Attachments B, C and D)

11 REFERENCES

11.1 U.S. Environmental Protection Agency. Method 200.7, Determination of Trace Elements by in Waters and Wastes by Inductively Coupled Plasma - Atomic Emission Spectrometry, Revision 4.4, EMMC Version, May 1994

11.2 Region 9 SOP 130, *Glassware Cleaning Procedures.*

11.3 Region 9 SOP 462, *Analysis of Total Suspended Solids By EPA Method 160.2.*

11.4 Region 9 SOP 830, *Notification Procedures for Results Exceeding the Safe Drinking Water Act Maximum Contaminant Level.*

11.5 Region 9 SOP 840, *Notebook Documentation and Control.*

11.6 Region 9 SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency.*

Table 1
Method Analytes and Potential Interfering Elements

Analyte	Wavelength - nm	Interfering Elements
Al	308.215	Ce, Mn, Mo, V, Fe
Sb	206.838	Ce, Cr, Mo, Ni, Ti, V, Sn, Fe, Zn
As	193.696	Al, Ce, Cr, Fe, Mo, Ni, V
Ba	493.409	Sr, Ce, Fe
Be	313.042	Ce, Mo, Ti, V
B	249.678	Fe, Co
Cd	226.502	Ce, Co, Fe, Mo, Ti, Ni
Ca	317.933*	Mn, Mo, V, Cr
Cr	267.716*	Cd, Ce, Mn, Mo, Ti, V
Co	228.616	Cd, Ce, Cr, Ba, Mo, Ti, Ni, Fe
Cu	324.754	Ce, Mo, Ti, V, Fe
Fe	259.940	Mn, Mo
Pb	220.353	Al, Ce, Co, Fe, Mo, Ti
Mg	279.079*	Ce, Co, Mn, Mo, Ti, V
Mn	257.610	Al, Ce, Mo, V, Mg
Mo	202.030*	Fe
Ni	231.604	Tl, Sb
K	766.491	None
Se	196.026	Ce
SiO_2	288.158	Ce, Cr, V
Ag	328.068	Ce, Mn, Mo, Ti, V
Na	588.995	None
Sr	421.553	None
Tl	190.894	Ce, Co, V, Ti
Sn	189.989	Ti
Ti	334.941	Ce, Cr
V	292.402	Ce, Cr, Mo, Fe, Ti, Mn
Zn	213.856	Co, Cu, Mo, Ni, Ti, V, Fe

* Wavelengths other than those recommended by Method 200.7

Table 2 - Calibration Standard Concentrations*

Analyte	Solution	Concentration mg/L	Analyte	Solution	Concentration mg/L
Ag	IV	0.50	Co	III	2.0
As	IV	10.0	V	III	2.0
B	IV	1.0	Al	II	10.0
Ba	IV	1.0	Cr	II	5.0
Cd	IV	2.0	Sn	II	4.0
Cu	IV	2.0	Zn	II	5.0
Mn	IV	2.0	SiO_2	II	10.0
Sb	VI	5.0	Be	I	1.0
Se	IV	5.0	Fe	I	10.0
Sr	IV	1.0	Mg	I	10.0
K	V	20.0	Ni	I	2.0
Mo	V	10.0	Pb	I	10.0
Na	V	10.0	Tl	I	5.0
Ti	V	10.0			
Ce	V	2.0			
Ca	V	10.0			

* Stock standard solutions are purchased as concentrated solutions and diluted by a factor of 100 to prepare the calibration standards. Ce and Ca are prepared with appropriate dilutions from 1000 g/mL single element stock standard solutions due to a problem with the mixed standards. These individual elements were added to solution V.

Table 3 - IPC, QCS, LFB/LFM/LFMD Concentrations

Analyte	IPC - mg/L	QCS - mg/L	LFB/LFM/LFMD - mg/L
Al	2.0	1.0	2.0
Sb	2.0	2.0	0.80
As	2.0	2.0	0.80
Ba	2.0	1.0	0.20
Be	2.0	1.0	0.20
B	2.0	1.0	0.30
Cd	2.0	1.0	0.20
Ca	2.0	1.0	1.0
Cr	2.0	1.0	0.40
Co	2.0	1.0	0.20
Cu	2.0	1.0	0.30
Fe	2.0	1.0	3.0
Pb	2.0	2.0	1.0
Mg	2.0	1.0	2.0
Mn	2.0	1.0	0.20
Mo	2.0	1.0	0.40
Ni	2.0	1.0	0.50
K	10.0	5.0	10.0
Se	2.0	1.0	2.0
SiO_2	10.0	5.0	N/A
Ag	0.25	0.25	0.075
Na	2.0	1.0	3.0
Sr	2.0	1.0	0.20
Tl	2.0	5.0	2.0
Sn	2.0	5.0	0.70
V	2.0	1.0	0.30
Zn	2.0	1.0	0.20
Ce	2.0	5.0	N/A
Ti	2.0	5.0	N/A

Attachment A
Deviations From Reference Method

A.1 Sample digestates are allowed to settle overnight. If undissolved material does not settle out, the sample digestate is filtered prior to analysis on the instrument. The laboratory does not centrifuge samples as suggested in the method.

A.2 Aqueous samples with less than 1% undissolved solids are brought up to a final volume of 50 mL (no preparation step is performed at the instrument).

A.3 The scope of this SOP does not include the digestion of water and solid samples or analysis of solid samples.

A.4 Region 9 Laboratory does not blank subtract the LRB results from the LFB results for calculation of LFB recoveries.

A.5 Calibration blank acceptance criteria of <½ the QL is being followed in this procedure.

A.6 SIC acceptance criteria of ½ the QL is being followed in this procedure.

A.7 The 3% RSD criteria for initial IPC is not being followed in this method

A.8 The percent recovery for potassium in the initial IPC and QCS was changed to ±10%.

Attachment B
Inorganic Standards and Reagents Preparation Log Book

INORGANIC STANDARDS AND REAGENTS PREPARATION LOG BOOK

STANDARD ID	DATE/ ANALYST	STANDARD NAME	ANALYTE	SOURCE SUPPLIER	SOURCE EXP. DATE	SOURCE LOT NO.	SOURCE CONC. /PURITY	ALIQUOT (WT or VOL)	FINAL VOLUME	FINAL CONC.	STD EXP. DATE

USEPA REGION 9 LABORATORY

Attachment C
MET-1 TJA ICAP 61E Run Log

MET-1 : TJA ICAP 61E RUN LOG

Run/File Name:________________ Date:__________ Analyst:__________
Site ID:______________________ Page______ of______
Case #:__________ SDG:__________ Cu Profile:__________

#	STD Sample ID	Comments	#	STD Sample ID	Comments

EPA REGION 9 LABORATORY

Reviewed by:______________ Date:__________

MET1.wk4 REVISED: 11/97

Attachment D
Analytical Spreadsheet

EPA REGION 9 LABORATORY-RICHMOND, CA
SUMMARY OF ANALYTICAL RESULTS

Case Number: R01S20 **Analysis:** Metals
Site: AAAZZZ **Matrix:** Water
SDG: 123456A
Date: 02/01/01

Sample No.	N/A				N/A				LRB-1				Quantitation
Sample I.D.	DUMMY				DUMMY				Reagent Blank				Limit
Date of Collection	01/23/01				01/24/01				N/A				N/A
Units	ug/L				ug/L				ug/L				ug/L
Analyte	Result		Q	Com	Result		Q	Com	Result		Q	Com	Result
Aluminum (200.7)	200	U			200	U			200	U			200
Antimony (200.8)	5	U			5	U			5	U			1
Arsenic (200.8)	20				20	U			20	U			5
Barium (200.8)	100				5	U			5	U			1
Beryllium (200.7)	1	U			1	U			1	U			1
Boron (200.7)	400				100	U			100	U			100
Cadmium (200.8)	5	U			5	U			5	U			1
Calcium (200.7)	80000				100	U			100	U			100
Chromium (200.7)	10	U			10	U			10	U			10
Cobalt (200.8)	5	U			5	U			5	U			1
Copper (200.8)	6				5	U			5	U			1
Iron (200.7)	100				100	U			100	U			100
Lead (200.8)	5	U			5	U			5	U			1
Magnesium (200.7)	30000				500	U			500	U			500
Manganese (200.8)	4		J	A	5	U			5	U			1
Mercury (245.1)									0.03	U			0.03
Molybdenum (200.8)	5	U			5	U			5	U			1
Nickel (200.7)	50	U			50	U			50	U			50
Potassium (200.7)	6000				5000	U			5000	U			5000
Selenium (200.8)	20	U			20	U			20	U			5
Silver (200.8)	5	U			5	U			5	U			1
Sodium (200.7)	240000				500	U			500	U			500
Thallium (200.8)	5	U			5	U			5	U			1
Vanadium (200.7)	20	U			20	U			20	U			20
Zinc (200.8)	120				20	U			20	U			5

Com - Comments refer to the corresponding section in the report narrative for each letter.
N/A - Not Applicable.
N/R - Not Required.
Q - Refer to data qualifiers.
U - The parameter was analyzed for, but was not detected. The associated value is the sample quantitation limit, adjusted for dilution, if any.
J - The associated value is an estimated quantity.

Filename: METSPDSHT.123

Attachment E
QC Summary Report

US E.P.A.
REGION 9 LABORATORY
June 20, 2000
Case Number: R00SXX
SDG: 00XXXA

Laboratory Fortified Matrix and Laboratory Fortified Matrix Duplicate

Analyzed Date	Sample ID	Analyte (Analysis)	LFM Result (ug/L)	LFMD Result (ug/L)	RPD	Q
01/01/01	AB00001	Aluminum (200.7)			??	
01/01/01	AB00001	Antimony (200.8)			??	
01/01/01	AB00001	Arsenic (200.8)			??	
01/01/01	AB00001	Barium (200.8)			??	
01/01/01	AB00001	Beryllium (200.7)			??	
01/01/01	AB00001	Boron (200.7)			??	
01/01/01	AB00001	Cadmium (200.8)			??	
01/01/01	AB00001	Calcium (200.7)			??	
01/01/01	AB00001	Chromium (200.7)			??	
01/01/01	AB00001	Cobalt (200.8)			??	
01/01/01	AB00001	Copper (200.8)			??	
01/01/01	AB00001	Iron (200.7)			??	
01/01/01	AB00001	Lead (200.8)			??	
01/01/01	AB00001	Magnesium (200.7)			??	
01/01/01	AB00001	Manganese (200.8)			??	
01/01/01	AB00001	Mercury (245.1)			??	
01/01/01	AB00001	Molybdenum (200.8)			??	
01/01/01	AB00001	Nickel (200.7)			??	
01/01/01	AB00001	Potassium (200.7)			??	
01/01/01	AB00001	Selenium (200.8)			??	
01/01/01	AB00001	Silver (200.8)			??	
01/01/01	AB00001	Sodium (200.7)			??	
01/01/01	AB00001	Thallium (200.8)			??	
01/01/01	AB00001	Vanadium (200.7)			??	
01/01/01	AB00001	Zinc (200.8)			??	

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 507

DETERMINATION OF TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY EPA METHOD 200.8

Prepared by:

Stephen Carroll, ESAT Region 9, ICF Consulting	Date

Review by:

Richard Bauer, Chemistry Team Leader	Date

Approved by:

Brenda Bettencourt, Laboratory Director	Date

Periodic Review:

Signature	Title	Date

STANDARD OPERATING PROCEDURE 507

DETERMINATION OF TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY EPA METHOD 200.8

This SOP was prepared by ICF Consulting for the United States Environmental Protection Agency (USEPA) under the Environmental Services Assistance Team (ESAT) contract (EPA contract No. 68-W-01-028).

APPROVED BY:

Osellie Salvador, Inorganic Group Leader	Date
Surender Kaushik, QA Task Manager	Date
Jerry Vail, ESAT Program Manager	Date

ESAT Document Control Number: B0101029-0485

CONTENTS

1 SCOPE AND APPLICATION 4

2 METHOD SUMMARY 5

3 DEFINITIONS 6

4 HEALTH AND SAFETY 8

5 SAMPLE HANDLING AND PRESERVATION 9

6 INTERFERENCES 9

7 APPARATUS AND MATERIALS 11

8 QUALITY CONTROL PROCEDURES 13

9 ANALYTICAL PROCEDURES 18

10 DOCUMENTATION 21

11 REFERENCES 22

Table 1: Internal Standards And Limitations of Use 23

Table 2: Recommended Elemental Equations for Data Calculations 24

Table 3: Recommended Analytical Isotopes and Additional Masses Which Must Be Monitored 25

Attachment A - Deviations From Reference Method
Attachment B - Inorganic Standards and Reagents Preparation Log Book
Attachment C - ICP-MS Runlog
Attachment D - Analytical Spreadsheet
Attachment E - QC Summary

1 SCOPE AND APPLICATION

1.1 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 (Rev. 5.4, May 1994). This SOP is applicable to the determination of the following elements:

Analyte	Chemical Abstract Services Registry Number (CAS #)
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Cadmium (Cd)	7440-43-9
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Lead (Pb)	7439-92-1
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-98-7
Nickel (Ni)	7440-02-0
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Thallium (Tl)	7440-28-0
Thorium (Th)	7440-29-1
Uranium (U)	7440-61-1
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

1.2 For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulations (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water), and the latest Federal Register announcements.

1.3 Dissolved elements are determined after suitable filtration and acid preservation. In order to reduce potential interferences, dissolved solids should not exceed 0.2% (w/v) (Section 6.4).

1.4 Where this method is approved for the determination of metal and metalloid contaminants in drinking water, samples are analyzed directly by pneumatic nebulization without acid digestion if the samples have been properly acid-preserved and have turbidity of < 1 NTU at the time of analysis. This total recoverable determination procedure is referred to as "direct analysis". Note the exception for silver discussed in Section 1.6.

1.5 For the determination of total recoverable analytes in aqueous samples containing particulate and suspended solids a digestion step is required prior to analysis.

1.6 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, succeeding smaller volume, well mixed sample aliquots must be prepared until the analysis solution contains < 0.1 mg/L silver.

1.7 The total recoverable sample digestion procedure given in Region 9 Laboratory 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.

2 METHOD SUMMARY

2.1 An aliquot of a well-mixed, homogeneous aqueous sample is accurately measured for sample processing. For total recoverable analysis of an aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. After cooling, the sample is made up to volume, mixed and allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in drinking water where sample turbidity is <1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then mixed before analysis.

2.2 The method describes the determination of trace elements in aqueous solutions by ICP-MS. 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 poly-atomic elemental interferences (Section 6).

3 DEFINITIONS

3.1 Analytical Sample - Any solution introduced into the ICP-MS instrument excluding calibration standards, calibration blanks, or instrument performance check samples (e.g., tuning solution sample).

3.2 Calibration Blank (CB) - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP-MS instrument. In addition, the stability of the calibration curve baseline must be monitored by analyzing a CB immediately after every IPC standard.

3.3 Calibration Standard (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.4 Dissolved Analyte Concentration - The concentration of analyte in an aqueous sample that is filtered through a 0.45- m membrane filter assembly prior to sample acidification.

3.5 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.

3.6 Field Reagent Blank (FRB) - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purposes of the FRB is to determine if method analytes or other interferences are present in the field environment. **Note:** Field reagent blanks cannot be used for LFM or LFMD analyses.

3.7 Instrument Performance Check (IPC) - A solution of method analytes used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.8 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 Table 1.

3.9 Laboratory Fortified Blank (LFB) - An aliquot of LRB to which known quantities of the method analytes are added. The LFB 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.

3.10 Laboratory Fortified Sample Matrix (LFM) - An aliquot of an environmental sample to which known quantities of the method analytes are added. The LFM is analyzed exactly like a sample. The LFM results are compared to the results for the un-fortified sample to determine whether the sample matrix contributes bias to the analytical results.

3.11 Laboratory Fortified Sample Matrix Duplicate (LFMD) - A duplicate aliquot of an analytical sample to which known quantities of the method analyte is added in the laboratory. The LFMD 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.

3.12 Laboratory Reagent Blank (LRB) - An aliquot of reagent water or other blank matrix 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.

3.13 Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear.

3.14 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.

3.15 Quality Control Sample (QCS) - A solution containing known concentrations of method analytes. The QCS source must be different than the source of calibration standards. It is used to check laboratory or instrument performance.

3.16 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.

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

3.18 Stock Standard Solution - A solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a commercial source. The stock standards are used to prepare the calibration standards.

3.19 Total Recoverable Analyte Concentration - The concentration of analyte in either a solid sample or an unfiltered aqueous sample after preparation by acid digestion. The sample preparation procedures are described in Region 9 Laboratory SOPs 403 and 405.

3.20 Tuning Solution - A solution contained 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.

3.21 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 AND SAFETY

4.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Concentrated nitric and hydrochloric acids present various hazards and according to MSDS may be fatal and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large amounts of water for at least 15 minutes or if inhalation occurs, remove to fresh air. ESAT personnel should contact the Group Leader or Health and Safety and Env. 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.

4.2 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. Refer to the Material Safety Data Sheets located in the library or in Room 413 for additional information.

4.3 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

4.4 The ICP-MS emits radio frequency and intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards.

4.5 Areas of high, lethal voltages exist within the instrument. Never touch parts of the instrument which are not intended for access by the instrument operator.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Samples should be collected in pre-cleaned plastic or glass bottles. Volume collected should be sufficient to insure 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 Samples are received at the Region 9 Laboratory by EPA staff in Room 503. Preservation and pretreatment of samples are verified against the chain-of-custody form and analytical request as follows:

5.2.1 Dissolved Analyte Samples: The samples must be filtered through a 0.45- m 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 (1+1) nitric acid immediately following filtration to pH<2 (normally, 3 mL of (1+1) nitric acid per liter of sample is sufficient).

5.2.2 Aqueous Total Recoverable Analyte Samples: Samples are preserved by acidifying with (1+1) nitric acid to pH<2 (normally, 3 mL of (1+1) 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 sample pH >2, more acid must be added and the sample held for sixteen hours until verified to be pH<2.

5.2.3 Drinking Water Samples: Samples are preserved by acidifying with (1+1) nitric acid to pH<2 (normally, 3 mL of (1+1) 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 <1 NTU, the sample can be analyzed directly without digestion.

5.3 The holding time for properly preserved samples is six months.

6 INTERFERENCES

6.1 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 Section 1.1 have at least one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method (Table 3), only molybdenum-98 (ruthenium) and selenium-82 (krypton) have isobaric elemental interferences. 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.

6.2 Abundance Sensitivity Interference - Abundance sensitivity interference refers to the degree of peak overlap that can occur between adjacent peaks. An interference can occur when the shoulder of a large peak significantly overlaps the peak of a neighboring of a minor peak, thereby contributing to its intensity. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

6.3 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. 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 which are listed in Table 2.

6.4 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 sampler 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).

6.5 Memory Interference - 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 may be achieved by aspirating a standard containing the analyte at a concentration ten times the LDR 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 a 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

7.1 Apparatus

Note: All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives and isolated from other laboratory glassware. Please refer to ESAT Region 9 SOP 130, Glassware Cleaning Procedures, for specific instructions (reference 3 of section 11).

7.1.1 ICP-MS System, comprised of following:
Fisons Genesis Inductively Coupled Plasma Mass Spectrometer
Gilson Autosampler
Gilson Minipuls3 peristaltic pump
Neslab CFT - 760 Refrigerated Circulator
Cetac U-5000+ Ultrasonic Nebulizer
Argon gas supply (high-purity grade, 99.99%)

7.1.2 Convection drying oven, with thermostatic control capable of maintaining 104±1°C.

7.1.3 Pipetters, capable of delivering volumes ranging from 10 to 1000 L, and associated metal-free disposable pipet tips.

7.1.4 Syringe with 0.45um Whatman disk filters.

7.1.5 Glassware - Class A volumetric flasks, graduated cylinders and funnels (glass and/or metal-free plastic).

7.1.6 Class A volumetric pipettes.

7.1.7 Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125-mL to 1-L capacities.

7.1.8 One-piece stem FEP wash bottle with screw closure, 500-mL capacity.

7.2 Materials and Reagents

Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society (ACS) specifications should be used. If the purity of a reagent is in question, analyze for contamination. All acids must be of ultra high-purity grade or equivalent. Suitable acids are available from a number of manufacturers, such as J.T. Baker or Mallinckrodt. Record the preparation of standards and reagents in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.2.1 Hydrochloric acid, concentrated (sp.gr. 1.19) - HCl.

7.2.2 Hydrochloric acid (1+1) - Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

7.2.3 Hydrochloric acid (1+4) - Add 200 mL concentrated HCl to 400 mL reagent water and dilute to 1 L

7.2.4 Nitric acid, concentrated (sp.gr. 1.41) - HNO_3.

7.2.5 Nitric acid (1+1) - Add 500 mL concentrated HNO_3 to 400 mL reagent water and dilute to 1L.

7.2.6 Reagent water - All references to reagent water in this method refer to ASTM Type II grade water.

7.2.7 Standard stock solutions (1000 g/mL) can be purchased from a commercial supplier such as Spex or Inorganic Ventures. The list of required elements is provided in Section 1.1.

7.2.8 Calibration Standards - Calibration standards (CAL Solution) should be prepared every two weeks or as needed. Dilute the stock standard solution to levels appropriate to the operating range of the instrument with 1% (v/v) nitric acid. The element concentrations in each CAL solution should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. The Region 9 Laboratory uses a multi-element standard prepared with element concentrations set at 50 g/L, with the exceptions of selenium at 250 g/L.

7.2.9 Instrument Performance Check (IPC) Solution - Prepare an aliquot of the CAL standard and use to verify instrument calibration.

7.2.10 Internal Standard Solution - Prepare a multi-element standard from 1000 g/mL stock standards to contain 500 g/L each of scandium, indium, terbium and bismuth.

7.2.11 Calibration Blank (CB) - Dilute concentrated nitric acid with reagent water to obtain a 1% (v/v) nitric acid solution.

7.2.12 Laboratory Reagent Blank (LRB) - Prepare the LRB to contain all of the reagents in the same volumes as used in processing the samples. The LRB is taken through the entire preparation and analytical sequence.

7.2.13 Laboratory Fortified Blank (LFB) and Laboratory Fortified Matrix (LFM) - Prepare the LFB by fortifying an aliquot of the laboratory reagent blank with the calibration stock standards to contain 100 g/L of each analyte, except for selenium. Selenium is fortified at 500 g/L. Prepare the LFM by fortifying an aliquot of the QC sample with the calibration stock standards to contain 100 g/L of each analyte, except for selenium. Selenium is fortified at 500 g/L. For direct analysis of drinking water samples (Sect. 9.1.2), reduce the LFB and LFM concentrations by a factor of 4; the added LFB/LFM will be 25 g/L of each analyte, except for selenium which will be fortified at 125 g/L. The LFB is taken through the entire preparation and analytical sequence.

7.2.14 Rinse Blank - Dilute concentrated nitric acid with reagent water to obtain a 2% (v/v) nitric acid solution.

7.2.15 Tuning Solution - Prepare a multi-element standard from 1000 g/mL stock standards to contain 500 g/L of barium and cerium and 10 g/L each of beryllium, magnesium, cobalt, indium, lead, and uranium.

7.2.16 Quality Control Sample (QCS) - Prepare a multi-element standard from 1000 g/mL stock standards to contain 100 g/L of each analyte, except for selenium at 500 g/L. The acid content of the QCS must be the same as the acid content of the calibration standards. The source of the QCS stock standards must be different than that of the calibration standard stock solutions.

7.2.17 Quantitation Limit Standard (QL) - Prepare a multi-element standard from 1000 g/mL stock standards to contain 1 g/L of each analyte, except for arsenic, selenium and zinc at 5 g/L, aluminum at 20 *ug*/L and vanadium at 10 g/L. The acid content of the QL must be the same as the acid content of the calibration standards.

8 QUALITY CONTROL PROCEDURES

8.1 EPA Region 9 Laboratory operates a formal quality control (QC) program. As it relates to this SOP, the QC program consists of an initial demonstration of laboratory and analyst capability (refer to Region 9 Laboratory SOP 880), and the periodic analysis of laboratory solutions as a continuing check on performance.

8.2 Method Characterization - Prior to routine use, the LDR and MDL for each analyte must be determined for each operating condition (including detector used), and average of triplicate analysis of the QCS must yield acceptable results.

8.2.1 LDR - The upper limit of the LDR must be established for each mass used in quantifying results. Analyze a series of standards with concentrations spanning the range from 1 to 100 times the highest calibration 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 reanalyzed. The LDR should be verified whenever the analytical conditions are changed.

8.2.2 MDL - A method detection limit must be confirmed annually and must be <½ QL or corrective action must be initiated.

8.2.3 QCS - Analyze a QCS in triplicate and take average results to demonstrate initial acceptable performance. The determined mean concentration from the 3 analyses of the QCS must be within ±10% of the stated QCS value or corrective action must be initiated. Analyze only prior to routine use of the procedure.

8.3 Routine Analytical Quality Control

8.3.1 Instrument performance check (IPC) solution - The laboratory must check instrument performance and verify that the instrument is properly calibrated on a continuing basis. To verify calibration, the IPC and the calibration blank are run as routine samples immediately following calibration, after every 10 analytical samples, and at the end of each run. For each analyte in the IPC, the percent recovery is calculated as follows:

$$\%R = \frac{IPC}{s} \times 100$$

where:

%R	=	percent recovery.
IPC	=	measured concentration of analyte in the IPC, g/L.
s	=	expected analyte concentration in the IPC, g/L.

The QC criteria for the initial IPC are 90-110%. If the %R for any analyte in the IPC 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 IPC is analyzed.

The QC criteria for continuing IPC samples are 90 -110%. If the %R for any analyte in the IPC falls outside of the QC criteria analysis must stop. If the out-of-control IPC analyte is within 85 - 115%, the results may be reported. The instrument must be recalibrated for at least the unacceptable out-of-control analytes. Once an acceptable calibration is obtained, the samples preceding the out-of-control IPC must be reanalyzed for the affected analytes.

8.3.2 CB - The stability of the calibration curve baseline must be monitored by analyzing a CB immediately after every IPC standard. If the absolute value of the CB result is less than ½ the QL, the result is acceptable. If the absolute value of the CB result equals or exceeds ½ the QL, the analysis must be terminated. 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 reanalyzed.

8.3.3 QCS - Analyze a QCS 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.

8.3.4 QL - Analyze a QL standard daily after calibration to verify acceptable data quality. The QL recoveries should be within 50-150% of the true value. If the measured concentration are not within ±50% of the true values, the method performance is unacceptable. The source of the problem must be identified and corrected before proceeding with analyses.

8.3.5 LRB - The laboratory must analyze at least one LRB with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment and sample preparation reagents. LRB values that exceed the QL indicate potential laboratory or

reagent contamination. If the potential contamination significantly impacts the analytical results, the LRB must be re-prepared along with the affected samples, and the affected analytes re-analyzed. Unless specified otherwise, the following statement describes when samples must be re-prepared:

1) If the LRB analyte concentration is ≥ the QL and the sample result is less than 5 times the LRB analyte concentration, the LRB and sample must be re-prepared and re-analyzed.

8.3.6 LFB - The laboratory must analyze at least one LFB with each batch of 20 or fewer samples of the same matrix. Calculate the percent recovery for each analyte using the following equation:

$$\%R = \frac{LFB}{s} \times 100$$

where:

%R	=	percent recovery.
LFB	=	measured concentration of analyte in the LFB, g/L.
s	=	expected analyte concentration in the LFB, g/L.

If the recovery falls outside the control limits of 85-115%, re-analyze once. If the recovery still falls outside the control limits of 85-115% upon re-analysis, 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 LFB must be re-prepared and re-analyzed.

8.3.7 LFM - Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. LFM results can be used to assess these matrix effects and potential impact to data usability.

One LFM must be prepared for every 10 routine samples of the same matrix in a sample batch (e.g., 1 LFM for batches containing 1-10 routine samples, 2 LFMs for batches containing 11-20 routine samples). Homogenize the routine sample selected as the LFM and spike a representative aliquot with the analytes of interest, prior to any sample preparation. For aqueous samples, the spiking level must be the same as that used for the LFB (Section 7.2.13). Calculate the percent recovery for each analyte using the following equation:

$$\%R = \frac{Clfm - C}{s} \times 100$$

where:

%R	=	percent recovery.
C_{lfm}	=	measured concentration of analyte in the LFM, corrected for sample preparation and any dilutions, g/L.
C	=	measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions, g/L.
s	=	expected analyte concentration in the LFM, corrected for sample preparation and any dilutions, g/L.

If the value of ***C*** is less than 4 times the value of ***s***, the acceptance window for ***%R*** is 70-130%. If the recovery of any analyte falls outside the acceptance window other QC data must be examined to determine if a matrix problem exists. If the laboratory performance for that analyte is in control (i.e., the IPC, QCS, and LFB results are acceptable), the poor LFM recovery is most likely matrix related. The problem should be discussed in the report narrative and the data user informed that the result for that analyte in the unfortified sample is suspect due either to the heterogeneous nature of the sample or a matrix effect and considered to be an estimated quantity. All affected results should be flagged with a "J" on the analytical spreadsheet.

8.3.8 LFMD - Sample homogeneity can affect the quality and interpretation of the data. LFMD results can be used to assess sample homogeneity. One LFMD must be prepared for every 10 routine samples of the same matrix in a sample batch (e.g., 1 LFMD for a batch containing 1-10 routine samples, 2 LFMDs for a batch containing 11-20 routine samples, etc.). Samples identified as field blanks cannot be used for LFMD sample analysis. Homogenize the routine sample selected as the LFMD, obtain a representative aliquot, and proceed with sample preparation and analysis, treating the LFMD sample as a routine sample. Calculate the recovery of analyte in the LFMD following the equation in Section 8.3.7 and the relative percent difference using the following equation:

$$RPD = \frac{|C_{lfmd} - C_{lfm}|}{(C_{lfmd} + C_{lfm})/2} \times 100$$

Where

RPD	=	relative percent difference.
C_{lfm}	=	measured concentration in the LFM corrected for sample preparation and any dilutions, mg/L.
C_{lfmd}	=	measured concentration in the LFMD corrected for sample preparation and any dilutions, mg/L.

The relative percent difference (RPD) must be ≤20%. If the control limits for an analyte are exceeded, flag the associated result for the analyte as estimated (J flag). Document actions in the report narrative.

8.3.9 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 shifts, dissolve 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, flush the instrument with the rinse blank and re-analyze the calibration blank and examine the internal standard intensities with the following actions:

1) If the intensities of the internal standards are acceptable, dilute a fresh aliquot of the sample in question by a factor of two or five, and re-analyze.
2) If the intensities of the internal standards are still out-of-limits, terminate the analysis and determine the cause of the drift. Routine maintenance of the sampling interface or re-tuning the mass spectrometer may be required. The system must be calibrated and any samples not bordered by acceptable IPC samples re-analyzed.

9 ANALYTICAL PROCEDURES

9.1 Sample Preparation

9.1.1 Aqueous Samples, Dissolved Analytes - For the determination of dissolved analytes in ground and surface waters, pipet a 20 mL aliquot of the filtered, acid preserved sample into a 50-mL polypropylene centrifuge tube. Add 0.40mL (1+1) nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis. For LFB and LFM analyses, the samples should be spiked at 25 g/L for all analytes and 125 g/L for selenium.

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.

9.1.2 Drinking Water Samples, Total Recoverable Analytes, Direct Analysis - Drinking water samples with turbidity <1 NTU may be acidified and analyzed directly without digestion. Pipet a 20 mL aliquot of the unfiltered, acid-preserved sample into a 50-mL polypropylene centrifuge tube. Add 0.40mL (1+1) nitric acid to adjust the acid concentration to 1% (v/v). The sample is now ready for analysis. For LFB and LFM analyses, the samples should be spiked at 25 g/L for all analytes and 125 g/L for selenium.

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.

9.1.3 Sample Preparation for Aqueous Samples (1% undissolved solids), Total Recoverable Analytes - The sample preparation procedure for samples to be analyzed by ICP-MS is found in Region 9 Laboratory SOP 403.

9.2 Calibration and Standardization

9.2.1 Instrument Set-up - Set-up the proper operating configuration of the instrument and data system. Ignite the plasma and allow to stabilize for at least 30 minutes. During this stabilization period, align the torch using 10 g/L indium standard (use the tuning solution) and verify and adjust the mass calibration and resolution. Resolution at the low mass is checked using the magnesium isotopes 24, 25, 26 and at the high mass with the lead isotopes 206, 207, 208. The spectrometer resolution should produce a peak width of approximately 0.75 amu at 5% peak height. Adjust the mass calibration to ensure 0.1 amu accuracy from unit mass.

Copy the operating procedure from the master for 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. As a minimum, those masses for the elements of interest prescribed in Table 3 must be monitored in the same scan as is used for the collection of the data.

After the plasma system (i.e., torch box, plasma, and spray chamber) has stabilized, analyze the tuning solution a minimum of five times. The RSD for each element must be less than 5% before the instrument can be calibrated and samples analyzed.

9.2.2 Internal Standardization - Add internal standards to all samples, standards, and blanks at identical levels to correct for instrument drift and physical transport interferences (for full mass range scans, a minimum of three internal standards must be monitored and used for calculation). The internal standards are added by mixing with the sample solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil. 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 initial concentration of the internal standard solution presently used for calculation contains 500 g/L of scandium, indium, terbium and bismuth, with holmium, lutetium and yttrium as alternate internal standards. The final concentration of the internal standard solution after mixing in the mixing coil with the sample is approximately 100 g/L, or one-fifth the initial concentration, of scandium, indium, terbium and bismuth. Samples are analyzed first with all internal standards present. If scandium is present in the samples, the sample data are re-processed, deleting scandium as the internal standard.

9.2.3 Calibration - A calibration blank and one calibration standard are used for calibration. Elemental equations recommended for sample data calculations are listed in Table 2.

9.3 Sample Analysis

9.3.1 Screening - For every new or unusual matrix, screen a test sample for elements with significantly high concentration of naturally occurring internal standard elements. Use the internal standard mix as a calibration standard. Calibrate the instrument, verify the calibration by running the CAL standard and CB as surrogate samples. The samples will be run to screen samples for internal standards above 2 g/L (or >1% internal standard). If internal standards are detected, that internal standard cannot be used for sample calculations. One sweep will be performed semiquantitively.

9.3.2 Analytical Run Sequence

Set-up and configure the instrument and data system.
Tune the instrument.
Calibrate the instrument.
Enter autosampler loading list into data system, including all required QC and routine samples.
Start autosampler analysis sequence and analyze samples.
Review results for QC compliance and off-scale results. Identify samples which must be re-analyzed in a different analytical run. Samples having analytes at concentrations higher than the linear dynamic range must be diluted into range and re-analyzed.

An example of a loading list for an analytical run sequence is listed in the table below.

Seq.	Desc.	Seq.	Desc.	Seq.	Desc.	Seq.	Desc.
1	IPC	13	IPC	25	IPC	37	IPC
2	CB	14	CB	26	CB	38	CB
3	QCS	15	S5	27	S13	39	S21
4	QL	16	S6	28	S14	40	S21-LFM
5	LRB	17	S7	29	S15	41	S21-LFMD
6	LFB	18	S8	30	S16	42	S22
7	S1	19	S09	31	S17	43	S23
8	S1-LFM	20	S10	32	S18	44	IPC
9	S1-LFMD	21	S11	33	S19	45	CB
10	S2	22	S11-LFM	34	S20		End
11	S3	23	S11-LFMD	35	LRB		
12	S4	24	S12	36	LFB		

9.4 Data Reduction, Rounding and Reporting - After set-up and calibration the instrument reports results for the analyzed solution in the units of g/L. The instrument calculations include elemental correction calculations, internal standard correction calculations, and calibration factors.

The concentrations reported by the instrument must be corrected for any dilutions performed as part of the sample preparation or analysis process. 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 ½ the QL. Values between ½ the QL and the QL will be flagged as estimated (J flag). For rounding results, adhere to the following rules:

- If the number following those to be retained is less than 5, round down;
- If the number following those to be retained is greater than 5, round up; or
- 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.

9.4.1 Aqueous Samples - Data for aqueous samples should be reported in units of g/L using the following calculation:

$$C = M \times \frac{V_f}{V_i} \times D$$

where:

C	=	final reported concentration, in g/L.
M	=	measured concentration reported by instrument, in g/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.

10 DOCUMENTATION

10.1 ICP-MS Run Log - Entries are made for the case number, SDG number, date of analysis, site name, file name, analyst initials, lab sample IDs, client sample IDs, and comments, if any. The run log is maintained in Room 301. (Attachment C)

10.2 Inorganic Standards and Reagents Preparation Log Book - Copies of all standard solution preparation entries (CAL, IPC, QL, LFB, LFM, LFMD, QCS, etc.) must be submitted with each data package. (Attachment B)

10.3 Report Narrative and Deliverable

The data package consists of the report narrative, forms, and data, as listed in the table below.

Data Package Contents
Report Narrative: Discusses any problems encountered, both technical and administrative, the corrective action taken, and the resolution. All universal analytical flags should also be discussed in the report narrative.
Tabulated sample results: On an analytical spreadsheet, with units, sample collection dates, client sample IDs, laboratory IDs and station locations. (Attachment D)
LRB data: Included on the analytical spreadsheet. (Attachment D)
LFM and LFMD results: On a QC summary form with calculated relative percent difference (RPD). (Attachment E)
LFM, LFMD and LFB results: On a QC summary form with calculated percent recoveries (%R). (Attachments E)
Raw sample, standard and QC data, including run logs and any work sheets, if applicable. (Attachments B and C)

11 REFERENCES

11.1 U.S. Environmental Protection Agency. Method 200.8, *Determination of Trace Elements by in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, EMMC Version, May 1994.*

11.2 U.S. Environmental Protection Agency. SW846 Method 6020, *Inductively Coupled Plasma-Mass Spectrometry, Revision 0, 9/94.*

11.3 Fisons-VG Genesis Users Manual.

11.4 Region 9 SOP 130, *Glassware Cleaning Procedures.*

11.5 Region 9 SOP 462, *Analysis of Total Suspended Solids By EPA Method 160.2.*

11.6 Region 9 SOP 715, *Glassware Cleaning Procedures.*

11.7 Region 9 SOP 830, *Notification Procedures for Results Exceeding the Safe Drinking Water Act Maximum Contaminant Level.*

11.8 Region 9 SOP 840, *Notebook Documentation and Control.*

11.9 Region 9 SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency.*

11.10 Region 9 SOP 403, *Sample Preparation for GFAA, ICP-AES and ICP-MS Spectrometry Analyses*

11.11 Region 9 SOP 110, *Sample Receipt, Login, and Storage*

Attachment D
Analytical Spreadsheet

EPA REGION 9 LABORATORY-RICHMOND, CA
SUMMARY OF ANALYTICAL RESULTS

Case Number: R01S20 **Analysis:** Metals
Site: AAAZZZ **Matrix:** Water
SDG: 123456A
Date: 02/01/01

Sample No.	N/A				N/A				LRB-1				Quantitation
Sample I.D.	DUMMY				DUMMY				Reagent Blank				Limit
Date of Collection	01/23/01				01/24/01				N/A				N/A
Units	ug/L				ug/L				ug/L				ug/L
Analyte	Result		Q	Com	Result		Q	Com	Result		Q	Com	Result
Aluminum (200.7)	200	U			200	U			200	U			200
Antimony (200.8)	5	U			5	U			5	U			1
Arsenic (200.8)	20				20	U			20	U			5
Barium (200.8)	100				5	U			5	U			1
Beryllium (200.7)	1	U			1	U			1	U			1
Boron (200.7)	400				100	U			100	U			100
Cadmium (200.8)	5	U			5	U			5	U			1
Calcium (200.7)	80000				100	U			100	U			100
Chromium (200.7)	10	U			10	U			10	U			10
Cobalt (200.8)	5	U			5	U			5	U			1
Copper (200.8)	6				5	U			5	U			1
Iron (200.7)	100				100	U			100	U			100
Lead (200.8)	5	U			5	U			5	U			1
Magnesium (200.7)	30000				500	U			500	U			500
Manganese (200.8)	4		J	A	5	U			5	U			1
Mercury (245.1)									0.03	U			0.03
Molybdenum (200.8)	5	U			5	U			5	U			1
Nickel (200.7)	50	U			50	U			50	U			50
Potassium (200.7)	6000				5000	U			5000	U			5000
Selenium (200.8)	20	U			20	U			20	U			5
Silver (200.8)	5	U			5	U			5	U			1
Sodium (200.7)	240000				500	U			500	U			500
Thallium (200.8)	5	U			5	U			5	U			1
Vanadium (200.7)	20	U			20	U			20	U			20
Zinc (200.8)	120				20	U			20	U			5

Com - Comments refer to the corresponding section in the report narrative for each letter.
N/A - Not Applicable.
N/R - Not Required.
Q - Refer to data qualifiers.
U - The parameter was analyzed for, but was not detected. The associated value is the sample quantitation limit, adjusted for dilution, if any.
J - The associated value is an estimated quantity.

Filename: METSPDSHT.123

Attachment E
QC Summary

US E.P.A.
REGION 9 LABORATORY
June 20, 2000
Case Number: R00SXX
SDG: 00XXXA

Laboratory Fortified Matrix and Laboratory Fortified Matrix Duplicate

Analyzed Date	Sample ID	Analyte (Analysis)	LFM Result (ug/L)	LFMD Result (ug/L)	RPD	Q
01/01/01	AB00001	Aluminum (200.7)			??	
01/01/01	AB00001	Antimony (200.8)			??	
01/01/01	AB00001	Arsenic (200.8)			??	
01/01/01	AB00001	Barium (200.8)			??	
01/01/01	AB00001	Beryllium (200.7)			??	
01/01/01	AB00001	Boron (200.7)			??	
01/01/01	AB00001	Cadmium (200.8)			??	
01/01/01	AB00001	Calcium (200.7)			??	
01/01/01	AB00001	Chromium (200.7)			??	
01/01/01	AB00001	Cobalt (200.8)			??	
01/01/01	AB00001	Copper (200.8)			??	
01/01/01	AB00001	Iron (200.7)			??	
01/01/01	AB00001	Lead (200.8)			??	
01/01/01	AB00001	Magnesium (200.7)			??	
01/01/01	AB00001	Manganese (200.8)			??	
01/01/01	AB00001	Mercury (245.1)			??	
01/01/01	AB00001	Molybdenum (200.8)			??	
01/01/01	AB00001	Nickel (200.7)			??	
01/01/01	AB00001	Potassium (200.7)			??	
01/01/01	AB00001	Selenium (200.8)			??	
01/01/01	AB00001	Silver (200.8)			??	
01/01/01	AB00001	Sodium (200.7)			??	
01/01/01	AB00001	Thallium (200.8)			??	
01/01/01	AB00001	Vanadium (200.7)			??	
01/01/01	AB00001	Zinc (200.8)			??	

$$\%R = \frac{Cm}{Ct} \times 100$$

Where

$\%R$	=	relative percent recovery.
C_m	=	measured mercury concentration in the QCS, μg/L or ng/L.
C_t	=	true mercury concentration in the QCS, μg/L or ng/L.

8.3.5 QL - The accuracy of the calibration at the quantitation limit shall be verified by the analysis of the QL standard. The QL must be analyzed at the beginning of each analytical run, immediately after the QCS. The recovery of mercury in the QL is calculated as follows:

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

Where

$\%R$	=	percent recovery of the standard.
M	=	measured concentration of the analyte, μg/L or ng/L.
T	=	true concentration of the mercury in the QL, μg/L or ng/L.

If the QL recovery exceeds the limits of 50-150%, the analysis shall be terminated. The cause of the poor recovery must be determined and the problem corrected. The instrument must be re-calibrated and all affected samples must be re-analyzed. If after re-calibration, the QL recovery still exceeds the 50-150% limits, the calibration standards must be re-prepared and the instrument re-calibrated.

8.3.6 LRB - One LRB must be prepared and analyzed 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 potential laboratory contamination. If the potential contamination significantly impacts the analytical results, the LRB must be re-prepared along with the affected samples, and re-analyzed. Unless specified otherwise by project data quality objectives (DQOs), the following statement describes when samples must be re-prepared and re-analyzed:

If the LRB analyte concentration is $\geq$ the QL and the sample result is less than 5 times the LRB analyte concentration, the LRB and sample must be re-prepared and re-analyzed.

8.3.7 LFB - One LFB must be prepared and analyzed with each batch of 20 or fewer samples of the same matrix. The recovery of mercury in the LFB is calculated as follows:

$$\%R = \frac{LFB}{s} \times 100$$

Where

$\%R$	=	percent recovery.
LFB	=	measured concentration of mercury in the LFB, μg/L or ng/L.
s	=	expected mercury concentration in the LFB, μg/L or ng/L.

The recovery of mercury in the LFB must be within the 85-115% limits. If the recovery of mercury exceeds the limits, re-analyze once. If the recovery is still out, it is judged to be out-of-control, and the source of the problem must be identified and resolved before continuing analyses. All samples associated with the out-of-control LFB must be re-prepared and re-analyzed.

8.3.8 LFM - The LFM is designed to provide information about the effect of sample matrix on the measurement system. One LFM must be prepared for every 10 routine samples of the same matrix in a sample batch (e.g., 1 LFM for a batch containing 1-10 routine samples, 2 LFMs for a batch containing 11-20 routine samples, etc.). Samples identified as field blanks cannot be used for LFM sample analysis. Homogenize the routine sample selected as the LFM, obtain a representative aliquot, and proceed with sample preparation and analysis, treating the LFM sample as a routine sample. The recovery of mercury in the LFM is calculated as follows:

$$\%R = \frac{C_{lfm} - C}{s} \times 100$$

Where

$\%R$	=	percent recovery.
C_{lfm}	=	measured concentration in the LFM corrected for sample preparation and any dilutions, μg/L or ng/L.
C	=	measured concentration of mercury in the routine sample corrected for sample preparation and any dilutions, μg/L or ng/L.
s	=	expected mercury concentration in the LFM, corrected for sample preparation and any dilutions, μg/L or ng/L.

If the value of ***C*** is less than 4 times the value of ***s***, the acceptance window for ***%R*** is 70-130%. If the recovery of analyte falls outside the acceptance window other QC data must be examined to determine if a matrix problem exists. If the laboratory performance is in control (i.e., the IPC, QL, QCS, and LFB results are acceptable), the poor LFM recovery is most likely matrix-related. The problem should be discussed in the report narrative and the data user informed that the result for the analyte in the unfortified sample is suspect due either to heterogeneous nature of the sample or a matrix effect. The affected results should be flagged with a "J" on the analytical spreadsheet.

8.3.9 LFMD - Sample homogeneity can affect the quality and interpretation of the data. LFMD results can be used to assess sample homogeneity. One LFMD must be prepared for every 10 routine samples of the same matrix in a sample batch (e.g., 1 LFMD for a batch containing 1-10 routine samples, 2 LFMDs for a batch containing 11-20 routine samples, etc.). Samples identified as field blanks cannot be used for LFMD sample analysis. Homogenize the routine sample selected as the LFMD, obtain a representative aliquot, and proceed with sample preparation and analysis, treating the LFMD sample as a routine sample. Calculate the LFMD recovery using the equation from Section 8.3.8 and the relative percent difference using the following equation:

$$\%RPD = \frac{|C_{lfmd} - C_{lfm}|}{(C_{lfmd} + C_{lfm})/2} \times 100$$

Where

$\%RPD$ = relative percent difference.

C_{lfm} = measured concentration in the LFM corrected for sample preparation and any dilutions, μg/L or ng/L.

C_{lfmd} = measured concentration in the LFMD corrected for sample preparation and any dilutions, μg/L or ng/L.

The relative percent difference (RPD) must be $\leq$20%. If the control limits are exceeded, flag the associated mercury result as estimated (J flag). Document actions in the report narrative.

9 ANALYTICAL PROCEDURES

9.1 Sample Preparation - The sample and standard preparation procedure for mercury analysis is found in Region 9 Laboratory SOP 415.

9.2 Calibration and Standardization for the Leeman PS200 Automated Mercury Analyzer - 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. Typical operating parameters for the Leeman PS200 Automated Mercury Analyzer are as follows:

Parameter	Setting
Argon Flow Rate	0.30 liter/min
Pump Rate	5.0 mL/min

9.3 Analytical Run Sequence (Leeman PS200 Automated Mercury Analyzer)

9.3.1 Set-up and configure the instrument and data system. The Leeman PS200 mercury analyzer will be operational from a cold start (i.e. Leeman PS200 turned off) after an approximate 2.5 hour warm-up period. Inspect the pump tubing for pinching. Replace the pump tubing if excessive wear is apparent. Clamp the pump tubings in the holder and snap to seal. Prepare a fresh magnesium perchlorate drying tube by lightly packing a small loose wad of fine glass wool into both caps. Pack just enough to stop bits of magnesium perchlorate from filtering through, but not enough to restrict gas flow. Do not pack tightly. Reattach one of the caps onto the clear tube body and fill the tube with large flake magnesium perchlorate. It is important that the tube is full, but loosely packed. Firmly reattach the other cap. Pour out the reservoir containing reagent water into a waste container and add 10% hydrochloric acid (7.3.8) to a level approximately 1 inch from the top. Lightly oil the autosampler traverse arm and wipe clean.

9.3.2 After the 2.5 hour warm-up sequence has been completed, check the aperture reading by getting into the **Utility** menu and then into the **Diagnostics** menu. The aperture should be -100 to +100 (an ideal reading is zero); if not, take off the front panel of the PS200 and, using the hex wrench provided, gently adjust the bottom nut (if the value is negative) or the top nut (if the value is positive) so that the aperture reading is within the range and then replace the front panel. Use the **User Name** menu to enter analyst initials and then get back to the **Main Menu**. Select the **Protocol** (Mercury) and enter in a file name (for example, 20003021 which corresponds to instrument #2 (the Leeman PS200), the date, and the first run of the day). Transfer the calibration standards (in order, 0, 0.2, 0.5, 1.0, 5.0 and 15.0 μg/L mercury) into the first 6 spots in the 50mL standards tube rack. Place the bottle of 10% $SnCl_2$ in 10% HCl onto a stirring plate, stir, and put the tubing for the reductant into the container.

9.3.3 Transfer the QA/QC standards and samples into clean autosampler vials and place into the 44-sample capacity rack.

9.3.4 Enter the autosampler loading list into data system using **Rack Entry** and **Setup**, including all required QC and routine samples. Print the autosampler entries by pressing the F3 key.

9.3.5 Calibrate the instrument using the six standards. After calibration, get into **Calibration** on the **Main Menu** and then get into the **Line Calibration** menu. The current curve will be highlighted on the graph. Check the correlation coefficient (r); the correlation coefficient of the curve must be $\geq$0.995 or the instrument must be re-calibrated. If the correlation coefficient meets the 0.995 requirement, press the **A** key to Accept the curve and press the F3 key to print the curve.

9.3.6 Start autosampler analysis sequence and analyze samples. Review results for QC compliance and off-scale results. Identify samples which must be re-analyzed in a different analytical run. Samples

having analytes at concentrations greater than 15 µg/L must be diluted into calibration range and re-analyzed.

An example of a loading list for an analytical run sequence is listed in the table below.

Seq.	Desc.	Seq.	Desc.	Seq.	Desc.
1	IPC	13	IPC	25	IPC
2	CB	14	CB	26	CB
3	QCS	15	S5	27	S13
4	QL	16	S6	28	S14
5	LRB	17	S7	29	S15
6	LFB	18	S8	30	S16
7	S1	19	S09	31	S17
8	S1-LFM	20	S10	32	S18
9	S1-LFMD	21	S11	33	S19
10	S2	22	S11-LFM	34	S20
11	S3	23	S11-LFMD	35	IPC
12	S4	24	S12	36	CB

9.4 Calibration and Standardization for the CETAC M6000A Mercury Analyzer - 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. Typical operating parameters for the CETAC M6000A Mercury Analyzer are as follows:

Parameter	**Setting**
Argon Flow Rate	40 mL/min
Pump Rate	Instrument Default Pump Rate

9.5 Analytical Run Sequence (CETAC M6000A Mercury Analyzer)

9.5.1 Set-up and configure the instrument and data system. To start the M-6000A from a completely cold condition, turn on the M-6000A, gas, lamp and ASX-500 Auto Sampler. Inspect the pump tubing for pinching, replace if excessive wear is apparent. Clamp the pump tubings in the holder and snap to seal (from bottom, yellow-yellow-gray-yellow). Prepare a fresh magnesium

perchlorate drying tube by lightly packing a small loose wad of fine glass wool into both caps. Pack just enough to stop bits of magnesium perchlorate from filtering through, but not enough to restrict gas flow. Do not pack tightly. Reattach one of the caps onto the clear tube body and fill the tube with large flake magnesium perchlorate. It is important that the tube is full, but loosely packed. Firmly reattach the other cap. This charge of magnesium perchlorate will last until the "wet line" has moved 1/2 to 2/3 the way across the tube. Fill the bottle connected to the rinse station with de-ionized water. Turn the pump power on, speed is maximum and direction is clockwise. Make sure that the oven radiator surface temperature is set to 125°C. It takes at least 90 minutes for the optical rail, lamp, detectors and analog electronics to thermally stabilize.

9.5.2 Prior to analysis, ensure that the gas-liquid separator (GLS) center post is fully wetted 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 de-ionized 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 drying tube.* Re-engage the quick-release clamps on the drain pump tubes, once the GLS has emptied, sample analysis can start.

9.5.3 Open the worksheet *LOW LEVEL MERCURY*. Then type the sample IDs using the *LABELS* tab . Transfer the calibration standards (0, 30, 50,100, 500, 1000 ng/L mercury) into the first 6 positions of the standards rack, IPC and CB into positions 8 and 9. Then pour the samples into clean autosampler vials and place into the sample rack, making sure they are in the right position as it was entered in the labels file. An example of a loading list for an analytical run sequence is listed in Section 9.3.6.

9.5.4 Define the *TIME PROFILE* by reading a test Absorbance Signal using the *READ* button on the *ANALYSIS* tab. Once this has been done, it will 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.

9.5.5 Zero the instrument using the *INSTRUMENT MENU*. Calibrate using the *INSTRUMENT MENU*. The correlation coefficient of the curve must be ≥0.995 or the instrument must be re-calibrated.

9.5.6 Start the overall analysis process using the *START* button on the *ANALYSIS* tab. Click on *Put on stand-by mode after last sample* and *Print data*. Review results for QC compliance and off-scale results. Identify samples which must be re-analyzed in a different analytical run. Samples having analytes at concentrations greater than 1000 ng/L must be diluted into calibration range and re-analyzed.

9.5.7 When analysis is done, rinse de-ionized water through the reagent and sample tube for several minutes. Next, withdraw the reagent uptake tube manually and use the M-6000A Software Controls to withdraw the autosampler probe from the rinse water. Continue pumping until the drain line runs empty, turn off the pump, unclasp the pump tubes and turn off the gas.

9.6 Data Reduction and Reporting - After set-up and calibration the Leeman PS200 software reports results for the analyzed solution in units of μg/L and the CETAC M6000A software reports results for the analyzed solutions in units of ng/L. Aqueous samples should be reported using the following equation:

$$C = M \times D$$

where

C	=	final reported concentration, in μg/L or ng/L.
M	=	measured concentration reported by instrument, in μg/L or ng/L.
D	=	dilution factor, to account for dilution performed after sample preparation.

The concentrations reported by the instrument must be corrected for any dilutions performed as part of the sample preparation or analysis process. 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 ½ the QL. Values between ½ 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.

10 DOCUMENTATION

10.1 Leeman PS200 Mercury Run Log - Entries are made for the case number, SDG number, date of analysis, site name, file name, analyst initials, lab sample IDs, client sample IDs, and comments, if any. The run log is maintained in Room 302.

10.2 CETAC M6000A Automated Mercury Analyzer Run Log - Entries are made for the case number, SDG number, date of analysis, site name, file name, analyst initials, lab sample IDs, client sample IDs, and comments, if any. The run log is maintained in Room 300.

10.3 Standards Documentation - Copies of all standard solution preparation entries (CAL, IPC, QL, LFB, LFM, QCS, etc.) must be submitted with each data package.

10.4 Report Narrative and Deliverable

The data package consists of the report narrative, reports and data, as listed in the table below.

Data Package Contents
Report Narrative: Discusses any problems encountered, both technical and administrative, the corrective action taken, and the resolution. All universal analytical flags should also be discussed in the report narrative.
Tabulated sample results: On an analytical spreadsheet, with units, sample collection dates, client sample IDs, laboratory IDs and station locations. (Attachment E)
Method blank data: Included on the analytical spreadsheet. (Attachment E)
LFM and LFMD results: On a QC summary report with calculated relative percent difference (RPD).
LFM and LFB results: On a QC summary report with calculated percent recoveries (%R).
Raw sample, standard and QC data, including run logs and any work sheets, if applicable.

11 REFERENCES

11.1 Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry, EPA Method 245.1, Environmental Monitoring Systems Laboratory, Revision 3.0, May 1994.

11.2 Leeman PS200 Operation and Maintenance Manual, Leeman Labs, Hudson, New Hampshire 03051, 1993.

11.3 CETAC M6000A Operation Manual, Omaha, Nebraska, 1998.

11.4 Region 9 Laboratory SOP 125, *Aqueous Sample Disposal.*

11.5 Region 9 Laboratory SOP 110, *Sample Receipt, Log-in and Storage.*

11.6 Region 9 Laboratory SOP 415, *Preparation of Water Samples for Mercury Analysis.*

11.7 Region 9 Laboratory SOP 830, *Notification of Exceeding Safe Drinking Water MCL.*

11.8 Region 9 Laboratory SOP 840, *Notebook Documentation and Control.*

11.9 Region 9 Laboratory SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency.*

Attachment A
Deviations From Reference Method

A.1 The sample and standard preparation procedures are covered in Region 9 Laboratory SOP 415.

A.2 This SOP uses the Leeman PS200 Mercury Analyzer and CETAC M6000A Mercury Analyzer (automated instruments) which requires only a small digested sample aliquot (approximately 5 mL) to perform the mercury analysis. Method 245.1 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 which are over-range require redigestion 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.

A.3 Laboratory duplicate (LD) sample is not analyzed in this method, instead a LFMD is analyzed to calculate for precision.

A.4 A linear dynamic range (LDR) is not determined in this method, but any sample with a concentration above the highest calibration standard is to be diluted.

Appendix B-7
Anions: Nitrate-N

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 530

ANALYSIS OF ANIONS BY ION CHROMATOGRAPHY

Prepared by:

Hongsheng Li, ESAT Region 9, LMES Date

Review by:

Richard Bauer, Team Leader Date

Approved by:

Brenda Bettencourt, Laboratory Director Date

Periodic Review:

Signature	Title	Date
_____	_____	_____

STANDARD OPERATING PROCEDURE 530

ANALYSIS OF ANIONS BY ION CHROMATOGRAPHY

This SOP was prepared by Lockheed Martin Environmental Services (LMES) for the United States Environmental Protection Agency (USEPA) under the Environmental Services Assistance Team (ESAT) contract (EPA contract No. 68D60005).

APPROVED BY:

Patrick Hirata, LMES Date

Kathy O'Brien, QA/QC Coordinator, LMES Date

Jack Berges, ESAT Team Manager, LMES Date

ESAT Document Control Number: ESAT-9B-968

CONTENTS

1	SCOPE AND APPLICATION	4
2	METHOD SUMMARY	4
3	DEFINITIONS	4
4	HEALTH AND SAFETY	6
5	SAMPLE HANDLING AND PRESERVATION	6
6	INTERFERENCES	6
7	APPARATUS AND MATERIALS	7
8	QUALITY CONTROL PROCEDURES	9
9	ANALYTICAL PROCEDURES	15
10	DOCUMENTATION	19
11	REFERENCES	20

Attachment A - Deviations from the Reference Method 300.0

Attachment B - Ion Chromatography Run Log

Attachment C - Analytical Spreadsheet

Attachment D - QC Summary Report

Attachment E - Inorganic Standards and Reagents Preparation Log Book

1 SCOPE AND APPLICATION

1.1 This method is applicable for drinking, ground, surface, and saline water, domestic and industrial wastes and solids leached with reagent water.

1.2 This method applies to the determination of the inorganic anions fluoride, chloride, nitrite, bromide, nitrate, ortho-phosphate and sulfate by Method 300.0.

1.3 The reporting limit (RL) is 0.10 mg/L for fluoride, nitrate (reported as mg/L N) and nitrite (reported as mg/L N), and 1.0 mg/L for chloride, bromide, ortho-phosphate (reported as mg/L P) and sulfate.

2 METHOD SUMMARY

2.1 A small volume of sample is injected onto and passed through a series of ion-exchange columns. The anions of interest are separated on the basis of their relative affinities to a low capacity, strongly basic anion exchanger. The separated anions are directed into a strongly acidic cation suppressor exchanger where they are converted to their highly conductive acid forms. The carbonate and bicarbonate eluent is converted to weakly conductive carbonic acid. The separated anions in their acid forms are detected by electrical conductivity and are qualitatively determined on the basis of retention time as compared to the standards. Quantitation is based on peak areas and a cubic calibration curve is used to determine concentrations in environmental samples.

3 DEFINITIONS

3.1 Analytical Sample - Any sample in which anions are being determined, excluding standards, blanks, or QC reference samples.

3.2 Calibration Blank (CB) - A volume of reagent water analyzed immediately after an IPC to check the stability of the calibration curve baseline.

3.3 Calibration Standard (CAL) - A solution prepared from the stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.4 Field Reagent Blank (FRB) - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purposes of the FRB is to determine if contamination is occurring in the field environment. Note: Field reagent blanks cannot be used for LD or LFM analyses.

3.5 Field Duplicates (FD) - Two separate samples collected at the same time and placed 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.

3.6 Instrument Performance Check Solution (IPC) - A solution of method analytes used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.7 Laboratory Fortified Blank (LFB) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB 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.

3.8 Laboratory Fortified Sample Matrix (LFM) - An aliquot of an analytical sample to which known quantities of the method analytes are added in the laboratory. The LFM 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 LFM corrected for background concentrations.

3.9 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.

3.10 Laboratory Reagent Blank (LRB) - An aliquot of reagent water or other blank matrix 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.

3.11 Calibration Range (CR) - The concentration range over which the instrument response is calibrated.

3.12 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.

3.13 Quality Control Sample (QCS) - A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

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

4 HEALTH AND SAFETY

4.1 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. Contact your Supervisor or Health and Safety Coordinator to determine if additional treatment is required.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis and minimize waste disposal.

5.2 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 Samples must be received and stored at 4 ±2°C. Any deviations from the 4 ±2°C temperature requirements must be noted in the case narrative.

5.4 Holding Times For IC Analytes - The maximum sample holding time for ortho-phosphate, nitrate and nitrite is 48 hours from the time of sample collection. For chloride, bromide, fluoride and sulfate, the holding time is 28 days.

6 INTERFERENCES

6.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification with concentrated eluent can be used to solve most interference problems associated with retention times.

6.2 The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (100X) to 100 mL of each standard and sample although this is not routinely employed in this procedure.

6.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

6.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

6.5 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

7 APPARATUS AND MATERIALS

7.1 Apparatus

7.1.1 Dionex Ion Chromatograph Model DX120 System - Includes the Advance Chromatography Module, pump, Conductivity Cell Detector, Dionex Advance Computer Interface and Dionex DX-120 Data Chromatography Software.
7.1.2 Dionex Autosampler.
7.1.3 Anion Guard Column - AG14 from Dionex or equivalent.
7.1.4 Anion Separator Column - AS14 from Dionex or equivalent.
7.1.5 Anion Suppressor device - Anion Self-Regenerating Suppressor ASRS-II from Dionex or equivalent.
7.1.6 Analytical Balance - capable of weighing accurately to ±0.0001 g.
7.1.7 Class "S" weights.
7.1.8 Stirrer Plate and stirring bars.
7.1.9 Disposable Syringe Filters, 0.20 micron and 0.45 micron.
7.1.10 10 mL Disposable Syringes with luer-lock fittings.
7.1.11 Dionex Polyvials, 5 mL capacity with filter caps (Dionex P/N 38141).

7.2 Glassware

7.2.1 Volumetric Class "A" Flasks - 1000 mL, 500 mL, 250 mL and 100 mL.
7.2.2 Volumetric Class "A" Pipettes - 50 mL, 25 mL, 10 mL and 5 mL.
7.2.3 Drying oven, capable of being controlled at 105 ± 5°C.
7.2.4 Desiccator.
7.2.5 Plastic or Teflon spray bottle.
7.2.6 Class "S" weights.

7.3 Materials and Reagents

Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society (ACS) specifications should be used. If the purity of a reagent is in question, analyze for contamination.

7.3.1 Reagent water - All references to reagent water in this method refer to ASTM Type II grade water, ASTM D1193.
7.3.2 Degassed reagent water - Reagent water that has been purged with helium for 2 minutes.
7.3.3 Sodium Bicarbonate ($NaHCO_3$), reagent grade.
7.3.4 Sodium Carbonate (Na_2CO_3), reagent grade.
7.3.5 Sulfuric Acid (H_2SO_4), concentrated, reagent grade.
7.3.6 Sodium Chloride (NaCl), reagent grade.
7.3.7 Sodium Fluoride (NaF), reagent grade.
7.3.8 Sodium Nitrate ($NaNO_3$), reagent grade.
7.3.9 Sodium Nitrite ($NaNO_2$), reagent grade.
7.3.10 Sodium Bromide (NaBr), reagent grade.
7.3.11 Potassium Phosphate (KH_2PO_4), reagent grade.
7.3.12 Potassium Sulfate (K_2SO_4), reagent grade.
7.3.13 Gases
7.3.13.1 Helium, UHP.
7.3.13.2 Nitrogen, UHP.

7.4 Preparation of Solutions and Standards

7.4.1 Eluent Solutions

7.4.1.1 Two eluent stock solution concentrates are required. The first eluent concentrate is 0.5 M sodium carbonate prepared by dissolving 26.49 g of sodium carbonate in 400 mL of reagent water and diluting to final volume of 500 mL. The second eluent concentrate is 0.5 M sodium bicarbonate prepared by dissolving 21.00 g of sodium bicarbonate in 400 mL of reagent water and diluting to final volume of 500 mL. Record the reagent preparation in Inorganic Standards and Reagents Preparation Log Book (Attachment E).

7.4.1.2 The working eluent solution is prepared by pipetting 7.0 mL of 0.5 M Na_2CO_3 plus 2.0 mL of 0.5 M $NaHCO_3$ into a 1L volumetric flask and diluting to volume with degassed reagent water. Record the reagent preparation in Inorganic Standards and Reagents Preparation Log Book (Attachment E).

7.4.2 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 1 month when stored at 4°C. Record the standard preparation in Inorganic Standards and Reagents Preparation Log Book (Attachment E).

7.4.2.1 Mixed Stock Standard 1: 1000 mg/L fluoride, chloride, nitrite, bromide, nitrate, ortho-phosphate and sulfate standard - Prepare by dissolving 2.2100 g NaF, 1.6485 g NaCl, 4.9257 g $NaNO_2$, 1.2878 g NaBr, 6.0679 g $NaNO_3$, 4.3937 g KH_2PO_4 and 1.8141 g K_2SO4 in reagent water and dilute to volume in a 1-L volumetric flask.

7.4.3 Calibration Standard 5: 50 mg/L fluoride, chloride, nitrite, bromide, nitrate, ortho-phosphate and sulfate standard - Pipet 5.0 mL of Mixed Stock Standard 1 (7.4.2.1) into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily.

7.4.4 Calibration Standard 4: 25 mg/L fluoride, chloride, nitrite, bromide, nitrate, ortho-phosphate and sulfate standard - Pipet 2.5 mL of Mixed Stock Standard 1 (7.4.2.1) into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily.

7.4.5 Calibration Standard 3: 5.0 mg/L fluoride, chloride, nitrite, bromide, nitrate, ortho-phosphate and sulfate standard - Pipet 0.5 mL of Mixed Stock Standard 1 (7.4.2.1) into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily.

7.4.6 Calibration Standard 2: 1.0 mg/L fluoride, chloride, nitrite, bromide, nitrate, ortho-phosphate and sulfate standard - Pipet 2.0 mL of Calibration Standard 5 (7.4.3) into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily.

7.4.7 Calibration Standard 1: 0.1 mg/L fluoride, chloride, nitrite, bromide, nitrate, ortho-phosphate and sulfate standard - Pipet 2.0 mL of Calibration Standard 3 (7.4.5) into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily.

7.4.8 Quality Control Sample (QCS) - Analysis of a QCS solution is required. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials. R9 laboratory uses a Custom Multi-Anion solution from Spex as the QCS containing 30 mg/L each ortho-phosphate, sulfate, 20 mg/L each bromide, chloride, nitrate, nitrite and 10 mg/L fluoride. Prepare fresh daily. Record the reagent preparation in Inorganic Standards and Reagents Preparation Log Book (Attachment E).

8 QUALITY CONTROL PROCEDURES

8.1 EPA Region 9 Laboratory operates a formal quality control (QC) program. As it relates to this SOP, the QC program consists of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks, performance evaluation samples and other laboratory solutions as a continuing check on performance. The laboratory maintains performance records that define the quality of the data that are generated.

8.2 Initial Demonstration of Performance - Prior to use in routine analysis, the method must be characterized in terms of calibration range verification and MDL study.

8.2.1 Calibration Range (CR) - The CR must be determined initially and verified every 6 months or whenever a significant change in instrument response is observed or expected. The initial demonstration must use sufficient standards to insure that the resulting curve is adequately defined. The verification must use a minimum of a blank and five standards. If any verification data exceeds the initial values by $\pm$10%, the calibration range must be reestablished.

8.2.2 MDL - MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit. An MDL in reagent water represents a best case situation and does not reflect possible matrix effects of real world samples.

To determine MDL values, process seven replicate aliquots of the fortified reagent water through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = t \times s$$

where: MDL = method detection limit
t = student t value for 99% at 99% confidence interval with n-1 degrees of freedom (t=3.14 for n=7)
s = standard deviation

If the relative standard deviation (RSD) for any analyte from the analyses of the seven aliquots is <10%, the concentration of the analyte in the reagent water may have been too high, which will bias the MDL value. In such a case, the MDL study should be repeated with a lower concentration of the analyte.
MDL's are determined every 6 months, when a new operator begins work or whenever analytical conditions are changed significantly.

The MDL must be less than 1/2 the reporting limit of 0.1 mg/L for nitrite, nitrate, ortho-phosphate and 1.0 mg/L for fluoride, chloride, bromide and sulfate. If any analyte fails, the process must be examined to determine the source of variability in the analyte measurement or the lack of sensitivity. The problem must be corrected before analytical samples are measured.

8.3 Routine Analytical Quality Control

8.3.1 IPC - The accuracy and stability of the calibration shall be verified by the periodic analysis of an IPC standard. It must be analyzed at the beginning of an analytical run, after every 10 samples, and at the end of an analytical run. The recovery of analytes in the IPC is calculated as follows:

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

Where

%R	=	percent recovery of the standard
M	=	measured concentration of analyte, mg/L
T	=	true concentration of analyte in the IPC, mg/L

If the IPC recovery exceeds the limits of 90-110%, the analysis shall be terminated. The cause of the poor recovery must be determined and the problem corrected. The instrument must be re-calibrated and all samples not bracketed by acceptable IPC results must be reanalyzed. The IPC analyzed immediately after calibration is also a QCS (30 mg/L each ortho-phosphate, sulfate, 20 mg/L each bromide, chloride, nitrate, nitrite and 10 mg/L fluoride); both have recovery limits of 90-110%. All subsequent IPCs have analyte concentrations at 25 mg/L (7.4.4).

8.3.2 CB - The stability of the calibration curve baseline must be monitored by analyzing a CB immediately after every IPC standard. If the absolute value of the CB result is less than or equal to the RL, the result is acceptable. If the absolute value of the CB result exceeds the RL, the analysis must be terminated. 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 reanalyzed.

8.3.3 QCS Analysis - The anion concentrations in a QCS sample must be measured daily or once per batch of 20 samples, whichever is more frequent. The first QCS analyzed is also the initial IPC (30 mg/L each ortho-phosphate, sulfate, 20 mg/L each bromide, chloride, nitrate, nitrite and 10 mg/L fluoride). The recoveries must be within 90-110% or the samples in the batch must be reanalyzed.

$$\%R = \frac{Cm}{Ct} \times 100$$

Where

$\%R$ = relative percent recovery
C_m = measured analyte concentration in the QCS
C_t = true analyte concentration in the QCS

8.3.4 Reporting Limit (RL) - To verify the ability to detect target analytes near the RL, RL standards must be analyzed at the RL level (Section 1.3) at the beginning of the analytical run but not before the initial IPC. R9 laboratory analyzed two RL standards, one with analyte concentrations at 0.1 mg/L (for fluoride, nitrate, nitrite) and the other with analyte concentrations at 1 mg/L (for chloride, bromide, ortho-phosphate, sulfate). The recovery of analytes in the RL is calculated as follows;

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

Where

%R = percent recovery of the standard
M = measured concentration of the analyte, mg/L
T = true concentration of the analyte in the RL, mg/L

If the RL 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. The instrument must be re-calibrated and all affected samples must be reanalyzed. If, after recalibration, the RL recovery still exceeds the 70-130% limits, the calibration standards must be reprepared and the instrument recalibrated.

8.3.5 LRB - The laboratory must analyze at least one LRB daily or with each batch of 20 or fewer samples of the same matrix, whichever is more frequent. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the MDL indicate potential laboratory contamination. If the potential contamination significantly impacts the analytical results, the LRB must be re-prepared along with the affected samples, and re-analyzed. Unless specified otherwise by project DQOs, the following statements describe when samples must be re-prepared and re-analyzed:

1) If the sample concentration is greater than or equal to 10 times the MDL and the LRB concentration is greater than 10% of the sample concentration, the LRB and sample must be re-prepared and re-analyzed
2) If the sample concentration is less than 10 times the MDL and the LRB concentration is greater than 2.2 times the MDL, the LRB and sample must be re-prepared and re-analyzed.

8.3.6 LFB - One LFB must be prepared and analyzed with each analytical run. R9 laboratory uses the same solution used for the QCS (30 mg/L chloride, sulfate, 20 mg/L bromide, nitrate, nitrite, ortho-phosphate and 10 mg/L fluoride) as the LFB. The recovery of analyte in the LFB is calculated as follows:

$$\%R = \frac{LFB}{s} \times 100$$

Where

$\%R$ = percent recovery
LFB = measured concentration of analyte in the LFB
s = expected analyte concentration in the LFB

The recovery of the analytes in the LFB must be within the 90-110% limits. If the recovery exceeds the limits, the analysis system is judged to be out-of-control, and the source of the problem must be identified and resolved before continuing analyses.

8.3.7 Laboratory Duplicate - 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 (e.g., 1 LD for a batch containing 1-10 routine samples, 2 LDs for a batch containing 11-20 routine samples, etc.). 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 analyte in the LD
C = measured analyte in the routine sample

The relative percent difference (RPD) for any analyte must be $\leq$20% for samples with analyte levels greater than or equal to 1.0 mg/L for nitrite (reported as N), nitrate (reported as N), ortho-phosphate (reported as P) and 10.0 mg/L for fluoride, chloride, bromide and sulfate. The absolute difference between duplicate results must be less than the reporting limit for samples containing less than 1.0 mg/L for nitrite, nitrate, ortho-phosphate and 10.0 mg/L for fluoride, chloride, bromide and sulfate. If the control limits are exceeded, flag all associated analyte results with an asterisk (*). Document actions in the case narrative.

8.3.8 LFM - The LFM is designed to provide information about the effect of sample matrix on the measurement system. One LFM must be prepared for every 10 routine samples of the same matrix in a sample batch. The same sample chosen as the LD should be used as the sample for the LFM. Samples identified as field blanks cannot be used for LFM sample analysis. The recovery of analyte in the LFM is calculated as follows:

$$\%R = \frac{C_{lfm} - C}{s} \times 100$$

Where
$\%R$ = percent recovery
C_{lfm} = measured concentration of analyte in the LFM, 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 LFM, corrected for sample preparation and any dilutions

If the value of s exceeds 3.3 times the value of C, the acceptance window for $\%R$ is 90-110% for drinking water samples and 75-125% for other samples. If the recovery falls outside the acceptance window other QC data must be examined to determine if a matrix problem exists. If the laboratory performance for that analyte is in control (i.e., the IPC, QCS, and LFB results are acceptable), the poor LFM recovery is most likely matrix related. Lab duplicate results should also be examined to gain additional insight as to whether the matrix components or matrix heterogeneity are the cause of the unacceptable recovery. In either case, the problem should be discussed in the case narrative and the data user informed that the result for that analyte in the unfortified sample is suspect due either to heterogeneous

nature of the sample or a matrix effect. Flag any out-of-control analytes with an "N". The spiking levels for the LFM are as follows:

Parameter	Recommended Spiking Level (mg/L)
Fluoride	20
Chloride	20
Nitrite-N	20
Bromide	20
Nitrate-N	20
O-Phosphate-P	20
Sulfate	20

8.3.9 QCS Analysis - The anion concentrations in a QCS sample must be measured daily or once per batch of 20 samples, whichever is more frequent. The recoveries must be within 90-110% or the samples in the batch must be reanalyzed.

$$\%R = \frac{Cm}{Ct} \times 100$$

Where

$\%R$ = relative percent recovery
C_m = measured analyte concentration in the QCS
C_t = true analyte concentration in the QCS

9 ANALYTICAL PROCEDURES

9.1 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.
Typical operating settings for the Dionex DX120 are as follows:

DX-120 Detector Parameters

Detector Type: DX-120
Data Collection time (minutes): 11.00
Data Collection Rate: 5.00
Real time plot scale maximum (us): 30.000
Real time plot scale minimum (us): -3.000

DX-120 Integration Parameters

Peak detection algorithm: Standard
Starting peak width (seconds):10.00
Peak threshold: 0.50
Peak area reject (area counts): 1000.00
Reference peak area reject (area counts): 1000.00

DX-120 Smoothing Parameters

Filter Type: No filter

DX-120 Integration Data Events

Time	Description
0.00	Stop peak detection
2.44	Start peak detection
2.45	Force baseline at start of this peak
2.65	Void volume treatment for this peak

DX-120 Calibration Parameters

External or internal calibration: EXTERNAL
Number of replicates for calibration:1
Rejection: Manual
Level Weighting: Equal
Calibration standard volume: 1.00
Default sample volume: 1.00
Amount units: mg/L
Replace retention time: Yes
Update response: Yes
Default dilution factor: 1.00
Default response factor for unknown peaks:0.00
Calculate unknowns by area or height: Area
Flow: 2 mL/min.

9.2 Initial Calibration

9.2.1 An initial calibration is performed by analysis of a blank and five standards of increasing analyte concentration (0.1, 1.0, 5.0, 25 and 50 mg/L for all analytes) with cubic fit. The initial calibration is considered valid as long as the instrument performance check (IPC) standard response is within the ±10% of the response for that standard level in the initial calibration. The correlation coefficient for the initial calibration must be ≥ 0.995 for the calibration to be valid. If the calibration does not meet the criteria, the analysis shall be terminated, the problem corrected, and a new calibration curve performed.

9.2.2 The QC samples in Section 8.3 must be analyzed and must be within the appropriate control limits before sample analyses are performed.

9.3 Sample Analysis

9.3.1 Fill a 5mL polyvial with well-mixed sample. Samples that contain particles larger than 0.45 microns require filtration to prevent damage to instrument columns and flow systems. Attach a 0.45 micron disposable syringe filter to a 10mL disposable syringe; pull out the plunger and pour approximately 10 mL of well-mixed sample into the syringe and reattach the plunger. Apply pressure to the plunger and filter the sample through the syringe filter and into the 5mL polyvial (discard the remaining sample into the waste container and the syringe assembly into a solid waste container). Attach a filter cap to the 5mL polyvial and push down the filter cap with the supplied tool until it is flush with the top of the polyvial. Label the contents of the polyvial and insert into the autosampler cassette.

9.3.2 Load and inject the sample. The sample loop will be flushed thoroughly.

9.3.3 The width of the retention time window used to make identifications is based upon measurements of actual retention time variations of standards over the course of the day. The manufacturer's suggested retention times were modified slightly due to instrument conditions and the experience of the analyst in the interpretation of the chromatograms. All chromatograms are reviewed to ensure that the correct peaks are integrated. The retention time windows currently used on the DX-120 are listed in the following table:

Parameter	Retention Time (min)	Retention Time Window (min)
Fluoride	2.62	2.35 - 2.88
Chloride	3.67	3.30 - 4.03
Nitrite-N	4.38	3.94 - 4.81
Bromide	5.50	4.95 - 6.05
Nitrate-N	6.10	5.49 - 6.71
O-Phosphate-P	7.80	7.02 - 8.58
Sulfate	9.35	8.41 - 10.28

9.3.4 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

An example of a loading list for an analytical run sequence is listed in the table below.

Seq.	Desc.	Seq.	Desc.	Seq.	Desc.	Seq.	Desc.
1	IPC/QCS	13	IPC	25	IPC	37	IPC
2	CB	14	CB	26	CB	38	CB
3	RL1	15	S5	27	S13	39	LFB
4	RL2	16	S6	28	S14	40	S21
5	LRB	17	S7	29	S15	41	S21-LD
6	LFB	18	S8	30	S16	42	S21-LFM
7	S1	19	S9	31	S17	43	S22
8	S1-LD	20	S10	32	S18	44	S23
9	S1-LFM	21	S11	33	S19	45	S24
10	S2	22	S11-LD	34	S20	46	S25
11	S3	23	S11-LFM	35	QCS	47	IPC
12	S4	24	S12	36	LRB	48	CB

9.4 Data Reduction and Reporting - After set-up and calibration the software reports results for the analyzed solution in units of mg/L.

The concentrations reported by the instrument must be corrected for any dilutions performed as part of the sample preparation or analysis process. All results should be reported using no more than three significant figures; however, no values of less significance than the MDL may be reported (values near the MDL will be reported with only two significant figures). Report down to ½ the RL. Values between ½ the RL and the RL will be flagged as estimated (J flag).

9.4.1 Aqueous Samples - Data for aqueous samples should be reported in units of mg/L using the following calculation;

$$C = M \times D$$

where: C = final reported concentration, in mg/L
M = measured concentration reported by software, in mg/L
D = sample analysis dilution factor, to account for any dilution

9.4.2 Solid Samples - Data for solid samples should be reported in units of mg/Kg using the following calculation;

$$C = M \times \frac{Vf}{Vi} \times D$$

where: C = final reported concentration, in mg/Kg
M = measured concentration reported by software, in mg/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

9.4.3 Reporting - Results will be reported to 1 significant figure for analyte concentrations less than 1 mg/L, 2 significant figures for analyte concentrations less than 10 mg/L and to 3 significant figures for analyte concentrations greater than or equal to 10 mg/L. 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.

10 DOCUMENTATION

10.1 Raw Data

10.1.1 Ion Chromatography Run Log - Entries are made for the case number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any. The run log is maintained in Room 207.

10.1.2 Inorganic Standards and Reagents Preparation Log Book - Copies of all standard solution preparation entries (CAL, IPC, RL, LFB, LFM, QCS, etc.) must be submitted with each data package.

10.1.3 Chromatograms and Quantitation Reports - The chromatograms must be scaled such that the baseline used for measuring the peak is visible.

Case Narrative and Deliverable

The data package consists of the case narrative, forms, and data, as listed in the table below.

Data Package Contents
Case Narrative: Discusses any problems encountered, both technical and administrative, the corrective action taken, and the resolution. All universal analytical flags should also be discussed in the case narrative.
Tabulated sample results on an analytical spreadsheet, with units, sample collection dates, client sample IDs, laboratory IDs and station locations. (Attachment C)
Method blank data included on the analytical spreadsheet. (Attachment C)
Duplicate results on a QC summary form with calculated relative percent difference (RPD). (Attachment D)
QCS, LFM and LFB results on a QC summary form with calculated percent recoveries (%R). (Attachment D)
Raw sample, standard and QC data, including run logs and any work sheets, if applicable. (Attachment B)

11 REFERENCES

11.1 EPA Method 300.0, Determination of Inorganic Anions by Ion Chromatography, Environmental Monitoring Systems Laboratory, Revision 2.1, August 1993.
11.2 Dionex DX-120 Operation and Maintenance Manual, Dionex Corp., Sunnyvale, California 94086, 1997.
11.3 Region 9 SOP 125, *Sample Disposal.*
11.4 Region 9 SOP 110, *Sample Receipt, Log-in and Storage.*
11.5 Regional Analytical Program Client Request Form - Anions (3001295.CRF) USEPA, Revision 12/22/95.
11.6 Region 9 SOP 835, *Chromatographic Integration Procedures.*

11.7 Region 9 SOP 830, *Notification Procedures for Results Exceeding the Safe Drinking Water Act Maximum Contaminant Level.*

Attachment A
Deviations From Reference Method

A.1 This SOP specifies the use of third-order regression (cubic) calibration. Review of instrument response using various calibration protocols demonstrates that instrument response is not linear at low concentrations (less than 1 mg/L) but that the data fit a third-order calibration model very well. Using these calibration protocols has resulted in acceptable performance evaluation samples from a variety of sources. Additionally, the SOP requires the analysis of a standard at the reporting limit on a daily basis to verify instrument performance and calibration.

A.2 The scope of this SOP does not include the analysis of the inorganic anions bromate, chlorate and chlorite.

Appendix B-8
1,2,3-Trichloropropane

1,2,3-TCP analysis approval process

Analysis for 1,2,3-Trichloropropane

Last Update: August 9, 2002
1,2,3-Trichloropropane (1,2,3-TCP) is a state Unregulated Chemical Requiring Monitoring. Both the action level and the DLR are 0.000005 mg/L (5 ng/L).
Due to the extremely low DLR, USEPA methods 502.2, and 524.2 are not applicable for determining this compound in drinking water. Consequently, the Sanitation and Radiation Laboratories (SRL) have developed two GC/MS methods (Purge and Trap GC/MS and Liquid-Liquid Extraction GC/MS) that are capable of 1,2,3-TCP quantification at the DLR.
Laboratories performing an analysis for 1,2,3-TCP may use one of the GC/MS methods above. Alternatively, EPA methods 504.1 or 551.1 may also be used if the laboratory can demonstrate that the method is capable of achieving the DLR of 0.000005 mg/L without method modification.
A laboratory using EPA method 504.1 or 551.1 will be required to do the following:

- Demonstrate that it can achieve the DLR,
- Demonstrate that the blank is not contaminated, and
- Confirm a positive detection that is at or above the DLR either by a second column analysis, or by one of the GC/MS methods above. This confirmation will be required only for the initial characterization of a water source. Confirmation will not be required on subsequent analyses of the same water source.

NOTE: A 1,2,3-TCP finding in a sample that has high TDS or volatile content, or otherwise precludes unambiguous confirmation, should be confirmed with one of the GC/MS methods above.
Certification Requirements
Once PE samples are available from the DHS Drinking Water Program, any laboratory wishing to perform the analysis for 1,2,3-TCP in drinking water must seek interim certification from the Environmental Laboratory Accreditation Program (ELAP) by doing the following. A laboratory must:

- Send in an ELAP application for certification,
- Conduct an initial demonstration of performance/capabilities,
- Provide a validation data package,
- Have a written SOP to demonstrate laboratory capability,
- Successfully analyze a DHS-provided performance evaluation (PE) sample, (two PE testing rounds will be scheduled by DHS during 2003). The PE samples will be distributed by SRL along with instructions for the study.

Upon passing a laboratory inspection by ELAP(to be conducted at the time of the regular site inspection), the laboratory will be granted full certification.
Interim certification may be granted based on the above and the laboratory inspection will be conducted at the time of the regular site visit.
For further details refer to the ELAP web page.
[If you have general certification questions, please call Shinae Park at (510) 540-2800, and for questions related to

DETERMINATION OF 1,2,3-TRICHLOROPROPANE IN DRINKING WATER BY CONTINUOUS LIQUID-LIQUID EXTRACTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1. Scope and Application

1.1. This method may be used to determine 1,2,3-trichloropropane (TCP), CAS No. 96-18-4, in water at concentrations below the quantifiable ranges of USEPA methods 504.1, 551.1 and 524.2.

1.2. The linear calibration range for TCP is from 5.0 to at least 500 ng/L. Higher concentrations of TCP have not been tested, as the purpose of this method is trace-level analysis. As a general guide, use methods 504.1 or 551.1 for TCP concentrations =100 ng/L and method 524.2 for TCP concentrations =500 ng/L.

1.3. While the ion trap mass spectrometer (MS) detector was used in the development of this method, the quadrupole MS detector may also be used. To achieve the sensitivity necessary for this method, the ion trap MS must be operated in the selected ion storage (SIS) mode, while the quadrupole MS must be operated in the selected ion monitoring (SIM) mode.

1.4. The applicable matrices include drinking water, ground water and surface water. Although not specifically tested, this method should also be applicable to wastewaters.

1.5. This method is recommended for use by analysts experienced in gas chromatography/mass spectrometry (GC/MS) and in the interpretation of the resulting ion chromatograms and mass spectra. Analysts using this method should be familiar with USEPA method 525.2.

1.6. Disclaimer: Mention of trade names or commercial products in this method does not constitute endorsement or exclusive recommendation for use. Laboratories may make equivalent product substitutions.

2. Summary of Method

2.1. A 1 L sample is extracted for approximately 16 hours (overnight) with methylene chloride using a continuous liquid-liquid extractor. After extraction the methylene chloride extract is isolated, dried, then concentrated to 1 mL and analyzed by GC/MS. TCP is identified by matching the retention time and mass fragment ions from the sample with those of the reference standard. Quantitation is performed by the isotopic dilution procedure. 1,2,3-trichloropropane-D_5 (TCP-D_5) is used as the internal standard, which is added to the samples and standards, such that the final concentrations in the sample extracts and standards are the same.

3. Interferences

3.1. Ensure that all solvents, reagents, glassware and equipment used in the analysis are free from interfering contaminants.

3.2. Organic compounds which coelute or nearly coelute with TCP or TCP-D_5 and which yield the same fragment ions as TCP or TCP-D_5 can be a major source of error. Due to the extreme sensitivity of this method, even low abundances of these ions can result in severe interference when the interfering compound is present at sufficiently high concentration.

4. Safety

4.1. The toxicity or carcinogenicity of chemicals used in this method has not been fully defined. When working with these chemicals, use appropriate protection to eliminate or minimize exposure to these chemicals. Observe and employ other safety precautions described in the material safety data sheets for these chemicals. When operating analytical instruments, observe the manufacturers safety precautions and safe operating procedures.

5. Equipment and Supplies

5.1. Continuous liquid-liquid extractor, one step, for heavier than water solvents, with all glass or PTFE connecting joints, 1 L sample capacity (Corning Pyrex, Accelerated One-Step Modular, or equivalent).
  5.1.1. Recirculating hot water bath, or equivalent, for methylene chloride distillation.
  5.1.2. Recirculating chiller, or equivalent, for the condenser.
5.2. Nitrogen evaporator for solvent evaporation (Organomation, or equivalent)
5.3. Gas chromatograph: Same as described in method 525.2.
  5.3.1. 30 meter x 0.25 mm DB-5ms with a 0.25 µm film thickness (J&W Scientific).
  5.3.2. An alternate column may be used if it provides the required separation and performance for this method.
5.4. Mass spectrometer and data system: Same as described in method 525.2, except the mass spectrometer and data system must be capable of the following.
  5.4.1. Ion trap mass spectrometer: Must be capable of operating in the selected ion storage mode (SIS).
  5.4.2. Quadrupole mass spectrometer: Must be capable of operating in the selected ion mode (SIM).
5.5. Sample containers: 1 L amber glass bottles with PTFE-lined screw-caps. The bottles may be purchased as pre-cleaned, level 2.
5.6. Assorted glass micro-syringes for preparing standards and fortification solutions.
5.7. Assorted volumetric flasks and vials with PTFE-lined screw-caps for the preparation and storage of standards and sample.

6. Reagents and Standards

6.1. Reagent water: free from TCP and other interfering contaminants.
6.2. Methylene chloride, capillary GC/trace analysis grade (Burdick & Jackson, or equivalent).
6.3. Methanol, pesticide grade.
6.4. Sodium sulfate, anhydrous, reagent grade. Heat at 400°C in a muffle furnace for 2 hours before use.
6.5. Primary standard: 1,2,3-Trichloropropane, 200 µg/mL in methanol (Ultra Scientific, or equivalent). Prepare a primary dilution standard in methylene chloride. Use the primary dilution standard to prepare the calibration standards in methylene chloride at the concentrations of 5.0, 10, 25, 50, 100 µg/L, or higher, as required.
6.6. QC solution: 1,2,3-Trichloropropane, 100 µg/mL in methanol (Chem Service, or equivalent). Prepare a 1.0 µg/mL primary dilution standard in methanol. Prepare the QC sample by adding 50 µL of the primary dilution standard to 1 L of reagent water to produce a TCP concentration of 50 ng/L.
6.7. Labeled internal standard: 1,2,3-Trichloropropane-D_5, 98% (Cambridge Isotopes, or equivalent). Ensure that the TCP-D_5 standard contains less than 0.5% of the native compound (TCP). Prepare a stock solution and a primary dilution standard in methanol. Spike all

(TCP). Prepare a working stock solution and a primary dilution standard in methanol. Spike all prepared standards, samples and blanks with the primary dilution standard before conducting the analysis. It is recommended that the internal standard concentration in the aqueous working samples should not exceed 50 ng/L.

7. Sample Collection, Preservation and Storage

7.1. Collect samples in duplicate in 40 mL amber VOA vials as described in method 524.2.

7.2. If the samples contain residual chlorine, add 25 mg of ascorbic acid to each vial before sample collection.

7.3. Store samples at 4°C until analysis. Protect from direct sunlight or other bright light sources. The sample storage area must be free from organic solvent vapors.

7.4. All samples must be analyzed within 14 days of collection.

8. Quality Control

8.1. An initial demonstration of capability

8.1.1. Prepare and analyze a laboratory reagent blank (LRB) to demonstrate that the preparation procedures, glassware, reagents and instrument system are free from interfering contaminants.

8.1.2. Prepare and analyze seven replicates of a laboratory fortified blank (LFB) containing TCP in the range of 20 to 50 ng/L. The mean recovery should be within 80-120% and the relative standard deviation (RSD) should be =20%.

8.1.3. Perform a method detection limit (MDL) study by preparing and analyzing a minimum of seven replicates of a 5.0 ng/L TCP standard over a period of three days, or more. Calculate the MDL as follows.

$$MDL = S \times t_{(n-1,\,1-a=0.99)}$$

where: S = standard deviation of the replicate analysis.
t = Student's t value for the 99% confidence level with n-1 degrees of freedom.
n = number of replicates.

8.1.4. The reporting level should be no less than three times the MDL. A TCP reporting level of 5.0 ng/L requires a MDL of 1.7 ng/L, or less.

8.2. Assessing laboratory performance

8.2.1. Before processing samples, a LRB must be analyzed to demonstrate that all glassware and reagents are free of interfering contaminants. A LRB must be analyzed with each batch of samples of 10 samples, or less, or when reagents are changed. LRB results should be non-detects (< MDL).

8.2.2. Each day that samples are analyzed, a LFB must be analyzed with each batch of 10 samples, or less. For the GC/MS-quadrupole system, prepare the LFB with a TCP concentration of 5.0 ng/L. For GC/MS-the ion trap system, prepare the LFB with a TCP concentration of 10 ng/L. The LFB recovery should be within the range of 80-120% of the fortified concentration.

8.2.3. In addition, the integrated areas of the TCP-D_5 responses should be monitored during the day, as another check on system sensitivity. (See Section 9.5.3.)
8.2.4. Analyze at least one sample in duplicate per batch of 10 samples, or less.
8.2.5. At least quarterly, analyze a TCP quality control sample from an external source to assess laboratory performance.

9. Calibration and Standardization

9.1. Calibrate the instrument by analyzing a minimum of five calibration standards in the range of 5.0 to 100 ng/L, or higher, as required.

9.2. The capillary columns and temperature programs listed in Table 1 provide sufficient separation between TCP and TCP-D_5. In addition, the two compounds do not interfere with each other's quantitation ion. Since corrections to isotopic abundances are not required when calculating the isotope ratio of TCP to TCP-D_5, a response factor (similar to the internal standard response factor calculation) for TCP may be calculated as follows.

$$RF = \frac{A_{TCP} Q_{TCP\text{-}D_5}}{A_{TCP\text{-}D_5} Q_{TCP}}$$

where:
A_{TCP} = integrated abundance of the m/z 75 quantitation ion for TCP.
$A_{TCP\text{-}D5}$ = integrated abundance of the m/z 79 quantitation ion for the internal standard, TCP-D_5.
Q_{TCP} = concentration of TCP in ng/L.
$Q_{TCP\text{-}D5}$ = concentration of the internal standard, TCP-D_5, in ng/L.

9.3. Calculate the mean response factor (RF_{mean}) and standard deviation of the five concentration levels. If the RSD for the initial calibration exceeds 20%, check for linearity and recalibrate.

9.4. As an alternative to calculating the mean response factor, a linear regression curve may be generated from the initial calibration data by plotting the ratio of $A_{TCP}/A_{TCP\text{-}D5}$ versus Q_{TCP}.

9.5. For continuing calibration, verify the calibration by analyzing a midpoint calibration standard during the course of sample analysis. The RF should be within 20% of RF_{mean} from the initial calibration, or within 20% of the true concentration if the calibration was performed by linear regression. If the RF or measured concentration exceeds 20%, a fresh standard should be prepared and then rerun. If the RF or measured concentration still exceeds 20%, a new calibration curve should be prepared.
9.5.1. Each set of samples must be bracketed by a calibration check standard or LFB.
9.5.2. During the continuing calibration, verify that the retention times have not drifted from those set in the initial calibration.
9.5.3. The absolute area of the quantitation ion of the TCP-D_5 in the LRB, LFB, and continuing calibration check standard should not have decreased by more than 20% from the initial calibration. If necessary, make appropriate adjustments to restore system sensitivity.

10. Procedure

10.1. See Table 1 for the instruments and instrument parameters that were used in the development of this method.

10.2. Bake out the trap on the purge and trap concentrator for 10 minutes before analyzing any standards or samples.

10.3. Prepare a 25 mL sample aliquot for analysis as in method 524.2, but use TCP-D_5 as the internal standard.

10.4. Analyze the sample as in method 524.2 using the instrument parameters from Table 1 in this method. The instrument parameters in Table 1 should be used as guidelines.

10.5. TCP is identified by matching the retention time and fragment ions and ion abundances from the sample with those of the reference standard. Identification requires expert judgment, especially when sample components are not completely resolved, or if TCP is present at very low concentration (near the detection limit). Background ions or interfering ions from coeluting compounds may make identification (and quantitation) difficult to achieve.

10.5.1. Quadrupole MS: Calculate the mean abundance ratio of the m/z 75 ion to the m/z 110 ion of TCP from the initial calibration data. Calculate and compare the abundance ratio of the sample with the reference mean value. The abundance ratio of the sample should compare within ±30% of the reference mean value.

10.5.2. Ion trap MS: Compare with the "spectrum" of the sample (m/z ranges 74 to 82, 96 to 104 and 109 to 116) with the "spectrum" of the reference standard. Care should be exercised when performing the comparison, as the SIS "spectrum" is composed of three discontinuous "m/z windows" and does not represent the complete spectrum.

10.6. Monitor the absolute area of the m/z 79 quantitation ion of the TCP-D_5 in samples. A significant increase in area may signify the additive effect of a m/z 79 ion from a coeluting compound.

10.6.1. If using the ion trap MS detector, compare the TCP-D_5 sample "spectrum" with the "spectrum" of the reference standard to help determine if any interfering compound may be present. The TCP-D_5 peak shapes in the extracted ion current profile (EICP) and the total ion current profile (TIC) should also be examined for possible coeluters.

10.6.2. If using the quadrupole MS detector and only the m/z 79 quantitation ion was measured for TCP-D5, examine the TCP-D_5 peak shapes in the EICP and the TIC for possible coeluters, or perform a sample matrix spike (a high TCP-D_5 response due to contribution from an interfering compound will result in a calculated TCP spike recovery that will be lower than normal).

10.6.3. Take appropriate corrective action, as necessary, to correct for interfering compounds.

11. Analysis and Calculations

11.1. Calculate the TCP sample concentration, using the multipoint calibration established in Section 9.

$$C_{TCP} = \frac{A_{TCP} Q_{TCP-D_5}}{A_{TCP-D_5}(RF_{mean})}$$

where:
C_{TCP} = concentration of TCP in ng/L in the water sample
A_{TCP} = integrated abundance of the m/z 75 quantitation ion for TCP.
A_{TCP-D5} = integrated abundance of the m/z 79 quantitation ion for the internal Standard, TCP-D_5.
Q_{TCP-D5} = concentration of the internal standard, TCP-D_5, in ng/L.

RF_{mean} = mean response factor of analyte from the initial calibration.

11.2. Alternatively, the TCP sample concentration may be computed from the linear regression line established in Section 9.

12. Method Performance

12.1. GC/MS-quadrupole (System 1 in Table 1): Single laboratory, single operator.

12.1.1. A MDL study (n=7) conducted over a period of three days using reagent water fortified with 5.0 ng/L of TCP resulted in a calculated MDL of 0.9 ng/L. The mean recovery and relative standard deviation were 104% and 5.6%, respectively.

12.1.2. The estimated reporting limit was 5.0 ng/L.

12.1.3. The mean recovery and relative standard deviation for LFB samples (n=8) containing 50.0 ng/L of TCP were 97% and 4.2%, respectively.

12.2. GC/MS-ion trap (System 2 in Table 1): Single laboratory, single operator performance (lab and operator different from 12.1).

12.2.1. A MDL study (n=8) conducted over a period of three days using reagent water fortified with 5.0 ng/L of TCP resulted in a calculated MDL of 2.3 ng/L. The mean recovery and relative standard deviation were 101% and 15%, respectively.

12.2.2. The estimated reporting limit was 10 ng/L.

12.2.3. The mean recovery and relative standard deviation for QC samples (n=18) containing 20.0 ng/L of TCP were 98% and 10%, respectively.

12.2.4. The mean recovery and relative standard deviation for LFB samples (n=10) containing 20.0 ng/L of TCP were 94% and 11%, respectively.

12.3. Fifteen groundwater samples that were analyzed on both the GC/MS-quadrupole and the GC/MS-ion trap systems were found to contain TCP at concentrations ranging from 8 to 300 ng/L. Linear regression analysis of the measurement results from the GC/MS-quadrupole system compared with those from the GC/MS-ion trap system resulted in a slope, intercept and correlation (r^2) of 0.985, 2.39 and 0.9981, respectively.

13. References

13.1. U. S. EPA. *Methods for the Determination of Organic Compounds in Drinking Water, Supplement III (Methods504.1, 524.2 and 551.1)*; EPA/600/R-95/131; U.S. Environmental Protection Agency, Office of Research and Development: Washington, DC, August 1995.

14. Acknowledgements

14.1. The GC/MS-ion trap method was developed by J. Remoy, J. Dhoot, H. S. Okamoto and S. K. Perera, CA Department of Health Services, Division of Drinking Water and Environmental Management, Sanitation and Radiation Laboratories Branch-North. The GC/MS-quadrupole method was developed by P. Hill and W. R. Steeber, CA Department of Health Services, Division of Drinking Water and Environmental Management, Sanitation and Radiation Laboratories Branch-South.

Table 1. Instruments and Parameter Settings Employed in the Development of this Method.

	System 1	System 2
Purge and Trap Concentrator	**Tekmar 3000 with Dry Purge and Sample Heater Jacket**	**Tekmar 3000 with Dry Purge and Sample Heater Jacket**
Sample volume	25 mL	25 mL
1,2,3-Trichloropropane-D_5 (internal standard) spike concentration in sample	400 ng/L	40 ng/L
Purge:		
Vessel type	25 mL fritted glass sparger?	25 mL fritted glass sparger
Time & temperature	11 min. at 40°C	11 min. at 40°C
Gas flow rate	40 cc/min.	40 cc/min.
Dry purge time	2 min.	5 min.
Trap:		
Desorb preheat temperature	245°C	245°C
Desorb time & temperature	4 min. at 250°C	4 min. at 250°C
Gas flow rate	20 cc/min.	30 cc/min.
Bake out time & temperature	8 min. at 270°C	10 min. at 260°C
Gas Chromatograph	**Agilent 6890**	**Varian CP-3800**
Injector:		
Split interface	20:1	20:1
Temperature	200°C	200°C
Column	30 m x 0.25 mm DB-5.625, 1.0 µm film thickness	60 m x 0.25 mm DB-VRX, 1.4 µm film thickness
He carrier gas flow rate	0.90 cc/min.	1.5 cc/min.
Column oven temperature program	Hold 35°C for 5 min., ramp at 4.0 °C/min. to 105°C, ramp at 30 °C/min. to 170°C.	Hold 45°C for 10 min., ramp at 12 °C/min. to 190°C, ramp at 6°C/min. to 225°C.
Retention Time:		
1,2,3-Trichloropropane-D_5	~20.36 min.	~20.86
1,2,3-Trichloropropane	~20.58 min.	~20.95
Mass Spectrometer	**Agilent 5973 MSD**	**Varian Saturn 2000 Ion Trap**
Ionization mode	EI, 70 eV, auto-tune	EI, 70 eV, auto-gain control
Filament & electron multiplier:		
Delay time (off)	19 min.	19 min.
Start/end times (on)	19.0/22.0 min	19.0/22.0 min.
Emission current	34.6 µA	100 µA
EM voltage	Set +300 V higher than for normal full scan mode.	Add +200 V to auto-gain setting, +200 V added by SIS mode.
Additional ion trap parameters:		
Waveform amplitude	Not applicable	25 V
SIS amplitude adjustment factor	Not applicable	200
Pre-ionization time	Not applicable	1500 µS
Scan mode	Selected ion monitoring Mass 1: 75 Mass 2: 79 Mass 3: 110	Selected ion storage Mass range 1: 74 to 82 Mass range 2: 96 to 104 Mass range 3: 109 to 116

Appendix B-9
Semivolatile Organic Compounds

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE #315

SEMIVOLATILE ORGANICS ANALYSIS

Signature & Title

Prepared by: _____ _____
Li-Pin Lee, ESAT Region 9, ICF Consulting Date

Reviewed by: _____ _____
Richard Bauer, Chemistry Team Leader Date

Approved by: _____ _____
Brenda Bettencourt, Lab. Director Date

Periodic Review:

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

STANDARD OPERATING PROCEDURE #315

SEMIVOLATILE ORGANICS ANALYSIS

This SOP was prepared by ICF Consulting for the United States Environmental Protection Agency (USEPA) under the Environmental Services Assistance Team (ESAT) contract (EPA contract No. 68D60005).

APPROVED BY:

Ziyad Rajabi, Organic Group Leader	Date
Surender Kaushik, QA/QC Task Manager	Date
Jerry Vail, ESAT Program Manager	Date

ESAT Document Control Number: B0101063-1371

TABLE OF CONTENTS

1 SCOPE AND APPLICATION 4

2 METHOD SUMMARY 4

3 DEFINITIONS 4

4 HEALTH & SAFETY 6

5 SAMPLE HANDLING AND PRESERVATION 7

6 INTERFERENCES 7

7 APPARATUS AND MATERIALS 7

8 QUALITY CONTROL 9

9 ANALYTICAL PROCEDURES 27

10 DOCUMENTATION 31

11 REFERENCES 37

APPENDIX A 38

APPENDIX B 40

APPENDIX C 42

APPENDIX D 44

APPENDIX E 46

ATTACHMENT A - Semivolatile Organics Run Log example page

ATTACHMENT B - GC/MS Semivolatile Standards Log example page

ATTACHMENT C - Maintenance Logbook example page

1 SCOPE AND APPLICATION

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 analytes of interest. This SOP is based on procedures contained in EPA Method SW-846 8270.

The applicability of these procedures to specific project data quality objectives must be assessed on a case by case basis. The QC criteria specified in the procedures do not meet compliance criteria for either drinking water or NPDES monitoring projects.

2 METHOD SUMMARY

Sample extracts, which have been fortified with surrogate analytes and internal standards, are injected into a gas chromatograph with a Mass Spectrometer (MS). Analytes are separated in the narrow-bore fused-silica capillary gas chromatographic column during temperature programming, then detected by the MS.

Target semivolatile organic compounds are identified in the sample extract by comparing the mass spectra and GC retention times of the target analytes to the mass spectra and retention times of standards analyzed under the same conditions as samples. A response factor is established for each target and surrogate compound during the initial calibration by comparing the MS response of the quantitation ion produced by the target and surrogate compounds to the MS response for the quantitation ion produced by the associated internal standard. Each target analyte and surrogate are quantitated using an internal standard method of calculation using the average response factors from the initial calibration.

Non-target compounds are identified by comparing the resulting mass spectra of the non-target compound to the mass spectra contained in the National Institute of Standards and Technology (NIST) Library in the MS database. An estimated quantitation is performed for the non-target compounds by comparing the total MS response to the nearest internal standard total MS response, assuming a 1:1 response factor.

3 DEFINITIONS

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

3.2 Surrogate Analyte (SA) - A pure analyte, which is extremely unlikely to be found in any sample, 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.

3.3 Laboratory Reagent Blank (LRB) - 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 LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the solvents, or the equipment.

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

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

3.6 GC/MS Performance Check Solution (decafluorotriphenylphosphine (DFTPP) - A solution of 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.

3.7 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.

3.8 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.

3.9 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

3.10 Quality Control Sample (QCS) – Equivalent to the mid-point initial calibration solution but prepared from a source different from the source of calibration standards. The QCS is used to check the accuracy of the initial calibration solutions.

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

3.12 System Performance Check Compounds (SPCC) - analytes that typically have low response factors. These compounds are used as indicators of deteriorating system performance.

3.13 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.

4 HEALTH & SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals should be minimized through the use of personal protective equipment and laboratory engineering and design. A reference file of material safety data sheets (MSDS) is available to all personnel involved in the chemical analysis and can be found in the library (Room 118) or Room 413.

4.2 Methylene chloride 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. Methylene chloride 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.

4.3 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

7.1 GCMS System

7.1.1 Gas Chromatograph (GC): Hewlett Packard 5890 Series 2 or equivalent 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).

7.1.2 GC column: 30 m, 0.25 mm ID, 0.25 μm df, DB-5MS or equivalent. A fused silica capillary column with a bonded phase coating of 5% phenyl-95% methyl silicone such as DB-5, DB-5MS, Rtx-5, XTI-5, or HP-5. 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.

7.1.3 Mass spectrometer: Hewlett Packard 5972 or equivalent. Capable of scanning from 35 to 500 amu every one second or less using 70 volts (nominal) electron energy in the electron impact ionization mode. Must be able to produce a mass spectrum that meets acceptance criteria when 50 ng of DFTPP is injected through the GC inlet.

7.1.4 Data system: HP EnviroQuant ChemStation G1701BA Version B.01.00 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 data base, 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 response factors and concentrations of analytes in samples.

7.2 Standard solutions

Document the preparation of all standards in the Semivolatile Standards logbook following EPA Region 9 Laboratory SOP # 840, Notebook Documentation and Control.

7.2.1 Internal Standard Solution (IS) - A solution of acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, 1,4-dichlorobenzene-d_4, perylene-d_{12}, and naphthalene-d_8 at 2,000 μg/mL each in dichloromethane. Restek catalog # 31206 or equivalent.

7.2.2 Surrogate solution (SA) - A solution of 2-fluorobiphenyl, nitrobenzene-d_5, p-terphenyl-d_{14}, and 1,2-dichlorobenzene-d_4 (B/N surrogates) at 100 μg/mL each and 2-fluorophenol, phenol-d_5, 2,4,6-tribromophenol, and 2-chlorophenol-d_4 (Acid surrogates) at 150 μg/mL each in dichloromethane. Prepare by diluting purchased

solutions - B/N surrogates: Restek catalog# 31002 or equivalent. Acid surrogates: Restek catalog# 31003 or equivalent.

7.2.3 Calibration Stock Standard. A solution of target analytes listed in Appendix B at a concentration of 2,000 µg/mL in dichloromethane. Restek SV calibration mix #2 (cat# 31008), #3 (cat# 31009), #4 (cat# 31010), #5 (cat# 31011), #7 (cat# 31013), and #8 (cat# 31026) or equivalent.

7.2.4 Calibration standards - A solution of target analytes listed in Appendix B at concentrations of 10, 25, 40, 60, and 80 µg/mL. Prepare by diluting from the calibration stock standard. Add 10 µL of the IS solution per 1.0 mL of standard.

7.2.5 GC/MS Performance Check Solution (DFTPP+). A solution of decafluorotriphenylphosphine (DFTPP), 4,4'-DDT, pentachlorophenol, and benzidine at 50 ng/µL each in methylene chloride. Prepare from a purchased solution - ULTRA Scientific cat# GCM-150 or equivalent.

7.2.6 Matrix Fortification Solution - A solution of 1,2,4-Trichlorobenzene, Acenaphthene, 2,4-Dinitrotoluene, Pyrene, n-Nitroso-di-n-propylamine, and 1,4-Dichlorobenzene (B/N spike mix) at 100 µg/mL each and Pentachlorophenol, Phenol, 2-Chlorophenol, 4-Chloro-3-methylphenol, and 4-Nitrophenol (Acid spike mix) at 150 µg/mL each in methanol. Prepare from purchased solutions - B/N spike mix: Restek catalog# 31004 or equivalent. Acid spike mix: Restek catalog# 31005 or equivalent.

7.2.7 Storage of Standard Solutions - Store the unopened ampulated stock standard solutions at 4°C (± 2°C). Store all other working standard solutions in glass bottles or vials with Teflon lined screw caps at ≤-10°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 quality control check samples indicates a problem. CAUTION: Analysts must allow all standard solutions to equilibrate to room temperature before use.

7.2.8 Methylene chloride -- High purity pesticide quality or equivalent.

7.2.9 Helium carrier gas - as contaminant free as possible.

7.3 Syringes (10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, 1-mL).

8 QUALITY CONTROL

8.1 Quality control requirements include the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified matrix samples.

8.2 The laboratory must perform an initial demonstration of capability with each sample preparation technique used in analyzing analytes of interest with this SOP before analyzing any samples. See EPA Region 9 SOP #880, *Initial and Continuing Demonstration of Capabilities and Proficiency* for requirements and procedures.

8.2.1 Analyze Laboratory Fortified Blanks (LFBs) containing all the analytes of interest at a concentration of 40 µg/L in aqueous samples and 1320 µg/Kg in solid samples, equivalent to 40 µg/mL in the extract, to demonstrate initial laboratory capability.

8.2.2 Analyze LFBs which have been fortified with all analytes of interest at 10 µg/L in water samples and 330 µg/Kg in soil samples, corresponding to 10 µg/mL in the extract for MDL determination.

8.3 Mass calibration.

8.3.1 Calibrate the mass axis of the mass spectrometer daily. You must also calibrate the mass axis whenever the mass spectrometer is shut down, or whenever there is a mass mis-assignment. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer. Perfluorotributylamine (FC43) is used to perform calibration of the mass axis. The FC43 spectrum with the following criteria are recommended:

Mass	Target % of Mass 69
69	100
131	25.0 - 40.0
219	25.0 - 40.0
414	1.4 - 4.0
502	0.5 - 2.0

8.3.2 Take corrective action if the FC43 spectrum does not meet the criteria listed above as DFTPP will probably not pass criteria. The corrective action may be as simple as

adjusting the mass gain and peak width or manually retuning the MS. Alternatively, retuning the MS by selecting target tune with mass ratio(s) set based on the failure on criteria in Section 8.4.4. If retuning the MS does not produce adequate FC43 spectra or repeated failure to meet DFTPP criteria, further maintenance such as cleaning the ion source may be required. See Section 9.4.

8.4 GC/MS System Performance Check

8.4.1 Prior to the analysis of any calibration standards, blanks, and samples (including LFM/LFMDs), the GC/MS system must meet the mass spectral ion abundance criteria for DFTPP. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target and non-target compounds.

8.4.2 Frequency of GC/MS Performance Check.

8.4.2.1 Analyze the DFTPP solution once at the beginning of each 12-hour period during which standards, blanks and samples are to be analyzed. The twelve-hour time period begins at the moment of injection of the DFTPP solution. The time period ends after twelve hours have elapsed. If a sample is injected after the 12-hour time period has elapsed it must be re-analyzed.

8.4.3 Analyze the DFTPP solution according to Section 9 of this SOP.

8.4.4 The ion abundance ratios must meet the following criteria:

Mass (m/z)	Relative Ion Abundance Criteria
51	30 - 60% of the base peak
68	less than 2% of mass 69
70	less than 2% of mass 69
127	40 -60% of the base peak
197	less than 1% of mass 198
198	Base peak (100% relative abundance)
199	5 - 9% of mass 198
275	10 - 30% of the base peak
365	Greater than 1% of the base peak
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17 - 23% of mass 442

8.4.4.1 If the ion abundances fail to meet the criteria listed above the DFTPP 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 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. See Section 9.4.

8.4.4.2 Evaluate the breakdown of DDT using Equation 1. Locate the degradation products of 4,4'-DDT (4,4'-DDD and 4,4'-DDE). If the percent breakdown calculated using peak areas based on each Quantitation ion (Qion) exceeds 20%, corrective maintenance must be taken

Equation 1:

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

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

8.4.4.3 Benzidine and pentachlorophenol responses should be at their expected levels in the DFTPP solution and peak tailing should be minimal. Replacing the inlet liner and /or the inlet seal and breaking off a portion of the column from the injector end should restore instrument performance.

8.5 Initial calibration.

8.5.1 Calibrate the GC/MS system whenever corrective action which may change instrument response (e.g., ion source cleaning, column replacement, etc.) is performed or if the continuing calibration acceptance criteria have not been met.

8.5.2 Analyze the 10 or 25 μg/mL calibration standard according to Section 9.

8.5.2.1 Evaluate the separations of anthracene /phenanthrene and benzo(a)anthracene/chrysene. Anthracene /phenanthrene should have baseline separation. Benzo(a)anthracene/chrysene should be separated by a valley whose height is less than 25% of the average height of the two peaks. If not, the GC column requires maintenance.

8.5.2.2 If any target analytes, surrogates or internal standards are mis-identified or not found, corrective action or system maintenance is required.

8.5.3 If all performance criteria are met, analyze the remaining initial calibration standards according to Section 9 of this SOP.

8.5.4 The data system calculates the relative response factor (RRF) for each target compound and surrogate for all five calibration standards using Equation 2. The quantitation ions and internal standard assignments are listed in Appendix C.

Equation 2:

$$RRF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

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 in μg/mL
C_{is} = Concentration of the associated internal standard in μg/mL

8.5.5 Calculate the average RRF for all analytes

8.5.6 Calculate the percent relative standard deviation (%RSD) of the RRF values for each compound using Equation 3.

Equation 3

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

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

8.5.7 Check the initial calibration for misidentified peaks due to retention time shifts. The most commonly mis-assigned compounds are the 1,3- and 1,4-dichlorobenzenes and the benzo(b) and benzo(k) fluoranthenes.

8.5.8 Verify that the minimum average RRF's in the initial calibration for the following system performance check compounds (SPCC's) is 0.050:

N-nitroso-di-n-propylamine
hexachlorocyclopentadiene
2,4-dinitrophenol
4-nitrophenol

Corrective action must be taken before sample analysis can begin if any SPCC fails the minimum RRF criterion.

8.5.9 All other analytes must meet the minimum RRF criteria in Appendix C.

8.5.10 Verify that the maximum %RSD for the following calibration check compounds (CCC's) in the initial calibration is ≤ 20:

acenaphthene	4-chloro-3-methylphenol
1,4-dichlorobenzene	2,4-dichlorophenol
hexachlorobutadiene	2-nitrophenol
di-n-octyl phthalate	phenol
fluoranthene	pentachlorophenol
benzo(a)pyrene	2,4,6-trichlorophenol

Corrective action must be taken before sample analysis can begin if any CCC fails the maximum %RSD criterion.

8.5.11 All other analytes should meet the maximum %RSD of 20. Any project specific analyte of interest must meet the maximum %RSD criterion. If one or more analytes exceed the RSD limit, the initial calibration may still be acceptable if the following conditions are met:

8.5.11.1 The %RSD of the analytes that exceed the limit is ≤ 30.

8.5.11.2 The mean of the RSD values for all analytes is less than or equal to 20%.

8.5.11.3 If an analyte that exceeds the %RSD limit is found in a sample extract, that extract must be re-analyzed using an initial calibration that meets QC limits for that analyte.

8.5.12 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 before sample analysis begins.

8.5.13 If the five point calibration fails the minimum RRF or maximum %RSD criteria for target analytes with on column quantitation limits of 25 ng listed in Appendix D, then a four-point calibration, excluding the 10 µg/mL standard, may be used if it meets the initial calibration criteria.

8.5.14 Remember that the lowest concentration standard defines the reporting limit for each compound. If appropriate reporting limits cannot be obtained by this procedure, the system must be repaired so that the criteria are satisfied before any samples are analyzed. If repairs are made to the system, then a new initial calibration must be performed.

8.5.15 No quantitation ion may saturate the detector.

8.5.16 Analyze a QCS sample immediately after each initial calibration. The RRF for each analyte in the QCS must be within 30% of the mean RRF in the initial calibration. If the QCS sample fails, the cause must be determined and corrected before analysis of samples can proceed.

8.5.17 If the initial calibration and the QCS meet the specified criteria, the remainder of the 12-hour analytical period may be used for the analysis of field and QC samples, using the average RRF from the initial calibration to quantitate the sample data.

8.5.18 Manual integration. There will be instances when the data system will not produce accurate integrations. Examples of this are misidentification of a peak, inaccurate dropping of a perpendicular between peaks, or failure to integrate the entire tail of a peak. When necessary, chromatograms can be manually integrated if the following steps are taken (see SOP 835, *Chromatographic Integration Procedures*):

8.5.18.1 Print a view of the chromatogram to be reintegrated using QEDIT. Include the background-subtracted spectrum of the apex of the peak and the reference spectrum. Indicate the reasons for manually integrating the chromatographic results on the chromatogram and initial and date the statement.

8.5.18.2 Reintegrate the peak and print the new view. Save the reintegrated value(s). Print the peak and reference spectra. Document the manual integration on the reintegrated chromatogram and initial and date the statement.

8.5.18.3 Print the new quant report and chromatogram after all manual integrations have been completed. Indicate each manual integration on the new quant report. Document the fact that there was manual integration in the instrument's run log and initial and date the statement.

8.5.18.4 Show the chromatograms, quant reports and log book to a supervisor, QA/QC coordinator or team leader for review and acceptance. The QA/QC coordinator or team leader will initial and date the integrations.

8.6 Calibration Verification

8.6.1 Verify the MS tune and initial calibration at the beginning of each 12-hour period (see Section 8.4.2.1 for definition of 12-hour time period) when analyses of field and QC samples are performed using the following procedure.

8.6.2 Analyze a DFTPP+ solution according to Section 9

8.6.2.1 Check that the DFTPP ion abundances meet the criteria in Section 8.4.4

8.6.2.2 Evaluate the DDT breakdown using the Equation 1 and the acceptance criteria in Section 8.4.4.2.

8.6.2.3 Evaluate the benzidine and pentachlorophenol responses according to the criteria in section 8.4.4.3.

8.6.3 Analyze the calibration verification standard (25 μg/mL) according to Section 9 of this SOP.

8.6.4 The responses of the internal standards in the calibration verification standard must meet the criteria in Section 8.11.2.

8.6.5 Check the calibration verification for misidentified peaks due to retention time shifts. The most commonly mis-assigned compounds are closely eluting pairs such as the benzo(b) and benzo(k)fluoranthenes. If any are found, corrective action must be taken and the chromatogram re-quantitated to ensure the corrective action was successful.

8.6.6 Calculate the relative response factor (RRF) for each target compound and surrogate using Equation 1. The quantitation ions and internal standard assignments are listed in Appendix C.

8.6.7 Calculate the percent difference (%D) between the continuing calibration RRF's and the average RRF's from the most recent initial calibration for each target compound and surrogate using Equation 4.

Equation 4

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

Where :

RRFc = relative response in the continuing calibration
Avg RRFi = average relative response in the initial calibration

8.6.8 Verify that the minimum RRF for the SPCC's listed in section 8.5.8 is 0.050.

8.6.9 All other analytes must meet the minimum RRF's listed in Appendix B.

8.6.10 Verify that the maximum %D for the CCC's listed in section 8.5.10 is ≤ 25.

8.6.11 All other analytes must meet the maximum %D criteria listed in Appendix B.

8.6.12 All project specific analytes of interest must meet the minimum RRF and maximum %D criteria in Appendix B. If one or more analytes exceed the minimum RRF and maximum %D limit, the calibration verification may still be acceptable if the following conditions are met:

8.6.12.1 The %D of the analytes that exceed the limit is ≤ 40.

8.6.12.2 The minimum RRF of the analytes that exceed the limit is 0.050.

8.6.12.3 The mean of the %D values for all analytes is less than or equal to 25.

8.6.12.4 If an analyte that exceeds the QC limits is found in a sample extract, that extract must be re-analyzed using a calibration verification that meets QC limits for that analyte.

8.6.13 If any of the criteria are not satisfied a second continuing calibration may be analyzed. Repeated failure requires the analysis of a new initial calibration before analysis of samples can begin. If repairs to the system are required then a new initial calibration must be performed.

8.6.14 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. See Section 9.4.

8.7 Quantitation Limit Standard analysis

8.7.1 Analyze a quantitation limit standard (QLS) in each 12-hour period (see Section 8.4.2.1 for definition of 12-hour time period) when analyses of field or QC samples are performed. The QLS is used to verify analytical system response at the quantitation limit.

8.7.2 Analyze the 10 μg/mL calibration standard according to Section 9 of this SOP

8.7.3 Calculate the percent of true value for each target compound using Equation 5.

Equation 5

$$\% \text{ True Value} = (Cd / Tv) \times 100$$

Where:

Cd = Concentration determined by analysis
Tv = True value

8.7.4 The accuracy for each analyte, expressed as a percentage of true value must be between 50 - 150%. If the QLS sample fails, the cause must be determined and corrected before analysis of samples can begin.

8.7.5 If the 10 μg/mL QLS standard fails for target analytes with on column quantitation limits of 25 ng listed in Appendix B, then analyze a 25 μg/mL standard. Calculate the % True Value using Equation 6. The %True Value must be between 50 - 150%. If the QLS sample fails, the cause must be determined and corrected before analysis of samples can begin.

8.7.6 If the QLS standard fails, a fresh QLS solution of that standard may be analyzed.

8.8 Laboratory Reagent Blank (LRB) analysis.

8.8.1 An LRB is extracted with each extraction batch in order to demonstrate that the entire analytical system - from extraction through GC/MS analysis - is free of contamination.

8.8.2 Analyze the LRB according to Section 9 of this SOP.

8.8.3 Evaluate the LRB as soon as possible after it has been analyzed to determine if the following criteria have been met:

The LRB is acceptable if it contains less than the quantitation limit (QL) of any single target compound. Exceptions are the target phthalate esters, each of which may be present at up to five times the QL.

8.8.4 The LRB internal standards must meet the criteria listed in Section 8.11.2

8.8.5 The LRB surrogate recoveries must meet the criteria listed in Section 8.12.1

8.8.6 Corrective action - If the LRB 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.

8.8.7 If surrogate or internal standard recoveries do not meet acceptance criteria, re-analyze the extract. If the surrogate recoveries still do not meet acceptance criteria, document failure in the report narrative.

8.9 Laboratory fortified matrix and duplicate analysis.

8.9.1 A laboratory fortified matrix and a duplicate sample are extracted and analyzed for each batch of twenty or fewer samples extracted as a group.

8.9.2 LFM and LFMD extracts should be analyzed as soon as possible following the analysis of the sample designated as the laboratory fortified matrix sample.

8.9.3 Analyze the LFM and LFMD according to Section 9 of this SOP.

8.9.4 The recovery and RPD criteria for the LFM and LFMD analyses are as follows:

	%Recovery		**RPD**	
Compound	**Water**	**Soil**	**Water**	**Soil**
Phenol	12 - 110	26 - 100	21	35
2-Chlorophenol	27 - 123	25 - 102	16	50
1,4-Dichlorobenzene	36 - 100	28 - 104	22	27

	% Recovery		RPD	
Compound	**Water**	**Soil**	**Water**	**Soil**
n-Nitroso-di-n-propylamine	41 - 116	41 - 126	38	38
1,2,4-Trichlorobenzene	39 - 100	38 - 107	28	23
4-Chloro-3-methylphenol	23 - 100	26 - 103	42	33
Acenaphthene	46 -118	31 - 137	31	19
2,4-Dinitrotoluene	24 - 100	28 - 100	38	50
4-Nitrophenol	10 - 100	11 - 114	50	47
Pentachlorophenol	9 - 103	17 - 109	50	107
Pyrene	26 - 127	35 - 142	31	36

8.9.5 Calculate the recovery of each compound using Equation 6.

Equation 6

$$\% \text{ Rec} = ((SSR - SR)/SA) \times 100$$

where,

SSR = Spiked sample result (volume/weight corrected)
SR = Sample result (volume/weight corrected)
SA = Spike added

8.9.6 Calculate the relative percent differences (RPD) of the recoveries of each compound in the matrix spike and matrix spike duplicate using Equation 7.

Equation 7

$$RPD = \frac{(LFMC - LFMDC)}{(LFMC + LFMDC)/2} \times 100$$

where:

LFMC = Measured concentration of analyte in LFM
LFMDC = Measured concentration of analyte in LFMD

8.9.7 The limits for LFM/LFMD recovery are advisory limits only. If the limits are not met, then no further action is required, as long as the LFB 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 30% of the expected values.

8.10 Laboratory Fortified Blank (LFB) An LFB is analyzed to demonstrate that the analytical system is in control. The LFB is extracted and analyzed once per batch or every 20 samples, whichever is more frequent. The LFB is an LRB spiked with laboratory fortified matrix solution.

8.10.1 All analytes and surrogates must be recovered within the QC limits listed in section 8.9.4. If not, the source of the problem must be determined prior to reporting any sample data. It usually indicates either a discrepancy between the spiking solution and the calibration standard, or a problem in the extraction laboratory.

8.10.2 The table below lists the action to be taken based on the LFB and LFM/LFMD results.

QC ACCEPTANCE MATRIX

+ = PASS − = FAIL

CASE	1	2	3	4	5	6	7	8
LFB - % REC	+	+	+	+	−	−	−	−
LFM/LFMD -% REC	+	−	+	−	+	−	+	−
LFM/LFMD - RPD	+	+	−	−	+	+	−	−

Case 1: Extraction batch is acceptable.

Case 2: Extraction batch is acceptable; matrix effect confirmed.

Cases 3 & 4: Extraction batch is unsatisfactory. Investigate LFM/LFMD problem and document findings in report narrative.

Case 5: Extraction batch is rejected. The batch may have to be re-extracted unless LFB problem is determined and documented.

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

8.11 Internal standard recovery.

8.11.1 Check the internal standard recovery, determined by total area, for all standards, blanks, samples, and spikes immediately after analysis in order to determine if all applicable criteria have been met.

8.11.2 If the total area of any internal standard in any blank, sample, or spike analysis changes by more than a factor of two (-50% to +100%) of the corresponding internal standard from the preceding 12-hour calibration standard, the system must be checked for malfunctions and the necessary corrections made (see Section 9.4). After the corrections are made, the analyses performed while the system was not in control must be repeated. Keep in mind that many "corrections" to the system will require a new initial calibration be performed prior to re-analysis of the samples.

8.11.3 If after re-analysis, the total areas for all internal standards are within the criteria, then the problem is considered to have been within the laboratory's control. Report the results from the re-analysis and submit the data for both analyses. Distinguish between the analysis and re-analysis by adding an "RI" suffix to the client sample ID on the re-analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.11.4 If re-analysis of the sample does not solve the problem, report the results from the first analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding an "RI" suffix to the client sample ID on the re-analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.11.5 Check internal standard retention times in all standards immediately after data acquisition. If the retention time for any internal standard changes by more than 0.2 minute from the latest daily calibration standard, the system must be inspected for malfunctions, and the necessary corrections made. 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 25 μg/L standard.

8.12 Surrogate recovery.

8.12.1 Calculate the surrogate recovery in all blanks, samples, and spike immediately after analysis using Equation 8 and compare to the following criteria.

Compound	**Water %R**	**Soil %R**	
2-Fluorophenol	21 - 110	25 - 121	
Phenol-d5	10 - 110	24 - 113	
Nitrobenzene-d5	35 - 114	23 - 120	
2-Fluorobiphenyl	43 - 116	30 - 115	
2,4,6-Tribromophenol	10 - 123	19 - 122	
Terphenyl-d14	33 - 141	18 - 137	
2-Chlorophenol-d4	33 - 110	20 - 130	(advisory)

Compound	Water %R	Soil %R	
1,2-Dichlorobenzene-d4	16 - 110	20 - 130	(advisory)

Equation 8

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

8.12.2 Take the following steps if the recovery of one or more of the surrogates is not within the limits.

8.12.2.1 Check to ensure that there are no calculation errors, and check the system performance.

8.12.2.2 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 (e.g., very large amounts of hydrocarbon).

8.12.2.3 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.

8.12.2.4 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 and report narrative.

8.12.2.5 Do not re-analyze the LFM or LFMD samples, even if the surrogates recoveries are outside the limits.

8.12.2.6 If the sample associated with the LFM/LFMD 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 discussed in the report narrative (See Section 10.2.1.1).

8.12.3 If the surrogate recoveries of the re-analysis of the extract are within limits, then:

8.12.3.1 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 an "RE" suffix to the client sample ID on the re-analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.12.3.2 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 "DL" suffix to the client sample ID on the diluted analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.12.4 If the sample was re-extracted and 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" suffix to the client sample ID in the re-analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.12.5 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 "RX" suffix to the client sample ID in the re-analysis. The problem must be documented in the report narrative (see Section 10.2.1.1).

8.13 Sample dilution.

8.13.1 Dilute and inject a new aliquot of the extract if the on-column concentration of any target compound in any sample exceeds the initial calibration range. Add more internal standard solution to the diluted extract to maintain the initial internal standard concentration. Use the following criteria in performing dilutions:

8.13.1.1 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

8.13.1.2 Keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument by choosing an appropriate dilution factor.

8.13.1.3 Do not dilute LFM/LFMD 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.

8.13.1.4 In the case of extremely contaminated samples several dilutions may be required.

8.13.1.5 Distinguish between the undiluted and diluted analysis by adding a "DL" suffix to the client sample ID on the diluted analysis.

8.13.2 Demonstrate that there is no carryover to subsequent analyses after a sample is analyzed that contains one or more target compounds at a level exceeding the initial calibration range of the system. This can be done by analyzing an instrument blank.

8.13.2.1 Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the limits above. The maximum contamination criteria are as follows:

8.13.2.2 The sample should not contain a concentration above the QL for the target compounds that exceeded the limits in the contaminated sample, unless other analytes present in the sample indicate that the presence of these compounds is likely. The most common scenario for this is when PNAs are found in both samples, and the pattern in the second sample does not follow the pattern in the first.

8.13.3 The most common cause of a carryover is hydrocarbon in the oil/asphalt range. This may require cleaning the injection port and analyzing an instrument blank.

8.14 Review of Target Analytes

Review each reported value for both qualitative and quantitative validity. This process, in particular the qualitative review of mass spectra, relies upon the technical judgement of the analyst.

8.14.1 Qualitative Review

Both the relative retention time and the mass spectra must match those of the standard's in order for a target compound to be identified as present in a sample.

8.14.1.1 Target analytes must elute within 0.06 relative retention time units of the analyte in the continuing calibration standard. The relative retention time is the retention time of the target divided by the retention time of the associated internal standard. If the relative retention time for the target analyte in the CCAL is 0.82 then the peak in the sample must have a relative retention time of 0.76 to 0.88.

8.14.1.2 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other.

8.14.1.3 The mass spectra used for qualitative identification must be obtained using the GCMS system used to analyze the samples.

8.14.1.3.1 All ions present in the standard mass spectra at a relative intensity of 10 percent of the most abundant ion must be present in the sample spectra.

8.14.1.3.2 The relative intensities of the ions must agree within ±30 % (absolute) between the standard and sample spectra.

8.14.1.3.3 Ions present in the sample at greater than 10 percent abundance but not present in the standard spectra must be reviewed and accounted for by the analyst making the comparison.

8.14.1.3.4 If a compound cannot be verified by these criteria but, in the technical judgement of the analyst, is present the supporting evidence must be indicated on the raw data and the analyte reported.

8.14.2 Quantitative Review

Review reported values to determine that the correct calculations were used to generate the results, that the RRFs from the associated continuing calibration standard were used, and that all other numbers are accurate.

8.14.2.1 Review of data system integrations

The analyst must review the data system integration to verify that the internal standards, surrogates and target compounds are integrated properly. In the

event that the analyst observes an incorrect integration, the analyst must manually correct the integration and document the correction following Section 8.5.11 of this SOP and EPA Region 9 SOP #835, *Chromatographic Integration Procedures.*

8.14.2.2 Water calculations

Calculate results for target analytes using Equation 9:

Equation 9:

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

where:

A_x = area of the quantitation ion of the compound
C_{IS} = concentration of internal standard in μg/mL (normally 20)
DF = dilution factor
A_iS = area of the quantitation ion of the associated internal standard
RRF = analyte's mean relative response factor from the initial calibration
V_o = volume of water extracted in mL
V_i = volume of extract injected in μL
V_t = volume of concentrated extract in μL

8.14.2.3 Soil calculations

Calculate results for target analytes using Equation 10:

Equation 10:

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

where:

A_x = area of the quantitation ion of the compound
C_{IS} = concentration of Internal Standard in μg/mL (normally 20)
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's 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

8.15 Review the Tentatively Identified Compound search results for the following:

8.15.1 Verify that all unknown peaks in the chromatogram greater than10 percent of the area of the nearest internal standard are accounted for in the summary.

8.15.2 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.

8.15.3 The relative intensities of the major ions should agree within 20 percent.

8.15.4 Molecular ions present in the reference spectrum should be present in the sample spectrum.

8.15.5 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.

8.15.6 Ions present in the reference spectrum but not within the scan range (35 to 500 amu) of the method should not be considered when making a tentative identification.

8.15.7 If, in the technical judgement 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.

8.16 If any of the data reports have been edited, or if manual integration or quantitation has been performed, the analyst must identify the changes. A supervisor, QA/QC coordinator, or team leader must review both the original and the changed data and indicate acceptance by initialing and dating the report. See SOP#835, *Chromatographic Integration Procedures*.

9 ANALYTICAL PROCEDURES

9.1 Analytical system preparation.

9.1.1 Calibrate the mass axis and optimize the peak width of the mass spectrometer using FC43 at the beginning of each 12-hour period during which standards or QC or field samples are to be analyzed.

9.1.2 Check the GC/MS system for leaks prior to the analysis of the DFTPP tuning compound. The system must also be checked for leaks after any disconnection and re-connection in the entire system, from the carrier gas source to the MS.

9.1.2.1 Acquire a scan of m/z's 18, 28, and 69. Observe the ratio of the water peak (m/z 18) to the nitrogen peak (m/z 28). If a leak is present in the mass spectrometer, the nitrogen peak will be greater than the water peak. Corrective action must be taken if a leak is detected. The ratios of these ions to the m/z 69 ion should be no more than 10%. Ratios between 10 and 20% indicate a problem that should be repaired as soon as practical, and ratios greater than 20% indicate problems that should be repaired immediately.

9.1.3 The GC/MS system must meet the mass spectral ion abundance criteria for DFTPP and the maximum breakdown criteria for DDT prescribed in Section 8.4 prior to the analysis of any calibration standards, blanks, or samples

9.1.3.1 Analyze the DFTPP+ solution using the system conditions in Appendix E. Obtain ion abundance ratios from a background subtracted average of three scans around the apex of the DFTPP peak or from any one or two of these scans with or without background subtraction. The ion abundance ratios must meet the criteria listed in Section 8.4.4. If not, appropriate corrective action must be taken before calibrations or extracts are analyzed. See Section 9.4.

9.1.3.2 Evaluate the percentage of DDT breakdown as described in Section 8.4.4.2. If it is greater than 20%, take corrective action.

9.2 Calibration - The target compounds for this method are listed in Appendix B.

9.2.1 Five-point initial calibration

Perform a five-point initial calibration in order to demonstrate that the GC/MS system provides a linear response over the desired concentration range.

9.2.1.1 Create a method (if not present already) to operate the GC and collect data as described in Appendix E. Create a sequence to use this method to analyze the standard solutions - 80, 60, 40, 25 and 10 μg/mL.

9.2.1.2 Analyze the 10 or 25 µg/mL standard. Verify that all of the peaks have been properly identified. Update the retention times in the method. Save the method and re-quantitate the chromatogram. Make sure that all of the standards are quantitated using the updated retention times.

9.2.1.3 Update the initial calibration response factors in the method by associating the correct data file with each calibration level. Save the method.

9.2.1.4 Generate the initial calibration summary report. Samples shall not be analyzed if the initial calibration does not meet the criteria specified in Appendix B of this SOP.

9.2.1.5 Analyze a QCS sample immediately after each initial calibration. The RRF for each analyte in the QCS must be within 30% of the mean RRF in the initial calibration. If the QCS sample fails, the cause must be determined and corrected before analysis of samples can proceed.

9.2.1.6 If the initial calibration and the QCS meet all the criteria specified in Section 8.5 of this SOP, the remainder of the 12-hour analytical period may be used for the analysis of blanks, spikes and samples, using the average RRF from the initial calibration to quantitate these data files.

9.2.2 Calibration Verification

Analyze a calibration verification standard once in every 12-hour analytical time period, after DFTPP tuning and prior to continuing with extract analysis. The calibration verification is performed in order to determine if the GC/MS system is operating within the acceptable range as demonstrated by the percent difference and the minimum response factor criteria meeting the appropriate QA/QC criteria. The continuing calibration is analyzed at a level of 25 µg/mL.

9.2.2.1 Analyze the 25 µg/mL standard. Verify that all compounds have been properly identified. Update the retention times in the method. Save the method. Re-quantitate the chromatogram, again verify that all compounds have been properly identified. Select Report Continuing Calibration to Printer. Examine the RRFs and %Ds for method compliance following sections 8.6.4 through 8.6.12 of this SOP. If the continuing calibration meets QC criteria, analysis of extracts can begin.

9.2.2.2 If any of the criteria are not satisfied a second continuing calibration may be analyzed. Repeated failure requires the analysis of a new initial calibration before analysis of samples can begin. If repairs to the system are required then a new initial calibration must be performed.

9.2.2.3 Take corrective action if the continuing calibration fails. This may consist of re-analyzing the standard, clipping the column and replacing the injection port seal, or creating a new five point calibration.

9.2.3 Sample analysis.

Samples can be analyzed only after the DFTPP tune and initial calibration or continuing a calibration meet all of the appropriate criteria specified in Section 8 of this SOP.

9.2.3.1 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Appendix E.

9.2.3.2 Set up a data acquisition sequence. The sample description shall include the client sample ID and the laboratory sample ID. Additional header information shall include the dilution factor, instrument ID, and the analyst's initials.

9.2.3.3 Add 10 μL of the IS solution to each 1 mL of field and QC sample extract.

9.2.3.4 Include all QC sample extracts. It is highly recommended that the LRB, LFB and LFM/LFMD extracts be analyzed as early as possible in the analysis of a batch.

9.2.3.5 After completion of analysis, quantitate the data using the appropriate initial calibration mean RRF's and print out quantitation reports and chromatograms for each field and QC sample.

9.2.3.6 Review the results as discussed in Section 8.14 for identification of target analytes. Manually cross out all reported hits which do not meet the qualitative criteria and document the reason on the quant report. Review all target compounds that are detected to verify they are integrated properly. Review the chromatogram for possible false negatives.

9.2.3.7 Document any required manual integrations as described in Section 8.5.11 and Region 9 SOP #835. Print out the updated quantitation report.

9.2.3.8 Check the sample's internal standard area counts and surrogate recoveries with the criteria in Section 8.11 and 8.12.

9.2.3.9 Dilute and re-analyze the sample extracts if any of the target analytes exceed the calibration range of the instrument. Dilute the extract so that the most prominent target compound will fall within the upper half of the initial calibration range of the instrument.

9.3 Tentatively Identified Compounds (TICs)

9.3.1 Load the data file of the most concentrated valid analysis of the sample.

9.3.2 Examine the spectra for each peak that is not a target, surrogate or internal standard. See how well it matches the tentative identifications given by the data system. Report any unique, likely match, if there is one. If none, so state. Try to give as much information as possible, e.g., "unknown polynuclear aromatic hydrocarbon," "unknown, molecular weight 205 daltons".

9.3.3 The concentration of TIC's should be estimated. Use the TIC area in Equations 9 and 10 and assume the RRF is 1. Use the nearest internal standard free of interferences.

9.3.4 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.

9.4 The following are suggested corrective actions which may improve method performance. Document all routine maintenance or corrective actions taken in the maintenance logbook.

9.4.1 Adjust the mass gain and peak width or re-calibrate the mass axis or retune the mass spectrometer.

9.4.2 Replace the injection liner and/or the inlet seal.

9.4.3 Break off a portion of the column (a few inches to a foot or more) from the injector end.

9.4.4 Prepare fresh standard solutions

9.4.5 Clean the ion source

10 DOCUMENTATION

10.1 Data from the Region 9 Laboratory is presented to the client in one of two general reporting formats: a complete data package or a summary report data package. For the former the laboratory provides summary forms of calibration, quality control, and sample results along with the raw data for standards and field and QC samples, logbook pages, a report narrative, and the analytical report spreadsheet to the client. If a summary package is all that is required the laboratory provides a report narrative, analytical results spreadsheet, and sample specific raw data for delivery to the client and collects all other data included in a complete data package and files it at the laboratory. Section 10.2 details the requirements of a complete data package and Section 10.3 lists the summary report requirements.

10.2 Assembly of a complete data package.

A data package for each SDG in each case requiring the delivery of a complete data package shall be assembled by the analyst, or other chemist, according to the following instructions, and in the following order. Each section of the data package shall have a cover sheet titled with the appropriate section name. The data package shall be sequentially numbered after assembly using a hand-operated numerator.

10.2.1 Report Narrative section.

10.2.1.1 The Report Narrative section contains a text narrative describing, but not limited to, the following.

10.2.1.1.1 Site name.

10.2.1.1.2 Case number.

10.2.1.1.3 SDG number.

10.2.1.1.4 Client sample ID - Laboratory sample ID cross reference

10.2.1.1.5 Date(s) the samples were received.

10.2.1.1.6 Protocol used to analyze the samples

10.2.1.1.7 LRB results

10.2.1.1.8 Surrogate recoveries

10.2.1.1.9 Internal standard recoveries.

10.2.1.1.10 LFM/LFMD results.

10.2.1.1.11 LFB results.

10.2.1.1.12 Analytical comments section to include:

10.2.1.1.12.1 Problems with analysis

10.2.1.1.12.2 Examples of calculations

10.2.2 Summary of Analytical Results spreadsheet

10.2.2.1 Include a spreadsheet containing a summary of the results for all target analytes for all samples and LRB's in the data package.

10.2.2.2 The header information for each sample contains the station location, Sample ID, and date sampled.

10.2.2.3 The results section contains the results for each target analyte as follows:

If an analyte is not detected then the quantitation limit with a "U" qualifier will be reported

If an analyte is detected then the value reported on the quant report and the associated qualifier (Section 10.2.5.1) will be reported.

If an analyte requires a dilution then value from the sample dilution will be reported.

10.2.3 Tracking Forms section.

The Tracking Form section contains the following forms.

10.2.3.1 A technical direction form

10.2.3.2 A copy of the chain of custody records received with each sample shipment.

10.2.3.3 A copy of the shipper's air bill, or bill of lading.

10.2.4 QA/QC Summary section.

The QA/QC section contains all of the QA/QC summary forms for the specific sample delivery group. All of the forms are checked by the analyst to ensure that all of the filenames are correct, and that all of the appropriate standards, blanks, samples and spikes have been included.

10.2.4.1 Data analysis of sample SDG matrix summary report

10.2.4.2 Surrogate recovery and internal standard area count data. In a chronological order by instrument.

10.2.4.3 LFB recovery data.

10.2.4.4 LFM and LFMD recovery data.

10.2.5 Initial Calibration section:

10.2.5.1 Copy of the peer reviewed instrument run log page(s).

10.2.5.2 DFTPP tuning report, which includes the pass/fail table, bar spectrum and tabulated mass listing.

10.2.5.3 Initial calibration summary form containing the response factors for each file, the average response factor for each compound, and the percent RSD for each compound in the initial calibration.

10.2.5.4 Quantitation reports and RICs.

10.2.5.5 Documentation of any required manual integrations as described in Section 8.5.11 and Region 9 SOP #835.

10.2.6 Daily Sample Package section.

The daily sample package section contains the following forms and raw data for each sample including QC samples of LFM/LFMD, LFB, and LRB in the data package, assembled in data file alphanumeric order. Each daily package is arranged in chronological order.

10.2.6.1 Quantitation report, data report form listing all detected target compounds, surrogates and internal standards and the levels detected in the sample. All analyses must be included, even those not used. The analyst shall check to be sure that the appropriate qualifier is added to the form as indicated below.

B This analyte was detected in the associated method blank as well as in the sample.

E The amount detected exceeds the calibration range of the instrument.

J The analyte was positively identified . The amount is less than QL but greater than or equal to ½ of QL and/or the associated numerical value is approximate. It is an estimated value.

10.2.6.2 The reconstructed ion chromatogram (RIC) of the data file.

10.2.6.3 The raw spectra and enhanced spectra of the target compounds, internal standards and surrogates detected in the sample, as well as the corresponding reference spectra in order of elution.

10.2.6.4 Documentation of any required manual integrations as described in Section 8.5.11 and Region 9 SOP #835.

10.2.6.5 Non-target compound report form detailing the compound names, retention times, the estimated concentrations, and the CAS number of up to twenty tentatively identified compounds. The exceptions are QC samples of LFB, LFM/LFMD.

10.2.6.6 Enhanced spectra of non-target compounds detected in the sample. Library search listing the three best fits of a forward library search of the non-target compounds.

10.2.6.7 Area summary showing results of integrating the RIC.

10.2.7 Logbooks and Miscellaneous Data.

All logbooks must be peer reviewed and complete in compliance with USEPA Region 9 Laboratory SOP #840, Notebook Documentation and Control.

10.2.7.1 Copies of all applicable standards preparation logbook pages.

10.2.7.2 Copies of extraction log pages.

10.2.7.3 Copies of Percent Solids logbook pages, if applicable.

10.2.7.4 Copies of GPC run log logbook pages, if applicable

10.2.7.5 Copies of applicable Semivolatile Organics Run Log pages

10.3 Summary Report and Raw Data

When the clients' requirements stipulate a summary data package, the laboratory prepares the report narrative, analytical results spreadsheet, and sample specific raw data and organizes other data associated with the package for filing in the event that future data review or validation is required.

10.3.1 Prepare the report narrative according to the requirements listed in Section 10.2.1.

10.3.2 Prepare the analytical results spreadsheet according to the specifications provided in Section 10.2.2.

10.3.3 Organize the raw data associated with the analysis of all the samples in the package for filing and present it for review along with the report narrative and the spreadsheet. No summary forms need be generated with the raw data but any forms which would normally be generated as part of the analysis must be included in the package. For example, the calibration summary reports generated by the data system and used by the analyst to assess the acceptability of the calibration should be filed with the raw data.

10.3.3.1 Include sample tracking information as detailed in Section 10.2.3 as the analyst has a copy of the information readily available.

10.3.3.2 Sample raw data organized by laboratory sample ID must include: the quantitation report; the RIC; the raw and enhanced spectra of the internal standards, surrogates and any target compounds detected in the sample, as well as the enhanced spectra of the corresponding compounds in the calibration file; and enhanced spectra of non-target compounds detected in the sample along with the library search listing the three best matches for the non-target compounds. (Sections 10.2.5.3 through 10.2.5.6)

10.3.3.3 Calibration data must include any available summary information and the quantitation reports and RICs for all initial calibrations and continuing calibrations associated with the SDG. This information must be organized by instrument and date. Additionally, any manual integration must be demonstrated by including the associated peak integration as described in Section 8.5.11.

10.3.3.4 Include raw data for QC samples. Tuning data and the associated summary used by the analyst to determine acceptability, blanks (quant report, RIC and spectra and TICs), LFM/LFMD data (quant report and RICs) should all be included in this order.

10.3.3.5 Runlogs and standard preparation logbooks need not be included in the raw data as these are already filed in an accessible manner in the laboratory.

10.4 Technical review.

Assign the data package an ESAT document control number after assembly. Each data package is reviewed by the GC Group Leader or a senior level chemist, other than the chemist who performed the analyses. All reviews are documented using the review form. After the peer review is performed, a cover letter is prepared and signed by the Group Leader. Final review of the data package is done by ESAT QA/QC Coordinator or ESAT Team Leader and the package is then paginated and submitted to EPA Region 9.

10.5 Injection logbook.

Maintain an injection logbook listing each field and QC sample injected for each instrument in accordance with ESAT SOP #840, *Notebook Documentation and Control.*

10.6 Standards' logbook

Maintain a logbook documenting the preparation of all standard solutions. Record the standard ID, preparation date, expiration date, solvent and solvent lot number used. Record the identification, supplier, lot number, concentration purity, and expiration date of the stock standard solution used. Record the aliquot weight or volume of the stock standard solution, final volume of the standard solution and the concentration of the analyte(s) in the standard. Document the calculations used in preparing the standard.

10.7 Maintenance logbook

Maintain a logbook for each instrument. Record the date, the problem and resolution, and documentation of return to control. Document all preventive or routine maintenance procedures, as well as repairs or corrective or remedial actions in accordance with ESAT SOP #840, *Notebook Documentation and Control.*

11 REFERENCES

1 EPA Method 8270C, *Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*, Revision 3, December 1996.

2 EPA 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

3 EPA Region 9 SOP #125. *Disposal Procedures for Unused Aqueous Environmental Samples*

4 HP 5972A MSD Hardware Manual

5 HP EnviroQuant Chemstation User's Guide

6 HP Environmental Analysis User's Guide

7 EPA Region 9 SOP #835, *Chromatographic Integration Procedures*

8 EPA Region 9 SOP #840, *Notebook Documentation and Control*

9 EPA Method 8000B, *Determinative Chromatographic Separations*, Revision 2, December 1996.

10 EPA Region 9 SOP #805, *Refrigerator Temperature Monitoring*

11 40 CFR, Part 136, Appendix B.

12 HP 5890 Gas Chromatograph Users Manual

13 HP 6890 Gas Chromatograph Users Manual

APPENDIX A

DEVIATIONS FROM SW-846 METHOD 8270C

1. There is no requirement in the reference method for the analysis of a quality control sample (QCS), or a second source standard.

2. This SOP uses a GC column with a 0.25 μm film instead of a 1 μm film as specified in the reference method.

3 The surrogate solution used in this SOP contains 1,2-dichlorobenzene-d_4 and 2-chlorophenol-d_4, neither of which are specified by method 8270.

4 The reference method recommends a concentration of 40 ng/μL in the sample extract for each internal standard; this SOP specifies 20 ng/μL instead.

5 SW-846 method 3500B referenced by method 8270C specifies a concentration of 200 mg/L for the acid matrix spiking solution; this SOP specifies 150 mg/L.

6 The reference method does not have criteria for the chromatographic separations of anthracene/phenanthrene or benzo(a)anthracene/chrysene.

7. This SOP allows for the re-analysis of certain calibration, QC, and sample solutions if the first analysis fails QC limits. This practice is not addressed in the reference method.

8. This SOP allows for a four-point calibration for certain analytes with on column quantitation limits of 25 ng (see Appendix D). The reference method requires a five-point calibration for all analytes.

9. There is no requirement in the reference method that a quantitation ion not saturate the detector.

10. There is no requirement in the reference method for the analysis of a quantitation limit standard (QLS).

11. This SOP allows the phthalate esters to be present at levels exceeding the QL in the laboratory reagent blank; the reference method does not.

12. The LFB/LFM/LFMD acceptance criteria are predetermined and fixed; they are not updated using laboratory data as in the reference method.

13. The retention times of internal standards must be within 0.2 minute from the latest daily calibration, instead of 0.5 minutes as in the reference method.

14. The acceptance criteria for surrogates are predetermined and fixed; they are not updated using laboratory data as in the reference method.

15. There is no requirement in the reference method that the response of the largest analyte peak in a dilution be kept in the upper half of the initial calibration range.

16. There is no requirement in the reference method that all ions present in the standard mass spectra at a relative intensity of 10 percent of the most abundant ion must be present in the sample spectra.

17. There is no requirement in the reference method that ions present in the sample at greater than 10 percent abundance but not present in the standard spectra must be reviewed and accounted for by the analyst making the comparison.

18. There is no requirement in the reference method that the GC/MS system is to be checked for leaks prior to the analysis of the tuning compound by monitoring m/z's 18, 28, and 69.

19. Diphenylamine is not used as a CCC in this SOP as in the reference method since it is not a target analyte in this SOP.

20. The maximum RSD of target analytes in the initial calibration in this SOP is 20%, not 15% as in the reference method.

21. The maximum RSD for any CCC in this SOP is 20%, not 30% as in the reference method.

22. The maximum %D for any CCC in this SOP is 25, not 20 as in the reference method.

23. The reference method has no %D criteria for analytes in the calibration verification other than the calibration check compounds (CCC's).

APPENDIX B
Calibration Criteria

SEMIVOLATILE COMPOUND	MINIMUM RRF	MAXIMUM %RSD	MAXIMUM %DIFF
Phenol	0.800	20	±25
bis(2-Chloroethyl)ether	0.700	20	±25
2-Chlorophenol	0.800	20	±25
1,3-Dichlorobenzene	0.600	20	±25
1,4-Dichlorobenzene	0.500	20	±25
benzyl alcohol	0.050	20	±25
1,2-Dichlorobenzene	0.400	20	±25
2-Methylphenol	0.700	20	±25
2,2'-oxybis(1-Chloropropane)	0.010	20	±25
4-Methylphenol	0.600	20	±25
N-Nitroso-di-n-propylamine	0.050	20	±25
Hexachloroethane	0.300	20	±25
Nitrobenzene	0.200	20	±25
Isophorone	0.400	20	±25
2-Nitrophenol	0.100	20	±25
2,4-Dimethylphenol	0.200	20	±25
bis(2-Chloroethoxy)methane	0.300	20	±25
2,4-Dichlorophenol	0.200	20	±25
1,2,4-Trichlorobenzene	0.200	20	±25
Naphthalene	0.700	20	±25
4-Chloroaniline	0.010	20	±25
Hexachlorobutadiene	0.010	20	±25
4-Chloro-3-methylphenol	0.200	20	±25
2-Methylnaphthalene	0.400	20	±25
Hexachlorocyclopentadiene	0.050	20	±25
2,4,6-Trichlorophenol	0.200	20	±25
2,4,5-Trichlorophenol	0.200	20	±25
2-Chloronaphthalene	0.800	20	±25
2-Nitroaniline	0.010	20	±25
Dimethylphthalate	0.010	20	±25
Acenaphthylene	0.900	20	±25
3-Nitroaniline	0.010	20	±25
2,6-Dinitrotoluene	0.200	20	±25
Acenaphthene	0.900	20	±25
2,4-Dinitrophenol	0.050	20	±25
4-Nitrophenol	0.050	20	±25
Dibenzofuran	0.800	20	±25
2,4-Dinitrotoluene	0.200	20	±25
Diethylphthalate	0.010	20	±25
4-Chlorophenyl-phenylether	0.400	20	±25
Fluorene	0.900	20	±25
4-Nitroaniline	0.010	20	±25
4,6-Dinitro-2-methylphenol	0.010	20	±25
N-Nitrosodiphenylamine	0.010	20	±25
4-Bromophenyl-phenylether	0.100	20	±25
Hexachlorobenzene	0.100	20	±25

SEMIVOLATILE COMPOUND	MINIMUM RRF	MAXIMUM %RSD	MAXIMUM %DIFF
Pentachlorophenol	0.050	20	±25
Phenanthrene	0.700	20	±25
Anthracene	0.700	20	±25
Carbazole	0.010	20	±25
Di-n-butylphthalate	0.010	20	±25
Fluoranthene	0.600	20	±25
Pyrene	0.600	20	±25
Butylbenzylphthalate	0.010	20	±25
3,3'-Dichlorobenzidine	0.010	20	±25
Benzo(a)anthracene	0.800	20	±25
bis(2-Ethylhexyl)phthalate	0.010	20	±25
Chrysene	0.700	20	±25
Di-n-octylphthalate	0.010	20	±25
Benzo(b)fluoranthene	0.700	20	±25
Benzo(k)fluoranthene	0.700	20	±25
Benzo(a)pyrene	0.700	20	±25
Indeno(1,2,3-cd)pyrene	0.500	20	±25
Dibenzo(a,h)anthracene	0.400	20	±25
Benzo(g,h,i)perylene	0.500	20	±25
SURROGATES			
Nitrobenzene-d5	0.200	20	±25
2-Fluorobiphenyl	0.700	20	±25
Terphenyl-d14	0.500	20	±25
Phenol-d5	0.800	20	±25
2-Fluorophenol	0.600	20	±25
2,4,6-Tribromophenol	0.010	20	±25
2-Chlorophenol-d4	0.800	20	±25
1,2-Dichlorobenzene-d4	0.400	20	±25

APPENDIX C

TARGET COMPOUND LIST FOR SEMIVOLATILE ORGANICS ANALYSIS

The following is the Target Compound List for semivolatile organics, as well as the associated internal standards and surrogates. Included are the internal standard reference for each target compound, as well as the quantitation mass for each analyte.

Compound	Primary Quant Ion	Secondary Ion(s)	Int. Std
Phenol	94	65, 66	1
bis(2-Chloroethyl)ether	93	63, 95	1
2-Chlorophenol	128	64, 130	1
1,3-Dichlorobenzene	146	148, 113	1
1,4-Dichlorobenzene	146	148, 113	1
benzyl alcohol	108	79, 77	1
1,2-Dichlorobenzene	146	148, 113	1
2-Methylphenol	108	107	1
2,2'-oxybis(1-Chloropropane)	45	77, 79	1
4-Methylphenol	108	107	1
N-Nitroso-di-n-propylamine	70	42, 101, 130	1
Hexachloroethane	117	201, 199	1
Nitrobenzene	77	123, 65	2
Isophorone	82	95, 138	2
2-Nitrophenol	139	65, 109	2
2,4-Dimethylphenol	107	121, 122	2
bis(2-Chloroethoxy)methane	93	95, 123	2
2,4-Dichlorophenol	162	164, 98	2
1,2,4-Trichlorobenzene	180	182, 145	2
Naphthalene	128	129, 127	2
4-Chloroaniline	127	129	2
Hexachlorobutadiene	225	223, 227	2
4-Chloro-3-methylphenol	107	144, 142	2
2-Methylnaphthalene	142	141	2
Hexachlorocyclopentadiene	237	235, 272	3
2,4,6-Trichlorophenol	196	198, 200	3
2,4,5-Trichlorophenol	196	198, 200	3
2-Chloronaphthalene	162	164, 127	3
2-Nitroaniline	65	92, 138	3
Dimethyl phthalate	163	194, 164	3
Acenaphthylene	152	151, 153	3
2,6-Dinitrotoluene	165	89, 121	3
3-Nitroaniline	138	108, 92	3
Acenaphthene	153	152, 154	3
2,4-Dinitrophenol	184	63, 154	3
4-Nitrophenol	109	139, 65	3
Dibenzofuran	168	139	3
2,4-Dinitrotoluene	165	63, 182	3
Diethylphthalate	149	177, 150	3
4-Chlorophenyl-phenylether	204	206, 141	3
Fluorene	166	165, 167	3
4-Nitroaniline	138	92, 108	3

Compound	Primary Quant Ion	Secondary Ion(s)	Int. Std
4,6-Dinitro-2-methylphenol	198	182, 77	4
N-Nitrosodiphenylamine	169	168, 167	4
4-Bromophenyl-phenylether	248	250, 141	4
Hexachlorobenzene	284	142, 249	4
Pentachlorophenol	266	264, 268	4
Phenanthrene	178	179, 176	4
Anthracene	178	179, 176	4
Carbazole	167	166, 139	4
Di-n-butylphthalate	149	150, 104	4
Fluoranthene	202	101, 100	4
Pyrene	202	101, 100	5
Butylbenzylphthalate	149	91, 206	5
3,3'-Dichlorobenzidine	252	254, 126	5
Benzo(a)anthracene	228	229, 226	5
bis(2-Ethylhexyl)phthalate	149	167, 279	5
Chrysene	228	226, 229	5
Di-n-Octyl phthalate	149	150, 279	6
Benzo(b)fluoranthene	252	253, 125	6
Benzo(k)fluoranthene	252	253, 125	6
Benzo(a)pyrene	252	253, 125	6
Indeno(1,2,3-cd)pyrene	276	138, 227	6
Dibenzo(a,h)anthracene	278	139, 279	6
Benzo(g,h,i)perylene	276	138, 277	6
SURROGATES			
Phenol-d5	99	42, 71	1
2-Fluorophenol	112	64	1
2,4,6-Tribromophenol	330	332, 141	4
Nitrobenzene-d5	82	128, 54	2
2-Fluorobiphenyl	172	171	3
Terphenyl-d14	244	122, 212	5
2-Chlorophenol-d4	132	68, 134	1
1,2-Dichlorobenzene-d4	152	115, 150	1
INTERNAL STANDARDS			
1,4-Dichlorobenzene-d4	152	115	1
Naphthalene-d8	136	68	2
Acenaphthene-d10	164	162, 160	3
Phenanthrene-d10	188	94, 80	4
Chrysene-d12	240	120, 236	5
Perylene-d12	264	260, 265	6

APPENDIX D

SEMIVOLATILES TARGET COMPOUND LIST AND QUANTITATION LIMITS

Semivolatiles	CAS Number	Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column ng
Phenol	108-95-2	10	330	10000	10
bis-(2-Chloroethyl)ether	111-44-4	10	330	10000	10
2-Chlorophenol	95-57-8	10	330	10000	10
1,3-Dichlorobenzene	541-73-1	10	330	10000	10
1,4-Dichlorobenzene	106-46-7	10	330	10000	10
benzyl alcohol	100-51-6	10	330	10000	10
1,2-Dichlorobenzene	95-50-1	10	330	10000	10
2-Methylphenol	95-48-7	10	330	10000	10
2,2'-oxybis (1-Chloropropane)	108-60-1	10	330	10000	10
4-Methylphenol	106-44-5	10	330	10000	10
N-Nitroso-di-n-propylamine	621-64-7	10	330	10000	10
Hexachloroethane	67-72-1	10	330	10000	10
Nitrobenzene	98-95-3	10	330	10000	10
Isophorone	78-59-1	10	330	10000	10
2-Nitrophenol	88-75-5	10	330	10000	10
2,4-Dimethylphenol	105-67-9	10	330	10000	10
bis(2-Chloroethoxy)methane	111-91-1	10	330	10000	10
2,4-Dichlorophenol	120-83-2	10	330	10000	10
1,2,4-Trichlorobenzene	120-82-1	10	330	10000	10
Naphthalene	91-20-3	10	330	10000	10
4-Chloroaniline	106-47-8	10	330	10000	10
Hexachlorobutadiene	87-68-3	10	330	10000	10
4-Chloro-3-methylphenol	59-50-7	10	330	10000	10
2-Methylnaphthalene	91-57-6	10	330	10000	10
Hexachlorocyclopentadiene	77-47-4	10	330	10000	10
2,4,6-Trichlorophenol	88-06-2	10	330	10000	10
2,4,5-Trichlorophenol	95-95-4	25	830	25000	25
2-Chloronaphthalene	91-58-7	10	330	10000	10
2-Nitroaniline	88-74-4	25	830	25000	25
Dimethylphthalate	131-11-3	10	330	10000	10
Acenaphthylene	208-96-8	10	330	10000	10
2,6-Dinitrotoluene	606-20-2	10	330	10000	10
3-Nitroaniline	99-09-2	25	830	25000	25
Acenaphthene	83-32-9	10	330	10000	10
2,4-Dinitrophenol	51-28-5	25	830	25000	25
4-Nitrophenol	100-02-7	25	830	25000	25
Dibenzofuran	132-64-9	10	330	10000	10
2,4-Dinitrotoluene	121-14-2	10	330	10000	10
Diethylphthalate	84-66-2	10	330	10000	10
4-Chlorophenyl-phenylether	7005-72-3	10	330	10000	10
Fluorene	86-73-7	10	330	10000	10
4-Nitroaniline	100-01-6	25	830	25000	25
4,6-Dinitro-2-methylphenol	534-52-1	25	830	25000	25
N-Nitroso-diphenylamine	86-30-6	10	330	10000	10
4-Bromophenyl-phenylether	101-55-3	10	330	10000	10
Hexachlorobenzene	118-74-1	10	330	10000	10
Pentachlorophenol	87-86-5	25	830	25000	25

Phenanthrene	85-01-8	10	330	10000	10
Anthracene	120-12-7	10	330	10000	10
Carbazole	86-74-8	10	330	10000	10
Di-n-butylphthalate	84-74-2	10	330	10000	10
Fluoranthene	206-44-0	10	330	10000	10
Pyrene	129-00-0	10	330	10000	10
Butylbenzylphthalate	85-68-7	10	330	10000	10
3,3'-Dichlorobenzidine	91-94-1	10	330	10000	10

Semivolatiles	CAS Number	Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column (ng)
Benzo(a)anthracene	56-55-3	10	330	10000	10
Chrysene	218-01-9	10	330	10000	10
bis(2-Ethylhexyl)phthalate	117-81-7	10	330	10000	10
Di-n-octylphthalate	117-84-0	10	330	10000	10
Benzo(b)fluoranthene	205-99-2	10	330	10000	10
Benzo(k)fluoranthene	207-08-9	10	330	10000	10
Benzo(a)pyrene	50-32-8	10	330	10000	10
Indeno(1,2,3-cd)-pyrene	193-39-5	10	330	10000	10
Dibenzo(a,h)-anthracene	53-70-3	10	330	10000	10
Benzo(g,h,i)perylene	191-24-2	10	330	10000	10

APPENDIX E

GC PARAMETERS

HP6890

Typical operating parameters for the gas chromatograph are as follows:

DFTPP analysis

PARAMETER	SETTING
Injector temperature	280°C
Column Stability time	0.5 minutes
MS Source Temp	230°C
MS Quad Temp	150°C
MSD Heater Temp	280°C
EPC split-splitless inlet	Pulsed splitless
Injection pulse pressure	20 psi until 0.55 min
Purge flow to split vent	20 ml/min @ 0.50 min
Initial Oven Temp	100°C
Initial Oven Time	0 minutes
Temperature Ramp	20°C/minute for 10 minutes
Final Oven Temp	300°C
Final Hold Time	2 minutes
Column Flow rate	~ 1 mL/min
Electron Energy	70 volts (nominal)
Injector	Front
Injection Volume	1.0 µL
Pre Injection	
Sample Washes	0
Solvent A Washes	1
Solvent B Washes	0
Post Injection	
Solvent A Washes	3
Solvent B Washes	3
Pumps	3
Syringe Size	10 µL
Viscosity	0
Plunger Speed	Fast Injection

Target Compound Analysis

PARAMETER	SETTING
Injector temperature	280°C
Column Stability time	0.5 minutes
MS Source Temp	230°C

MS Quad Temp	150°C
MSD Heater Temp	280°C
EPC split-splitless inlet	Pulsed splitless
Injection pulse pressure	20 psi until 0.55 min
Purge flow to split vent	20 ml/min @ 0.50 min
Initial Oven Temp	40°C
Initial Oven Time	1 minutes
Temperature Ramp	20°C/minute
Final Oven Temp	130°C
Temperature Ramp A	12°C/minute
Final Oven Temp A	270°C
Temperature Ramp B	4°C/minute
Final Oven Temp B	313°C
Final Hold Time	2 minutes
Column Flow rate	~ 1 mL/min
Electron Energy	70 volts (nominal)
Injection Volume	1.0 µL
Pre Injection	
Sample Washes	0
Solvent A Washes	1
Solvent B Washes	0
Post Injection	
Solvent A Washes	3
Solvent B Washes	3
Pumps	3
Syringe Size	10 µL
Viscosity	0
Plunger Speed	Fast Injection

Appendix B-10
Flashpoint

U. S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P. O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490; FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES

Client Request

_____ Regional Transmittal _____ Telephone Request

A. EPA Region/Client: Region 9

B. Region Contact: [redacted]

C. Date of Request:

D. Site Name:

E. City/State:

F. 2 Digit Superfund Site Identifier:

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address all applicable questions. Incomplete or erroneous information may result in a delay in the processing of your request. If you need to provide additional information not addressed by the questions, please attach additional sheets of paper.

1. General description of analytical service requested:

   The determination of ignitability (flash point) of soil/sludge samples by modified EPA Method 1010 and modified ASTM Method D93-80.

2. Definition and number of work units involved (specify whether whole samples or fraction; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium or high concentration):

3. Purpose of analysis (specify whether Superfund [enforcement or remedial action], RCRA, NPDES, etc.):

4. Estimated date(s) of collection (provide a sampling schedule):

5. Estimated date(s) and method of shipment:

Federal Express - shipped same day as collection for next day delivery.

6. Number of days analysis and data required after laboratory receipt of samples:

The determination of ignitability should be performed within 14 days after sample receipt at the laboratory.

Data packages and all other deliverables are required within 35 days from receipt of last sample in each Sample Delivery Group (SDG). A SDG is defined as all samples received within a 14 day period or 20 samples, whichever is reached first.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Method Summary: The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame causes the vapor above the sample to ignite. The sample is deemed to have flashed when a large flame appears and instantaneously propagates itself over the surface of the sample.

Follow EPA Method 1010 and ASTM Method D93-80, with the following specification and modifications:

1. Use a Pensky-Martens Closed Flash Tester and thermometer as described in Section 6 of ASTM Method D93-80.

2 Weight out an appropriate aliquot of soil/sludge and place it in the test cup. A 30 to 50 gram sample aliquot is recommended.

3. The ignitability of each sample is to be determined twice. Report the average of these two determinations. If the duplicate results differ by more than 2°C, repeat and report the average of the four determinations.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

a. Calibration Procedure and Criteria: Not applicable.

b. Internal Quality Control Checks, Control Limits and Corrective Actions:

1. The ignitability of a laboratory control sample (LCS), composed of p-xylene, must be determined before any samples are analyzed and at a frequency of one per sample delivery group. The laboratory must report at least three determinations of the ignitability of the p-xylene standard. The laboratory is to report the average of these determinations and the percent relative standard deviation (%RSD). The %RSD is not to exceed 10%.

2. The laboratory must determine the percent moisture of each sample using a separate sample aliquot for this determination.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.) If not completed, format of results will be left to program discretion.

a. Data Calculations and Reporting Units:

Follow Section 11 of ASTM Method D93-80. Sample results are to be reported in degrees Celsius (°C). All records of determinations and calculations must be legible and sufficient to recalculate all sample results. Include an example of the calculations in the data package.

b. Documentation and Deliverables:

Deliverables (in the form of a purge file - i.e., original documents) for each Sample Delivery Group shall include all deliverables required by the IFB, including, but not limited to:

1. All Sample Tracking Reports (i.e., signed SAS Packing Lists/Chain-of-Custody forms).

2. A copy of the SAS, as provided by SMO (so that any SMO changes will be known). Only the technical portion of the SAS is required.

3. Any telephone logs referring to the samples.

4. A Case Narrative, signed by the laboratory manager or his or her designee, certifying the accuracy and validity of all data reported and describing any problems encountered during the analyses and documenting their resolution(s).

5. Tabulated sample results with units. Report all sample

6. Analysis run logs.

7. Laboratory control sample results with calculated %RSD.

8. Percent moisture determinations.

9. Raw sample data, including:

   a. instrument output
   b. bench sheets and worksheets
   c. tabulated results

10. Other (use additional sheets or attach supplementary information, as needed):

Attached is a copy of the "U. S. EPA Region 9 Laboratory QC Summary Report" form. This form is to be completed by the Laboratory Manager or his/her designee and submitted with each data package. The form is to reflect the conditions contained within the data package with which it is submitted. Laboratories may make additional copies of this form as needed.

11. Name of sampling/shipping contact:

Phone: ( )

12. Data Requirements:

Parameter	Contract Required Detection Limit
Not applicable.	

13. QC Requirements:

QC Required	Frequency of QC	Limits (% or Conc.)
LCS	Beginning of analysis and 1 per SDG	≤10% RSD

14. Action required if limits are exceeded:

If above control limits are exceeded, take appropriate actions to identify the problem. Corrective action should be taken before additional samples are analyzed.

Appendix B-11
pH

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 582

pH in SOLID SAMPLES

Prepared by:

Osellie L. Salvador, ESAT Region 9, ICF Consulting _____ Date

Review by:

Richard Bauer, Chemistry Team Leader _____ Date

Approved by:

Brenda Bettencourt, Laboratory Director _____ Date

Periodic Review:

Signature	Title	Date

STANDARD OPERATING PROCEDURE 582

pH in SOLID SAMPLES

This SOP was prepared by ICF Consulting for the United States Environmental Protection Agency (USEPA) under the Environmental Services Assistance Team (ESAT) contract (EPA contract No. 68-W-01-028).

APPROVED BY:

Osellie L. Salvador, Inorganic Group Leader	Date
Surender Kaushik, QA Task Manager	Date
Jerry Vail, ESAT Program Manager	Date

ESAT Document Control Number: B0101023-0320

CONTENTS

1 SCOPE AND APPLICATION 4

2 METHOD SUMMARY 4

3 DEFINITIONS 4

4 HEALTH AND SAFETY 5

5 SAMPLE HANDLING AND PRESERVATION 5

6 INTERFERENCES 5

7 APPARATUS AND MATERIALS 6

8 QUALITY CONTROL PROCEDURES 6

9 ANALYTICAL PROCEDURES 7

10 DOCUMENTATION 9

11 REFERENCES 10

Attachment A - Deviations From Reference Method

Attachment B - pH Reporting Benchsheet

Attachment C - Analytical Spreadsheet

Attachment D - QC Summary Page

1 SCOPE AND APPLICATION

1.1 This procedure is applicable for measuring the pH of multiphase wastes where the aqueous phase constitutes at least 20% of the total volume of the sample. This procedure is based on EPA Method 9040B.

1.2 This procedure is also applicable for measuring pH in soils, sediments, sludges or other solid samples where water constitutes less than 20% of the total volume of the sample. This procedure is based on EPA Method 9045C.

2 METHOD SUMMARY

2.1 The pH of a sample is determined electrometrically using a combination electrode attached to a pH meter with automatic temperature compensation (ATC).

3 DEFINITIONS

3.1 Analytical Sample - Any sample in which pH is being determined, excluding QC reference samples.

3.2 Automatic Temperature Compensation (ATC) - A probe that electronically adjusts for differences in temperature in the sample.

3.3 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.

3.4 Instrument Performance Check Solution (IPC) - Periodic analysis of the calibration standards performed to monitor calibration drift.

3.5 Laboratory Duplicate (LD) - An aliquot of sample 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.

3.6 Quality Control Sample (QCS) - A secondary solution containing a known pH. The QCS is obtained from a commercial source. It is used to check laboratory performance.

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

4 HEALTH AND SAFETY

4.1 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. Contact your Group Leader or Health & Safety and Env. Compliance Task Manager to determine if additional treatment is required.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Samples are received at the Region 9 Laboratory by EPA staff in Room 503. Sample IDs and dates and times of collection are verified against the chain-of-custody form.

5.2 Samples must be stored at 4 ± 2 C.

5.3 Samples must be analyzed as soon as possible.

6 INTERFERENCES

6.1 The electrode, in general, is not subject to interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.

6.2 Coatings of oily material or particulate matter can impair electrode response time. These coatings may be removed by gently wiping or washing the electrode with detergent. An additional treatment with hydrochloric acid (1+9) may be necessary to remove any remaining film.

6.3 The sample temperature affects pH measurement in two manners:

1) The electrode response will vary with changes in temperature. Using a pH meter with ATC can minimize this variability.
2) Sample pH is dependent upon the sample temperature, i.e., the true pH of a sample is different at different temperatures. Consequently, the sample temperature must be recorded as part of the pH measurement process.

7 APPARATUS AND MATERIALS

7.1 Apparatus

7.1.1 Orion Expandable IonAnalyzer EA 940 pH meter or equivalent.
7.1.2 Orion Combination pH Electrode Model 91-56 or equivalent.
7.1.3 Automatic Temperature Compensation probe, Epoxy Body, Beckman No. 592373 or equivalent.

7.2 Glassware and Incidentals

7.2.1 Plastic or Teflon spray bottle.
7.2.2 Beakers - 50mL or 100mL capacity.
7.2.3 Magnetic Stirrer Plate.
7.2.4 Magnetic Stirrer Bars - 0.5" to 1" in length.
7.2.5 Analytical Balance: capable of weighing 0.1 g.

7.3 Standards and Reagents

Reagents may contain impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society (ACS) specifications should be used.

7.3.1 pH Buffers - pH buffers at 2, 4, 7,10 and 12 pH (Fisher or equivalent).
7.3.2 Quality Control Sample (QCS) - A second source pH buffer (pH 7) obtained from a commercial vendor such as E.R.A., Inorganic Ventures or equivalent.
7.3.3 Orion Storage Solution or equivalent.
7.3.4 Orion Filling Solution (4M KCl saturated with AgCl) or equivalent.
7.3.5 Reagent water - All references to water in this method refer to ASTM Type II grade water.

8 QUALITY CONTROL PROCEDURES

8.1 EPA Region 9 Laboratory operates a formal quality control (QC) program. As it relates to this SOP, the QC program consists of an initial demonstration of laboratory capability (refer to R9 SOP 880), and the periodic analysis of laboratory solutions as a continuing check on performance.

8.2 Routine Analytical Quality Control

8.2.1 QCS - The pH in a QCS sample must be measured daily or once per batch of 20 samples, whichever is more frequent. The QCS must have a pH value within the range of the current calibration (normally pH 7). If the measured concentrations are not within $\pm$0.1 pH units, the

method performance is unacceptable. The source of the problem must be identified and corrected before proceeding with analyses.

8.2.2 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 20 routine samples of the same matrix in a sample batch.

The pH readings on duplicate samples should agree within 0.1 pH units of the original sample. Otherwise, reanalyze using a fresh aliquot. If four different aliquots of the same sample show results that differ by more than 0.1 pH units, the problem may be the sample. Flag all associated sample results. Document actions in the report narrative.

8.2.3 Instrument Performance Check - Measure the pH of the calibration standards immediately after calibration, after every 10 samples and at the end of every analysis sequence. If the measured concentrations are not within $\pm$0.1 pH units of the true values, the method performance is unacceptable. Re-calibrate the system and re-analyze all samples since the last acceptable IPC analysis. If some samples have a pH below 4, measure a buffer at pH 2 as part of the Instrument Performance Check. If some samples have a pH of above 10, measure a buffer at pH 12 as part of the Instrument Performance Check.

9 ANALYTICAL PROCEDURES

9.1 The analyst is advised to follow the recommended operating conditions provided by the instrument 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.

9.2 Method Characterization - Prior to routine use, it must be demonstrated that the pH meter, electrode, and ATC are in working condition.

9.2.1 ATC Temperature Measurement - Measure the temperature of two solutions (room temperature water and ice water) using both the ATC probe and a NIST-traceable thermometer. Compare the measurements for the ATC probe and thermometer. If the difference exceeds 0.5°C, refer to the ATC manual for corrective action.

9.3 Calibration and Standardization - The analyst must select the appropriate calibration range for the samples. The pH meter may be calibrated with the pH 4 and pH 7 buffers or with pH 7 and pH 10 buffers. Every sample must be analyzed under a calibration which brackets the sample pH. This may require analyzing a set of samples under one calibration, recalibrating the meter using the other calibration range, and reanalyzing the samples which have sample pHs within the second

calibration range. Samples with pH below 4, calibrate with pH 4 and pH 7 buffers and for samples with pH above 10, calibrate with pH 7 and pH 10 buffers.

9.3.1 Place a clean magnetic stirrer bar into a clean 50-mL beaker and pour about 30 to 40-mL of the lowest of the two calibration buffer to be used for calibration. Immerse the ATC probe and the pH electrode into the buffer and measure the pH while the buffer is being gently stirred (i.e., no visible vortex). Perform a temperature calibration by pressing **speed** and the number **7** on the pH meter. Press **yes** when the question "SET TEMPERATURE?" appears on the screen. The temperature reading on the buffer will appear on the screen. Press **yes** if the temperature reading is correct. If it is incorrect, punch in the correct temperature. Use a NIST-traceable thermometer to verify the temperature of the buffer. Record the temperature of both the ATC probe and the NIST thermometer and the time of analysis in the pH Analysis Run Log.

9.3.2 To calibrate with the buffer, press **speed** and **0**. Press **yes** to calibrate the pH and enter the number of pH buffers to be used, which is **2**. Press the **yes** button to do automatic calibration, and **yes** again to indicate that the electrode is in buffer 1 (the lower pH solution). When the pH reading is stable, the instrument will indicate the determined value of the buffer and what it should be according to its temperature. It will calibrate with that number when you press **yes**. Rinse the pH electrode and the ATC probe with reagent water and blot them dry with Kimwipes. Place a clean magnetic stirrer bar into a 50-mL beaker and pour approximately 30 to 40-mL of buffer 2 (the higher pH solution). Immerse the ATC probe and the pH electrode into the buffer and measure the pH while the buffer is being gently stirred. Calibrate with the buffer 2 by pressing **yes** to "ELECTRODE IN BUFFER 2?". Press **yes** again to calibrate with the number the pH meter determines the reading should be. The determined slope will appear.

9.3.3 Review the calibration slope results. The calibration slope must be within 95-105%. If the slope is acceptable press **yes** to continue. Record the slope in the pH Analysis Run Log. If the slope is unacceptable, troubleshoot the system and re-calibrate. An acceptable calibration must be obtained before samples can be analyzed. Rinse the pH electrode and the ATC probe with reagent water and blot them dry with Kimwipes.

9.4 Sample Preparation and Analysis

9.4.1 To determine if the aqueous phase of the sample constitutes less than 20% or more of the total sample volume, do the following: Transfer the sample in a beaker and approximately determine the volume of the aqueous phase and compare it to the total volume of the sample. If aqueous phase is less than 20% follow Section 9.4.3 and if it is at least 20% follow Section 9.4.2.

9.4.2 For multiphase samples where the aqueous phase constitutes at least 20% of the total volume of the sample, no preparation step is needed. Either pour the sample into a beaker or immerse the electrode directly into the sample container and follow Section 9.4.4.

9.4.3 For samples where water constitutes less than 20% of the total volume of the sample, measure 20 g of the sample in a 50-mL beaker and add 20 mL of reagent water, cover and stir the suspension for 5 minutes and let it stand for about 30 minutes to settle out the suspension or filter/centrifuge off the aqueous phase for pH measurement and follow Section 9.4.4.

Note: If the sample is hygroscopic and absorbs all the reagent water, begin the procedure again using 20 g of sample and 40 mL of reagent water.

9.4.4 Immerse the ATC probe and the pH electrode into the beaker containing the sample to be measured just below the suspension and measure the pH. When a stable reading is obtained, record the time, temperature and pH. Rinse the pH electrode and the ATC probe with reagent water and blot the probes dry with Kimwipes after each sample analysis. A typical run sequence is listed in the following table.

Seq.	Description	Seq.	Description	Seq.	Description
1	IPC-Low Buffer	11	S7	21	S15
2	IPC-High Buffer	12	S8	22	S16
3	QCS	13	IPC-Low Buffer	23	S17
4	S1	14	IPC-High Buffer	24	S18
5	S1-LD	15	S9	25	IPC-Low Buffer
6	S2	16	S10	26	IPC-High Buffer
7	S3	17	S11		
8	S4	18	S12		
9	S5	19	S13		
10	S6	20	S14		

9.5 Data Reduction and Reporting - The pH meter reports pH results directly in pH units and temperature results in °C. Record and report pH results to 0.1 pH unit and the temperature to the nearest degree. 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.

10 DOCUMENTATION

10.1 pH Analysis Run Log - Entries are made for the pH buffer solutions, case number, SDG number, slope of the calibration, lab sample IDs, client sample IDs, sample volume in mL, time of analysis, pH result, analyst initials, date of analysis and comments, if any. The run log is maintained in Room 304 (Attachment B).

10.2 Report Narrative and Deliverable

The data package consists of the report narrative, forms, and data, as listed in the table below.

Data Package Contents
Report Narrative: Discusses any problems encountered, both technical and administrative, the corrective action taken, and the resolution. All universal analytical flags should also be discussed in the report narrative.
Tabulated sample results: On an analytical spreadsheet, with units of pH, sample collection dates, client sample IDs, laboratory IDs and station locations. (Attachment C)
Duplicate results on a QC summary form with calculated relative percent difference (RPD). (Attachment D)
QCS results on a QC summary form with true value and found result. (Attachment D)
Raw sample, standard and QC data, including bench sheets and any work sheets, if applicable.

11 REFERENCES

11.1 SW-846 Method 9040B, Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, Revision 2, January 1995.
11.2 SW-846 Method 9045C, Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, Revision 3, January 1995.
11.3 Orion Combination pH Electrode Instruction Manual, 1991 Orion Research, Incorporated.
11.4 EA 940 Expandable IonAnalyzer Instruction Manual, 1985 Orion Research, Incorporated..
11.5 *Method 4500-H^+ pH Value*, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998.
11.6 Region 9 SOP 840, *Notebook Documentation and Control.*
11.7 Region 9 SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency.*

Attachment A
Deviations From Reference Method

A.1 This SOP includes routine QC procedures based on EPA Region 9 Laboratory policy in addition to those listed in EPA Method 9040B and 9045C. This include the analysis of a laboratory duplicate.

ATTACHMENT B

pH ANALYSIS RUN LOG

pH Buffer #1: _____ Case: _____

pH Buffer #2: _____ SDG: _____

Slope: _____

	Lab ID	EPA ID	Soil Weight (g)	Water Volume (mL)	Time	pH	Comments
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							

Analyst: _____ Date: _____

BOOK #3

filename: pH_book.log Reviewed by:

ATTACHMENT C

EPA REGION 9 LABORATORY-RICHMOND, CA
SUMMARY OF ANALYTICAL RESULTS

Case Number:	**R01S36**	**Analysis:**	**pH**
Site:	**LYNX/HASSAYAMPA WATERSHED**	**Matrix:**	**Soil/Sediment**
SDG:	**01134B**		
Date:	**06/11/01**		

Sample No.	N/A			N/A			N/A			N/A			N/A			N/A		
Sample I.D.	HR-GGV-SS-02			HR-SC-SS-02			HR-MCT-SD-BCMD			HR-SUN-SS-01			HR-MCT-SD-BCSCD			HR-MCT-SD-01		
Lab Sample I.D.	AB30980			AB30981			AB30982			AB30983			AB30984			AB30985		
Date of Collection	05/10/01			05/10/01			05/10/01			05/10/01			05/10/01			05/10/01		
Units	units of pH			units of pH			units of pH			units of pH			units of pH			units of pH		
Analyte	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result	Q	Com
pH	6.9			2.8			3.2			3.6			4.1			2.9		

Com- Comments refer to the corresponding section in the report narrative for each letter.
N/A - Not Applicable.
N/R - Not Required.
Q - Refer to data qualifiers.
U - The parameter was analyzed for, but was not detected; The associated value is the sample quantitation limit, adjusted for dilution, if any.
J - The associated value is an estimated quantity.

ATTACHMENT D

US E.P.A.
REGION 9 LABORATORY
June 11, 2001
Case Number: R01S36
SDG: 01130B

Laboratory Duplicate Sample

Analyzed	Sample ID	Analysis	Sample	Duplicate	Difference	Q
05/14/01	HR-LH-SD-	pH	6.53	6.59	0.06	
05/18/01	HR-WM-SD-	pH	3.03	3.07	0.04	
05/18/01	HR-GGV-	pH	6.79	6.85	0.06	

Quality Control Sample (pH)

Analyzed Date	Sample ID	True Value (units of pH)	Result (units of pH)	Difference (units of pH)
05/14/01	QCS	7.0	7.01	0.01
05/18/01	QCS	7.0	6.99	0.01
05/18/01	QCS	7.0	7.01	0.01
06/05/01	QCS	4.0	4.00	0

Appendix B-12
8260 VOCs

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE #305

VOLATILE ORGANICS ANALYSIS

	Signature & Title	
Prepared by:	_____	_____
	Kathy O'Brien, ESAT Region 9, Lockheed Martin	Date
Reviewed by:	_____	_____
	Richard Bauer, Chemistry Team Leader	Date
Approved by:	_____	_____
	Brenda Bettencourt, Lab. Director	Date

Periodic Review:

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

STANDARD OPERATING PROCEDURE #305

VOLATILE ORGANICS ANALYSIS

This SOP was prepared by Lockheed Martin for the United States Environmental Protection Agency (USEPA) under the Environmental Services Assistance Team (ESAT) contract (EPA contract No. 68D60005).

APPROVED BY:

_____ _____
Kathy O'Brien, QA/QC Coordinator, Lockheed Martin Date

_____ _____
Jack Berges, ESAT Team Manager, Lockheed Martin Date

ESAT Document Control Number: ESAT-9B-3094

TABLE OF CONTENTS

1 SCOPE AND APPLICATION
2 METHOD SUMMARY
3 DEFINITIONS
4 HEALTH AND SAFETY
5 SAMPLE HANDLING AND PRESERVATION
6 INTERFERENCES
7 APPARATUS AND MATERIALS
8 QUALITY CONTROL
- 8.1 Mass calibration.
- 8.2 GC/MS System Performance Check (BFB analysis.)
- 8.3 Initial calibration.
- 8.4 Continuing Calibration
- 8.5 Laboratory Control Sample (LCS)
- 8.6 Low Level Quantitation Verification Standard.
- 8.7 Method blank analysis.
- 8.8 Storage blank analysis.
- 8.9 Instrument blanks
- 8.10 Internal standard recovery.
- 8.11 System monitoring compound recovery.
- 8.12 Matrix spike and matrix spike duplicate analysis.
- 8.13 Sample dilution.
- 8.14 Review of Target Analytes
- 8.15 Review the Tentatively Identified Compound

9 ANALYTICAL PROCEDURES
- 9.1 Analytical system preparation
- 9.2 Leak Checking
- 9.3 GC/MS Performance Check
- 9.4 Analysis of waters (5 mL sample volume).
- 9.5 Analysis of low detection limit waters (25 mL)
- 9.6 Analysis of low level soils
- 9.7 Analysis of soils using medium level soil extraction method
- 9.8 Autosampler operation

10 DOCUMENTATION
11 REFERENCES
12 DEVIATIONS FROM REFERENCE METHOD

APPENDIX A - 5 mL Water and Soil Calibration Criteria
APPENDIX B - 25 mL Water Calibration Criteria
ATTACHMENT A - Target Compound List For Volatile Organics Analysis
ATTACHMENT B - Purge and Trap Concentrator Parameters
ATTACHMENT C - Autosampler Parameters
ATTACHMENT D - GC Parameters
ATTACHMENT E - Data File Naming Convention

1 SCOPE AND APPLICATION

The function of the Region 9 Volatile Organics laboratory is to analyze water, soil and sediment samples for volatile organic compounds in support of the EPA's Superfund, RCRA, WQM, NPDES, UIC, and Drinking Water programs. The applicability of these procedures to specific project data quality objectives must be assessed on a case by case basis. The QC criteria specified in the procedures do not meet compliance criteria for either drinking water or NPDES monitoring projects.

2 METHOD SUMMARY

This Standard Operating Procedure (SOP) describes the procedures used for the analysis of volatile organic compounds in the Region 9 Laboratory. Volatile organic compounds are purged from water samples in a fritted sparge cell. Low level water samples use a 25 mL sample volume. Low level soil samples are purged by adding a 5-mL aliquot of water to 5 grams of the sample, and purging with a needle sparger while heating to 40°C. Medium level soil samples are extracted in methanol and an aliquot of the extract is purged out of 5 mL of water. An inert gas (helium) is bubbled through the sample in the sparge cell, which causes the purgeable volatile organics to be transferred from the aqueous phase to the vapor phase. The vapor phase is swept through a column, or trap, containing a sorbent material at ambient temperature, where the volatile organics are trapped. After the purging of the sample is completed, the sorbent trap is heated and back flushed with helium which desorbs the volatile organics onto a capillary column in a gas chromatograph (GC). The GC is temperature programmed, which separates the volatile organic compounds. They are then introduced into, and detected by, a mass spectrometer (MS).

The samples are spiked with internal standards (IS) and system monitoring compounds (SMC) before they are purged. The target volatile organic compounds and system monitoring compounds are identified in the sample by analyzing standards under the exact same conditions employed for samples, and comparing the resulting mass spectra and GC retention times. A response factor is established for each target and system monitoring compound during the initial and continuing calibrations by comparing the MS response of the primary ion produced by the target and system monitoring compounds to the MS response for the primary ion produced by the associated internal standard. Each target and system monitoring compound is quantitated by comparing the responses of the target and system monitoring compound responses to the internal standard responses, using the response factors from the most recent continuing calibration.

Non-target compounds are identified by comparing the resulting mass spectra of the non-target compound to the mass spectra contained in the National Institute of Standards and Technology (NIST) Library in the MS database. An estimated quantitation is performed for the non-target compounds by comparing the total MS response to the nearest internal standard total MS response, assuming a response factor of 1.0.

3 DEFINITIONS

3.1	GC/MS	Gas Chromatograph / Mass Spectrometer
3.2	BFB	4-Bromofluorobenzene, the compound used as the system performance check for the GC/MS. Also used as a surrogate.

3.3	IS	Internal Standard
3.4	SMC	System Monitoring Compound, also known as Surrogate
3.5	SDG	Sample Delivery Group
3.6	GC	Gas Chromatograph
3.7	MS	Mass Spectrometer
3.8	MS/MSD	Matrix spike and matrix spike duplicate
3.9	ESAT	Environmental Services Assistance Team
3.10	FC43	Perfluorotributylamine. Compound used to tune the MS.
3.11	QL	Quantitation Limit (see Attachment A).
3.12	RIC	Reconstructed Ion Chromatogram
3.13	NIST	National Institute of Standards and Technology
3.14	CLP SOW	Contract Laboratory Program Statement of Work
3.15	LCS	Laboratory control sample
3.16	EPA	Environmental Protection Agency
3.17	WAM	Work Assignment Manager
3.18	USEPA	United States Environmental Protection Agency
3.19	SOP	Standard Operating Procedure
3.20	MSDS	Material safety data sheets
3.21	PTFE	polytetrafluoroethylene
3.22	%RSD	percent relative standard deviation
3.23	%D	percent difference
3.24	RRF	relative response factor
3.25	RPD	relative percent difference

4 HEALTH & SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals should be minimized through the use of personal protective equipment and laboratory engineering and design. A reference file of material safety data sheets (MSDS) is available to all personnel involved in the chemical analysis and can be found in the library (Room 118) or Room 413.

4.2 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, methylene chloride and vinyl chloride. Primary standards of these toxic compounds must be prepared in a hood. Routine procedures in this SOP do not require contact with concentrated or neat solutions of these materials. All standard preparation procedures associated with this SOP should be performed in a hood.

4.3 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 fumehood. The analyst must wear appropriate personal protective equipment (laboratory coat, nitrile gloves and safety glasses). Store methanol in a flammables storage cabinet away from oxidizers and sources of ignition.

4.4 Due to the unknown and potentially hazardous characteristics of samples all sample handling and preparation must be performed in a laboratory fumehood.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Sample receipt at the Region 9 Laboratory is performed under strict chain-of-custody procedures.

5.2 VOA samples are in the sample refrigerator in the volatile organics laboratory, room 201. The refrigerator shall be maintained at 4°C ± 2°C, and the freezer shall be maintained at less than -10°C. The temperatures shall be recorded daily in the temperature logbook as described in SOP 805. Samples and standards shall not be stored in the same refrigerator.

5.3 The following information shall be checked by an analyst to ensure that the information on the sample containers corresponds to the information on the tracking sheets and the chain-of-custody record.

5.3.1 EPA sample number.
5.3.2 Region 9 Laboratory number.
5.3.3 Case number.
5.3.4 Sample Delivery Group number.

5.4 The analyst shall confirm that the integrity of the samples has not been compromised by checking the samples for the following items. Any problems should be noted in the injection logbook and mentioned in the report narrative.

5.4.1 Broken chain-of-custody seals on the sample containers.
5.4.2 Leaking or broken sample containers.
5.4.3 Altered sample information on the sample containers.
5.4.4 The presence of head space or air bubbles.

5..5 Samples shall be sorted according to date sampled, so that samples can be analyzed in order of date sampled to prevent missed holding times.

5.6 Samples must be analyzed in an efficient and timely manner such that no analytical holding times are exceeded. Generally, samples should be analyzed on the GC/MS system which is set up for the type of analysis which is required, (i.e., if one of the systems is already set up to analyze soils, then soils should be assigned to that system). Samples should be analyzed in the order of their sampling date, if

possible.

5.7 Samples shall be analyzed within 14 days of the time of sampling.

5.8 Excess samples shall be stored at 4°C in the sample refrigerator in room 201. Thirty (30) days after the close date for an SDG the excess samples for the entire SDG shall be removed from refrigerated storage and placed on the shelves in Room 211, for a period of 60 days after the submission of the data deliverables associated with the SDG. After 60 days, the samples may be disposed of in the appropriate manner as specified in SOP 125, unless otherwise directed by the EPA Chemistry Team Leader (who is also the WAM for the ESAT analytical work assignment).

6 INTERFERENCES

6.1 Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapor/s 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 9. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

6.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during storage and handling.

6.3 Contaminations 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 a detergent solution between analyses, rinse it with distilled water, and then dry it in an oven at 105 °C. 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.

6.4 Solvents and other compounds which are target analytes must never be introduced into the laboratory where volatiles analysis is performed. Methylene chloride, acetone and other common laboratory chemicals are target analytes under this SOP and must be rigorously excluded from Room 201and 203. Particular attention must be paid to the possibility of transport of solvent vapors on individuals. Analysts should never enter Room 201or 203 after being in the extraction laboratories or glassware washing area (acetone is used to remove writing from glassware).

7 APPARATUS AND MATERIALS

7.1 The volatiles laboratory employs GC/MS analytical systems for the analysis of volatile organic compounds. The Incos-50A and Incos-XL systems allow for the sequential analysis of up to 16 water samples, standards, or method blanks. The HP5973 systems are equipped with automated sample heater & stir bar for the analysis of low level soil samples. The four (4) GC/MS analytical systems are summarized below.

Region 9 GC/MS Volatiles Analytical Systems

System Name	Incos 50A	Incos XL	HP5973H	HP5973J
Purge and Trap Concentrator	Tekmar LSC 2000	OI 4560	Hewlett Packard (Tekmar 3000)	Hewlett Packard (Tekmar 3000)
Autosampler	Tekmar ALS 2016	OI DPM-16	Varian Archon	Varian Archon
Gas Chromatograph	HP 5890	Varian 3400	HP 6890 Plus	HP 6890 Plus
Mass Spectrometer	Finnigan Incos 50	Finnigan Incos XL	Hewlett Packard HP 5973	Hewlett Packard HP 5973
Data System	Galaxy 2000/HP Chemstation	Galaxy 2000/HP Chemstation	HP Chemstation	HP Chemstation
Column type	DB-624 75M x 0.53 mm, 3 micron film	DB-624 30M x 0.32 mm, 1.8 micron film	DB-624 25M x 0.2mm id 1.12μm film	DB-624 25M x 0.2mm id 1.12μm film

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 Standard solutions (Region 9 Lab SOP 255).

7.2.1 Internal Standard and System Monitoring Compounds Solution (IS/SMC 50 ng/μL).

7.2.2 Internal Standard and System Monitoring Compound Solution (IS/SMC 250 ng/μL).

7.2.3 Internal Standard and System Monitoring Compound Solution (IS/SMC 125 ng/μL).

7.2.4 Matrix Spike Solution (MS Solution, 50 ng/μL).

7.2.5 Calibration Mix (Low level RAP CAL Mix, 25/250 ng/μL). The concentration of acetone, 2-butanone, 4-methyl-2-pentanone, and 2-hexanone is 250 ng/μL; and the concentration of the rest of the analytes is 25 ng/μL.

7.2.6 Calibration Mix (RAS CAL Mix, 50 ng/μL).

7.2.7 4-Bromofluorobenzene Tuning Solution (BFB Solution, 50 ng/μL).

7.2.8 Low level Laboratory Control Sample Spike Solution (LCS Spike Solution, 25/250 ng/μL). The concentration of acetone, 2-butanone, 4-methyl-2-pentanone, and 2-hexanone is 250 ng/μL; and the concentration of the rest of the analytes is 25 ng/μL.

7.2.9 RAS Laboratory Control Sample Spike Solution (LCS Spike Solution, 50 ng/μL).

7.3 Organic-free method blank water (Region 9 Lab SOP 205).

7.4 Gas-tight syringes (5-μL, 10-μL, 25-μL, 50-μL, 100-μL, 250-μL, 500-μL, 1-mL, 5-mL, and 25-mL).

7.5 Fritted sparge vessels (5-mL and 25-mL).

7.6 Fritless sparge vessels (5-mL and 25-mL).

7.7 Soil sparge kits.

7.8 Screw-cap vials, 40-mL, with teflon-lined septa, pre-cleaned with sodium bisulfate preservative and magnetic stir-bar (ESS Part # QC-4039-5035, or equivalent).

7.9 Stainless steel spatulas.

7.10 Disposable Pasteur pipettes.

7.11 Top-loading balance (weighing to the nearest 0.01 g).

7.12 Methanol (Purge & Trap grade).

7.13 pH paper (pH 0-14 range).

7.14 Trap K (VOCARB 3000, or equivalent).

7.15 Trap I (VOCARB 4000, or equivalent)

7.16 Sand, sea washed (VWR Cat. # VW3358-3, or equivalent).

8 QUALITY CONTROL

This section describes the QA/QC criteria which shall be followed in the analysis of samples for volatile organic compounds.

8.1 Mass calibration.

8.1.1 Mass calibration of the analytical system shall be performed whenever the mass spectrometer is shut down, or whenever there is a mass miss-assignment. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer. Perfluorotributylamine (FC43) is the compound which shall be used to perform the mass calibration of the instrument. The FC43 spectrum must meet the following criteria:

Mass	Target % of Mass 69
69	100

131	25.0-70.0
219	25.0-70.0
414	1.4-4.0
502	0.8-4.0

Isotope Ratio

Mass Ratio	Target %
70/69	0.8-1.3
132/131	2.0-3.4
220/219	3.5-5.2
415/414	7.2-10.8
503/502	8.1-12.1

8.1.2 If the FC43 spectrum does not meet the criteria listed above, 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 and rods may be required.

8.2 GC/MS System Performance Check (BFB analysis.)

8.2.1 Prior to the analysis of any calibration standards, blanks, and samples (including MS/MSDs), 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.

8.2.2 Frequency of GC/MS Performance Check.

BFB must be injected once at the beginning of each 12-hour period during which standards, blanks and samples are to analyzed. The twelve-hour time period begins at the moment of injection of the BFB. The time period ends after twelve hours have elapsed. If a sample is injected after the 12-hour time period has elapsed it must be re-analyzed.

8.2.3 Analyze the BFB according to Section 9 of this SOP.

8.2.4 The ion abundance ratios must meet the following criteria.

Mass (m/z)	Relative Ion Abundance Criteria
50	8.0 - 40.0 percent of mass 95
75	30.0 - 66.0 percent of mass 95
95	Base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of mass 95
173	less than 2 percent of mass 174
174 *	50.0 - 120.0 percent of mass 95
175	4.0 - 9.0 percent of mass 174
176	93.0 - 101.0 percent of mass 174
177	5.0 - 9.0 percent 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 up to 120 percent that of m/z 95.

If the ion abundances fail to meet the 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 also be necessary to clean the ion source, or take other corrective action to achieve the ion abundance criteria.

8.3 Initial calibration.

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

8.3.2 For 5-mL water (and medium level soils) and low level soil analysis, the initial and continuing calibration criteria are listed in Appendix A.

8.3.3 For 25-mL water analysis, the initial and continuing calibration criteria are listed in Appendix B. A four point calibration at 2 µg/L, 5 µg/L 10µg/L and 25 µg/L is performed for DBCP. All other compounds require a five point calibration.

8.3.4 Analyze the initial calibration standards according to Section 9 of this SOP.

8.3.5 The data system calculates the relative response factor (RRF) for each target compound and system monitoring compound for all five calibration standards using equation 1. The quantitation ions and internal standard assignments are listed in Attachment A.

Eq. 1

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

Where
Ax = Area of quantitation ion of compound x
Ais = Area of quantitation ion for associated internal standard
Cx = Concentration of compound x
Cis = Concentration of the associated internal standard

8.3.6 Calculate the average RRF for all analytes

8.3.7 Calculate the percent relative standard deviation (%RSD) of the RRF values for each compound using equation 2.

EQ. 2

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

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

8.3.8 Immediately after the initial calibration is performed, the data files shall be processed and checked to ensure that all of the minimum RRFs and maximum %RSD criteria have been satisfied (Appendices A and B). Up to two volatile compounds may fail to meet the minimum RRF and maximum %RSD criteria listed in Appendix A or Appendix B. However, these two must have an average RRF greater than or equal to 0.010, and the %RSDs must be less than or equal to 40%. If any of the criteria have not been met because of a single concentration point in the curve, then that single point can be reanalyzed once, and the data checked against the criteria. 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 repairs are made to the system, then a new initial calibration must be performed. 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 and 4-methyl-2-pentanone and 2-hexanone.

8.3.9 No quantitation ion may saturate the detector, with the exceptions of combined xylenes (*meta*- and *para*-xylenes).

8.3.10 If the initial calibration meets all the specified criteria, the remainder of the 12-hour analytical period may be used for the analysis of blanks, LCS, QL standards and samples, using the calibration standard that is the same concentration as the continuing calibration to quantitate the blank and sample data.

8.4 Continuing Calibration

8.4.1 A continuing calibration standard must be analyzed at the beginning of each 12-hour analytical period (see Section 8.2.2 for definition of 12-hour time period). The continuing calibration standard is used to quantitate analytical results during the associated 12-hour time period.

8.4.2 For 5-mL water (and medium level soils) and low level soil analysis, the initial and continuing calibrations must meet the criteria listed in Appendix A.

8.4.3 For 25-mL water analysis, the initial and continuing calibrations must meet the criteria listed in Appendix B.

8.4.4 Analyze the continuing calibration standard according to Section 9 of this SOP.

8.4.5 Calculate the relative response factor (RRF) for each target compound and system monitoring compound using equation 1. The quantitation ions and internal standard assignments are listed in Attachment A.

8.4.6 Calculate the percent difference (%D) between the continuing calibration RRF and the most recent initial calibration average RRF for each target compound and surrogate using equation 3.

EQ 3.

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

8.4.7 The minimum relative response factors must be satisfied. The percent difference must be calculated and compared with the maximum percent difference criteria listed in Appendix A or Appendix B. Up to two volatile compounds may fail to meet the minimum RRF and maximum %D criteria. However, the RRFs of those two compounds must be greater than or equal to 0.010, and the %Ds must be less than or equal to 40% for the continuing calibration to be acceptable. Compounds which have minimum RRF requirements but no %D requirements are not counted as part of the two allowable failing compounds. If any of the criteria is not satisfied a second continuing calibration may be analyzed. Repeated failure requires the analysis of a new initial calibration. 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 relative response, loss of classes of compounds, etc. which may signal the need for instrument maintenance.

Check the continuing calibrations for mis-identified peaks due to retention time shifts. The most commonly mis-assigned compounds are the 1,3- and 1,4-dichlorobenzenes and 4-methyl-2-pentanone and 2-hexanone.

8.5 Laboratory Control Sample (LCS)

A LCS is analyzed daily to demonstrate that the calibration standards used to calibrate the instrument are appropriate. Specifically the LCS verifies that the standards include the appropriate compounds at the correct concentration. This is done by preparing the LCS spiking mixture from a source (or sources) entirely separate from those used to calibrate the instrument. The LCS must be analyzed immediately after the initial or continuing calibrations.

8.5.1 Prepare the LCS as a method blank except add the volume of the LCS standard which results in a concentration equal to the concentration of the mid-point (level 3) of the calibration range.

8.5.2 Analyze the LCS exactly as a sample is analyzed. Quantitate the LCS using the daily calibration standard RRFs.

8.5.3 90% of the analytes must be recovered at 60 to 140 percent accuracy or the source of the

discrepancy determined prior to reporting any sample data. This may require preparing fresh standards (either the calibration standard, the LCS, or both) which may require a new initial calibration. Dichlorodifluormethane, acetone, 2-butanone, 4-methyl-2-pentanone, and 2-hexanone are exempt from this criteria.

8.6 Low Level Quantitation Verification Standard.

8.6.1 A low level quantitation standard at the concentration of the lowest point of the initial calibration must be analyzed immediately after the LCS for each 12-hour analytical period. In the event that an initial calibration is analyzed the lowest standard of the initial calibration satisfies this requirement.

8.6.2 Analyze the low level quantitation standard according to Section 9 of this SOP.

8.6.3 The observed concentration of 90% of the analytes must be 50 to 150 percent of the actual concentration. Dichlorodifluormethane, acetone, 2-butanone, 4-methyl-2-pentanone, and 2-hexanone are exempt from this criteria.

8.6.4 For low level water analysis (25mL) the low level quantitation standard is analyzed at 0.5 µg/L. This requires the analysis of this standard after an initial calibration. The observed concentration of five compounds; vinyl chloride, 1,2-dichloroethane, carbon tetrachloride, cis-1,3-dichloropropene, and trans-1,3-dichloropropene; must be between 0.25 µg/L to 0.75 µg/L (50 -150 % recovery).

8.6.5 If the requirements of 8.6.3 or 8.6.4 are not met corrective action must be taken. The standard can be reanalyzed once. Repeated failure indicates a possible problem with the standards or that maintenance is required to improve instrument performance.

8.7 Method blank analysis.

8.7.1 A method blank must be analyzed immediately after the calibration standards and the QL verification standard -- before the samples are analyzed -- in order to demonstrate that the instrument is free of contamination.

8.7.2 Analyze the method blank according to Section 9 of this SOP.

8.7.3 The method blank RIC and quantitation report must be checked immediately after it is analyzed, or as soon as possible, to determine that the following criteria have been met:

The method blank is acceptable if it contains less than or equal to 2.5 times the QL of methylene chloride, acetone, and 2-butanone, and less than or equal to the QL of any other volatile target compound. The total area of any non-target compound detected must be less than 50 percent of the total area of the nearest internal standard. If the method blank does not meet these requirements, a new blank shall be prepared and reanalyzed before any samples can be analyzed. If the second blank fails to meet the above criteria corrective action must be initiated and documented.

8.7.4 The method blank internal standards must meet the criteria listed in Section 8.10.

8.7.5 The method blank surrogate recoveries must meet the criteria listed in Section 8.11.

8.7.6 All volatile analyses associated with a blank that does not meet the above requirements must be reanalyzed.

8.8 Storage blank analysis.

8.8.1 A storage blank must be analyzed once every week. The storage blank indicates whether contamination may have occurred during sample storage.

8.8.2 Every Monday morning, or the first work day of the week, three 40-mL screw-cap volatile vials with PTFE-faced silicone septum must be filled with reagent water and stored with the samples, in the sample storage refrigerator in room 201.

8.8.3 The storage blank must be analyzed the following Monday, or on the first work day of that week, and new storage blanks placed in the refrigerator.

8.8.4 Analyze the storage blank according to Section 9 of this SOP.

8.8.5 The storage blank internal standards must meet the criteria listed in Section 8.10 or reanalysis is required.

8.8.6 The storage blank surrogate recoveries must meet the criteria listed in Section 8.11 or reanalysis is required.

8.9 Instrument blanks

8.9.1 In the event that a sample is analyzed which exceeds the calibration range of the instrument, an instrument blank must be analyzed on the same autosampler port to demonstrate that the system is free of carryover contamination prior to the analysis of another sample using that autosampler port. The Archon autosamplers do not use discreet ports for each sample. If the sample analyzed immediately after the high concentration sample is free of carryover as defined in Section 8.13.2 then the system is free of contamination.

8.9.2 Analyze the instrument blanks according to Section 9 of this SOP.

8.9.3 The instrument blank is acceptable if it contains less than or equal to the QL of methylene chloride, acetone, and 2-butanone, and less than or equal to the QL of any other volatile target compound. The total area of any non-target compound detected must be less than 50 percent of the total area of the nearest internal standard. If the instrument blank does not meet these requirements, the autosampler port must be cleaned and a new instrument blank must be reanalyzed on that autosampler port to demonstrate the absence of contamination before any samples can be analyzed on the autosampler port. This is an iterative process which must be repeated until the port has been demonstrated to be free of contamination.

8.9.4 The instrument blanks can be analyzed beyond the twelve-hour tune time period.

8.9.5 Instrument blanks do not need to meet the surrogate recovery criteria listed in Section 8.11.

8.9.6 Instrument blanks must meet the internal standard criteria listed in Section 8.10.

8.10 Internal standard recovery.

8.10.1 The internal standard recovery, determined by total area, for all standards, blanks, samples, and spikes shall be checked immediately after analysis in order to determine if all applicable criteria have been met.

8.10.2 If the total area of any internal standard in any blank, sample, or spike analysis changes by more than a factor of two (-50% to +100%) of the corresponding internal standard from the preceding 12-hour calibration standard, the system must be checked for malfunctions and the necessary corrections must be made. After the corrections are made, the analyses performed while the system was malfunctioning must be repeated. Keep in mind that many "corrections" to the system will require that the initial calibration be performed prior to reanalysis of the samples.

8.10.3 If after reanalysis, the total area for all internal standards are within the criteria, then the problem is considered to have been within the laboratory's control. The data form the reanalysis must be used for calculating sample results.

8.10.4 If reanalysis of the sample does not solve the problem, submit the data for both analyses. Distinguish between the analysis and reanalysis by adding an "RE" suffix to the EPA sample number on the reanalysis. The problem must be documented in the Report Narrative (see Section 10.2.1.9).

8.10.5 The internal standard retention times in all standards must be checked immediately after data acquisition. If the retention time for any internal standard changes by more than 0.25 minutes from the latest daily calibration standard, the system must be inspected for malfunctions, and the necessary corrections made. Blanks, samples, and spikes analyzed within the 12-hour analytical period of the initial calibration shall be compared to the 50 μg/L standard, or the 5 μg/L standard for low detection limit waters.

8.11 System monitoring compound recovery.

8.11.1 The system monitoring compound (SMC) recovery in all blanks, samples, and spike must be calculated and checked immediately after analysis and compared to the following criteria.

Compound	Water % Recovery	Soil % Recovery

1,2-Dichloroethane-d4	76 - 114	70 - 121
Toluene-d8	88 - 110	84 - 138
Bromofluorobenzene	86 - 115	59 - 113

%R = (Amount Found/Amount Spiked)*100

8.11.2 If the recovery of one or more of the system monitoring compounds is not within the limits, the following steps must be taken.

8.11.2.1 Check to ensure that there are no calculation errors, and check the system performance.

8.11.2.2 Reanalyze the sample if a system performance problem or calculation error is not evident.

8.11.2.3 Do not reanalyze undiluted samples with SMC recoveries outside the limits if the diluted analysis with acceptable SMC recoveries is being submitted. Report the event in the runlog and report narrative.

8.11.2.4 Do not reanalyze the matrix spike or matrix spike duplicate samples, even if the SMC recoveries are outside the limits.

8.11.2.5 If the sample associated with the matrix spike and duplicate analyses does not meet the SMC recovery criteria, it should be reanalyzed only if the matrix spike and duplicate SMC 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 reanalysis. The similarity in SMC recoveries in the sample and spike analyses must be discussed in the Report Narrative (See Section 10.2.1.9.).

8.11.3 If the SMC recoveries of the reanalysis are within limits, then the problem was within the laboratory's control. Therefore, the analysis with the SMC recoveries within limits shall be considered the initial analysis.

8.11.4 If the reanalysis does not solve the problem, then submit the data from both analyses. Distinguish between the original analysis and the reanalysis by adding the "RE" suffix to the EPA sample number in the reanalysis.

8.11.5 If the SMC recovery for a medium level soil analysis is outside the limits, then reanalysis of the extract shall be done first. If the SMC recovery continues to be outside the limits, then the sample shall be re-extracted and analyzed. Submit data according to Sections 8.11.3 and 8.11.4.

8.12 Matrix spike and matrix spike duplicate analysis.

8.12.1 In order to determine the matrix effect upon the analytical methodology, a matrix spike and matrix spike duplicate analysis must be performed according to the following scheme, whichever is most frequent:

One MS/MSD for each case of samples received.

One MS/MSD for each SDG within a case.

One MS/MSD each 14 calendar day period during which field samples in a case are received, beginning with the receipt of the first sample in the sample delivery group (SDG).

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. The analyst shall not designate any obvious field blanks as the QC sample.

8.12.2 Matrix spike and matrix spike duplicate samples shall be analyzed immediately following the analysis of the sample designated as the matrix spike sample.

8.12.3 Analyze the MS and MSD according to Section 9 of this SOP.

8.12.4 The recovery and RPD criteria for matrix spike and matrix spike duplicate analyses are as follows:

Compound	Water % Recovery	Soil % Recovery	Water RPD	Soil RPD
1,1-Dichloroethene	61 - 145	59 - 172	14	22
Benzene	76 - 127	66 - 142	11	21
Trichloroethene	71 - 120	62 - 137	14	24
Toluene	76 - 125	59 - 139	13	21
Chlorobenzene	75 - 130	60 - 133	13	21
1,2-Dibromoethane	75 - 125	50 - 150	30	50
1,2-dibromo-2-chloropropane	75 - 125	50 - 150	30	50
1,3-Dichloropropane	75 - 125	50 - 150	30	50
1,2,3-Trichloropropane	75 - 125	50 - 150	30	50

8.12.5 Calculate the recovery of each compound as follows:

$$\% \text{ Rec} = ((SSR - SR)/SA)*100$$

where,

SSR = Spiked sample result
SR = Sample result
SA = Spike added

8.12.6 Calculate the relative percent differences (RPD) of the recoveries of each compound in the matrix spike and matrix spike duplicate as follows:

$$RPD = \frac{|MSR - MSDR|}{(½)(MSR + MSDR)} \times (100)$$

where,

MSR = Matrix spike recovery
MSDR = Matrix spike duplicate recovery

8.12.7 The limits for matrix spike and matrix spike duplicate recovery are advisory limits only. If the limits are not met, then no further action is required since the purpose of these analyses is to determine matrix effects on compound recovery. A comment regarding the matrix spike recoveries must be included in the report narrative. 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 check the matrix spike solution by spiking a method blank sample and checking the recoveries of the spike compounds. A new solution should be prepared if the recoveries are outside the limits.

8.13 Sample dilution.

8.13.1 If the on-column concentration of any target compound in any sample exceeds the initial calibration range, a new aliquot of that sample must be diluted and purged. The following criteria shall be used in performing dilutions.

8.13.1.1 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

8.13.1.2 The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

8.13.1.3 Do not dilute matrix spike or matrix spike duplicate 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.

8.13.1.4 In the case of extremely contaminated samples several dilutions may be required.

8.13.2 After a sample is analyzed that contains one or more target compounds at a level exceeding the initial calibration range of the system, it must be demonstrated that there is no carryover to subsequent analyses. The laboratory must:

8.13.2.1 Analyze an instrument blank immediately after the contaminated sample. If the autosampler was used, the instrument blank must be analyzed using the same sparge cell as the contaminated sample. The instrument blank must meet the acceptance criteria in Section 8.10.

8.13.2.2 Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the limits above. The maximum contamination criteria are as follows: the sample must not contain a concentration above the QL for the target compounds that exceeded the limits in the contaminated sample. If the autosampler is used, the next sample analyzed using the same sparge cell that was used for the contaminated sample must also meet the maximum contamination criteria.

8.14 Review of Target Analytes

Each reported value must be reviewed for both qualitative and quantitative validity. This process, in particular the qualitative review of mass spectra, relies upon the technical judgement of the analyst.

8.14.1 Qualitative Review

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

8.14.1.1 For relative retention time, the peak must elute within 0.06 relative retention time units of the analyte in the continuing calibration standard. The relative retention time is the retention time of the target divided by the retention time of the associated internal standard. If the relative retention time for the target analyte in the CCAL is 0.82 then the peak in the sample must have a relative retention time of 0.76 to 0.88.

8.14.1.2 The mass spectra used for qualitative identification must be obtained using the GCMS system used to analyze the samples.

8.14.1.2.1 All ions present in the standard mass spectra at a relative intensity of 10 percent of the most abundant ion must be present in the sample spectra.

8.14.1.2.2 The relative intensities of the ions must agree within ±20 % between the standard and sample spectra.

8.14.1.2.3 Ions present in the sample at greater than 10 percent abundance but not present in the standard spectra must be reviewed and accounted for by the analyst making the comparison.

8.14.1.3 If a compound cannot be verified by these criteria but, in the technical judgement of the analyst, is present the supporting evidence must be indicated on the raw data and the analyte reported.

8.14.2 Quantitative Review

Reported values must be reviewed to determine that the correct calculations were used to generate the results, that the RRFs from the associated continuing calibration standard were used, and that all other numbers are accurate.

8.14.2.1 Review of data system integrations

The analyst must review the data system integration to verify that the internal standards, surrogates and target compounds are integrated properly. In the event that the analyst observes an incorrect integration the analyst must manually correct the integration and document the correction as per Region 9 Lab SOP 835.

8.14.2.2 Water calculations

Results for target analytes are calculated using the following equation:

$$\text{Conc. } (\mu g/L) = A_x * AMT_{IS} * DF / (A_{IS} * RRF)$$

where:
A_x = area of the characteristic ion of the compound
AMT_{IS} = amount of internal standard in μg/L (5 μg/L for low level waters and 50 μg/L for medium level)
DF = dilution factor
A_{IS} = area of the characteristic ion of the associated internal standard
RRF = analyte's relative response factor from the daily calibration

8.14.2.3 Low level soil calculations

Results for target analytes are calculated using the following equation:

$$\text{Conc. } (\mu g/Kg) = A_x * AMT_{IS} / (A_{IS} * RRF* W*D)$$

where:
A_x = area of the characteristic ion of the compound

AMT_{IS} = amount of internal standard in (250 ng)
D = dry weight factor ((100 - %Moisture)/100)
W = weight of sample in grams
A_{IS} = area of the characteristic ion of the associated internal standard
RRF = analyte's relative response factor from the daily calibration

8.14.2.4 Medium level soil calculations

Results for target analytes are calculated using the following equation:

$$\text{Conc. } (\mu g/Kg) = A_x * AMT_{IS} * Vt * 1000(\mu L/mL) * DF / (A_{IS} * RRF * Va * W * D)$$

where:
A_x = area of the characteristic ion of the compound
AMT_{IS} = amount of internal standard in ng (250 ng)
D = dry weight factor ((100 - %Moisture)/100)
W = weight of sample extracted in grams
A_{IS} = area of the characteristic ion of the associated internal standard
RRF = analyte's relative response factor from the daily calibration
Vt = Total volume of the extract in mL
Va = Volume of aliquot of extract purged, in μL
DF = Dilution factor for medium level soils is defined as:

$$\frac{\text{volume of extract use + volume of clean solvent}}{\text{volume of extract used}}$$

8.15 Review the Tentatively Identified Compound search results for the following:

8.15.1 Verify that all unknown peaks in the RIC greater than 10 percent of the area of the nearest internal standard are accounted for in the summary.

8.15.2 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.

8.15.3 The relative intensities of the major ions should agree within 20 percent.

8.15.4 Molecular ions present in the reference spectrum should be present in the sample spectrum.

8.15.5 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.

8.15.6 Ions present in the reference spectrum but not within the scan range (35 to 300 amu) of the method should not be considered when making a tentative identification.

8.15.7 If, in the technical judgement 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.

9 ANALYTICAL PROCEDURES

9.1 Analytical system preparation.

Mass calibration of the analytical system shall be performed according to the schedule prescribe in Section 8.1. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer. Perfluorotributylamine (FC43) is the compound which shall be used to perform the mass calibration of the instrument.

9.1.1 Enter the control program of the instrument and enable the analyzer voltages.

9.1.2 Enter the tuning program of the instrument. Turn the filament and electron multiplier on and enable the scan function.

9.1.3 Open the calibration gas valve and allow the FC43 to infuse into the analyzer.

9.1.4 Adjust the voltages according to the manufacturer's instruction manual and specifications to obtain the proper mass ratio, peak shape, and isotope peak resolution.

9.1.5 Calibrate the mass spectrometer as specified in the manufacturer's instruction manual.

9.1.6 The data system will automatically acquire a FC43 spectrum, process the FC43 spectrum data, and calibrate the mass spectrometer.

Check the mass spectrum/peak ratios with the specifications listed in Section 8.1. The specifications shall be met or the instrument must be re-tuned and recalibrated.

9.2 Leak Checking

The mass spectrometer shall be checked for leaks after system maintenance, prior to the analysis of 4-bromofluorobenzene (BFB) tuning compound.

9.2.1 Enter the control program and check that the analyzer temperatures are set to the following values:

9.2.1.1 Transfer line body @ 250°C.

9.2.1.2 Transfer line nozzle @ 250°C.

9.2.1.3 Ion source @ 180°C.

9.2.1.4 If the display indicates that the analyzer temperatures are not at the desired set points, corrective action must be performed according to the operator's manual.

9.4.1.2.6 Gently place the vial in the appropriate autosampler position. Avoid causing any hairline cracks in the vial, as this may result in the vial disintegrating in the autosampler.

9.4.1.2.7 Analyze the standards. The autosampler will analyze a 25 mL aliquot and add 1 μL of the 250 ng/μL IS/SMC solution.

9.4.1.3 Press the start button on the concentrator to begin purging the sample. The purge and trap concentrator parameters are found in Attachment B.

9.4.1.4 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment D.

9.4.1.5 Analyze the standard and acquire the data.

9.4.1.6 Quantitate the data and print out a quantitation report and chromatogram.

9.4.1.7 Analyze the four other initial calibration standards following the procedures outlined above.

9.4.1.8 Update the initial calibration response factors in the method by associating the correct data file with each calibration level. Save the method.

9.4.1.9 Generate the initial calibration summary report. Samples shall not be analyzed if the initial calibration does not meet the criteria specified in Appendix A of this SOP.

9.4.1.10 If the initial calibration meets all the criteria specified in Section 8.3 of this SOP, the remainder of the 12-hour analytical period may be used for the analysis of LCS, blanks and samples, using the 50 μg/L calibration standard to quantitate the blank and sample data files.

9.4.2 Continuing calibration

A continuing calibration standard shall be run once every 12-hour analytical time period, after BFB tuning and prior to a method blank analysis. The continuing calibration check is performed in order to determine if the GC/MS system is operating within the acceptable range as demonstrated by the percent difference and the minimum response factor criteria meeting the appropriate QA/QC criteria. The continuing calibration is analyzed at a level of 50 μg/L.

9.4.2.1 Prepare and load a 50 μg/L calibration standard as described in Section 9.4.1. and Appendix A.

9.4.2.2 Press the start button on the concentrator to begin purging the standard.

9.4.2.3 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment D.

9.4.2.4 Analyze the standard and acquire the data.

9.4.2.5 Quantitate the data and print out a quantitation report and chromatogram.

9.4.2.6 Update the response factors for each analyte in the method and save the new response factors.

9.4.2.7 Generate the continuing calibration summary report. Samples shall not be analyzed if the continuing calibration does not meet the criteria specified in Section 8.4 of this SOP.

9.4.2.8 If the continuing calibration meets all the criteria specified in Section 8.4, the remainder of the 12-hour analytical period may be used for the analysis of blanks and samples, using the RRFs from the daily 50 µg/L continuing calibration file to quantitate the blank and sample data files.

9.4.3 Laboratory Control Standard (LCS)

A LCS is analyzed once every 12-hour analytical time period, immediately after the initial or continuing calibration. An LCS is analyzed to demonstrate that the calibration standards used to calibrate the instrument are appropriate. Specifically the LCS verifies that the standards include the appropriate compounds at the correct concentration. This is done by preparing the LCS spiking mixture from a source (or sources) entirely separate from those used to calibrate the instrument. The LCS is analyzed at a level of 50 µg/L.

9.4.3.1 Analysis on Incos-50A, and Incos-XL systems

9.4.3.1.1 Fill a 5-mL syringe with method blank water. Invert the syringe, remove any air bubbles, and bring the level to 5 mL by displacement with the plunger.

9.4.3.1.2 Lay the syringe on the lab bench in the hood and spike the water with 5 µL of IS/Surr Solution. The amount used results in final concentration 50 µg/L.

9.4.3.1.3 Spike the water with 5 µL of RAS LCS Spike Solution, (50 ng/µL). The amount used results in final concentration 50 µg/L.

9.4.3.1.4 Attach the 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. Remove the syringe from the mount

9.4.3.2 Analysis on HP5973H & HP5973J system.

9.4.3.2.1 The LCS is prepared in 50-mL gas tight syringe and then transferred to 40mL VOA vials which is pre-cleaned.

9.4.3.2.2 Fill a 50-mL gas-tight syringe with method blank water. Invert the syringe, remove any air bubbles, and bring the level to 50-mL by displacement with the plunger.

9.4.3.2.3 Spike the water with 50 µL of RAS LCS Spike Solution, (50 ng/µL). The amount used results in final concentration 50 µg/L.

9.4.3.2.4 Cap the end of the syringe. Rotate and invert the closed syringe to mix. Let the standard solution equilibrate in the syringe for about 1 minutes. While the standard solution is equilibrating, label the 40-mL vial with information about the standard.

9.4.3.2.5 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.

9.4.3.2.6 Gently place the vial in the appropriate autosampler position. Avoid causing any hairline cracks in the vial, as this may result in the vial disintegrating in the autosampler.

9.4.3.2.7 Analyze the standards. The autosampler will analyze a 25 mL aliquot and add 1 µL of the 250 ng/µL IS/SMC solution.

9.4.3.3 Press the start button on the concentrator to begin purging the standard.

9.4.3.4 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment D.

9.4.3.5 Analyze the standard and acquire the data.

9.4.3.6 Quantitate the data and print out a quantitation report and chromatogram.

9.4.3.7 Evaluate the calculated concentrations against the criteria listed in Section 8.5.3. Samples shall not be analyzed if the LCS does not meet the criteria specified in Section 8.5.3.

9.4.3.8 If the LCS meets all the criteria specified in Section 8.5.3, the remainder of the 12-hour analytical period may be used for the analysis of blanks and samples.

9.4.4 Quantitation Limit Standard

A low level quantitation standard at the concentration of the lowest point of the initial calibration must be analyzed immediately after the LCS for each 12-hour analytical period. In the event that an initial calibration is analyzed the lowest standard of the initial calibration satisfies this requirement

9.4.4.1 Prepare and load the quantitation limit standard (10μg/L) as described in Section 9.4.1 and Appendix A.

9.4.4.2 Press the start button on the concentrator to begin purging the standard.

9.4.4.3 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment D.

9.4.4.4 Analyze the standard and acquire the data.

9.4.4.5 Quantitate the data and print out a quantitation report and chromatogram.

9.4.4.6 Evaluate the calculated concentrations against the criteria listed in Section 8.6.3. Samples shall not be analyzed if the QL standard does not meet the criteria specified in Section 8.6.3.

9.4.4.7 If the QL standard meets all the criteria specified in Section 8.6.3, the remainder of the 12-hour analytical period may be used for the analysis of blanks and samples.

9.4.5 Method blank analysis.

After the initial or continuing calibration is performed and before samples are analyzed, a method, or laboratory blank analysis shall be conducted.

9.4.5.1 Analysis on Incos-50A, and Incos-XL systems

9.4.5.1.1 Fill a 5-mL syringe with method blank water. Invert the syringe, remove any air bubbles, and bring the level to 5 mL by displacement with the plunger.

9.4.5.1.2 Lay the syringe on the lab bench in the hood and spike the water with 5 μL of IS/Surr Solution. The amount used results in final concentration 50 μg/L.

9.4.5.1.3 Attach the 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. Remove the syringe from the mount

9.4.5.2 Analysis on HP5973H & HP5973J system.

9.4.5.2.1 Gently fill a 40-mL vial with method blank water. Overfill the vial to

form an inverted meniscus. Cap the vial. Invert the vial to ensure that there are no air bubbles present.

9.4.5.2.2 Gently place the vial in the appropriate autosampler position. Avoid causing any hairline cracks in the vial, as this may result in the vial disintegrating in the autosampler.

9.4.5.2.3 Analyze the method blank. The autosampler will analyze a 5 mL aliquot and add 1 µL of the 250 ng/µL IS/SMC solution.

9.4.5.3 Press the start button on the concentrator to begin purging the sample.

9.4.5.4 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment D.

9.4.5.5 Analyze the method blank and acquire the data.

9.4.5.6 Quantitate the data and print out a quantitation report and chromatogram.

9.4.5.6.1 Review the results as discussed in Section 8.14 for qualitative identification of target analytes. Review all target compounds that are detected to verify they are integrated properly. Review the chromatogram for possible false negatives.

9.4.5.6.2 Print out the updated quantitation report.

9.4.5.6.3 Samples shall not be analyzed if the method blank does not meet the criteria specified in Section 8.7 of this SOP.

9.4.5.6.4 If the method blank meets all the specified criteria, the remainder of the 12-hour analytical period may be used for the analysis of samples.

9.4.6 Sample analysis.

Samples shall be analyzed only after the BFB tune, initial calibration, continuing calibration, and method blank analyses meet all of the appropriate criteria specified in Section 8 of this SOP. If time still remains in the 12-hour time period after meeting the initial calibration criteria, samples may be analyzed. It is not necessary to analyze a continuing calibration standard within this 12-hour time period, if the initial calibration standard that is at the same concentration as the continuing calibration standard meets the continuing calibration acceptance criteria.

9.4.6.1 Allow the sample to reach ambient temperature before analysis.

9.4.6.2 The analyst shall again check that the numbers on the vials coincide with the numbers

on the routing forms to ensure that the correct sample is being analyzed.

9.4.6.3 Break the chain of custody seal on the vial with a scalpel or other appropriate implement, again making note in the runlog if the seal is missing or compromised in any way.

9.4.6.4 The analyst shall take note if the sample has an unusual color or other physical characteristic such as more than one phase, presence of a precipitate or unusual viscosity. If any physical signs of contamination are present a screening analysis to protect the analytical system from damage or contamination, and to determine the appropriate subsequent dilution is required. If a screening is necessary, it shall be at a 1:50 dilution, unless the laboratory supervisor decides otherwise.

9.4.6.5 The analyst shall also note if there is head space present in the sealed sample vial.

9.4.6.6 Analysis on Incos-50A, and Incos-XL systems

9.4.6.6.1 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. Any excess sample displaced from the syringe should be placed in the aqueous waste containers.

9.4.6.6.2 Lay the syringe on the lab bench in the hood and spike the sample with 5 μL of IS/Surr Solution. The amount used results in final concentration 50 μg/L.

9.4.6.6.3 Attach the syringe to the luer lock mount on the purge and trap concentrator. Open the mount valve and inject the contents of the syringe into the sparge cell and close the valve. Remove the syringe from the mount.

9.4.6.7 Analysis on HP5973H and HP5973J system.

9.4.6.7.1 Gently place the sample vial in the appropriate autosampler position Avoid causing any hairline cracks in the vial, as this may result in the vial disintegrating in the autosampler.

9.4.6.7.2 The autosampler will analyze a 5 mL aliquot and add 1 μL of the 250 ng/μL IS/SMC solution.

9.4.6.8 Press the start button on the concentrator to begin purging the sample.

9.4.6.9 The analyst shall observe the initial purging of the sample to determine if the sample is liable to foam during the purging process. 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 the analyst feels that the sample is going to foam

excessively, the purging shall be discontinued by pressing the "step to standby" button twice. The sparge cell shall be drained, rinsed with method blank water, and drained again. The sample waste and rinstate must be placed in the aqueous waste container. The trap and the GC shall be baked out for 6 minutes before additional samples are analyzed. A 1:10 dilution of the sample, or other appropriate dilution to prevent foaming, shall be analyzed, even though the detection limits are elevated. A NOTE must be made in the runlog regarding sample foaming.

9.4.6.10 Check the pH of the sample using pH 0-14 range pH paper. Record the pH in the injection logbook. If any samples have a pH greater than 2 this needs to be noted in the report narrative.

9.4.6.11 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment D.

9.4.6.12 Set up a data acquisition. The sample description shall include the EPA sample number and the laboratory sample number. Additional header information shall include the sample volume or weight, GC and scan descriptors, instrument ID, and the analyst's initials.

9.4.6.13 Quantitate the data and print out a quantitation report and chromatogram.

9.4.6.14 Review the results as discussed in Section 8.14 for qualitative identification of target analytes. Delete all reported hits which do not meet the qualitative criteria. Review all target compounds that are detected to verify they are integrated properly. Review the chromatogram for possible false negatives.

9.4.6.15 Print out the updated quantitation report.

9.4.6.16 Check the sample's surrogate and internal standard recoveries with the criteria in the QA/QC Section of this SOP.

9.4.6.17 In addition to the full strength analysis, the sample must be diluted and reanalyzed if any of the target analytes exceed the calibration range of the instrument. The sample should be diluted so that the target compound(s) which was originally outside of the calibration range, will fall within the upper half of the initial calibration range of the instrument.

9.4.7 Analysis of matrix spike and matrix spike duplicate samples.

A matrix spike and matrix spike duplicate analysis must be performed in order to determine matrix effects, if any, on the sample analysis.

9.4.7.1 Matrix spike and matrix spike duplicate analyses shall be performed according to the schedule specified in Section 8.12 of this SOP

9.4.7.2 For the Incos-50A and Incos-XL systems, matrix spike and matrix spike duplicate samples shall be analyzed according to the instructions for sample analysis (Section 9.4.6), except that the sample shall be spiked with 5 uL of Matrix Spike Solution, after spiking the sample with the IS/SMC Solution.

9.4.7.3 For the HP5973 systems, MS/MSD samples shall be analyzed according to the instructions for sample analysis (Section 9.4.6), except that the sample shall be spiked with 40μL of the 50 ng/μL MS solution. Using a microliter syringe, inject the MS solution directly into the sample, through the teflon-lined septum of the 40-mL screw cap vial. Assuming the vial contains 40 mL of sample, the final spike concentration is 50μg/L.

9.4.8 Analysis of storage blank samples.

9.4.8.1 A storage blank analysis must be performed according to the schedule specified in Section 8.8 of this SOP.

9.4.8.2 Storage blank samples shall be analyzed according to the instructions for sample analysis, Section 9.4.6 of this SOP.

9.5 Analysis of low detection limit waters (25 mL)

The 12-hour analytical time period for this method begins with the injection of BFB and ends 12 hours after the injection time. Standards, blanks, and samples shall be analyzed within this 12-hour analytical time period.

9.5.1 Five point initial calibration.

The purge and trap concentrator shall be set up for analysis using 25-mL sparge cells.

9.5.1.1 Analysis on Incos-50A and Incos-XL systems.

9.5.1.1.1 The five concentration points are listed in Appendix B.

9.5.1.1.2 Fill a 25-mL syringe with method blank water. Invert the syringe, remove any air bubbles, and bring the level to 25 mL by displacement with the plunger.

9.5.1.1.3 Spike the water with 2.5 μL of IS/SMC Solution. The amount used results in a final concentration of 5 μg/L.

9.5.1.1.4 Spike the water with the appropriate amount of RAP Calibration Mix for the specific point being analyzed.

9.5.1.1.5 Attach the 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. Remove the syringe from the mount.

9.5.1.2 Analysis on HP5973H & HP5973J system.

9.5.1.2.1 The five concentration points are listed in Appendix B. Standards are prepared in 50-mL gas tight syringe and then transferred to 40mL VOA vials which are pre-cleaned.

9.5.1.2.2 Fill a 50-mL gas-tight syringe with method blank water. Invert the syringe, remove any air bubbles, and bring the level to 50 mL by displacement with the plunger.

9.5.1.2.3 Spike the water with the appropriate amount of RAP Calibration Mix for the specific point being analyzed.

9.5.1.2.4 Cap the end of the syringe. Rotate and invert the closed syringe to mix. Let the standard solution equilibrate in the syringe for about 1 minutes. While the standard solution is equilibrating, label the 40-mL vial with information about the standard.

9.5.1.2.5 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.

9.5.1.2.6 Gently place the vial in the appropriate autosampler position. Avoid causing any hairline cracks in the vial, as this may result in the vial disintegrating in the autosampler.

9.5.1.2.7 Analyze the standards. The autosampler will analyze a 25 mL aliquot and add 1 μL of the 125 ng/μL IS/SMC solution.

9.5.1.3 Follow the instructions for the 5-mL five-point initial calibration analysis in Sections 9.4.1 through 9.4.1.9 for each of the five calibration levels.

9.5.1.4 Update the initial calibration response factors for each the method by associating the current data file with each calibration level. Save the method.

9.5.1.5 Generate the initial calibration summary report. Samples shall not be analyzed if the initial calibration does not meet the criteria specified in Appendix B.

9.5.1.6 If the initial calibration meets all the criteria specified in Section 8.3 of this SOP, the remainder of the 12-hour analytical period may be used for the analysis of QL standard (0.5 μg/L), LCS, blanks and samples, using the 5 μg/L calibration standard to quantitate the blank and sample data files.

9.5.2 Continuing calibration.

A continuing calibration standard shall be run every 12-hour analytical time period, after BFB

tuning and prior to a method blank analysis. The continuing calibration check is performed in order to determine if the percent difference and the minimum response factor criteria meet the appropriate QA/QC criteria. The continuing calibration is analyzed at a level of 5 µg/L.

9.5.2.1 Prepare the mid-level standard as described in Sections 9.5.1.1 for the Incos-50A, and Incos-XL systems and 9.5.1.2 for the HP5973H, and HP5973J systems. The amounts used result in a final concentration of 5 µg/L.

9.5.2.2 Follow the instructions for the 5-mL continuing calibration analysis in Section 9.4.2.2 to 9.4.2.5 of this SOP.

9.5.2.3 Update the response factors for the continuing calibration and generate the continuing calibration summary form.

9.5.2.4 The continuing calibration must meet all the criteria specified in Section 8.4 of this SOP.

9.5.3 Laboratory Control Standard (LCS)

A LCS is analyzed once every 12-hour analytical time period, immediately after the initial or continuing calibration. An LCS is analyzed to demonstrate that the calibration standards used to calibrate the instrument are appropriate. Specifically the LCS verifies that the standards include the appropriate compounds at the correct concentration. This is done by preparing the LCS spiking mixture from a source (or sources) entirely separate from those used to calibrate the instrument. The LCS is analyzed at a level of 5 µg/L.

9.5.3.1 Analysis on Incos-50A, and Incos-XL systems

9.5.3.1.1 Fill a 25-mL syringe with method blank water. Invert the syringe, remove any air bubbles, and bring the level to 25 mL by displacement with the plunger.

9.5.3.1.2 Lay the syringe on the lab bench in the hood and spike the water with 2.5 µL of IS/Surr Solution. The amount used results in final concentration 5 µg/L.

9.5.3.1.3 Spike the water with 5 µL of the Low level Laboratory Control Sample Spike Solution (LCS Spike Solution, 25/250 ng/µL). The amount used results in final concentration 5/50/L.

9.5.3.1.4 Attach the 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. Remove the syringe from the mount

9.5.3.2 Analysis on HP5973H & HP5973J system.

9.5.3.2.1 The LCS is prepared in 50-mL gas tight syringe and then transferred

to 40-mL VOA vial which is pre-cleaned.

9.5.3.2.2 Fill a 50-mL gas-tight syringe with method blank water. Invert the syringe, remove any air bubbles, and bring the level to 50 mL by displacement with the plunger.

9.5.3.2.3 Spike the water with 50 µL of the Low level Laboratory Control Sample Spike Solution (LCS Spike Solution, 25/250 ng/µL). The amount used results in final concentration 5/50 µg/L.

9.5.3.2.4 Cap the end of the syringe. Rotate and invert the closed syringe to mix. Let the standard solution equilibrate in the syringe for about 1 minutes. While the standard solution is equilibrating, label the 40-mL vial with information about the standard.

9.5.3.2.5 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.

9.5.3.2.6 Gently place the vial in the appropriate autosampler position. Avoid causing any hairline cracks in the vial, as this may result in the vial disintegrating in the autosampler.

9.5.3.2.7 The autosampler will analyze a 25 mL aliquot and add 1 µL of the 125 ng/µL IS/SMC solution.

9.5.3.3 Press the start button on the concentrator to begin purging the standard.

9.5.3.4 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment D.

9.5.3.5 Analyze the standard and acquire the data.

9.5.3.6 Quantitate the data and print out a quantitation report and chromatogram.

9.5.3.7 Evaluate the calculated concentrations against the criteria listed in Section 8.5.3. Samples shall not be analyzed if the LCS does not meet the criteria specified in Section 8.5.3.

9.5.3.8 If the LCS meets all the criteria specified in Section 8.5.3, the remainder of the 12-hour analytical period may be used for the analysis of blanks and samples.

9.5.4 Quantitation Limit Standard

A QL standard at a concentration of 0.5 µg/L must be analyzed to verify that the low detection limits for vinyl chloride, 1,2-dichloroethane, carbon tetrachloride, cis-1,3-

dichloropropane, and trans-1,3-dichloropropane can be achieved. Prepare and analyze the QL standard in a manner analogous to the continuing calibration standard except use 0.5 µL of the RAP CAL solution.

9.5.4.1 Analysis on Incos-50A, and Incos-XL systems

9.5.4.1.1 Fill a 25-mL syringe with method blank water. Invert the syringe, remove any air bubbles, and bring the level to 25 mL by displacement with the plunger.

9.5.4.1.2 Lay the syringe on the lab bench in the hood and spike the water with 2.5 µL of IS/Surr Solution. The amount used results in final concentration 5 µg/L.

9.5.4.1.3 Spike the water with 0.5 µL of the Low level RAP CAL Mix, 25/250 ng/µL. The amount used results in final concentration 0.5/5 µg/L.

9.5.4.1.4 Attach the 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. Remove the syringe from the mount

9.5.4.2 Analysis on HP5973H & HP5973J system.

9.5.4.2.1 The QL Standard is prepared in 50-mL gas tight syringe and then transferred to 40mL VOA vials which is pre-cleaned.

9.5.4.2.2 Fill a 50-mL gas-tight syringe with method blank water. Invert the syringe, remove any air bubbles, and bring the level to 50-mL by displacement with the plunger.

9.5.4.2.3 Spike the water with 1 µL of the Low level RAP CAL Mix, 25/250 ng/µL. The amount used results in final concentration 0.5/5 µg/L.

9.5.4.2.4 Cap the end of the syringe. Rotate and invert the closed syringe to mix. Let the standard solution equilibrate in the syringe for about 1 minutes. While the standard solution is equilibrating, label the 40-mL vial with information about the standard.

9.5.4.2.5 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.

9.5.4.2.6 Gently place the vial in the appropriate autosampler position. Avoid causing any hairline cracks in the vial, as this may result in the vial disintegrating in the autosampler.

9.5.4.2.7 The autosampler will analyze a 25 mL aliquot and add 1 µL of the 125 ng/µL IS/SMC solution

9.5.4.3 Press the start button on the concentrator to begin purging the standard.

9.5.4.4 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment D.

9.5.4.5 Analyze the standard and acquire the data.

9.5.4.6 Quantitate the data and print out a quantitation report and chromatogram.

9.5.4.7 Evaluate the calculated concentrations against the criteria listed in Section 8.6.4. Samples shall not be analyzed if the QL standard does not meet the criteria specified in Section 8.6.4.

9.5.4.8 If the QL standard meets all the criteria specified in Section 8.6.4, the remainder of the 12-hour analytical period may be used for the analysis of blanks and samples.

9.5.5 Method blank analysis.

After the initial or continuing calibration is performed and before samples are analyzed, a method, or laboratory blank analysis shall be conducted.

9.5.5.1 Analysis on Incos-50A, and Incos-XL systems

9.5.5.1.1 Fill a 25-mL syringe with method blank water. Invert the syringe, remove any air bubbles, and bring the level to 25 mL by displacement with the plunger.

9.5.5.1.2 Lay the syringe on the lab bench in the hood and spike the water with 2.5 µL of IS/Surr Solution. The amount used results in final concentration 5 µg/L.

9.5.5.1.3 Attach the 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. Remove the syringe from the mount

9.5.5.2 Analysis on HP5973H & HP5973J system.

9.5.5.2.1 Gently fill a 40-mL vial with method blank water. Overfill the vial to form an inverted meniscus. Cap the vial. Invert the vial to ensure that there are no air bubbles present.

9.5.5.2.2 Gently place the vial in the appropriate autosampler position. Avoid causing any hairline cracks in the vial, as this may result in the vial disintegrating in the autosampler.

9.5.5.2.3 Analyze the method blank. The autosampler will analyze a 5 mL aliquot and add 1 µL of the 250 ng/µL IS/SMC solution.

9.5.5.3 Follow the instructions for the 5-mL method blank analysis in Sections 9.4.5.2 to 9.4.5.4 of this SOP.

9.5.5.4 Follow the file processing instructions for the 5-mL method blank in Section 9.4.5 of this SOP.

9.5.5.5 Review the results as discussed in Section 8.14 for qualitative identification of target analytes. Delete all reported hits which do not meet the qualitative criteria. Review all target compounds that are detected to verify they are integrated properly. Review the chromatogram for possible false negatives.

9.5.5.6 If the method blank meets all the criteria specified in Section 8.7, the remainder of the 12-hour analytical period may be used for the analysis of samples.

9.5.6 Sample analysis.

Samples shall be analyzed only after the BFB tune, initial calibration, continuing calibration, LCS, QL standard, and method blank analysis meet all of the appropriate criteria specified in the QA/QC section of this SOP.

9.5.6.1 Allow the sample to reach ambient room temperature before analysis.

9.5.6.2 The analyst shall again check that the numbers on the vials coincide with the numbers on the routing forms to ensure that the correct sample is being analyzed.

9.5.6.3 For the Incos-50A, and Incos-XL systems, break the chain of custody seal on the vial with a scalpel or other appropriate implement, again making note if the seal is missing or compromised in any way.

9.5.6.4 The analyst shall take note if the sample has an unusual color or other physical characteristic such as more than one phase, presence of a precipitate or unusual viscosity. If any physical signs of contamination are present a screening analysis to protect the analytical system from damage or contamination, and to determine the appropriate subsequent dilution is required. If an initial screening is necessary, it shall be at a 1:50 dilution, unless the laboratory supervisor decides otherwise.

9.5.6.5 The analyst shall also note in the runlog if there is head space present in the sealed sample vial.

9.5.6.6 For the Incos-50A, and Incos-XL systems, fill a 25-mL syringe with the sample. Invert the syringe, remove any air bubbles, and bring the level to 25-mL by displacement with the plunger. Any excess sample displaced from the syringe should be either place back into the sample vial or placed in the aqueous waste containers.

Spike the water with 2.5 µL of IS/SMC solution. The amounts used result in a final concentrations of 5 µg/L.

Attach the syringe to the luer lock mount on the appropriate autosampler position sparge apparatus. Open the mount valve and inject the contents of the syringe into the sparge cell and close the valve. Remove the syringe from the mount.

9.5.6.7 For the HP5973 systems, gently place the vial in the appropriate autosampler position. The autosampler will analyze a 25 mL aliquot and add 1 µL of the IS solution.

9.5.6.8 Follow the sample analysis instructions for the 5-mL sample in Sections 9.4.6.9 through 9.4.6.18.

9.5.6.9 Review the results as discussed in Section 8.14 for qualitative identification of target analytes. Delete all reported hits which do not meet the qualitative criteria. Review all target compounds that are detected to verify they are integrated properly. Review the chromatogram for possible false negatives.

9.5.7 Analysis of matrix spike and matrix spike duplicate samples.

9.5.7.1 Matrix spike and matrix spike duplicate analyses shall be performed according to the schedule prescribed in Section 8.12 of this SOP.

9.5.7.2 For the Incos-50A, and Incos-XL systems, matrix spike and matrix spike duplicate samples shall be analyzed according to the instructions for sample analysis (Section 9.5.4), except that the sample shall be spiked with 2.5 uL of Matrix Spike Solution, after spiking the sample with the IS/SMC Solution.

9.5.7.3 For the HP5973 systems, MS/MSD samples shall be analyzed according to the instructions for sample analysis (Section 9.5.4), except that the sample shall be spiked with 4 µL of the 50 ng/µL MS solution. Using a microliter syringe, inject the MS solution directly into the sample, through the teflon-lined septum of the 40-mL screw cap vial. Assuming the vial contains 40 mL of sample, the final spike concentration is 5 µg/L.

Since spiking of each vial for MS/MSD analysis occurs, the MS/MSD analysis will proceed only if a sufficient number of sample vials have been submitted to the laboratory.

9.5.8 Analysis of storage blanks.

9.5.8.1 A storage blank analysis must be performed according to the schedule specified in Section 8.8 of this SOP.

9.5.8.2 Storage blank samples shall be analyzed according to the instructions for sample analysis, Section 9.5.4 of this SOP.

9.6 Analysis of low level soils

The 12-hour analytical time period for this method begins with the injection of BFB and ends 12 hours after the injection time. Standards, blanks, and samples shall be analyzed within this 12-hour analytical time period. A sample heater is integrated into the Varian Archon autosampler for heating soil samples. The purging is conducted at 40°C. The analysis of low level soils is restricted to systems configured with Archon autosamplers.

9.6.1 Five-point initial calibration.

9.6.1.1 Standards are prepared in 40-mL vials which are pre-cleaned and contain a magnetic stir-bar and 5-mL of sodium bisulfate preservative.

9.6.1.2 Using a top-loading balance, tare the vial, weigh 5.0 g of purified soil into the vial, cap the vial, and record the weight in the runlog. Ensure that there is no sand on the top edge of the vial nor in the threads of the vial before capping because sand may compromise the seal of the vial.

9.6.1.3 For each calibration standard, uncap the vial, spike the appropriate amount of calibration standard (see Appendix A) directly into the sand, and quickly replace the cap on the vial. Use gas-tight microliter syringes for measuring the calibration standard.

9.6.1.4 Gently place the vial in the appropriate autosampler position to avoid causing any hairline cracks in the vial Any hairline cracks may result in a leak or the vial disintegrating in the autosampler.

9.6.1.5 Analyze the standards. The autosampler will add 5 mL of water and 1 µL of the IS/SMC solution to the standards.

9.6.1.6 If the initial calibration meets all the criteria specified in Section 8.3, the remainder of the 12-hour analytical period may be used for the analysis of LCS, blanks and samples, using the 50 µg/Kg calibration file to quantitate the blank and sample data files.

9.6.2 Continuing calibration.

The continuing calibration standard is analyzed at a concentration of 50 µg/Kg.

9.6.2.1 Follow Sections 9.6.1.1 through 9.6.1.5 for the analysis of the continuing calibration. The autosampler will add 5 mL of water and 1 µL of the IS/SMC solution to the standard.

9.6.2.2 Follow the instructions for the 5-mL water continuing calibration analysis in Section 9.4.2 except use the purified soil matrix and a heated purge.

9.6.2.3 If the continuing calibration meets all the criteria specified in Section 8.4, the

remainder of the 12-hour analytical period may be used for the analysis of blanks and samples, using the updated 50 µg/Kg continuing calibration file to quantitate the blank and sample data files.

9.6.3 Analysis of laboratory control sample.

After the initial or continuing calibration is performed a LCS shall be analyzed.

9.6.3.1 Follow Sections 9.6.1.1 and 9.6.1.2 for the LCS vial preparation.

9.6.3.2 Inject 10 µL of the 25 ng/µL LCS Spike Solution directly into the purified soil matrix. Gently tilt the vial containing the soil sample so that the tip of the microliter syringe is inserted into the soil itself. The final spike concentration is 50 µg/Kg.

9.6.3.3 Follow Sections 9.6.1.4 and 9.6.1.5. The autosampler will add 5 mL of method blank water and 1 uL of IS/SMC solution. Heat the sample to 40°C.

9.6.3.4 If the LCS meets all the criteria specified in Section 8.5, the remainder of the 12-hour analytical period may be used for the analysis of samples.

9.6.4 Quantitation Limit Standard

A quantitation standard at the concentration of the lowest point of the initial calibration must be analyzed immediately after the LCS for each 12-hour analytical period. In the event that an initial calibration is analyzed the lowest standard of the initial calibration satisfies this requirement

9.6.4.1 Prepare and load the quantitation limit standard (10µg/Kg) as described in Section 9.6.1 and Appendix A.

9.6.4.2 Press the start button on the concentrator to begin purging the standard.

9.6.4.3 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment D.

9.6.4.4 Analyze the standard and acquire the data.

9.6.4.5 Quantitate the data and print out a quantitation report and chromatogram.

9.6.4.6 Evaluate the calculated concentrations against the criteria listed in Section 8.6.3. Samples shall not be analyzed if the QL standard does not meet the criteria specified in Section 8.6.3.

9.6.4.7 If the QL standard meets all the criteria specified in Section 8.6.3, the remainder of the 12-hour analytical period may be used for the analysis of blanks and samples.

9.6.5 Method blank analysis.

After the initial or continuing calibration is performed and before samples are analyzed, a method blank analysis shall be performed.

9.6.5.1 Follow Sections 9.6.1.2, 9.6.1.4, and 9.6.1.5 for the analysis of the method blank. The autosampler will add 5 mL of water and 1 μL of the IS/SMC solution. The sample heaters must be used for the soil method blanks.

9.6.5.2 Follow the instructions for the 5-mL water method blank analysis in Sections 9.4.5.2 through 9.4.5.5 except use the purified soil matrix and a heated purge.

9.6.5.3 If the method blank meets all the criteria specified in Section 8.7, the remainder of the 12-hour analytical period may be used for the analysis of samples.

9.6.6 Sample analysis.

Samples shall be analyzed only after the BFB tune, initial calibration, continuing calibration, laboratory control sample, and method blank analysis meet all of the appropriate criteria specified in the QA/QC Section of this SOP. Low level soil samples for VOA should be received in screw-cap 40-mL VOA vials, with approximately 5 grams of sample, 5 mL of sodium bisulfate preservative solution, and magnetic stir-bar. Section 9.6.7 addresses sample preparation of soil samples that are received in Encore samplers or Soil cores.

9.6.6.1 Gloves must be worn when handling the sample vial since the vial has been tared. If any soil is noted on the exterior of the vial or cap, it must be carefully removed.

9.6.6.2 The analyst shall again check that the numbers on the container coincide with the numbers on the routing forms to ensure that the correct sample is being analyzed.

9.6.6.3 Remove the sample vial from the refrigerator and allow it to warm to room temperature. Shake the vial gently to ensure that the contents move freely and that stirring will be effective.

9.6.6.4 Weigh the vial and contents to the nearest 0.1 g and record the weight in the runlog. The weight obtained in the laboratory is compared to the weight obtained in the field to verify that the sample weight is accurate. Any discrepancies in the weights are to be noted in the report narrative.

9.6.6.5 Follow Sections 9.6.1.4 and 9.6.1.5 for the analysis of each sample. The autosampler will add 5 mL of method blank water and 1 μL of the IS/SMC solution to each sample.

9.6.6.6 Heat the sample to 40°C and follow the instructions for 5-mL water sample analysis in Sections 9.4.6.9 and 9.4.6.12 through 9.4.6.17.

9.6.6.7 If sample dilution is required, analyze the methanol preserved soil sample according to the instructions provided in Section 9.7. The sample should be diluted so that the target compound which was originally outside of the calibration range will fall within the upper hal

of the initial calibration range of the instrument, if possible.

It should be noted that results between 200 µg/Kg (upper calibration concentration for 5 g sample) and 1000 µg/Kg (lower calibration concentration for 100 µL aliquot of 5 g sample preserved in 10 mL of methanol) may not be determined accurately due to limitations with EPA Method 5035. This data gap is to be noted in the report narrative.

9.6.6.8 Determine the percent moisture following EPA Region 9 Lab SOP 460 using the separate soil aliquot provided by the sampler for this purpose. The concentrations of the target analytes will be reported based on the dry weight of the sample.

Note: If the sampler did not provide an aliquot of soil for determination of the moisture content then the results must be reported on a wet weight basis and the deviation indicated in the report narrative and on the spreadsheet.

9.6.7 Low Level Soil Sample Preparation

In the event that soil samples are received in Encore samplers or Soil core tubes, the following procedures must be used to transfer an aliquot of the sample into a 40mL VOA vial.

9.6.7.1 Preparation of Vials

All 40-mL VOA vials must contain 1 gram of sodium bisulfate, 5 mL of organic free water, and a magnetic stir bar. After all of these items have been added to the vial the vial must be weighed prior to the addition of the soil aliquot. Record the weight of these Vials in the VOA extraction logbook.

9.6.7.2 Samples in 5 gram Encore containers

9.6.7.2.1 Attach the Encore sampler to the extrusion tool. Then remove the end cap. Insert the Encore sampler into a pre-weighed 40-mL VOA vial. Press the plunger of the extrusion tool to add the sample aliquot to the vial. Immediately cap the vial.

9.6.7.2.2 Immediately after the sample aliquot is added to the vial the vial must be weighed. Record the weight of the vial on the appropriate line in the VOA extraction logbook and calculate the exact weight of the sample added to the vial.

9.6.7.2.3 Analyze the sample according to Section 9.6.6.

9.6.7.2.4 25 gram Encore Containers must be analyzed as medium level soils. The diameter of these sample containers prevents the direct addition of the soil aliquot into a 40-mL VOA vial.

9.6.7.3 Samples in Soil Core tubes.

9.6.7.3.1 Cut off the end of a 10-mL disposable plastic syringe.

9.6.7.3.2 Open an end of the soil core and jam the cut off syringe into the soil core to approximately the 5 mL mark. Remove the syringe containing the soil aliquot.

9.6.7.3.3 Insert the syringe containing the soil into a pre-weighed 40-mL VOA vial. Press the plunger of the syringe to add the sample aliquot to the vial. Immediately cap the vial.

9.6.7.3.4 Immediately after the sample aliquot is added to the vial the vial must be weighed. Record the weight of the vial on the appropriate line in the VOA extraction logbook and calculate the exact weight of the sample added to the vial.

9.6.7.3.5 Analyze the sample according to Section 9.6.6.

9.6.8 Analysis of matrix spike and matrix spike duplicate samples.

9.6.8.1 Matrix spike and matrix spike duplicate analyses shall be performed according to the schedule prescribed in Section 8.12 of this SOP when these samples are provided by the field sampler.

9.6.8.2 Matrix spike and matrix spike duplicate samples shall be analyzed according to the instructions for sample analysis (Section 9.6.6), except that 5 μL of the 50 ng/μL MS Solution will be injected directly into the soil sample vial. Gently tilt the vial containing the soil sample so that the tip of the microliter syringe is inserted into the soil itself. The final spike concentration is 50 μg/Kg. The autosampler will add 5 mL of method blank water and 1 uL of IS/SMC solution. Heat the sample to 40°C.

9.6.9 Analysis of storage blank samples.

9.6.9.1 A storage blank analysis must be performed according to the schedule specified in Section 8.8 of this SOP.

9.6.9.2 Storage blank samples shall be analyzed according to the instructions for sample analysis, Section 9.4.6 of this SOP.

9.7 Analysis of soils using medium level soil extraction method.

The medium level soil extraction method shall be used to analyze soils that are expected to contain high levels of volatile organics, for screening soil samples before analysis by the low level method, or to perform a dilution required on a soil sample analyzed by the low level method . The 12 hour analytical time period for this method begins with the injection of BFB and ends 12 hours after the injection time. Standards, blanks, and samples shall be analyzed within this 12 hour analytical time period. The purge and trap concentrator should be equipped with 5-mL sparge cells.

9.7.1 Initial calibration.

Because the methanol extract and method blank water mixture is purged at ambient temperature, the initial calibration for 5-mL water samples (Section 9.4.1) shall be used for this method.

9.7.2 Continuing calibration

Because the methanol extract and method blank water mixture is purged at ambient temperature, the continuing calibration for 5-mL water samples (Section 9.4.2) shall be used for this method.

9.7.3 Laboratory Control Sample

Because the methanol extract and method blank water mixture is purged at ambient temperature, the LCS for 5-mL water samples (Section 9.4.3) shall be used for this method.

9.7.4 QL Standard

Because the methanol extract and method blank water mixture is purged at ambient temperature, the QL standard for 5-mL water samples (Section 9.4.4) shall be used for this method.

9.7.5 Method blank analysis.

After the initial or continuing calibration is performed and before samples are analyzed, a method, or laboratory blank analysis shall be conducted.

9.7.5.1 Using a top loading balance, weigh 5.0 g of purified soil into a tared 15-mL vial. Record the actual weight to the nearest 0.1 g in the log book.

9.7.5.2 Quickly add 10.0 mL of purge and trap grade methanol to the vial. Cap and shake the vial for 2 minutes. The steps in Sections 9.7.3.1 and 9.7.3.2 must be done rapidly in order to prevent the loss of volatile organics from the soil.

9.7.5.3 Using a disposable pipette, transfer approximately 1 mL of extract to a GC vial for storage in the volatiles laboratory refrigerator at 4°C. This method blank extract shall be used for all medium level soils extracted at the same time.

9.7.5.4 Analyze 100 µL of the extract in 4.9 mL of method blank water according to the instructions for 5-mL water method blank analysis, in Section 9.4.5.

9.7.5.5 If the method blank meets all the criteria specified in Section 8.7, the remainder of the 12-hour analytical period may be used for the analysis of samples.

9.7.6 Sample analysis.

Samples shall be analyzed only after the BFB tune, initial calibration, continuing calibration, LCS, QL standard and method blank analysis meet all of the appropriate criteria specified in the QA/QC section of this SOP.

9.7.6.1 Follow the steps in Section 9.6.6 regarding the procedures for the sequence of analysis and checking the sample integrity.

9.7.6.2 Unpreserved soil samples.

9.7.6.2.1 Samples in 5g Encore containers

9.7.6.2.1.1 Attach the Encore sampler to the extrusion tool. Then remove the end cap. Insert the Encore sampler into a pre-weighed 40mL VOA vial. Press the plunger of the extrusion tool to add the sample aliquot to the vial. Immediately cap the vial.

9.7.6.2.1.2 Immediately after the sample aliquot is added to the vial the vial must be weighed. Record the weight of the vial on the appropriate line in the VOA extraction logbook and calculate the exact weight of the sample added to the vial.

9.7.6.2.1.3 Add the 10mL of purge & trap grade methanol to the vial. Shake the vial for 1 minute.

9.7.6.2.1.4 Using a disposable pipette, transfer approximately 1 mL of extract to a GC vial for storage in the volatile laboratory refrigerator at 4°C. This extract shall be used for the analysis and any subsequent dilutions which may be necessary.

9.7.6.2.2 Samples in 25g Encore containers

9.7.6.2.2.1 Attach the Encore sampler to the extrusion tool. Then remove the end cap. Insert the Encore sampler into a pre-weighed 4 oz jar. Press the plunger of the extrusion tool to add the sample aliquot to the vial. Immediately cap the jar.

9.7.6.2.2.2 Immediately after the sample aliquot is added to the jar the jar must be weighed. Record the weight of the jar on the appropriate line in the VOA extraction logbook and calculate the exact weight of the sample added to the jar.

9.7.6.2.2.3 Quickly add 50.0 mL of purge and trap grade methanol to the jar. Cap and shake the jar for 1 minutes. The steps in Sections 9.7.4.2.2.1through 9.7.4.2.2.3 must be done rapidly in order to prevent the loss of volatile organics from the sample.

9.7.6.2.2.4 Using a disposable pipette, transfer approximately 1 mL of extract to a GC vial for storage in the volatile laboratory refrigerator at 4°C. This extract shall be used for the analysis and any subsequent dilutions which may be necessary.

9.7.6.2.3 Samples in Soil Core tubes.

9.7.6.2.3.1 Cut off the end of a 10mL disposable plastic syringe.

9.7.6.2.3.2 Open an end of the soil core and jam the cut off syringe into the soil core to approximately the 5 mL mark. Remove the syringe containing the soil aliquot.

9.7.6.2.3.3 Insert the syringe containing the soil into a pre-weighed 40-mL VOA vial. Press the plunger of the syringe to add the sample aliquot to the vial. Immediately cap the vial.

9.7.6.2.3.4 Immediately after the sample aliquot is added to the vial the vial must be weighed. Record the weight of the vial on the appropriate line in the VOA extraction logbook and calculate the exact weight of the sample added to the vial.

9.7.6.2.3.5 Quickly add 10.0 mL of purge and trap grade methanol to the vial. Cap and shake the vial for 1 minutes. The steps in Sections 9.7.4.2.3.3 through 9.7.4.2.3.5 must be done rapidly in order to prevent the loss of volatile organics from the sample.

9.7.6.2.3.6 Using a disposable pipette, transfer approximately 1 mL of extract to a GC vial for storage in the volatile laboratory refrigerator at 4°C. This extract shall be used for the analysis and any subsequent dilutions which may be necessary.

9.7.6.3 Soil samples preserved with methanol.

9.7.6.3.1 Gloves must be worn when handling the sample vial since the vial has been tared. If any soil is noted on the exterior of the vial or cap, it must be carefully removed.

9.7.6.3.2 Remove the sample from the refrigerator and allow it to warm to room temperature. Shake the vial gently to ensure that the contents move freely and that stirring will be effective.

9.7.6.3.3 Weigh the vial and contents to the nearest 0.1 g and record the weight in the runlog. The weight obtained in the laboratory is compared to the weight obtained in the field to verify that the sample weight is accurate. Any discrepancies in the weights are to be noted in the report narrative.

9.7.6.3.4 Using a disposable pipette, transfer approximately 1 mL of extract to a GC vial for storage in the volatile laboratory refrigerator at 4°C. This extract shall be used for the analysis and any subsequent dilutions which may be necessary.

9.7.6.4 Analyze 100 µL of the extract in 4.9 mL of method blank water according to the instructions for 5-mL sample analysis in Sections 9.4.6.

9.7.6.5 If any of the target compounds exceed the initial calibration range of the instrument, a dilution shall be performed using a smaller aliquot of the extract combined with method blank water to a total volume of 5 mL. The sample should be diluted so that the target compound(s) which was originally outside of the calibration range will fall within the upper range of the initial calibration of the instrument.

9.7.7 Analysis of matrix spike and matrix spike duplicate samples.

9.7.7.1 Matrix spike and matrix spike duplicate analyses shall be performed according to the schedule prescribed in Section 8.12 of this SOP.

9.7.7.2 Add 9.0 mL of methanol and 1.0 mL of matrix spike solution to each of the two aliquots of the soil sample chosen for spiking.

9.7.7.3 Using a 100 µL aliquot of the extract, analyze the matrix spike and matrix spike duplicate sample according to the instructions for medium level soil sample analysis (Section 9.7.4).

9.7.8 Analysis of storage blank samples.

9.7.8.1 A storage blank analysis must be performed according to the schedule specified in Section 8.8 of this SOP.

9.7.8.2 Storage blank samples shall be analyzed according to the instructions for sample analysis, Section 9.4.6 of this SOP.

9.8 Autosampler operation.

The Tekmar ALS2016, OI DPM-16, and Varian Archon autosamplers may be employed in any of the methods described in Sections 9.4 through 9.7. The operating parameters of the autosamplers are found in Attachment C at the end of this SOP.

9.8.1 Outfit the autosampler with the appropriate type and size glassware required for the method used, e.g. 25 mL fritted sparge cell or 40-mL vial for Low Level VOA analysis.

9.8.2 Prepare and deliver each standard, blank, or sample into a separate sparge cell or 40-mL vial according to the instructions set forth in the analysis sections of this SOP.

9.8.3 Display the ALS function on the purge and trap concentrator and select the purge positions

which are to be used in the autosampler sequence (total possible are 1 through 16 for the Tekmar and OI autosamplers and 1- 50 for the Varian Archon autosampler).

9.8.4 Position the concentrator to the first cell to be used in the sequence.

9.8.5 The analytical sequence file must be created using the data acquisition software. Complete the header information for each sample and save the file. Load and run the sequence.

9.8.6 Press the start button on the concentrator to start the sequence.

9.8.7 Each data file will be automatically quantitated. The files should be processed in accordance with the instructions found in the sample analysis section relevant to the type of analysis being conducted.

10 DOCUMENTATION

10.1 Data from the Region 9 Laboratory is presented to the client in one of two general reporting formats: a complete, validatible data package or a summary report. For the former the laboratory prepares summary forms of calibration, quality control, and sample results and provides this information along with the raw data, a Report Narrative, and an analytical report spreadsheet to the client. If a summary report is all that is required the laboratory prepares a Report Narrative and the analytical spreadsheet for delivery to the client and collects the raw data which will be filed at the laboratory. Section 10.2 details the requirements of a complete data package and Section 10.3 lists the summary report requirements.

10.2 Data package assembly.

The analyst, or other chemist, shall assemble a discrete data package for each SDG in each case requiring the delivery of a validatible data package according to the following instructions, and in the following order. Each section of the data package shall have a cover sheet titled with the appropriate section name. The data package shall be sequentially numbered after assembly using a hand operated numerator.

10.2.1 Report Narrative section.

The Report Narrative section shall contain a text narrative describing, but not limited to, the following. A report narrative template, VOA2_TEMP.wpd is avialable on the network in G:\user\share\esat_data\templates\

10.2.1.1 Site name.
10.2.1.2 Case number.
10.2.1.3 SDG number.
10.2.1.4 Date(s) the samples were received.
10.2.1.5 EPA sample number.
10.2.1.6 Region 9 laboratory sample number.
10.2.1.7 Summary of the analyses performed.
10.2.1.8 Problems with the analyses.

10.2.1.9 Summary of the QA/QC results.

10.2.2 Analytical report spreadsheet

10.2.2.1 A spreadsheet (Lotus 123, Version 4) containing a summary of the results for all target analytes for all samples and blanks will be included in the data package. The report spreadsheet templates are avialable on the network in G:\user\share\esat_data\templates\

10.2.2.2 The header information for each sample will contain the station location, Sample ID, Lab Sample ID, and date sampled.

10.2.2.3 The results section will contain the results for each target analyte as follows:

If an analyte is not detected then the quantitation limit with a "U" qualifier will be reported

If an analyte is detected the following qualifier may be used:

J	The reported concentration is an estimated value.
N	The qualification (chemical identity) is uncertain.

In the event that a result is qualified, a comment letter must be defined in the report narrative. This letter must be present on the spreadsheet next to the affected result.

10.2.3 Tracking Forms section.

The Tracking Form section shall contain the following forms.

10.2.3.1 Region 9 sample cross reference form.
10.2.3.2 A copy of the chain of custody record received with each sample shipment.
10.2.3.3 A copy of the shipper's airbill, or bill of lading.

10.2.4 QA/QC Summary section.

The QA/QC section shall contain all of the QA/QC summary forms for the specific sample delivery group. Forms are generated using the EnviroQuant software. All of the forms shall be checked by the analyst to ensure that all of the filenames are correct, and that all of the appropriate standards, blanks, samples, spikes, and tune files have been included.

10.2.4.1 System Monitoring Compound / Internal Standard area summary data in chronological order. Include all analyses for each day. Note any data not used or not part of the SDG.

10.2.4.2 MS/MSD recovery report.

10.2.5 Sample section.

The sample section shall contain the following forms and raw data for each sample in the sample delivery group, assembled in laboratory ID order.

Quantitation report
Reconstructed ion chromatogram (RIC) of the data file
Extracted Ion chromatogram (EIC), spectra and reference spectra of target compounds detected, internal standards and surrogates.
Documentation of manual integrations reviewed by supervisors.
Library search compounds
Integrations
Chromatogram
Library comparison
LSC summary

All sample analyses must be included. Sample dilutions and analyses that failed QC criteria do not require Library search compounds. Data for each individual sample should be arranged as follows:

Full strength/least diluted analysis
Sample dilutions
Any analyses not being used.

10.2.6 MS/MSD Data Section

The MS/MSD Data Section shall contain the following raw data.

Quantitation report
Reconstructed ion chromatogram (RIC) of the data file
Extracted Ion chromatogram (EIC), spectra and reference spectra of target compounds detected, internal standards and surrogates.
Documentation of manual integrations reviewed by supervisors.
Library search compounds.

10.2.7 Instrument QC Section

The instrument QC section shall be arraigned in chronological order by instrument and shall include the following:

10.2.7.1 Reviewed Initial Calibration package
Copy of peer reviewed instrument run logbook page
Tune data (background subtracted spectra, mass listing, and labeled RIC)
Initial Calibration summary form
Each point of the ICAL arrange in chronological order

Quantitation report
Reconstructed ion chromatogram (RIC) of the data file
Extracted Ion chromatogram (EIC), spectra and reference spectra of all manual integrations, in order of elution
Manual integrations must be initialed and dated by a supervisor

10.2.7.2 Daily Analytical Packets. In chronological order immediately after applicable ICAL
Copy of peer reviewed instrument run logbook page
Tune data (background subtracted spectra, mass listing, and labeled RIC)
Continuing Calibrations
- Continuing Cal summary form
- Quantitation report
- Reconstructed ion chromatogram (RIC) of the data file
- Extracted Ion chromatogram (EIC), spectra and reference spectra of all manual integrations, in order of elution
- Manual integrations must be initialed and dated by a supervisor

LCS data (same as Ccal)
Quantitation Limit Standard (same as Ccal)

All Continuing cals, LCS, and QL standards need to be included. For example if the first Ccal fail criteria and the second Ccal passes, both must be included in the data package. Any standards that are not used must be in chronological order immediately after the standard(s) that passed QC limits.

Method blank data (same as for sample)

All method blanks analyzed must be included in the data package. For example if the first method blank fails QC criteria and the second method blank is analyzed and it passes, the second method blank will be used for reporting, but the first method blank data must be included in the date package. Any blanks that failed QC criteria must be in chronological order immediately after the blank that passed QC limits.

10.2.8 Logbooks and Miscellaneous Data.

10.2.8.1 Copies of all applicable standards preparation logbook pages.

10.2.8.2 Copies of all Sample weight logbooks for low level soils (if applicable.)

10.2.8.3 Copies of all extraction logbook pages for medium level soil analysis (if applicable.)

10.2.8.4 Copies of all balance calibration logbooks (if applicable.)

10.2.8.5 Storage Blank Data

10.3 Summary Report and Raw Data

When the client requirements stipulate a summary report the laboratory prepares the Report Narrative, analytical results spreadsheet, and organizes the raw data associated with each SDG for filing in the event that future data review or validation is required.

10.3.1 The Report Narrative is prepared according to the requirements listed in Section 10.2.1.

10.3.2 The analytical results spreadsheet is prepared according to the specifications provided in Section 10.2.2.

10.3.3 The raw data associated with the analysis of all the samples in the SDG must be organized for filing and presented for review along with the Report Narrative and the spreadsheet. No summary forms need be generated with the raw data but any forms which would normally be generated as part of the analysis must be included in the package. For example, the calibration summary reports generated by the data system and used by the analyst to assess the acceptability of the calibration should be filed with the raw data.

10.3.3.1 Sample tracking information as detailed in Section 10.2.3 should be included as the analyst has a copy of the information readily available.

10.3.3.2 Sample raw data organized by EPA sample ID must include: the quantitation report; the RIC; the raw and enhanced spectra of the target compounds detected in the sample, as well as the enhanced spectra of the corresponding target compound in the calibration file; and enhanced spectra of non-target compounds detected in the sample along with the library search listing the three best matches for the non-target compounds. (Section 10.2.5.3 through 10.2.5.6)

10.3.3.3 Calibration data must include any avialable summary information and the quantitation reports and RICs for all initial calibrations and continuing calibrations associated with the SDG. This information must be organized by instrument and date. Additionally, any manual integration must be demonstrated by including the associated peak integration.

10.3.3.4 Raw data for QC samples must be included. Tuning data and the associated summary used by the analyst to determine acceptability, blanks (quant report, RIC and spectra and TICs), MS/MSD data (quant report and RICs) should all be included in this order.

10.3.3.5 Runlogs and standard preparation logbooks need not be included in the raw data as these are already filed in an accessible manner in the laboratory.

10.4 Technical review.

Each data package shall be reviewed by the GC/MS Group Leader or a senior level chemist, other than the chemist who performed the analyses. After the peer review is performed, the Report

Narrative shall be signed by the ESAT Assistant Team Leader and the data package shall be submitted to Region 9.

10.5 Injection logbook.

A logbook shall be maintained for each instrument in accordance with the instructions in ESAT SOP #850

10.6 Refrigerator temperature log.

A refrigerator temperature log shall be maintained for each refrigerator or freezer according to SOP #805. The temperatures shall be recorded on a daily basis whenever the refrigerator is in use.

11 REFERENCES

11.1 Region 9 SOP 255. Standard Preparation for Volatile Organics Lab.
11.2 Region 9 SOP 205. Preparation of Organic Free Method Blank Water.
11.3 Region 9 SOP 835. Chromatographic Integration Procedures.
11.4 Region 9 SOP 805, Refrigerator Temperature Monitoring.
11.5 Finnigan Incos-50 Operator's Manual.
11.6 Tekmar LSC2000 and ALS2016 Operator's Manuals.
11.7 OI 4560 and DPM16 Operator's Manuals.
11.8 Region 9 SOP 125. Sample Disposal
11.9 Region 9 SOP 460. Percent Moisture Determination.
11.10 EPA Method 524.2 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry; Revision 4, August 1992.
11.11 EPA Method 8260A Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry: Capillary Column Technique; Revision 1, September 1994.
11.12 EPA Method 5035 Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples; Revision 0, December 1996.

12 DEVIATIONS FROM REFERENCE METHOD

12.1 The BFB Ion Abundance criteria differs from the reference methods.

12.2 Bromochloromethane is used as an internal standard.

12.3 The Initial Calibration criteria differs from the reference methods.

12.4 The Continuing Calibration criteria differs from the reference methods.

12.5 The minimum RRFs for Bromoform and 1,1,2,2-tetrachloroethane are lower than the minimum RRFs in 8260B.

12.6 The RRFs from the daily continuing calibration or corresponding point of the initial calibration are used to calculate sample results.

12.7 The Surrogate recoveries listed in Section 8.11 are slightly different than the reference method

Appendix A
5 mL Water and Soil
Calibration Criteria

For all samples analyzed with a 5 mL purge volume, the response factors of the compounds listed below must meet the minimum RRF criteria at each concentration level, and maximum %RSD criteria for the initial calibration, with allowance made for up to two volatile compounds. However, the RRFs for those two compounds must be greater than or equal to 0.010, and the %RSD of those two compounds must be less than or equal to 40.0% for the initial calibration to be acceptable.

Compound	Min RRF	Max %RSD	Max %D
Dichlorodifluoromethane	0.100	20	25
Chloromethane	0.010	NA	NA
Vinyl chloride	0.100	20	25
Bromomethane	0.100	20	25
Chloroethane	0.010	NA	NA
Trichlorofluoromethane	0.100	20	25
1,1-Dichloroethene	0.100	20	25
Acetone	0.010	NA	NA
Carbon disulfide	0.010	NA	NA
Methylene chloride	0.010	NA	NA
trans-1,2-Dichloroethene	0.010	NA	NA
Methyl Tert-Butyl Ether	0.100	20	25
1,1-Dichloroethane	0.200	20	25
Ethyl Tert-Butyl Ether	0.010	NA	NA
cis-1,2-Dichloroethene	0.010	NA	NA
2-Butanone	0.010	NA	NA
Chloroform	0.200	20	25
1,2-Dichloroethane-d4 (SMC)	0.010	NA	NA
1,2-Dichloroethane	0.100	20	25
t-Amyl-methyl ether	0.010	NA	NA
1,1,1-Trichloroethane	0.100	20	25
Carbon tetrachloride	0.100	20	25
Benzene	0.500	20	25
Trichloroethene	0.200	20	25
1,2-Dichloropropane	0.010	NA	NA
Bromodichloromethane	0.200	20	25
cis-1,3-Dichloropropene	0.100	20	25
trans-1,3-Dichloropropene	0.080	20	25
1,1,2-Trichloroethane	0.080	20	25
Dibromochloromethane	0.100	20	25
4-Methyl-2-pentanone	0.010	NA	NA

Compound	Min RRF	Max %RSD	Max %D
Toluene	0.400	20	25
Tetrachloroethene	0.200	20	25
1,3-Dichloropropane	0.100	20	25
2-Hexanone	0.010	NA	NA
1,2-Dibromoethane	0.100	20	25
Chlorobenzene	0.500	20	25
Ethylbenzene	0.100	20	25
Xylene (m & p)	0.300	20	25
Xylene (ortho)	0.300	20	25
Styrene	0.300	20	25
Bromoform	0.100	20	25
Bromofluorobenzene (SMC)	0.200	20	25
1,1,2,2-Tetrachloroethane	0.300	20	25
1,2,3-Trichloropropane	0.080	20	25
1,3-Dichlorobenzene	0.400	20	25
1,4-Dichlorobenzene	0.400	20	25
1,2-Dichlorobenzene	0.400	20	25
1,2-Dibromo-3-chloropropane	0.010	NA	NA

Toluene-d8 (SMC)	0.010	NA	NA

NA - These compounds have no associated %RSD or %D criteria.

Appendix A

5-mL Calibration Standard Amounts
Incos-50A & Incos-XL

CALIBRATION POINT	Amount IS/Surr Solution 50 ng/µL	Amount RAS CAL Mix 50 ng/µL
200 µg/L	5 µL	20 µL
100 µg/L	5 µL	10 µL
50 µg/L	5 µL	5 µL
20 µg/L	5 µL	2 µL
10 µg/L	5 µL	1 µL

5 mL/5 g Calibration Standard Amounts
HP5973H & HP5973J with Arcon Autosamplers

CALIBRATION POINT	Amount RAS CAL Mix 50 ng/µL
200 µg/L	200 µL
100 µg/L	100 µL
50 µg/L	50 µL
20 µg/L	20µL
10 µg/L	10 µL

Appendix B
25 mL Water
Calibration Criteria

For all samples analyzed with a 25 mL purge volume, the response factors of the compounds listed below must meet the minimum RRF criteria at each concentration level, and maximum %RSD criteria for the initial calibration, with allowance made for up to two volatile compounds. However, the RRFs for those two compounds must be greater than or equal to 0.010, and the %RSD of those two compounds must be less than or equal to 40.0% for the initial calibration to be acceptable.

Compound	Min RRF	Max %RSD	Max %D
Dichlorodifluoromethane	0.100	30	30
Chloromethane	0.010	NA	NA
Vinyl chloride	0.100	30	30
Bromomethane	0.100	30	30
Chloroethane	0.010	NA	NA
Trichlorofluoromethane	0.100	30	30
1,1-Dichloroethene	0.100	30	30
Acetone	0.010	NA	NA
Carbon disulfide	0.010	NA	NA
Methylene chloride	0.010	NA	NA
trans-1,2-Dichloroethene	0.010	NA	NA
Methyl Tert-Butyl Ether	0.100	30	30
1,1-Dichloroethane	0.200	30	30
Ethyl Tert-Butyl Ether	0.010	NA	NA
cis-1,2-Dichloroethene	0.010	NA	NA
2-Butanone	0.010	NA	NA
Chloroform	0.200	30	30
1,2-Dichloroethane-d4 (SMC)	0.010	NA	NA
1,2-Dichloroethane	0.100	30	30
t-Amyl-methyl ether	0.010	NA	NA
1,1,1-Trichloroethane	0.100	30	30
Carbon tetrachloride	0.100	30	30
Benzene	0.400	30	30
Trichloroethene	0.200	30	30
1,2-Dichloropropane	0.010	NA	NA
Bromodichloromethane	0.200	30	30
cis-1,3-Dichloropropene	0.100	30	30
trans-1,3-Dichloropropene	0.080	30	30
1,1,2-Trichloroethane	0.080	30	30
Dibromochloromethane	0.080	30	30
4-Methyl-2-pentanone	0.010	NA	NA

Compound	Min RRF	Max %RSD	Max %D
Toluene	0.400	30	30
Tetrachloroethene	0.200	30	30
1,3-Dichloropropane	0.100	30	30
2-Hexanone	0.010	NA	NA
1,2-Dibromoethane	0.080	30	30
Chlorobenzene	0.500	30	30
Ethylbenzene	0.100	30	30
Xylene (m & p)	0.300	30	30
Xylene (ortho)	0.300	30	30
Styrene	0.300	30	30
Bromoform	0.040	30	30
Bromofluorobenzene (SMC)	0.200	30	30
1,1,2,2-Tetrachloroethane	0.080	30	30
1,2,3-Trichloropropane	0.080	30	30
1,3-Dichlorobenzene	0.400	30	30
1,4-Dichlorobenzene	0.400	30	30
1,2-Dichlorobenzene	0.400	30	30
1,2-Dibromo-3-chloropropane	0.010	NA	NA

Toluene-d8 (SMC)	0.010	NA	NA

NA - These compounds have no associated %RSD or %D criteria.

Appendix B

25-mL Calibration Standard Amounts
Incos-50A & Incos-XL

CALIBRATION POINT	Amount IS/Surr Solution 50 ng/µl	Amount RAP CAL Mix 25 - 250 ng/µL *
25 µg/L	2.5 µL	25 µL
10 µg/L	2.5 µL	10 µL
5 µg/L	2.5 µL	5 µL
2 µg/L	2.5 µL	2 µL
1 µg/L	2.5 µL	1 µL

25 mL Calibration Standard Amounts
HP5973H & HP5973J with Arcon Autosamplers

CALIBRATION POINT	Amount RAP CAL Mix 25 - 250 ng/µl *
25 - 250 µg/L	50 µl
10 - 100 µg/L	20 µl
5 - 50 µg/L	10 µl
2 - 20 µg/L	4 µl
1 - 10 µg/L	2 µl

*Ketones are at 10 times the concentration of the other target compounds.

These aqueous calibration standards for HP5973H and the HP5973J are prepared at a final volume of 50mL. The Arcon autosampler automatically adds 1 uL of 125 ug/mL internal standard/surrogate to the 25mL of these standards that is used when analyzed.

ATTACHMENT A

Target Compound List and Quantitation Limits for Volatile Organic Compound Analysis

The following table lists the Target Compound list for VOC analysis. The table also includes the CAS number, internal standard reference, quantitation mass (m/z), and quantitation limits for each compound.

Compound Name	CAS Number	ISTD #	Surr #	Quant Ion (m/z)	Quantitation limits			
					Water Samples 5 mL (µg/L)	Water Samples 25 mL (µg/L)	Soil Samples (µg/Kg)	
							Low	Med
Bromochloromethane	460-0-4	1		128				
1,4-Difluorobenzene	540-36-3	2		114				
Chlorobenzene-d5	3114-55-4	3		117				
1,2-Dichloroethane-d4	17060-7-0	1	1	65				
Toluene-d8	2037-26-5	3	2	98				
4-Bromofluorobenzene	460-0-4	3	3	174				
Dichlorodifluoromethane	75-71-8	1	1	85	10	1	10	1000
Chloromethane	74-87-3	1	1	50	10	1	10	1000
Bromomethane	74-83-9	1	1	94	10	1	10	1000
Vinyl Chloride	75-1-4	1	1	62	10	0.5	10	1000
Chloroethane	75-0-3	1	1	64	10	1	10	1000
Trichlorofluoromethane	75-69-4	1	1	101	10	1	10	1000
1,1-Dichloroethene	75-35-4	1	1	96	10	1	10	1000
Acetone	67-64-1	1		43	10	10	10	1000
Carbon disulfide	75-15-0	1		76	10	1	10	1000
Methylene chloride	75-9-2	1	1	84	10	1	10	1000
trans-1,2-Dichloroethene	156-60-5	1	1	96	10	1	10	1000
Methyl Tert-Butyl Ether	1634-4-4	1		73	10	1	10	1000
1,1-Dichloroethane	75-34-3	1	1	63	10	1	10	1000
Ethyl Tert-Butyl Ether	637-92-3	1		59	10	1	10	1000
cis-1,2-Dichloroethene	156-59-2	1	1	96	10	1	10	1000
2-Butanone	78-93-3	1		43	10	10	10	1000
Chloroform	67-66-3	1	1	83	10	1	10	1000
1,2-Dichloroethane	107-6-2	1	1	62	10	0.5	10	1000
tert-Amyl methyl ether	994-05-8	1		73	10	10	10	1000
1,1,1-Trichloroethane	71-55-6	2	1	97	10	1	10	1000
Carbon tetrachloride	56-23-5	2	1	117	10	0.5	10	1000
Benzene	71-43-2	2	2	78	10	1	10	1000
Trichloroethene	79-1-6	2	1	130	10	1	10	1000
1,2-Dichloropropane	78-87-5	2	1	63	10	1	10	1000

Compound Name	CAS Number	ISTD #	Surr #	Quant Ion (m/z)	Quantitation limits			
					Water Samples 5 mL (µg/L)	Water Samples 25 mL (µg/L)	Soil Samples (µg/Kg)	
							Low	Med
Bromodichloromethane	75-27-4	2	1	83	10	1	10	1000
cis-1,3-Dichloropropene	10061-1-5	2	1	75	10	0.5	10	1000
trans-1,3-Dichloropropene	10061-2-6	2	1	75	10	0.5	10	1000
1,1,2-Trichloroethane	79-0-5	2	3	97	10	1	10	1000
Dibromochloromethane	124-48-1	2	3	129	10	1	10	1000
4-Methyl-2-Pentanone	108-10-1	3		43	10	10	10	1000
Toluene	108-88-3	3	2	92	10	1	10	1000
Tetrachloroethene	127-18-4	3	3	164	10	1	10	1000
1,3-Dichloropropane	142-28-9	3	3	76	10	1	10	1000
2-Hexanone	591-78-6	3		43	10	10	10	1000
1,2-Dibromoethane (EDB)	106-93-4	3	3	107	10	1	10	1000
Chlorobenzene	108-90-7	3	3	112	10	1	10	1000
Ethylbenzene	100-41-4	3	2	106	10	1	10	1000
p & m-Xylene	1330-20-7	3	2	106	10	1	10	1000
o-Xylene	95-47-6	3	2	106	10	1	10	1000
Styrene	100-42-5	3	2	104	10	1	10	1000
Bromoform	75-25-2	3	3	173	10	1	10	1000
1,1,2,2-Tetrachloroethane	79-34-5	3	3	83	10	1	10	1000
1,2,3-Trichloropropane	96-18-4	3	3	75	10	1	10	1000
1,3-Dichlorobenzene	541-73-1	3	3	146	10	1	10	1000
1,4-Dichlorobenzene	106-46-7	3	3	146	10	1	10	1000
1,2-Dichlorobenzene	95-50-1	3	3	146	10	1	10	1000
1,2-Dibromo-3-chloropropane	96-12-8	3	3	157	10	2	10	1000

ATTACHMENT B

PURGE & TRAP CONCENTRATOR PARAMETERS

Tekmar LSC2000 Concentrator (Incos-50A)

The operating method for the TEKMAR LSC2000 A purge & trap concentrator which is interfaced with the Incos-50A GC/MS and the Tekmar ALS2016 Autosampler is as follows.

PARAMETER	SETTING
Standby temperature	30°C
Preheat temperature	N/A
Prepurge time	N/A
Sample temperature	Ambient for waters/40°C for soils
Purge Time	11 minutes
Dry purge	1 minute
Purge Flow	35 - 40 mL/min
Desorb preheat temperature	245°C
Desorb	6.00 minutes @ 250°C
Bake	4 minutes @ 260°C
Auto drain	On for waters/Off for soils
Bake gas bypass	Off for waters/ On for soils
Valve temperature	120°C
Mount temperature	40°C
Line temperature	120°C
Bottom of trap temperature	150°C

OI 4560 Concentrator (Incos-XL)

The operating method for the OI 4560 purge & trap concentrator which is interfaced with the Incos-XL GC/MS and the DPM-16 autosampler is as follows.

PARAMETER	SETTING
Standby temperature	30°C
Preheat temperature	N/A
Prepurge time	N/A
Sample temperature	Ambient for waters
Purge Time	11 minutes
Dry purge	3 minutes
Purge Flow	35 - 40 mL/min
Desorb preheat temperature	NA
Desorb	4.00 minutes @ 250°C
Bake	5 minutes @ 260°C
Valve temperature	100°C
Mount temperature	40°C
Line temperature	100°C
DPM160 transfer line	120°C

ATTACHMENT B

PURGE & TRAP CONCENTRATOR PARAMETERS

Tekmar 3000 Concentrator (HP5973)

The operating method for the TEKMAR 3000 A purge & trap concentrator which is interfaced with the HP5973 GC/MS and Archon Autosampler is as follows.

PARAMETER	SETTING
Standby temperature	32°C
Preheat temperature	N/A
Prepurge time	N/A
Sample temperature	Ambient for waters/40°C for soils
Purge Time	11 minutes
Dry purge	2minute
Purge Flow	35 - 40 mL/min
Desorb preheat temperature	245°C
Desorb	6.00 minutes @ 250°C
Bake	6 minutes @ 260°C
Auto drain	On for waters/Off for soils
Bake gas bypass	Off for waters/ On for soils
Valve temperature	120°C
Mount temperature	40°C
Line temperature	120°C
Bottom of trap temperature	NA

ATTACHMENT C

AUTOSAMPLER PARAMETERS

Tekmar ALS2016 Autosampler

The operating method for the ALS2016 autosampler which is interfaced with the Tekmar LSC2000 and an Incos-50 GC/MS is as follows.

PARAMETER	SETTING
Valve temperature	125°C
Line temperature	120°C
Sample temperature	Ambient for waters/40°C for soils
Auto drain	On for waters/Off for soils

OI DPM-16 Autosampler

The operating method for the DPM-16 autosampler which is interfaced with the OI 4560 and the Incos-XL GC/MS is as follows.

PARAMETER	SETTING
Valve temperature	100°C
Line temperature	100°C

Archon Autosampler

The 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

ATTACHMENT D

GC PARAMETERS

HP5890 GC Incos 50 A

The operating methods for the Gas Chromatographs which are interfaced with the Finnigan Incos-50 MS are as follows:

BFB analysis

PARAMETER	SETTING
Injector temperature	220°C
Separator temperature	225°C
Column Stability time	0.5 minutes
Ion Source	180°C
Transfer Line	240°C
Initial Oven Temp	120°C
Initial Oven Time	0.2 minutes
Temperature Ramp	10°C/minute for 7 minutes
Final Oven Temp	190°C
Final Hold Time	1.0 minutes
Column Flow rate	~ 35 mL/min
Electron Energy	70 volts (nominal)

VOA analysis

PARAMETER	SETTING
Injector temperature	220°C
Separator temperature	225°C
Column Stability time	0.5 minutes
Ion Source	180°C
Transfer Line	240°C
Initial Oven Temp	10°C
Initial Oven Time	3.0 minutes
Temperature Ramp	10°C/minute for 18 minutes
Final Oven Temp	190°C
Final Hold Time	2.0 minutes
Column Flow rate	~ 35 mL/min
Electron Energy	70 volts (nominal)

Varian 3400 GC Incos-XL

The operating methods for the gas chromatographs which are interfaced with the Finnigan Incos-50 XL are as follows:

BFB analysis

PARAMETER	SETTING
Injector temperature	220°C
Column Stability time	0.5 minutes
Ion Source	180°C
Transfer Line	220°C
Initial Oven Temp	100°C
Initial Oven Time	0.5 minutes
Temperature Ramp	10°C/minute for 5.5 minutes
Oven Temp	155°C
Hold Time	0 minutes
Temperature Ramp	36°C/minute for 1.8 minutes
Final Oven Temp	220°C
Hold Time	5 minutes
GC Head Pressure	10 psi
Split Valve Open	0.5 minutes
Split Flow	20 mL/min
Electron Energy	70 volts (nominal)

VOA analysis

PARAMETER	SETTING
Injector temperature	220°C
Column Stability time	0.3 minutes
Ion Source	180°C
Transfer Line	220°C
Initial Oven Temp	0°C
Initial Oven Time	4.0 minutes
Temperature Ramp	10°C/minute for 4 minutes
Oven Temp	40°C
Hold Time	0 minutes
Temperature Ramp	8°C/minute for 12.5 minutes
Oven Temp	140°C
Hold Time	0 minutes
Temperature Ramp	31°C/minute for 1.6 minutes
Final Oven Temp	190°C
Final Hold Time	1.0 minutes
GC Head Pressure	10 psi
Split Valve Open	Always
Split Flow	20 mL/min
Electron Energy	70 volts (nominal)

HP5973 H & J

The operating methods for the gas chromatographs which are interfaced with the HP5973 are as follows:

BFB analysis

PARAMETER	SETTING
Injector temperature	200°C
Column Stability time	0.5 minutes
Ion Source	180°C
Transfer Line	200°C
Initial Oven Temp	100°C
Initial Oven Time	0.5 minutes
Temperature Ramp	10°C/minute for 5.5 minutes
Oven Temp	155°C
Hold Time	0 minutes
Temperature Ramp	36°C/minute for 1.8 minutes
Final Oven Temp	220°C
Hold Time	5 minutes
GC Head Pressure	10 psi
Split Valve Open	0.06 minutes

VOA analysis

PARAMETER	SETTING
Injector temperature	200°C
Column Stability time	0.3 minutes
Ion Source	180°C
Transfer Line	200°C
Initial Oven Temp	35°C
Initial Oven Time	3.0 minutes
Temperature Ramp	8°C/minute
Oven Temp	150°C
Hold Time	0 minutes
Temperature Ramp	20°C/minute
Oven Temp	200°C
Final Hold Time	0.62 minutes
GC Head Pressure	12.85 psi
Split Valve Open	Always
Split ratio	20.0:1

ATTACHMENT E

File Naming Convention

Sub directory naming convention
A subdirectory must be made daily where the data for that day will be stored.

MMDDYY

25 mL waters analyzed on Incos-50A on 01/31/99

X:\I50A\013199 where x: is the drive....

Instrument & Matrix Identifiers

Instrument	File Name Identifier	Matrix	File Name Identifier
Incos-50A	A	R9 Low Level Water (25mL)/524	W
Incos-50B	B	Soil (5 g Heated P & T)	S
Incos-XL	C	Water (5 mL)	Z
HP5973H	H		
HP5973J	J		

BFB
(No Matrix Identifier Required)

BF?MMDD?
The first BFB analyzed on Incos-XL on 01/05/98 = BFC0105A
The second BFB analyzed on Incos-XL on 01/05/98 = BFC0105B

Initial Calibrations
I??MMDD?

25 mL water Initial calibration analyzed on HP5973H on 01/10/98

Concentration	Calibration ID	Filename
25 µg/L	VSTD025	IWH0110A
10 µg/L	VSTD010	IWH0110B
5 µg/L	VSTD005	IWH0110C
2 µg/L	VSTD002	IWH0110D
1 µg/L	VSTD001	IWH0110E

Continuing Calibrations

C??MMDD?

First 25 mL water continuing calibration analyzed on Incos-50A on 01/11/98

CWA0111A

Laboratory Control Sample (LCS)
L??MMDD?

First LCS of the day = A
Second LCS of the day = B.....

Instrument	File ID
Incos-50A	LWA0101A
Incos-XL	LWC0530A
HP5973H	LWH0101A
HP5973J	LWJ0101A

QL Standard

Q??MMDD?
First QL standard analyzed on Incos-50A on 01/12/98

QWA0112A

Method Blanks

M??MMDD?

First blank of the day = A
Second blank of the day = B.....

Instrument	File ID/Blank ID
Incos-50A	MWA0101A
Incos-XL	MWC0530A
HP5973H	MWH0101A
HP5973J	MWJ0101A

Storage Blanks (waters only)

S??MMDD?

LAB ID = SBMMDD
where mmdd is the day the storage blank was placed in the sample refrigerator.

Instrument	File ID	LAB ID
Incos-50A	SWA0101A	SBMMDD
Incos-XL	SWC0530A	SBMMDD

HP5973H	SWH0101A	SBMMDD
HP5973J	SWJ0101A	SBMMDD

Samples including MS/MSD, Instrumnet Blanks, etc.

YY?####

YY = Federal Fiscal year (Starts October 1st)
? = Instrument Identifier
= sequential number (first sample analysis in the fiscal year = 0001)

The 100th sample analysis on Incos-XL

98C0100

Appendix B-13
Total Petroleum Hydrocarbons-CA LUFT

TOTAL PETROLEUM HYDROCARBONS (TPH) as Gasoline and Diesel

SW-846 Method 8015B (Revision 2, December 1996)

Table 1A. Summary of Contract Required Quantitation Limits, Holding Times, and Preservation for Total Petroleum Hydrocarbons (TPH) as Gasoline and Diesel

Analytical Parameter [a]	**Technical and Contract Holding Times**	**Preservation**
Total Petroleum Hydrocarbons (TPH) as Gasoline in Water Samples	Technical: 7 days from collection; Contract: 5 days from receipt at laboratory	Cool to 4°C ±2°C
TPH as Gasoline in Water Samples	Technical: 14 days from collection; Contract: 10 days from receipt at laboratory	HCl or H_2SO_4 to pH<2; Cool to 4°C ±2°C
TPH as Gasoline in Soil Samples	Technical: 48 hours Contract: 48 hours	Cool to 4°C ±2°C; sealed zero headspace containers; freezing can extend the holding time [b,c]
TPH as Gasoline in Soil Samples	Technical: 14 days from collection; Contract: 10 days from receipt at laboratory	Preserved samples: in methanol [d] or sodium bisulfate [e]
TPH as Diesel in Water Samples	Technical to Extraction: 14 days from collection; Contract to Extraction: 10 days from receipt at laboratory Technical and Contract to Analysis: 40 days from extraction	Cool to 4°C ±2°C; HCl or H_2SO_4 to pH<2 [f]
TPH as Diesel in Soil Samples	Technical to Extraction: 14 days from collection; Contract to Extraction: 10 days from receipt at laboratory Technical and Contract to Analysis: 40 days from extraction	Cool to 4°C ±2°C

[a] Individual target compounds are listed in Table 1B.
[b] Freezing the sample can extend the holding time; however, 48 hours unfrozen holding time will be considered cumulative.
[c] Use Method 5021 for headspace analysis.
[d] Use Method 5030 for purge and trap.
[e] Use Method 5035 for purge and trap.
[f] Diesel analysis does not require acidification; however, acidified samples can be analyzed for diesel.

Data Calculations and Reporting Units:

Calculate the sample results using calibration factors determined according to Sections 7.7.2 of Method 8015B and 7.4.2 and 7.8.1 of SW-846 Method 8000A.

Report water sample results in concentration units of milligrams per liter (mg/L). Report soil sample results on a dry-weight basis in milligrams per kilogram (mg/kg).

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.

All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QC results. Include an example calculation in the data package.

TABLE 1B. Target Compound List and Contract Required Detection Limits (CRQL) for SW-846 Method 8015B

COMPOUND	CRQL Water mg/L	CRQL Soil mg/kg
Gasoline - Purge and Trap	0.5	10
Gasoline - Headspace	5.0	5
Diesel	0.5	10

Table 2. Summary of Calibration Procedures for Total Petroleum Hydrocarbons (TPH) as Gasoline and Diesel by SW-846 Method 8015B

Calibration Element	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (minimum blank + 5 points for each analyte) (ICAL) [a, b, c]	Initially; whenever required, due to failure of CCV	RSD for CFs ≤20%; or, if using a linear calibration curve, a correlation coefficient (r) of ≥0.99 for each compound	1. Terminate analysis 2. Re-calibrate and verify before sample analysis
Continuing Calibration Verification (CCV) at midpoint of ICAL	Beginning of each 12 hour time period, after every 10 samples and end of run	%D between calculated amount and nominal amount within ±25%	1. Re-calibrate and verify 2. Re-analyze samples back to last good CCV
Retention time evaluation CCV standards	Each analysis of CCV standards	±3 x the SD of the avg ICAL RT for surrogate, See footnote [c] for GRO and DRO	1. Re-calibrate and verify 2. Re-analyze samples back to last good IPC

[a] The ICAL low standard must be above but near the CRQL. The low ICAL standard must have a signal to noise ratio ≥5:1. If this requirement cannot be met, the laboratory must submit a MDL study as part of the data package.

[b] Gasoline Range Organics (GRO): C_6-C_{10}; Diesel Range Organics (DRO): C_{10}-C_{28}

[c] Establish and report retention time (RT) windows for GRO and DRO as described in Section 7.4 of Method 8015B and 7.6 of Method 8000B. Calculate RT windows for GRO and DRO based on the lower limit of the RT window for the first eluting component and the upper limit of the RT window for the last eluting component. Determine RT windows for surrogate compounds as ±3 x the standard deviation (SD) of the average ICAL RT for each analyte.

Table 3. Summary of Internal Quality Control Procedures for Total Petroleum Hydrocarbons (TPH) as Gasoline and Diesel by SW-846 Method 8015B

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Gasoline: One per each 12 hour time period and after unusually concentrated samples Diesel: One per Batch or SDG[a] (1 per 20 samples minimum) and for each instrument used	< CRQL for each compound	1. Investigate source of contamination and document corrective action measures 2. Re-extract and re-analyze all samples processed with a method blank that is out-of-control
Surrogate Spike [b]	Every sample and MB at midpoint of calibration range	Water Samples: 75-125% of expected value Soil Samples: 60-125% of expected value	1. Re-analyze all samples with non-compliant surrogate recoveries
Matrix Sike and Matrix Spike Duplicate (MS/MSD)	One MS/MSD set per batch or SDG (1 MS/MSD set per 20 samples minimum)	65-135% of expected value; ≤30 RPD between MS and MSD	1. Report in case narrative
Laboratory Control Sample (LCS)	Gasoline: one each 12-hour period; Diesel: one per Batch or SDG	80-120% of expected value	1. Re-extract and re-analyze all samples processed with out-of-control LCS

[a] SDG - Sample Delivery Group - each case of field samples received; or each 20 field samples within a case; or each 14 calendar day period during which field samples in a case are received.
[b] Surrogates for GRO: 4-bromofluorobenzene and 1,1,1-trifluorotoluene;
Surrogate for DRO: hexacosane or ortho-terphenyl

Dilute and reanalyze samples with one or more analytes at concentrations exceeding the range of the calibration curve. Results for such reanalyses should fall within the mid-range of the calibration curve. Report results and submit documentation for both analyses.

Appendix B-14
TTLC Metals

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 503

DETERMINATION OF TRACE ELEMENTS IN SOLIDS BY INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETRY

Prepared by:

Stephen Carroll, ESAT Region 9, Lockheed Martin	Date

Review by:

Richard Bauer, Chemistry Team Leader	Date

Approved by:

Brenda Bettencourt, Laboratory Director	Date

Periodic Review:

Signature	Title	Date

STANDARD OPERATING PROCEDURE 503

DETERMINATION OF TRACE ELEMENTS IN WATER BY INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETRY

This SOP was prepared by Lockheed Martin for the United States Environmental Protection Agency (USEPA) under the Environmental Services Assistance Team (ESAT) contract (EPA contract No. 68D60005).

APPROVED BY:

Patrick Hirata, Senior Chemist, Lockheed Martin	Date
Sujith Kumar, QA/QC Coordinator, Lockheed Martin	Date
Jack Berges, ESAT Team Manager, Lockheed Martin	Date

ESAT Document Control Number: ESAT-9B-3939

CONTENTS

1 SCOPE AND APPLICATION 4

2 METHOD SUMMARY 5

3 DEFINITIONS 5

4 HEALTH AND SAFETY 7

5 SAMPLE HANDLING AND PRESERVATION 7

6 INTERFERENCES 7

7 APPARATUS AND MATERIALS 9

8 QUALITY CONTROL PROCEDURES 11

9 ANALYTICAL PROCEDURES 16

10 DOCUMENTATION 18

11 REFERENCES 19

Table 1: Method Analytes and Interfering Elements 20

Table 2: Calibration Standards 21

Table 3: IPC, QCS, LFB/LFM/LFMD Concentrations 22

Attachment A - Deviations from Reference Method 6010B
Attachment B - Inorganic Standards and Reagents Preparation Log Book
Attachment C - Acid Digestion Log for Metals Preparation
Attachment D - MET-1 TJA ICAP 61E Run Log
Attachment E - Analytical Spreadsheet
Attachment F - QC Summary Report
Attachment G - IEC Tables

1 SCOPE AND APPLICATION

1.1 This SOP provides procedures for the determination of trace elements in solution by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) in environmental samples. It is applicable to sediments, sludges, solids and soils. The samples are analyzed using the TJA ICAP-61E. The preparation of samples analyzed in this method is detailed in Region 9 SOP #405. This SOP is based on EPA Method 6010B and is applicable to the determination of the following elements:

Analyte	Chemical Abstract Services Registry Number (CASRN)	Current Region 9 Laboratory Quantitation Limits (mg/Kg)
Aluminum (Al)	7429-90-5	200
Antimony (Sb)	7440-36-0	20
Arsenic (As)	7440-38-2	50
Barium (Ba)	7440-39-3	10
Beryllium (Be)	7440-41-7	0.2
Boron (B)	7440-42-8	20
Cadmium (Cd)	7440-43-9	1
Calcium (Ca)	7440-70-2	100
Chromium (Cr)	7440-47-3	2
Cobalt (Co)	7440-48-4	4
Copper (Cu)	7440-50-8	4
Iron (Fe)	7439-89-6	1000
Lead (Pb)	7439-92-1	30
Magnesium (Mg)	7439-95-4	100
Manganese (Mn)	7439-96-5	10
Molybdenum (Mo)	7439-98-7	10
Nickel (Ni)	7440-02-0	50
Potassium (K)	7723-14-0	1000
Selenium (Se)	7782-49-2	50
Silver (Ag)	7440-22-4	2
Sodium (Na)	7440-23-5	100
Thallium (Tl)	7440-28-0	100
Vanadium (V)	7440-62-2	4
Zinc (Zn)	7440-66-6	4

2 METHOD SUMMARY

2.1 A representative 1 gram (wet weight) aliquot of a well-mixed sediment, sludge, solid or soil sample is accurately weighed and digested using the appropriate sample preparation method (Region 9 SOP #405).

2.2 The method describes the multi-elemental determination of trace elements in digestate solutions by ICP-AES using a simultaneous instrument. The instrument measures the characteristic atomic-line emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Photo currents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of the analytes. Background must be measured adjacent to the analyte wavelength during analysis.

3 DEFINITIONS

3.1 Analytical Sample - Any solution introduced into the ICP-AES instrument excluding calibration standards, calibration blanks, or instrument performance check samples.

3.2 Calibration Blank (CB) - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP-AES instrument.

3.3 Calibration Standard (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.4 Instrument Detection Limit (IDL) - The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength.

3.5 Instrument Performance Check Solution (IPC) - A solution of method analytes used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.6 Laboratory Fortified Blank (LFB) - An aliquot of LFB to which known quantities of the method analytes are added. The LFB 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. For this SOP, the LFB also serves as a solid laboratory control sample (LCSS).

3.7 Laboratory Fortified Sample Matrix (LFM) - An aliquot of an analytical sample to which known quantities of the method analyte is added in the laboratory. The LFM 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 analyte in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.8 Laboratory Fortified Matrix Duplicate (LFMD) - A duplicate aliquot of an analytical sample to which known quantities of analytes are added in the laboratory. The LFMD 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 concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.9 Laboratory Reagent Blank (LFB) - An aliquot of reagent water, blank sand or other blank matrix that is treated exactly as a sample. The LFB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment.

3.10 Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear.

3.11 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.

3.12 Quality Control Sample (QCS) - A solution containing known concentrations of method analytes. The QCS source must be different than the source of calibration standards. It is used to check laboratory or instrument performance.

3.13 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.

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

3.15 Solid Sample - For the purpose of this method, a sample taken from matrices classified as soil, sludge, solid or sediment.

3.16 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 interelement spectral interferences with respect to a defined set of method criteria.

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

3.18 Total Recoverable Analyte Concentration - The concentration of analyte in a solid sample after preparation by acid digestion. The sample preparation procedures are described Region 9 SOP #405.

4 HEALTH AND SAFETY

4.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Specifically, concentrated nitric and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large amounts of water for at least 15 minutes. Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing when working with these reagents.

4.2 The ICP-AES emits radio-frequency and intense UV radiation. Personnel should not stand near the plasma while the ICP is in operation.

4.3 Areas of high, lethal voltages exist within the instrument. Never touch parts of the instrument which are not intended for access by the instrument operator.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Sample handling and preservation procedures are covered in Region 9 SOP #405.

6 INTERFERENCES

6.1 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.

6.1.1 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 (interelement or molecular) or adequately corrected to reflect the same change in background intensity that occurs at the wavelength peak.

6.1.2 Spectral overlaps can be compensated for by equations that correct for the inter-element contributions, which involves measuring the interfering elements. When present and uncorrected, these interferences will produce false-positive results and be reported as analyte concentrations.

6.1.3 When interelement corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions. Interelement 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. Interelement 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. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. It should not be forgotten that some samples may contain uncommon elements that could contribute spectral interferences.

6.1.4 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, 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 interelement 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, 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.

6.1.5 When interelement corrections are **not** used, the on-going SIC solutions (Sect. 7.3.10) must be analyzed to verify the absence of interelement 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 may not be available for all matrices. In these circumstances the analyte must be determined using another approved test procedure.

6.2 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.

6.3 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.

6.4 Memory Interference - 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.

7 APPARATUS AND MATERIALS

7.1 Apparatus

7.1.1 ICP-AES System, comprised of following: Thermo Jarrell Ash Inductively Coupled Plasma-Atomic Emission Spectrometer (ICAP-61E) and Thermo Jarrell Ash Autosampler.
7.1.2 Argon gas supply (high-purity grade, 99.99%).
7.1.3 Pipettors - variable volume, LabIndustries Repipet II, or equivalent, for dispensing reagents and acids.
7.1.4 Pipettes - calibrated fixed volume and digital variable volume, Eppendorf Model 4800, or equivalent, with associated metal-free disposable pipet tips.
7.1.5 Disposable syringes with 0.45um Whatman disk filters.

7.2 Glassware and Incidentals

Note: All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives and isolated from other laboratory glassware. Please refer to Region 9 SOP 130, Glassware Cleaning Procedures, for specific instructions (reference 11.2).

7.2.1 Volumetric Class "A" Flasks - 1000-mL, 500-mL, 200-mL and 100-mL.
7.2.2 Volumetric Class "A" Pipettes - 50-mL, 25-mL, 10-mL and 5-mL.
7.2.3 Plastic or Teflon Wash Bottles.

7.3 Materials and Reagents

Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society (ACS) specifications should be used. If the purity of a reagent is in question, analyze for contamination. Record all standard and reagent preparations in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.3.1 Reagent water. All references to reagent water in this method refer to ASTM Type II grade water.

7.3.2 Hydrochloric acid, (HCl) concentrated (sp.gr. 1.19) - trace metals grade or better.

7.3.3 Nitric acid, (HNO_3) concentrated (sp.gr. 1.41) - trace metals grade or better.

7.3.4 Standard stock solutions (1000 g/mL) can be purchased from a commercial supplier such as CPI, Spex or Inorganic Ventures. The list of elements required for this method is provided in Section 1.1.

7.3.5 Calibration Standards - Calibration stock standard solutions are purchased from Inorganic Ventures and the final concentrations are listed in Table 2. Each calibration standard is prepared by diluting an appropriate amount of the calibration stock standard to 1000 mL with 2% (v/v) nitric acid/5% (v/v) hydrochloric acid.

7.3.6 Calibration Blank (CB) - Dilute concentrated nitric acid and hydrochloric acid with reagent water to obtain a 2% (v/v) nitric acid/5%(v/v) hydrochloric acid solution.

7.3.7 Rinse Blank - Dilute concentrated nitric acid and hydrochloric acid with reagent water to obtain a 2% (v/v) nitric acid/5% (v/v) hydrochloric acid solution.

7.3.8 Instrument Performance Check (IPC) Solution - The IPC solution is used to verify instrument performance during analysis. The IPC is purchased from Inorganic Ventures and consists of the same solutions used to prepare the calibration standards. The IPC is prepared by adding 2.0 mL each of the three Cal Standard solutions, and 1.0 ml of the 1000ppm individual stock standards of B, Mo, Sn, Ti and Sr and diluting to 200 mL with 2% (v/v) nitric acid/5% (v/v) hydrochloric acid. The concentrations of the IPC are given in Table 3.

7.3.9 Quality Control Sample (QCS) - Analysis of a QCS is required for the initial verification of the calibration standards and instrument performance. The QCS is purchased from Inorganic Ventures and is from a source different from the standard stock solutions and prepared with 2% (v/v) nitric acid/5% (v/v) hydrochloric acid. The concentrations of the QCS standard are given in Table 3.

7.3.10 Spectral Interference Check (SIC) solutions - When interelement corrections are applied, SIC solutions are needed containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors. The SIC solutions used are 200 mg/L Al, 300 mg/L Fe and 50 mg/L of all other SIC analytes (Exceptions are made for those SIC analytes with LDRs less than 50 mg/L. These shall be prepared at a concentration near the upper LDR) . The SIC solutions are prepared by diluting the 1000 g/mL single element stock solutions in 2% (v/v) nitric acid/5%(v/v) hydrochloric acid.

7.3.11 Profile Solution - A solution of 10 mg/L copper and manganese is needed to profile the instrument prior to analysis. The solution is made by diluting 5.0 mL each of 1000 g/mL copper and manganese stock standard to 500 mL with 2% (v/v) nitric acid/5%(v/v) hydrochloric acid.

8 QUALITY CONTROL PROCEDURES

8.1 Method Characterization - Prior to routine use of this method, there must be data available documenting initial demonstration of performance. The required data document the selection criteria of background points, linear dynamic ranges, method detection limits and inter-element correction factors.

8.2 EPA Region 9 Laboratory operates a formal quality control (QC) program. As it relates to this SOP, the QC program consists of an initial demonstration of laboratory capability (refer to Region 9 SOP #880), and the periodic analysis of laboratory solutions as a continuing check on performance.

8.2.1 LDR - The upper limit of the LDR must be established for each element used in quantifying results. Analyze a minimum of three series of standards with concentrations spanning the range from 1 to 100 times the highest calibration 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 reanalyzed. The LDR is verified every six months or whenever the analytical conditions are changed.

8.2.2 MDL - A method detection limit must be confirmed annually and must be <½ the QL or corrective action must be initiated.

8.2.3 LFB - Analyze a LFB in quadruplicate and take average results to demonstrate initial acceptable performance.

8.2.4 SIC - The laboratory must establish and initially verify an interelemental 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 limits of the calibration blank for the analyte. Once established the interferences must be verified annually, or whenever there is a change in instrument operating conditions. Only a portion of the correction routine must be verified more frequently or daily. The test criteria and the solutions are as follows:

8.2.4.1 For interferences from aluminum and iron, only those correction factors (positive or negative) when multiplied by 100 which exceed ± ½ the QL are tested daily.

8.2.4.2 For all other interfering elements, only those correction factors (positive or negative) when multiplied by 10 which exceed ± ½ the QL are tested daily.

8.2.4.3 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interfering solution should fall within a specific concentration range. The range shall be the greater of either (1) ± ½ the QL or (2) a concentration range that is calculated by multiplying 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 redetermined and updated prior to sample analysis.

8.2.4.4 If the nature of the samples analyzed is such that they do not contain concentrations of the interfering elements at the 10 mg/L level, daily verification is not required; however, all interelement spectral correction factors must be verified annually, or whenever there is a change in instrument operating conditions.

8.3 Routine Analytical Quality Control

8.3.1 Instrument performance check (IPC) solution - The laboratory must check instrument performance and verify that the instrument is properly calibrated on a continuing basis. To verify calibration, the IPC and the calibration blank are run as routine samples immediately following calibration, after every 10 analytical samples, and at the end of each run. For each analyte in the IPC, the percent recovery is calculated as follows:

$$\%R = \frac{IPC}{s} \times 100$$

where:

$\%R$	=	percent recovery.
IPC	=	measured concentration of analyte in the IPC, mg/L.
s	=	expected analyte concentration in the IPC, mg/L.

8.3.1.2 The QC criteria for initial and continuing IPC samples is ±10%. If the %R for any analyte in the IPC falls outside of the QC criteria analysis must stop. The instrument must be re-calibrated for at least the unacceptable out-of-control analytes. Once an acceptable calibration is obtained, the samples preceding the out-of-control IPC must be re-analyzed for the affected analytes.

8.3.1.3 The results for analytes measured in the CBs analyzed after IPCs are compared to the QL. If any analyte in the initial CB exceeds ½ the QL, the instrument must be recalibrated. Samples cannot be analyzed until an acceptable initial CB is analyzed. If the concentration of any analyte in a continuing CB exceeds ½ the QL, the instrument must be recalibrated

for the out-of-control analytes. Once an acceptable calibration is obtained, the samples preceding the out-of-control CB must be reanalyzed for the affected analytes.

8.3.2 QCS Analysis - The analyte concentrations in a QCS sample must be measured daily. The concentrations of analytes in the QCS are listed in Table 3. The recovery of analytes in the QCS is calculated as follows:

$$\%R = \frac{C_m}{C_t} \times 100$$

Where

$\%R$	=	relative percent recovery.
C_m	=	measured analyte concentration in the QCS, mg/L.
C_t	=	true analyte concentration in the QCS, mg/L.

The recovery must be within 90-110% or the analyses must be terminated. The cause of the poor recovery must be determined and the problem corrected. The instrument must be re-calibrated and all affected samples must be re-analyzed. If, after re-calibration, the QCS recovery still exceeds the 90-110% limits, the calibration standards and QCS standard must be re-prepared and the instrument re-calibrated.

8.3.3 QL - The accuracy of the calibration 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 run, immediately after the QCS. The recovery of analytes in the QL is calculated as follows:

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

Where

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

If the QL recovery exceeds the limits of 50 - 150%, the analysis shall be terminated. The cause of the poor recovery must be determined and the problem corrected. The instrument must be recalibrated and all affected samples must be reanalyzed. If, after re-calibration, the QL recovery still exceeds the 50-150% limits, the calibration standards must be re-prepared and the instrument re-calibrated.

8.3.4 SIC - Analyze daily SIC solutions to test interelemental spectral correction factors. If the SIC solutions do not meet the test criteria given in Section 8.2.4, 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 ½ the QL, daily verification is not required. If the corrected concentration of the analyte due to spectral interference is less than 10% the total analyte concentration, daily verification is not required.

8.3.5 LRB - The laboratory must analyze at least one LRB with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment and sample preparation reagents. LRB values that exceed the QL indicate potential laboratory or reagent contamination. If the potential contamination significantly impacts the analytical results, the LRB must be re-prepared along with the affected samples, and the affected analytes re-analyzed. Unless specified otherwise by project DQOs, the following statements describe when samples must be re-prepared:

1) If the LRB analyte concentration is ≥ the QL and the sample result is less than 5 times the LRB analyte concentration, the LRB and sample must be re-prepared and re-analyzed.

8.3.6 LFB - The laboratory must analyze at least one LFB (Section 3.6) with each batch of 20 or fewer samples of the same matrix. Calculate the percent recovery for each analyte using the following equation:

$$\%R = \frac{LFB}{s} \times 100$$

where:

%R	=	percent recovery.
LFB	=	measured concentration of analyte in the LFB, mg/L.
s	=	analyte concentration in the LFB, mg/L.

If the recovery falls outside the manufacturer's acceptance limits, re-analyze once. If the recovery still falls outside the manufacturer's acceptance limits upon re-analysis, 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 LFB must be re-prepared and re-analyzed.

8.3.7 LFM - Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. LFM results can be used to assess these matrix effects and potential impact to data usability. One LFM must be prepared for every 20 routine samples of the same matrix in a sample batch. Calculate the percent recovery for each analyte using the following equation:

$$\%R = \frac{Clfm - C}{s} \times 100$$

where:

$\%R$	=	percent recovery.
C_{lfm}	=	measured concentration of analyte in the LFM, corrected for sample preparation and any dilutions, mg/L.
C	=	measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions, mg/L.
s	=	analyte concentration in the LFM, corrected for sample preparation and any dilutions, mg/L.

If the value of ***C*** is less than 4 times the value of ***s***, the acceptance window for ***%R*** is 75-125%. If the recovery of analyte falls outside the acceptance window other QC data must be examined to determine if a matrix problem exists. If the laboratory performance is in control (i.e., the IPC, QL, QCS, and LFB results are acceptable), the poor LFM recovery is most likely matrix-related. The affected analyte result must be flagged as estimated (J) on the analytical spreadsheet and a comment added on the spreadsheet and report narrative informing the data user that matrix effects may be present in samples of similar composition.

8.3.8 LFMD - Sample homogeneity can affect the quality and interpretation of the data. LFMD results can be used to assess sample homogeneity. One LFMD must be prepared for every 20 routine samples of the same matrix in a sample batch. Calculate the relative percent difference using the following equation:

$$\%RPD = \frac{|Clfmd - Clfm|}{(Clfmd + Clfm)/2} \times 100$$

Where

$\%RPD$	=	relative percent difference.
C_{lfm}	=	measured concentration in the LFM corrected for sample preparation and any dilutions, mg/L.
C_{lfmd}	=	measured concentration in the LFMD corrected for sample preparation and any dilutions, mg/L.

If the recovery of analyte falls outside the acceptance window other QC data must be examined to determine if a matrix problem exists. If the laboratory performance is in control (i.e., the IPC, QL, QCS, and LFB results are acceptable), the poor LFMD recovery is most likely matrix-related. The affected analyte result must be flagged as estimated (J) on the analytical spreadsheet

and a comment added on the spreadsheet and report narrative informing the data user that matrix effects may be present in samples of similar composition.

The relative percent difference (RPD) between the LFM and LFMD must be $\leq$20%. If the control limits are exceeded, the affected analyte result must be flagged as estimated (J) on the analytical spreadsheet and a comment added on the spreadsheet and report narrative informing the data user that sample imprecision may be present in samples of similar composition.

9 ANALYTICAL PROCEDURES

9.1 Calibration and Analysis

9.1.1 Instrument Set-up - Check the condition of the pump tubing for wear. Replace as needed. Tighten the pump tubing on the pump. 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. Check torch for salt build up. Verify that the drain tubing is tight and check the waste container.

9.1.2 Select the appropriate method file and change the data file name to correspond to the correct day (i.e.; 10101221, indicating ICP instrument number (1), present date (year/month/day), and analytical run number(1)). Check the flush times and change to desired time, minimally 60 seconds. Save all changes.

9.1.3 Set up the autosampler table with the desired sample run. Old autosampler files may be written over and re-saved. Print the autosampler file and place the standards and samples in the racks as indicated by autosampler file and enter into the Run Log (Attachment C).

9.1.4 The Profile procedure is to align the optical path of the instrument prior to calibration and sample analysis. Profile the instrument using the 10 mg/L Cu/Mn solution (Section 7.3.11). Aspirate the profile solution and run the profile routine as per the manufacturer's procedure. Adjust the profile position with the profile adjustment knob. Repeat the procedure until the profile peak position is $\pm$0.05 as indicated by the profile plot observed on the computer monitor. Print the acceptable profile plot.

9.1.5 Calibration - A calibration blank and two mixed calibration standards (7.2.7) are presently used for calibration. The calibration standards are given in Table 2. The calibration is automatically updated in the method file as they are run.

9.1.6 Sample Analysis - After calibration the autosampler continues with the samples and QC. Load SIC solutions according to the requested analyte list. An example of a loading list for an analytical run sequence is listed in the table below:

Seq.	Desc.	Seq.	Desc.	Seq.	Desc.	Seq.	Desc.
1	IPC	13	IPC	25	IPC	37	IPC
2	CB	14	CB	26	CB	38	CB
3	QCS	15	Ti SIC	27	S7	39	S17
4	QL	16	Mo SIC	28	S8	40	S18
5	Fe SIC	17	LRB	29	S9	41	S19
6	Al SIC	18	LFB	30	S10	42	S20
7	V SIC	19	S1	31	S11	43	S20-LFM
8	Mn SIC	20	S2	32	S12	44	S20-LFMD
9	Cr SIC	21	S3	33	S13	45	IPC
10	Co SIC	22	S4	34	S14	46	CB
11	Ni SIC	23	S5	35	S15	47	
12	Cu SIC	24	S6	36	S16	48	

9.1.7 Review results for QC compliance and off-scale results. Identify samples which must be re-analyzed in a different analytical run. Samples having analytes at concentrations higher than 90% of the linear dynamic range must be diluted into range and re-analyzed.

9.2 Data Reduction and Reporting - After set-up and calibration the TJA ICAP-61E software reports results for the analyzed solution in units of mg/L. Solid samples should be reported using the following equation:

$$R = \frac{Mx(0.2L)xD}{(W)x(1Kg/1000g)x(\%solids/100)}$$

where:

R	=	final reported concentration, in mg/Kg.
M	=	measured concentration reported by instrument, in mg/L.
D	=	dilution factor, to account for dilution performed after sample preparation.
W	=	Weight of sample, in grams.

The concentrations reported by the instrument must be corrected for any dilutions performed as part of the sample preparation or analysis process. 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 ½ the QL. Values between ½ 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.

10 DOCUMENTATION

10.1 Acid Digestion Log for Metals Preparation - Entries are made for the case number, SDG number, date of preparation, date of completion, site name, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, initial aliquot volume or weight, pH of sample (if applicable), concentration and volume of added acids and final volume of digestate. A copy of the acid digestion log for metals digestion must be submitted with the raw data. The digestion log is maintained in Room 302. (Attachment C)

10.2 MET-1 TJA ICAP 61E Run Log - Entries are made for the case number, SDG number, date of analysis, site name, file name, analyst initials, lab sample IDs, client sample IDs, and comments, if any. The run log is maintained in Room 303. (Attachment D)

10.3 Inorganic Standards and Reagents Preparation Log Book - Copies of all standard solution preparation entries (CAL, IPC, QCS, QL, SIC, LFM, LFMD, etc.) must be submitted with each data package. (Attachment B)

10.4 ESAT Region 9 Laboratory Solids Determination Log - Copies of all solids determination entries must be submitted along with the calculated dry weight with each data package.

10.5 Report Narrative and Deliverable

The data package consists of the report narrative, reports, and data, as listed in the table below.

Data Package Contents
Report Narrative: Discusses any problems encountered, both technical and administrative, the corrective action taken, and the resolution. All universal analytical flags should also be discussed in the report narrative.
Tabulated sample results on an analytical spreadsheet, with units, sample collection dates, client sample IDs, laboratory IDs and station locations. (Attachment E)
LRB data included on the analytical spreadsheet. (Attachment E)
LFM and LFM duplicate results on a QC summary report with calculated relative percent difference (RPD). (Attachment F)
LFM, LFM duplicate and LFB results on a QC summary report with calculated percent recoveries (%R). (Attachment F)
Raw sample, standard and QC data, including run logs and any work sheets, if applicable. (Attachments B, C and D)

11 REFERENCES

11.1 U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Method 3050B, Acid Digestion of Sediments, Sludges, and Soils, Revision 2, December 1996.

11.2 U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Method 6010B, Inductively Coupled Plasma - Atomic Emission Spectrometry, Revision 2, December 1996.

11.3 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed.; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1996; SW-846.

11.4 Region 9 SOP 405, *Preparation of Solid Samples for GFAA and ICP-AES Analysis.*

11.5 Region 9 SOP 125, *Sample Disposal.*

11.6 Region 9 SOP 130, *Glassware Cleaning Procedures.*

11.7 Region 9 SOP 840, *Notebook Documentation and Control.*

11.8 Region 9 SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency.*

Table 1 - Method Analytes and Potential Interfering Elements

Analyte	Wavelength - nm	Interfering Elements
Al	308.215	Mn, Mo, Ti, V, Fe
Sb	206.838	Cr, Mo, Ni, Ti, V, Sn, Zn
As	193.696	Al, Cr, Fe, Ti, V
Ba	493.409*	Fe
Be	313.042	Mo, Ti, V
B	249.678	Fe, Ni, Co
Cd	226.502	Co, Fe, Mo, Ti, Ni
Ca	317.933	Mn, Mo, Ti, V, Cr
Cr	267.716	Cd, Mn, Mo, Ti, V
Co	228.616	Cd, Cr, Ba, Mo, Ti, Ni, Fe
Cu	324.754	Mo, Ti, V, Fe
Fe	259.940	Mn, Mo, V
Pb	220.353	Al, Co, Fe, Mo, Ni, Ti
Mg	279.079	Co, Cr, Mn, Mo, Ti, V
Mn	257.610	Al, Mo, V
Mo	202.030	Fe
Ni	231.604	Tl, Sb
K	766.491	None
Se	196.026	Co
Ag	328.068	Mn, Mo, Ti, V
Na	588.995	None
Sr	421.553*	None
Tl	190.894	Co, Fe, Mo, V
Sn	189.989	Ti
Ti	334.941	Co, Cr
V	292.402	Cr, Fe, Mn, Mo, Ti
Zn	213.856	Co, Cu, Mo, Ni, Ti, V, Fe

* Wavelengths other than those recommended by Method 6010B.

Table 2 - Current Calibration Standard Concentrations*

Analyte	Solution	Concentration mg/L	Analyte	Solution	Concentration mg/L
Al	S1	20.0	Ag	S1	2.5
Sb	S1	10.0	Na	S1	50.0
As	S1	10.0	Tl	S1	10.0
Ba	S1	2.0	V	S1	5.0
Cd	S1	5.0	Zn	S1	5.0
Ca	S1	50.0	B	S2	5.0
Cr	S1	2.0	Mo	S2	5.0
Co	S1	5.0	Sr	S2	5.0
Cu	S1	2.5	Sn	S2	5.0
Fe	S1	10.0	Ti	S2	5.0
Pb	S1	10.0			
Mg	S1	50.0			
Mn	S1	5.0			
Ni	S1	5.0			
K	S1	50.0			
Se	S1	10.0			

* Stock standard solutions are purchased as concentrated solutions and diluted by a factor of 100 to prepare the calibration standards. B, Mo, Sr, Sn and Ti are prepared with appropriate dilutions from 1000 g/mL single element stock standard solutions. Additional calibration standards can be prepared from 1000 g/mL or 10,000 g/mL single element stock standard solutions as needed.

Table 3 - IPC, QCS, LFM/LFMD Concentrations

Analyte	IPC - mg/L	QCS - mg/L	LFM/LFMD - mg/L
Al	4.0	2.0	0.5
Sb	2.0	1.0	2.0
As	2.0	1.0	2.0
Ba	4.0	2.0	2.0
Be	0.1	0.05	0.05
B	1.0	0.5	2.0
Cd	1.0	0.5	0.05
Ca	10.0	5.0	10.0
Cr	0.4	0.2	0.2
Co	1.0	0.5	0.50
Cu	0.5	0.25	0.25
Fe	2.0	1.0	1.0
Pb	2.0	1.0	0.5
Mg	10.0	5.0	10.0
Mn	1.0	0.5	0.50
Mo	1.0	0.5	0.50
Ni	1.0	0.5	0.50
K	10.0	5.0	10.0
Se	2.0	1.0	2.0
Ag	0.5	0.25	0.05
Na	10.0	5.0	10.0
Sr	1.0	0.5	N/A
Tl	2.0	1.0	2.0
Sn	1.0	0.5	N/A
Ti	1.0	0.5	N/A
V	1.0	0.5	0.50
Zn	1.0	0.5	0.50

Attachment A:
Deviations From Reference Method 6010B

A.1 The following differences in nomenclature from Method 6010B are used at Region 9: IPC for CCV, QCS for ICV, SIC for ICS and LFB for LCS.

A.2 The scope of this SOP does not include the digestion of solid samples.

A.3 Calibration blank acceptance criteria was changed to ½ the QL.

A.4 SIC acceptance criteria was changed to ½ the QL.

A.5 The minimum concentration of interfering element considered to be significant was changed to 10 mg/L instead of $\pm$ one reporting limit from zero.

A.6 SICs will be calculated annually, or whenever there is a change in instrument operating conditions, rather than every six months.

Attachment G:

CURRENT 6010B IEC 08/31/00

(Table exp 06/20/01)

ALUMINUM
QL - 1.000 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Fe	-.000104		N	06/20/00
Mn	.000724		N	06/20/00
Mo	.018		N	06/20/00
Ti	-.000174		N	06/20/00
V	.01433		N	06/20/00

ANTIMONY
QL - 0.100 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Cr	.012507	**+/-.063**	Y	06/20/00
Mo	.004045		N	06/20/00
Ni	-.002389		N	06/20/00
Sn	-.01489	**+/-.074**	Y	06/20/00
Ti	.000999		N	06/20/00
V	-.007536	**+/-.050**	Y	06/20/00
Zn	-.000379		N	06/20/00

ARSENIC
QL - 0.250 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Al	.004282	**+/-.125**	Y	06/20/00
Cr	.001509		N	06/20/00
Fe	.000433		N	06/20/00
Ti	.000816		N	06/20/00
V	.016552	**+/-0.125**	Y	06/20/00

BARIUM
QL 0.050 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Fe	.000004		N	06/20/00

BERYLLIUM
QL - 0.001 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Mo	-.000044		N	06/20/00
Ti	.00001		N	06/20/00
V	-.000964	**+/-.0039**	Y	06/20/00

BORON
QL - 0.100 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Co	-.000256		N	06/20/00
Fe	.001797	**+/-.054**	Y	06/20/00
Ni	.00135		N	06/20/00

CADMIUM
QL - 0.005 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Co	.000112		N	06/20/00
Fe	.000104	**+/-.0031**	Y	06/20/00
Mo	.000088		N	06/20/00
Ni	-.000106		N	06/20/00
Ti	.000147		N	06/20/00

CALCIUM
QL - 0.500 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Cr	.000558		N	06/20/00
Mn	.000134		N	06/20/00
Mo	.000261		N	06/20/00
Ti	.000093		N	06/20/00
V	.000483		N	06/20/00

CHROMIUM
QL - 0.010 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Cd	-.000401		N	06/20/00
Mn	.000225		N	06/20/00
Mo	.00019		N	06/20/00
Ti	.000053		N	06/20/00
V	-.00131	+/-.0052	Y	06/20/00

COBALT
QL - 0.020 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Ba	-.000352		N	06/20/00
Cd	.000251		N	06/20/00
Cr	.000139		N	06/20/00
Fe	.000045		N	06/20/00
Mo	.000174		N	06/20/00
Ni	.000296		N	06/20/00
Ti	.001728	+/-0.010	Y	06/20/00

COPPER
QL - 0.020 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Fe	.000017		N	06/20/00
Mo	.000343		N	06/20/00
Ti	-.000463		N	06/20/00
V	-.00029		N	06/20/00

IRON
QL - 1.000 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Mn	-.003035		N	06/20/00
Mo	-.000351		N	06/20/00

LEAD
QL - 0.150 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Al	.000894	**+/-.075**	Y	06/20/00
Co	-.002368		N	06/20/00
Fe	.000124		N	06/20/00
Mo	.0001095		N	06/20/00
Ni	.000397		N	06/20/00
Ti	.000554		N	06/20/00

MAGNESIUM
QL - 0.500 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Co	-.000749		N	06/20/00
Cr	-.000611		N	06/20/00
Mn	-.004926		N	06/20/00
Mo	-.032707	**+/-.250**	Y	06/20/00
Ti	-.004694		N	06/20/00
Ti	-.000263		N	06/20/00

MANGANESE
QL -0.050 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Al	.00001		N	06/20/00
Mo	-.000117		N	06/20/00
V	-.000138		N	06/20/00

MOLYBDENUM
QL - 0.050 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Fe	-.000044		N	06/20/00

NICKEL
QL -0.050 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Sb	-.000954		N	06/20/00
Tl	-.000411		N	06/20/00

SELENIUM
QL -0.250 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Co	.000892		N	06/20/00

SILVER
QL -0.010 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Mn	000048		N	06/20/00
Mo	-.000312		N	N
Ti	-.000051		N	06/20/00
V	-.003692	+/-.015	Y	06/20/00

SILVER
QL -0.010 mg/L

Mo	-.000312		N	06/20/00
Ti	-.000051		N	06/20/00
V	-.003692	**+/-.015**	Y	06/20/00

THALLIUM
QL -0.500 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Co	-.004901		N	06/20/00
Fe	.000815		N	06/20/00
Mo	-.016425		N	06/20/00
V	.0026		N	06/20/00

TIN
QL - 0.100 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Ti	-.0268	N/A	Y	06/20/00

TITANIUM
MDL -0.010 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Cr	.000232		N	06/20/00
Co	.000014		N	06/20/00

VANADIUM
QL -0.020 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Cr	.000167		N	06/20/00
Fe	.000088		N	06/20/00
Mn	-.00007		N	06/20/00
Mo	-.012259	**+/-.061**	Y	06/20/00
Ti	.000589		N	06/20/00

ZINC
QL -0.020 mg/L

Affecting Elem	Factor	QC Limits	Daily Y/N	Date Determined
Co	-.000063		N	06/20/00
Cu	.002248	**+/-.011**	Y	06/20/00
Fe	.000076		N	06/20/00
Mo	-.000065		N	06/20/00
Ni	.004131	**+/-.021**	Y	06/20/00
Ti	.000131		N	06/20/00
V	.000068		N	06/20/00

The test to see if ICS must be run daily is as follows: For Al and Fe, multiply the IEC factor by 100 and compare to ½ the QL. For all others, multiply by 10 and compare to ½ the QL. All factors that exceed ½ the QL after the multiplication must be tested daily.

Al, Fe, Cr, Cu, Fe, Mo, Ni, Sn, Ti and V IECs must be tested daily and are presented in bold. Al and Sn may be mixed, as no common interferences occur with these two elements. Fe and Cr may be mixed, though As, Co and V have commom interferences with these two interferents, they do not require daily testing. The other ICS solutions shall be run individually. The concentration of Fe is 300ppm. the concentration of Al is 200ppm. The concentrations for all others are 50ppm (V is limited to 40ppm due to linear range constraints).

Acceptance criteria is the greater of (1) +/- ½ the QL or (2) a range found by multiplying the factor by the concentration of the ICS and dividing by 10.

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 405

PREPARATION OF SOLID SAMPLES FOR GFAA AND ICP-AES ANALYSIS

Prepared by:

Osellie Salvador, ESAT Region 9, ICF Consulting	Date

Review by:

Richard Bauer, Chemistry Team Leader	Date

Approved by:

Brenda Bettencourt, Laboratory Director	Date

Periodic Review:

Signature	Title	Date

STANDARD OPERATING PROCEDURE 405

PREPARATION OF SOLID SAMPLES FOR GFAA AND ICP-AES ANALYSIS

This SOP was prepared by ICF Consulting for the United States Environmental Protection Agency (USEPA) under the Environmental Services Assistance Team (ESAT) contract (EPA contract No. 68-W-01-028).

APPROVED BY:

Osellie Salvador, Inorganic Group Leader	Date
Surender Kaushik, QA Task Manager	Date
Jerry Vail, ESAT Program Manager	Date

ESAT Document Control Number: B0101000-0375

CONTENTS

1 SCOPE AND APPLICATION 4

2 METHOD SUMMARY 5

3 DEFINITIONS 5

4 HEALTH AND SAFETY 6

5 SAMPLE HANDLING AND PRESERVATION 7

6 INTERFERENCES 7

7 APPARATUS AND MATERIALS 7

8 QUALITY CONTROL PROCEDURES 9

9 ANALYTICAL PROCEDURES 10

10 DOCUMENTATION 14

11 REFERENCES 14

Attachment A - Deviations from Reference Method (EPA 3050B)

Attachment B - Acid Digestion Log for Metals Preparation

Attachment C - Inorganic Standards and Reagents Preparation Log Book

1 SCOPE AND APPLICATION

1.1 This method provides two separate sample preparation procedures, one for the preparation of sediment, sludge and soil samples for analysis by Graphite Furnace Atomic Absorption (GFAA) and one for the preparation of sediment, sludge and soil samples for analysis by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES). The analyses of samples prepared in this method is detailed in Region 9 SOPs 503 and 513. This SOP is based on EPA Method 3050B and is applicable for the following analytes:

Analyte	Chemical Abstract Services Registry Number (CASRN)
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Boron (B)	7440-42-8
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-98-7
Nickel (Ni)	7440-02-0
Potassium (K)	7723-14-0
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Strontium (Sr)	7440-28-6
Thallium (Tl)	7440-28-0
Tin (Sn)	7440-31-5
Vanadium (V)	7440-62-2

Zinc (Zn) 7440-66-6

1.2 This method is not a **total** digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment. If absolute total digestion is required use Method 3052.

2 METHOD SUMMARY

2.1 For the digestion of solid samples, a representative 1 gram (wet weight) sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2).

2.2 For GFAA analysis, the resultant digestate is reduced in volume while heating and then diluted to a final volume of 200 mL. The digestate is analyzed using the Perkin-Elmer 5100 graphite furnace atomic absorption spectrophotometer and is detailed in Region 9 SOP 513.

2.3 For ICP-AES analysis, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed and then diluted to a final volume of 200 mL. The digestate is analyzed using the Thermo Jarrell Ash ICP-61E atomic emission spectrophotometer and is detailed in Region 9 SOP 503.

2.4 A separate sample aliquot shall be dried for a total percent solids determination.

3 DEFINITIONS

3.1 Analytical Sample - Any sample in which metals are being determined, excluding standards, method blanks, or QC reference samples.

3.2 Field Duplicates (FD) - Two separate samples collected at the same time and placed 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.

3.3 Laboratory Fortified Blank (LFB) - An aliquot of a characterized solid matrix with the elements of interest, or alternatively, an aliquot of blank matrix to which known quantities of the elements of interest are added in the laboratory. The LFB 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. For this SOP, the LFB also serves as a solid laboratory control sample (LCSS).

3.4 Laboratory Fortified Sample Matrix (LFM) - An aliquot of an analytical sample to which known quantities of the method analyte is added in the laboratory. The LFM 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 analyte in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.5 Laboratory Fortified Matrix Duplicate (LFMD) - A duplicate aliquot of an analytical sample to which known quantities of analytes are added in the laboratory. The LFMD 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 concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.6 Laboratory Reagent Blank (LRB) - An aliquot of blank matrix 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.

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

3.8 Solid Sample - For the purpose of this method, a sample taken from matrices classified as soil, sludge, solid or sediment.

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

4 HEALTH AND SAFETY

4.1 The toxicity and carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in the library and Room 413 for additional information.

4.2 Hydrogen peroxide, concentrated nitric and hydrochloric acids present various hazards and according to MSDS may be fatal and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood and if eye or skin contact occurs, flush with large amounts of water for at least 15 minutes or if inhalation occurs, remove to fresh air. Contact the Inorganic Group Leader

or Health & Safety and Env. Compliance Task Manager immediately to determine if additional treatment is required.

4.3 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples must be done in a fume hood. Use of safety glasses and acid resistant gloves is required whenever handling concentrated acids or metals standards.

4.4 Areas of high, lethal voltages exist within the hot block digestor. Never touch parts of the hot block digestor which are not intended for access by the operator.

4.5 Digestion of samples must be done in a fume hood.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Samples should be collected in wide mouth glass jars with screw caps with plastic liners. All jars must be thoroughly cleaned and rinsed with reagent water. Sample collected should be sufficient to insure a representative sample, allow for replicate analysis, allow for percent solids determinations and minimize waste disposal.

5.2 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. Any deviations from the preservation requirements must be noted in the report narrative.

5.3 Samples must be received and stored at 4 ±2 °C. Any deviations from the 4 ±2 °C temperature requirements must be noted in the report narrative.

5.4 The technical holding time for properly preserved samples is six months.

6 INTERFERENCES

6.1 In sample preparation, contamination is of prime concern. The work area, including bench tops and fume hoods, should be periodically cleaned in order to eliminate environmental contamination.

7 APPARATUS AND MATERIALS

7.1 Apparatus

7.1.1 Environmental Express Hot Block Digestion apparatus, 36-place or 54-place, or equivalent.
7.1.2 Analytical balance capable of weighing to the nearest 0.01 g.
7.1.3 Pipettors - variable volume, LabIndustries Repipet II, or equivalent, for dispensing reagents and acids.
7.1.4 Pipettes - calibrated fixed volume and digital variable volume, Eppendorf Model 4800, or equivalent, with appropriate plastic tips.
7.1.5 Polycarbonate racks.

7.2 Glassware and Incidentals

7.2.1 Volumetric Class "A" Flasks - 1000-mL, 500-mL, 200-mL and 100-mL.
7.2.2 Volumetric Class "A" Pipettes - 50-mL, 25-mL, 10-mL and 5-mL.
7.2.3 100-mL plastic graduated cylinders.
7.2.4 250-mL LDPE bottles with screw caps, ESS part #0250-1010, or equivalent.
7.2.5 Plastic powder funnels.
7.2.6 Whatman 41 filter paper.
7.2.7 Plastic or Teflon Wash Bottles.
7.2.8 50-mL polypropylene digestion vessel, Environmental Express part #SC499, or equivalent.
7.2.9 Class "S" weights.
7.2.10 Polypropylene watch glasses, Environmental Express part #SC505, or equivalent.
7.2.11 Stainless steel or Teflon spatulas.

7.3 Materials and Reagents

Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society (ACS) specifications should be used. If the purity of a reagent is in question, analyze for contamination. Record all standard and reagent preparations in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.3.1 Reagent water - All references to reagent water in this method refer to ASTM Type II grade water.

7.3.2 Nitric Acid (HNO_3), concentrated, ACS Reagent Grade or better, suitable for trace metals analysis.

7.3.3 Hydrochloric Acid (HCl), concentrated, ACS Reagent Grade or better, suitable for trace metals analysis.

Note: Concentrated nitric and hydrochloric acids present various hazards and according to MSDS may be fatal and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood. The use of heavy gloves is recommended when working with hydrochloric acid.

7.3.4 Nitric acid (1+1) - Add 1000 mL concentrated HNO_3 (7.3.2) to 800 mL reagent water and dilute to 2L. Store in a clean glass 2.5L bottle.

7.3.5 30% Hydrogen Peroxide (H_2O_2) - ACS Reagent Grade or better, suitable for trace metals analysis.

7.3.6 Standard stock solutions can be purchased from a reputable supplier such as JTBaker, Spex or Inorganic Ventures. These solutions (usually made at concentrations of 1000 *ug*/mL or 10,000 *ug*/mL) have a shelf life of one year and come with NIST-traceable documentation. The use of these standards is the most convenient and time-saving approach.

7.3.6.1 Arsenic - 1000 *ug*/mL ICP Standard, Inorganic Ventures, Spex, CPI or equivalent.
7.3.6.2 Lead - 1000 *ug*/mL ICP Standard, Inorganic Ventures, Spex, CPI or equivalent.
7.3.6.3 Selenium - 1000 *ug*/mL ICP Standard, Inorganic Ventures, Spex, CPI or equivalent.
7.3.6.4 Thallium - 1000 *ug*/mL ICP Standard, Inorganic Ventures, Spex, CPI or equivalent.
7.3.6.5 Boron - 10,000 *ug*/mL ICP Standard, Inorganic Ventures, Spex, CPI or equivalent.
7.3.6.6 Molybdenum - 1000 *ug*/mL ICP Standard, Inorganic Ventures, Spex, CPI or equivalent.

7.3.7 Cation Spiking Solution, 5000 *ug*/mL each calcium, magnesium, potassium and sodium, CPI part #4400-ICAL1-100 or equivalent.

7.3.8 Soil Spike Concentrate Solution, 2000 *ug*/mL each aluminum, arsenic, barium, selenium, thallium, 1000 *ug*/mL iron, 500 *ug*/mL each antimony, cobalt, lead, manganese, nickel, vanadium, zinc, 250 *ug*/mL copper, 200 *ug*/mL chromium, 50 *ug*/mL each beryllium, cadmium, silver, Inorganic Ventures part #CLPP-SPK-SET or equivalent.

7.3.9 GFAA Laboratory Fortified Matrix spiking solution - Pipet 0.40 mL each of arsenic (7.3.6.1), lead (7.3.6.2), selenium (7.3.6.3) and thallium (7.3.6.4) into 50 mL reagent water, add 2.0 mL of nitric acid (7.3.2) and dilute to 100 mL with reagent water. The concentration of this spiking solution is 4.0 mg/L arsenic, lead, selenium and thallium. Addition of 2.0 mL of this spiking solution to 1 gram of soil sample and dilution to the final volume of 200 mL will produce a LFM of 40 *ug*/L arsenic, lead, selenium and thallium in the digestate.

7.3.10 ICP-AES Laboratory Fortified Matrix spiking solution - Pipet 10 mL soil spike concentrate (7.3.8), 20 mL of cation spiking solution (7.3.7), 5.0 mL of molybdenum (7.3.6.6) and 2.0 mL

boron into 10.0 mL reagent water, add 2.0 mL of nitric acid (7.3.2) and dilute to 100 mL with reagent water. The concentration of this spiking solution is 1000 mg/L calcium, magnesium, potassium, sodium, 200 mg/L aluminum, arsenic, barium, boron, selenium, thallium, 100 mg/L iron, 50 mg/L antimony, cobalt, lead, manganese, molybdenum, nickel, vanadium, zinc, 25 mg/L copper, 20 mg/L chromium, and 5.0 mg/L beryllium, cadmium, silver. Addition of 2.0 mL of this spiking solution to 1 gram of soil sample and dilution to the final volume of 200 mL will produce a LFM of 10.0 mg/L calcium, magnesium, potassium, sodium, 2.0 mg/L aluminum, arsenic, barium, boron, selenium, thallium, 1.0 mg/L iron, 0.50 mg/L antimony, cobalt, lead, manganese, molybdenum, nickel, vanadium, zinc, 0.25 mg/L copper, 0.20 mg/L chromium, and 0.05 mg/L beryllium, cadmium, silver.

7.3.11 Solid Laboratory Control Sample - Order a solid laboratory control sample from a manufacturer such as E.R.A. or the QATS contractor. This solid should have concentrations of arsenic, lead, selenium and thallium at least 10 times greater than the quantitation limit. This will be used as the LFB for solid samples.

8 QUALITY CONTROL PROCEDURES

8.1 Specific quality control procedures for QA/QC samples prepared in this SOP are provided in Region 9 Laboratory SOP #513 "Determination of Arsenic, Lead, Selenium and Thallium in Solids by Graphite Furnace Atomic Absorption Spectrophotometry" and SOP #503 "Determination of Trace Elements in Solids by Inductively-Coupled Plasma - Atomic Emission Spectrometry." The preparation of the QA/QC samples are detailed in Section 9.4.

8.2 A LRB and a LFB must be prepared and digested for each batch of 20 samples of the same matrix or for every SDG, whichever is more frequent. An additional LRB and LFB must be prepared for each subsequent batch of 20 samples or for every subsequent SDG. For example, a set of 30 sediment samples would require 2 LRBs and 2 LFBs.

8.3 One LFM and one LFM duplicate must be prepared for every 20 routine samples of the same matrix in a sample batch (e.g., 1 LFM and 1 LFM duplicate for a batch containing 1-20 routine samples, 2 LFMs and 2 LFM duplicates for a batch containing 21-40 routine samples, etc.).

8.4 One batch of 20 samples may contain samples from several sites or SDGs. In this case the matrix QC (Section 8.3) must be prepared for each site or SDG but multiple sets of the rest of the QC samples (LRB and LFB) are not required.

9 ANALYTICAL PROCEDURES

9.1 Initiate a Metals Digestion Log, one for each batch of samples to be digested, before beginning with any preparations. Prepare a removable label for each sample using the VPP Labelmaker. Complete the Metals Digestion Log as given in Section 10.1 and Attachment B. Most samples will require both the ICP-AES and GFAA digestions. However, there may be occasions where only the ICP-AES or GFAA analyses are required. Check the technical direction form (TDF) for the requested analyses.

9.2 ICP-AES Solid Sample Preparation

9.2.1 Mix the sample thoroughly and weigh out a representative 1.0 $\pm$0.05g aliquot in a 50-mL polypropylene digestion vessel. Large rocks, branches and other nonfriable materials should not be used in the digestion. Decant any standing water into a waste container. (**Note**: Do **NOT** decant RCRA waste samples - check with the EPA TOPO regarding decanting of standing water for RCRA projects). Record the sample weight in the Metals Digestion Log. Perform percent solids determination on another aliquot following Region 9 SOP 460.

9.2.2 To the vessel add 10.0 mL of (1+1) HNO_3 and mix the slurry. Cover the vessel with a watch glass. Place the vessel into a polycarbonate rack and place in the hot block for reflux digestion of the analytes. The hot block must be located in a fume hood and previously adjusted to provide a reflux temperature of approximately 95°C. (See the following note.)

Note: For proper heating adjust the temperature control of the hot block such that an uncovered digestion vessel containing 50 mL of water placed in the hot block can be maintained at a temperature approximately but no higher than 85°C. (Once the vessel is covered with a watch glass the temperature of the water will rise to approximately 95°C.)

9.2.3 Heat the sample and gently reflux for 15 minutes without boiling. Remove the rack(s) containing the digestion vessels from the hot block and allow the samples to cool to room temperature.

9.2.4 To the vessel add 5.0 mL of conc. HNO_3, replace the cover and mix the slurry. Place the rack(s) containing the digestion vessels back into the hot block and reflux for approximately 3 hours. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5.0 mL of conc. HNO_3) ONCE. If brown fumes continue to be given off the sample will require preparation using microwave digestion (Region 9 SOP 420). The sample volume should be less than 10 mL after the 3 hour digestion period. Remove the rack(s) containing the digestion vessels from the hot block and allow the samples to cool to room temperature.

9.2.5 To the vessel add 2.0 mL reagent water and 3.0 mL 30% H_2O_2 (7.3.5), replace the cover and mix the slurry. Place the rack(s) containing the digestion vessels back into the hot block and gently warm the samples for one minute. (Note: **This step must be monitored closely.** Hydrogen

peroxide will react with the sample and excessively vigorous effervescence will cause the sample to overflow out of the digestion vessel if the sample is allowed to heat! Samples which boil over are to be discarded and re-prepared with appropriate QC.) Remove the rack(s) containing the digestion vessels from the hot block and allow the samples to cool to room temperature.

9.2.6 To the vessel add an additional 3.0 mL 30% H_2O_2 (7.3.5), replace the cover and mix the slurry. Place the rack(s) containing the digestion vessels back into the hot block and warm the samples for one minute (see Note in 9.2.5). If vigorous effervescence still occurs, continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. Do not add more than 10 mL 30% H_2O_2. Remove the rack(s) containing the digestion vessels from the hot block and allow the samples to cool to room temperature.

9.2.7 To the vessel add 10.0 mL conc. HCl (7.3.3), replace the cover and mix the slurry. Place the rack(s) containing the digestion vessels back into the hot block and gently warm the samples for one minute (see Note in 9.2.5). Remove the rack(s) containing the digestion vessels from the hot block and allow the samples to cool to room temperature.

9.2.8 Quantitatively transfer the digest to a Whatman 41 filter paper and collect the digest in a 100-mL graduated cylinder. Dilute to volume with reagent water and transfer to an acid-washed 250-mL LDPE bottle. Wash down the sides of the same filter paper with reagent water and collect the rinsings in the same 100-mL graduated cylinder. Dilute to volume with reagent water and add the rinsings to the original sample filtrate and mix. The final volume of digestate is now 200 mL. The sample digestate is now ready for analysis.

9.2.9 The Acid Digestion Log for Metals Preparation needs to be peer-reviewed for completeness and signed off by the reviewer. Make a copy to accompany the digestates. The digestates are now ready for analysis by inductively-coupled plasma - atomic emission spectrometry (ICP-AES), Region 9 SOP #503.

9.3 GFAA Solid Sample Preparation

9.3.1 Mix the sample thoroughly and weigh out a representative 1.0 $\pm$0.05g aliquot in a 50-mL polypropylene digestion vessel. Large rocks, branches and other nonfriable materials should not be used in the digestion. Decant any standing water into a waste container. (**Note**: Do **NOT** decant RCRA waste samples - check with the EPA TOPO regarding decanting of standing water for RCRA projects). Record the sample weight in the Metals Digestion Log. Perform percent solids determination on another aliquot following Region 9 SOP 460.

9.3.2 To the vessel add 10.0 mL of (1+1) HNO_3 and mix the slurry. Cover the vessel with a watch glass. Place the vessel into a polycarbonate rack and place in the hot block for reflux digestion of the analytes. The hot block must be located in a fume hood and previously adjusted to provide a reflux temperature of approximately 95°C. (See the following note.)

Note: For proper heating adjust the temperature control of the hot block such that an uncovered digestion vessel containing 50 mL of water placed in the hot block can be maintained at a temperature approximately but no higher than 85°C. (Once the vessel is covered with a watch glass the temperature of the water will rise to approximately 95°C.)

9.3.3 Heat the sample and gently reflux for 15 minutes without boiling. Remove the rack(s) containing the digestion vessels from the hot block and allow the samples to cool to room temperature.

9.3.4 To the vessel add 5.0 mL of conc. HNO_3, replace the cover and mix the slurry. Place the rack(s) containing the digestion vessels back into the hot block and reflux for approximately 3 hours. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5.0 mL of conc. HNO_3) ONCE. If brown fumes continue to be given off the sample will require preparation using microwave digestion (Region 9 SOP 420). The sample volume should be less than 10 mL after the 3 hour digestion period. Remove the rack(s) containing the digestion vessels from the hot block and allow the samples to cool to room temperature.

9.3.5 To the vessel add 2.0 mL reagent water and 3.0 mL 30% H_2O_2 (7.3.5), replace the cover and mix the slurry. Place the rack(s) containing the digestion vessels back into the hot block and gently warm the samples for one minute. (Note: **This step must be monitored closely.** Hydrogen peroxide will react with the sample and excessively vigorous effervescence will cause the sample to overflow out of the digestion vessel if the sample is allowed to heat! Samples which boil over are to be discarded and re-prepared with appropriate QC.) Remove the rack(s) containing the digestion vessels from the hot block and allow the samples to cool to room temperature.

9.3.6 To the vessel add an additional 3.0 mL 30% H_2O_2 (7.3.5), replace the cover and mix the slurry. Place the rack(s) containing the digestion vessels back into the hot block and warm the samples for one minute (see Note in 9.2.5). If vigorous effervescence still occurs, continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. Do not add more than 10 mL 30% H_2O_2. Remove the rack(s) containing the digestion vessels from the hot block and allow the samples to cool to room temperature.

9.3.7 Quantitatively transfer the digest to a Whatman 41 filter paper and collect the digest in a 100-mL graduated cylinder. Dilute to volume with reagent water and transfer to an acid-washed 250-mL LDPE bottle. Wash down the sides of the same filter paper with reagent water and collect the

rinsings in the same 100-mL graduated cylinder. Dilute to volume with reagent water and add the rinsings to the original sample filtrate and mix. The final volume of digestate is now 200 mL. The sample digestate is now ready for analysis.

9.3.8 The Acid Digestion Log for Metals Preparation needs to be peer-reviewed for completeness and signed off by the reviewer. Make a copy to accompany the digestates. The digestates are now ready for analysis by graphite furnace atomic absorption (GFAA), Region 9 SOP #513.

9.4 Quality Control Sample Preparation for Solids

Refer to Section 8 of this SOP for a discussion of the frequency of QC sample preparation.

9.4.1 LRB Preparation - Weigh 1.00 gram of blank sand into a 50-mL digestion vessel. Process as described in Section 9.2. Weigh 1.00 gram of blank sand into a 50-mL digestion vessel. Process as described in Section 9.3.

9.4.2 LFB Preparation - Weigh 1.00 gram of the solid characterized soil sample (7.3.11) into a 50-mL digestion vessel. Process as described in Section 9.2. Weigh 1.00 gram of the solid characterized soil sample (7.3.11) into a 50-mL digestion vessel. Process as described in Section 9.3.

9.4.3 LFM preparation - Transfer 1.00 grams of the designated QC sample into a 50-mL digestion vessel. Pipet 2.0 mL of ICP-AES laboratory fortified matrix spiking solution (7.3.10) onto the sample. Select a second QC sample for LFM preparation if there are more than 20 samples in the batch. Process as described in Section 9.2. Transfer 1.00 gram of the designated QC sample into a 50-mL digestion vessel. Pipet 2.0 mL of GFAA laboratory fortified matrix spiking solution (7.3.9) onto the sample. Select a second QC sample for LFM preparation if there are more than 20 samples in the batch. Process as described in Section 9.3.

9.4.4 LFMD preparation - Transfer 1.00 gram of the designated QC sample into a 50-mL digestion vessel. Pipet 2.0 mL of ICP-AES laboratory fortified matrix spiking solution (7.3.10) onto the sample. Select a second QC sample for LFMD preparation if there are more than 20 samples in the batch. Process as described in Section 9.2. Transfer 1.00 gram of the designated QC sample into a 50-mL digestion vessel. Pipet 2.0 mL of GFAA laboratory fortified matrix spiking solution (7.3.9) onto the sample. Select a second QC sample for LFMD preparation if there are more than 20 samples in the batch. Process as described in Section 9.3.

10 DOCUMENTATION

10.1 Acid Digestion Log for Metals Preparation - Entries are made for the case number, SDG number, date of preparation, date of completion, site name, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, initial aliquot volume or weight, pH of sample (if applicable), concentration and volume of added acids and final volume of digestate. A copy of the acid digestion log for metals digestion must be submitted with the raw data. The digestion log is maintained in Room 302.

10.2 Standards Documentation - Copies of all standard solution preparation entries (LFM, LFB, spiking solutions, etc.) must be submitted with each raw data package.

11 REFERENCES

11.1 U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Method 3050B, Acid Digestion of Sediments, Sludges, and Soils, Revision 2, December 1996.
11.2 U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Method 6010B, Inductively Coupled Plasma - Atomic Emission Spectrometry, Revision 2, December 1996.
11.3 U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Method 7010, Graphite Furnace Atomic Absorption Spectrophotometry, Revision 0, January 1998.
11.4 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed.; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1996; SW-846.

11.5 Region 9 SOP 503, *Determination of Trace Elements in Solids by Inductively-Coupled Plasma - Atomic Emission Spectrometry.*
11.6 Region 9 SOP 513, *Determination of Arsenic, Lead, Selenium and Thallium in Solids by Graphite Furnace Atomic Absorption Spectrophotometry.*
11.7 Region 9 SOP 125, *Sample Disposal.*
11.8 Region 9 SOP 110, *Sample Receipt, Log-in and Storage.*
11.9 Region 9 SOP 420, *Microwave Digestion of Solid Samples.*
11.10 Region 9 SOP 840, *Notebook Documentation and Control.*
11.11 Region 9 SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency.*

Attachment A
Deviations From Reference Method (EPA 3050B)

A.1 Analytical procedures are documented in Region 9 SOPs 503 and 513.

A.2. Sample digestates are brought up to a final volume of 200 mL. The reference method uses a final volume of 100 mL.

A.3. Two 3.0 mL aliquots of 30% H_2O_2 are added to each sample initially. The reference method uses 3.0 mL and then 1.0 mL increments up to 10 mL of 30% H_2O_2

A.4 A hot block digestion apparatus is used instead of a hot plate. Digestion times have been increased for the addition of the conc. HNO_3 and decreased for the addition of H_2O_2 and HCl.

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 517

ANALYSIS OF SOLID SAMPLES FOR MERCURY

Prepared by:

Patrick Hirata, ESAT Region 9, Lockheed Martin	Date

Review by:

Richard Bauer, Chemistry Team Leader	Date

Approved by:

Brenda Bettencourt, Laboratory Director	Date

Periodic Review:

Signature	Title	Date

STANDARD OPERATING PROCEDURE 517

ANALYSIS OF SOLID SAMPLES FOR MERCURY

This SOP was prepared by Lockheed Martin for the United States Environmental Protection Agency (USEPA) under the Environmental Services Assistance Team (ESAT) contract (EPA contract No. 68D60005).

APPROVED BY:

Patrick Hirata, Senior Chemist, Lockheed Martin	Date
Sujith Kumar, QA/QC Coordinator, Lockheed Martin	Date
Jack Berges, ESAT Team Manager, Lockheed Martin	Date

ESAT Document Control Number: ESAT-9B-3941

CONTENTS

1 SCOPE AND APPLICATION 4

2 METHOD SUMMARY 4

3 DEFINITIONS 4

4 HEALTH AND SAFETY 6

5 SAMPLE HANDLING AND PRESERVATION 6

6 INTERFERENCES 7

7 APPARATUS AND MATERIALS 7

8 QUALITY CONTROL PROCEDURES 10

9 ANALYTICAL PROCEDURES 14

10 DOCUMENTATION 20

11 REFERENCES 21

Attachment A - Deviations from Reference Method (EPA 7471B)

Attachment B - Inorganic Standards and Reagents Preparation Log Book

Attachment C - Mercury Digestion Log

Attachment D - Leeman PS200 Mercury Run Log

Attachment E - Analytical Spreadsheet

Attachment F - QC Summary Report

1 SCOPE AND APPLICATION

1.1 This SOP describes the standard and sample preparation steps of solid samples and the instrumental analytical procedures for mercury by cold vapor atomic absorption (CVAA) The samples are analyzed using the Leeman PS200 Automated Mercury Analyzer. This method is applicable for the preparation of soils, solids, sludges and tissues for total mercury (organic + inorganic) by EPA Method 7471B.

1.2 The Region 9 Laboratory quantitation limit (QL) is 0.04 mg/Kg for total mercury analyzed using the Leeman PS200.

2 METHOD SUMMARY

2.1 An aliquot of a solid sample is transferred to a BOD bottle or equivalent closed-system container. The sample is digested with aqua regia, and a dilute potassium permanganate-potassium persulfate solution for 30 minutes at 95 °C. The digestion oxidizes all forms of mercury to Hg(II). The Hg(II) in the digested sample is reduced with stannous sulfate to elemental mercury which is sparged from the sample and detected by atomic absorption.

3 DEFINITIONS

3.1 Analytical Sample - Any sample in which mercury is being determined, excluding standards, method blanks, or QC reference samples.

3.2 Calibration Blank (CB) - A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes.

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

3.4 Field Duplicates (FD) - Two separate samples collected at the same time and placed 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.

3.5 Instrument Performance Check Solution (IPC) - A standard containing mercury which is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout an analysis sequence.

3.6 Laboratory Fortified Blank (LFB) - An aliquot of a characterized solid matrix with the elements of interest, or alternatively, an aliquot of blank matrix to which known quantities of the elements of interest are added in the laboratory. The LFB 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. For this SOP, the LFB also serves as a solid laboratory control sample (LCSS). The Region 9 Laboratory currently uses a LFB with a true mercury concentration of 12.3 mg/Kg (acceptable range is 7.8 to 16.9 mg/Kg).

3.7 Laboratory Fortified Sample Matrix (LFM) - An aliquot of an analytical sample to which known quantities of mercury is added in the laboratory. The LFM 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 analyte in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.8 Laboratory Fortified Matrix Duplicate (LFMD) - A duplicate aliquot of an analytical sample to which known quantities of mercury is added in the laboratory. The LFMD 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 concentrations of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.9 Laboratory Reagent Blank (LRB) - An aliquot of reagent water or other blank matrix 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.

3.10 Performance Evaluation Sample (PE) - A mercury solid sample obtained from a second-source (Environmental Resource Associates, QATS or equivalent) and distributed by the Region 9 Laboratory QA officer for analysis. Results of analyses are used by the Region 9 Laboratory to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.

3.11 Quality Control Sample (QCS) - An independent solution of mercury of known concentration. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance with externally prepared test materials.

3.12 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 dataquality. Region 9 laboratory currently has a QL standard of 0.2 μg/L (which corresponds to 0.04 mg/Kg for total mercury in solid).

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

3.14 Solid Sample - For the purpose of this method, a sample taken from matrices classified as soil, sludge, solid or tissue.

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

4 HEALTH AND SAFETY

4.1 The toxicity and carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. Specifically, concentrated nitric and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large amounts of water for at least 15 minutes. Contact your Supervisor or Health and Safety Coordinator to determine if additional treatment is required.

4.2 Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Exhaust or carrier gases should be vented to a fume hood. The analyst should use chemical resistant gloves when handling concentrated mercury standards.

4.3 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

4.4 Areas of high, lethal voltages exist within the water bath. Never touch parts of the water bath which are not intended for access by the operator.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Samples should be collected in pre-cleaned glass jars. Approximately 20 grams should be sufficient to insure a representative sample, percent solids determination, allow for replicate analysis and minimize waste disposal.

5.2 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 Samples must be received and stored at 4 ± 2 °C. Any deviations from the 4 ± 2 °C temperature requirements must be noted in the report narrative.

5.4 Holding Time - The maximum sample holding time for mercury is 28 days from the time of collection.

6 INTERFERENCES

6.1 Interferences have been reported for waters containing sulfide, chloride, copper and tellurium. Organic compounds which have broad band UV absorbance (around 253.7 nm) are confirmed interferences. The concentration levels for interferants are difficult to define. This suggests that quality control procedures (Sect. 8) must be strictly followed.

6.2 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).

6.3 Volatile materials (e.g. chlorine) which absorb at 253.7 nm will cause a positive interference. The Leeman PS200 Automated Mercury Analyzer mixes digested sample and stannous sulfate reductant in a liquid/gas separator. Any interfering volatile materials should be eliminated during this mixing step.

7 APPARATUS AND MATERIALS

7.1 Apparatus

7.1.1 Leeman PS200 Mercury Analyzer - includes optical cell, mercury lamp, peristaltic pump, drying tube, liquid/gas separator, sample and reagent tubing and Leeman PS200 software.

7.1.2 Okidata Microline 320 printer, or equivalent.

7.1.3 Stirrer plate and stirring bars.
7.1.4 50-mL plastic standard cups (Leeman P/N 116-2102).
7.1.5 Disposable borosilicate autosampler vials, 16x100 mm (VWR P/N 60825-618)
7.1.6 Class "S" weights.
7.1.7 Plastic or Teflon spray bottle.
7.1.8 Analytical balance capable of weighing to the nearest 0.01 g.
7.1.9 Pipettors - variable volume, LabIndustries Repipet II, or equivalent, for dispensing reagents and acids.
7.1.10 Pipettes - calibrated fixed volume and digital variable volume, Eppendorf Model 4800, or equivalent, with appropriate trace metals-free plastic tips.
7.1.11 Water bath capable of maintaining 95 ± 5 °C with 2 to 3 cu. ft. capacity.

7.2 Glassware and Incidentals

7.2.1 Volumetric Class "A" Flasks - 1000-mL, 500-mL, 250-mL and 100-mL.
7.2.2 Volumetric Class "A" Pipettes - 50-mL, 25-mL, 10-mL and 5-mL.
7.2.3 300-mL BOD bottles, or equivalent.
7.2.4 100-mL plastic graduated cylinders.
7.2.5 Quartz wool or glass wool.
7.2.6 Glass or teflon stirring rod.
7.2.7 Stainless steel spatulas.

7.3 Materials and Reagents

Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society (ACS) specifications should be used. If the purity of a reagent is in question, analyze for contamination. Record all standard and reagent preparations in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.3.1 Reagent water - All references to reagent water in this method refer to ASTM Type II grade water.
7.3.2 Nitric Acid (HNO_3), concentrated, ACS Reagent Grade or better, suitable for trace metals analysis.
7.3.3 Hydrochloric Acid (HCl), concentrated, ACS Reagent Grade or better, suitable for trace metals analysis.
7.3.4 Sulfuric Acid (H_2SO_4), concentrated, ACS Reagent Grade or better, suitable for trace metals analysis.
7.3.5 Potassium permanganate, $KMnO_4$, ACS Reagent Grade or better, suitable for mercury determination.

7.3.6 Potassium persulfate, $K_2S_2O_8$, ACS Reagent Grade or better, suitable for mercury determination.

7.3.7 Hydroxylamine hydrochloride, $NH_2OH \cdot HCl$, ACS Reagent Grade or better, suitable for mercury determination.

7.3.8 Sodium chloride, NaCl, ACS Reagent Grade or better, suitable for mercury determination.

7.3.9 5% Potassium permanganate solution - Dissolve 125 g of potassium permanganate (7.3.5) in 2500 mL of reagent water. Prepare fresh every 6 months.

7.3.10 5% Potassium persulfate solution - Dissolve 125 g of potassium persulfate (7.3.6) in 2500 mL of reagent water. Prepare fresh every 6 months.

7.3.11 12% Sodium chloride-Hydroxylamine hydrochloride solution - Dissolve 120 g of hydroxylamine hydrochloride (7.3.7) and 120 g of sodium chloride (7.3.8) in 1000 mL of reagent water. Prepare fresh every 6 months.

7.3.12 1000 *ug*/mL Mercury Primary Stock Standard - JT Baker, CPI or equivalent.

7.3.13 1000 *ug*/mL Mercury Secondary Stock Standard - SPEX, Inorganic Ventures or equivalent (used for QCS analysis).

7.3.14 Aqua Regia - Prepare immediately before use by carefully adding 3 volumes of concentrated HCl (7.3.3) to one volume of concentrated HNO_3 (7.3.2).
Note: 5 mL of aqua regia is needed for each standard and sample. Prepare enough aqua regia for the entire analytical batch.

7.3.15 Stannous chloride, $SnCl_2$, ACS Reagent Grade or better, suitable for mercury determination.

7.3.16 10% $SnCl_2$ in 10% H_2SO_4 - Dissolve 100 g of stannous chloride (7.3.15) in 100 mL H_2SO_4 (7.3.4) and dilute to 1L with reagent water. Place a stirring bar into the solution. Prepare fresh monthly.

7.3.17 Argon gas, ICP grade.

7.3.18 Magnesium perchlorate (Anhydrone), granular or powder.

7.3.19 10% HCl - Add 200 mL HCl (7.3.3) to approximately 1.5 liters reagent water and dilute to 2L with reagent water.

7.3.20 Solid Laboratory Control Sample - Order a solid laboratory control sample from a manufacturer such as E.R.A. or the B.P.A. QATS contractor. This solid should have a concentration of mercury at least 10 times greater than the quantitation limit. The current solid laboratory control sample has a true mercury concentration of 12.3 mg/Kg. This will be used as the LFB for solid samples.

7.4 Standards Preparation

7.4.1 Mercury Primary Working Standard, 10 mg/L. Prepare by pipetting 1.00 mL of 1000 *ug*/mL mercury primary stock standard into a 100-mL Class A volumetric flask containing 50 mL of reagent water. Add 1.0 mL concentrated HNO_3, dilute to volume with reagent water and mix. Prepare this standard monthly.

7.4.2 Mercury Primary Daily Standard, 100 *ug*/L. Prepare by pipetting 1.00 mL of 10 mg/L mercury primary working standard into a 100 mL Class A volumetric flask containing 50 mL of reagent water. Add 1.0 mL concentrated nitric acid, dilute to volume with reagent water and mix. Prepare daily. This 100 *ug*/L mercury primary working standard will be used for calibration standards, IPC, QL, LFB, LFM and LFMD solutions.

7.4.3 Mercury Secondary Working Standard, 10 mg/L. Prepare by pipetting 1.00 mL of 1000 *ug*/mL mercury secondary stock standard into a 100-mL Class A volumetric flask containing 50 mL of reagent water. Add 1.0 mL concentrated HNO_3, dilute to volume with reagent water and mix. Prepare this standard monthly.

7.4.4 Mercury Secondary Daily Standard, 100 *ug*/L. Prepare by pipetting 1.00 mL of 10 mg/L mercury secondary working standard into a 100-mL Class A volumetric flask containing 50 mL of reagent water. Add 1.0 mL concentrated HNO_3, dilute to volume with reagent water and mix. Prepare daily. This 100 *ug*/L mercury secondary working standard will be used for the QCS solution.

8 QUALITY CONTROL PROCEDURES

8.1 EPA Region 9 Laboratory operates a formal quality control (QC) program. As it relates to this SOP, the QC program consists of an initial 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.

8.2 Initial Demonstration of Proficiency - Prior to use in routine analysis, each analyst must perform the procedures noted in Region 9 Laboratory SOP 880.

8.3 Routine Analytical Quality Control

8.3.1 Calibrate the instrument using the standards prepared in Section 9.4. Check the correlation coefficient (r); the correlation coefficient of the curve must be $\geq$0.995 or the instrument must be re-calibrated. All five standards and the blank **MUST** be used when determining the correlation coefficient.

8.3.2 IPC - The accuracy and stability of the calibration is verified by the periodic analysis of an IPC standard. It must be analyzed immediately after calibration, after every 10 samples, and at the end of an analytical run. The concentration of mercury in the IPC is 2.0 μg/L. The recovery of mercury in the IPC is 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 IPC, μg/L.

Recovery of the IPC analyzed immediately after calibration must be within 95-105% or the analysis must be terminated. Subsequent analyses of the IPC solution must be within 90 - 110% or the analyses must be terminated. The cause of the poor recovery must be determined and the problem corrected. The instrument must be re-calibrated and all samples not bracketed by acceptable IPC results must be re-analyzed.

8.3.3 CB - The stability of the calibration curve baseline must be monitored by analyzing a CB immediately after every IPC standard. If the absolute value of the CB result is less than ½ the QL, the result is acceptable. If the absolute value of the CB result equals or exceeds ½ the QL, the analysis must be terminated. 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.

8.3.4 QCS Analysis - The mercury concentrations in a QCS sample must be measured daily or once per batch of 20 samples, whichever is more frequent. The concentration of mercury in the QCS is 2.0 μg/L. The recovery of mercury in the QCS is calculated as follows:

$$\%R = \frac{Cm}{Ct} \times 100$$

Where

$\%R$	=	relative percent recovery.
C_m	=	measured mercury concentration in the QCS, μg/L.
C_t	=	true mercury concentration in the QCS, μg/L.

The recovery must be within 90-110% or the analyses must be terminated. The cause of the poor recovery must be determined and the problem corrected. The instrument must be re-calibrated and all affected samples must be re-analyzed. If, after re-calibration, the QCS recovery still exceeds the 90-110% limits, the calibration standards and QCS standard must be re-prepared and the instrument re-calibrated.

8.3.5 QL - The accuracy of the calibration at the quantitation limit shall be verified by the periodic analysis of an QL standard. The QL must be analyzed at the beginning of each analytical run, immediately after the QCS. The concentration of mercury in the QL is 0.2 μg/L. The recovery of mercury in the QL is 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 mercury in the QL, μg/L.

If the QL recovery exceeds the limits of 50-150%, the analysis shall be terminated. The cause of the poor recovery must be determined and the problem corrected. The instrument must be re-calibrated and all affected samples must be re-analyzed. If, after re-calibration, the QL recovery still exceeds the 50-150% limits, the calibration standards must be re-prepared and the instrument re-calibrated.

8.3.6 LRB - The laboratory must analyze at least one LRB daily or with each batch of 20 or fewer samples of the same matrix, whichever is more frequent. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the QL indicate potential laboratory contamination. If the potential contamination significantly impacts the analytical results, the LRB must be re-prepared along with the affected samples, and re-analyzed. Unless specified otherwise by project DQOs, the following statements describe when samples must be re-prepared and re-analyzed:

1) If the LRB analyte concentration is $\geq$ the QL and the sample result is less than 5 times the LRB analyte concentration, the LRB and sample must be re-prepared and re-analyzed.

8.3.7 LFB - The laboratory must analyze at least one LFB daily or with each batch of 20 or fewer samples of the same matrix, whichever is more frequent. The Region 9 Laboratory currently uses a LFB with a true mercury concentration of 12.3 mg/Kg (acceptable range is 7.8 to 16.9 mg/Kg). The recovery of mercury in the LFB is calculated as follows:

$$\%R = \frac{LFB}{s} \times 100$$

Where

$\%R$	=	percent recovery.

LFB	=	measured concentration of mercury in the LFB, mg/Kg.
s	=	expected mercury concentration in the LFB, mg/Kg.

The recovery of mercury in the LFB must be within the manufacturer's acceptance limits. If the recovery of mercury exceeds the limits, it is judged to be out-of-control, and the source of the problem must be identified and resolved before continuing analyses.

8.3.8 LFM - The LFM is designed to provide information about the effect of sample matrix on the measurement system. One LFM must be prepared for every 20 routine samples of the same matrix in a sample batch (e.g., 1 LFM for a batch containing 1-20 routine samples, 2 LFMs for a batch containing 21-40 routine samples, etc.). Homogenize the routine sample selected as the LFM, obtain a representative aliquot, and proceed with sample preparation and analysis, treating the LFM sample as a routine sample. The recovery of mercury in the LFM is calculated as follows:

$$\%R = \frac{C_{lfm} - C}{s} \times 100$$

Where

$\%R$	=	percent recovery.
C_{lfm}	=	measured concentration in the LFM corrected for sample preparation and any dilutions, mg/Kg.
C	=	measured concentration of mercury in the routine sample corrected for sample preparation and any dilutions, mg/Kg.
s	=	expected mercury concentration in the LFM, corrected for sample preparation and any dilutions, mg/Kg.

If the value of C is less than 4 times the value of s, the acceptance window for $\%R$ is 75-125%. If the recovery of mercury falls outside the acceptance window other QC data must be examined to determine if a matrix problem exists. If the laboratory performance is in control (i.e., the IPC, QL, QCS, and LFB results are acceptable), the poor LFM recovery is most likely matrix-related. The affected mercury result should be flagged as estimated (J) on the analytical spreadsheet and a comment added on the spreadsheet and report narrative informing the data user that matrix effects may be present in samples of similar composition.

8.3.9 LFMD - Sample homogeneity can affect the quality and interpretation of the data. LFMD results can be used to assess sample homogeneity. One LFMD must be prepared for every 20 routine samples of the same matrix in a sample batch (e.g., 1 LFMD for a batch containing 1-20 routine samples, 2 LFMDs for a batch containing 21-40 routine samples, etc.). Homogenize the routine sample selected as the LFMD, obtain a representative aliquot, and proceed with sample

preparation and analysis, treating the LFMD sample as a routine sample. Calculate the recovery of mercury in the LFMD as in Section 8.3.8. Calculate the relative percent difference using the following equation:

$$\%RPD = \frac{|C_{lfmd} - C_{lfm}|}{(C_{lfmd} + C_{lfm})/2} \times 100$$

Where

$\%RPD$ = relative percent difference.

C_{lfm} = measured concentration in the LFM corrected for sample preparation and any dilutions, mg/Kg.

C_{lfmd} = measured concentration in the LFMD corrected for sample preparation and any dilutions, mg/Kg.

If the recovery of mercury falls outside the acceptance window other QC data must be examined to determine if a matrix problem exists. If the laboratory performance is in control (i.e., the IPC, QL, QCS, and LFB results are acceptable), the poor LFMD recovery is most likely matrix-related. The affected mercury result should be flagged as estimated (J) on the analytical spreadsheet and a comment added on the spreadsheet and report narrative informing the data user that matrix effects may be present in samples of similar composition.
The relative percent difference (RPD) must be $\leq$20%. If the control limits are exceeded, the affected mercury result should be flagged as estimated (J) on the analytical spreadsheet and a comment added on the spreadsheet and report narrative informing the data user that sample imprecision may be present in samples of similar composition.

8.4 A set of six calibration standards, an IPC standard, a CB, a QL standard and a QCS standard must be prepared for a SDG or with a batch of similar samples. Multiple SDGs or batches may be digested and analyzed with the set of calibration standards as long as each of the LFM and LFMD samples are spiked with the same mercury primary daily standard which were used to prepare the calibration standards, IPC and QL standards.

8.5 A LRB and a LFB must be prepared and digested for each batch of 20 samples of the same matrix. An additional LRB and LFB must be prepared for each subsequent batch of 20 samples. For example, a set of 30 solid samples would require 2 LRBs and 2 LFBs.

8.6 One LFM and one LFMD must be prepared for every 20 routine samples of the same matrix in a sample batch or SDG (e.g. 1 LFM and 1 LFMD for a batch containing 1-20 routine samples, 2 LFMs and 2 LFMDs for a batch containing 21-40 routine samples, etc.)

8.7 One batch of 20 samples may contain samples from several sites or SDGs. In this case the matrix QC (Sections 8.3.8 and 8.3.9) must be prepared for each site or SDG but multiple sets of the rest of the QC samples are not required.

9 ANALYTICAL PROCEDURES

9.1 Initiate a Mercury Digestion Log, one for each batch of samples to be digested, before beginning with any preparations. Complete the Mercury Digestion Log as given in Sections 9.5.5, 9.5.6, 9.5.7, 9.5.8 and Attachment C.

9.2 Balance Calibration Verification - On a daily basis, prior to use, check the analytical balance with Class S weights of 200 mg, 1 g, 10 g and 100 g. The relative difference between the measured weight and the certified weight must be less than 0.5 %. The results of the balance verification must be recorded in the balance logbook.

9.3 Solid Sample Preparation. On a laboratory cart or bench top in the designated sample prep area, arrange the samples in alpha-numeric order according to laboratory ID. Place a corresponding 300-mL BOD bottle in front of each sample and record the BOD bottle number in the digestion log for each sample.

9.3.1 Weigh approximately 0.5 grams of a well-mixed sample to the 300-mL BOD bottle. Large rocks, branches and other nonfriable materials should not be used in the digestion. Decant any standing water into a waste container. (**Note**: Do **NOT** decant RCRA waste samples - check with the EPA work assignment manager (WAM) regarding decanting of standing water for RCRA projects). Record the sample weight in the preparation log. Add 15 mL of reagent water. Swirl the bottle to mix.

9.3.2 Add 5 mL of aqua regia (7.3.14). Swirl the bottle to mix.

9.3.3 Heat at 95 $\pm$5°C on a hot plate for two minutes. Allow to cool to room temperature.

9.3.4 Add 35 mL reagent water and 15 mL of the 5% potassium permanganate solution (7.3.9) and swirl the bottle to mix. The solution should turn a purplish color.

NOTE: 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, MnO_2, which 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. If additional potassium permanganate is required, that amount must be added to all standards and samples. (The calibration curve is generated assuming that the volumes of samples and standards are constant, approximately 134 mL. 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 + reagent volume.)

9.3.5 Add 8 mL of the 5% potassium persulfate solution (7.3.10) and swirl the bottle to mix.

9.3.6 Place the 300-mL BOD bottles containing the samples in the water bath for 30 minutes at 95 $\pm$5°C. Record the time the samples were placed in the water bath and the initial temperature (in °C).

9.3.7 At the end of the 30 minute heating period, remove the bottles from the water bath, mix well, and allow to cool to room temperature.

NOTE: All calibration standard, QA/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 30 minute water bath digestion repeated.

9.3.8 Add 50 mL of reagent water and 6 mL of the sodium chloride-hydroxylamine hydrochloride solution (7.3.11) 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 3 mL increments until the purple color disappears. If additional sodium chloride- hydroxylamine solution is required, that amount must be added to **all** standards and samples. 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 is required, that amount must be added to **all** standards and samples.

9.3.9 The completed Mercury Digestion Log must be peer-reviewed for completeness and correctness and signed off by the reviewer. A copy of the log is made and should accompany the digestates.

9.4 Leeman PS200 Calibration Standards. Prepare calibration standards by pipetting 0.0, 0.2, 0.5, 1.0, 5.0 and 15.0 mL aliquots of the 100 *ug*/L mercury primary daily standard (Sect.

7.4.2) to a series of 300-mL BOD bottles. Dilute the standard aliquots to 15 mL with reagent water and process as described in Sections 9.3.2 through 9.3.9. (Note: If additional potassium permanganate was added to ANY sample, the same amount of potassium permanganate must be added to **all** standards and samples to keep the sample + reagent volumes constant.)

Calibration Standard ID	mL 100 *ug*/L Daily Standard Solution	Reagent water volume added to Daily Standard Solution (mL)	Final Standard Concentration after addition of reagents and reagent water (*ug*/L)
S1	0	15	0
S2	0.2	~15	0.2
S3	0.5	14.5	0.5
S4	1.0	14	1.0
S5	5.0	10	5.0
S6	15.0	0	15.0

9.5 Quality Control Sample Preparation

Refer to Section 8 of this SOP for a discussion of the frequency of QC sample preparation.

9.5.1 IPC Preparation. Pipet 2.0 mL of 100 *ug*/L mercury primary daily standard (7.4.2) into a 300-mL BOD bottle and add 98 mL of reagent water. The concentration of the QL is 2.0 *ug*/L. Process as described in Sections 9.3.2 through 9.3.9.

9.5.2 CB Preparation. Transfer 100 mL of reagent water to a 300-mL BOD bottle. Process as described in Sections 9.3.2 through 9.3.9.

9.5.3 QL Standard Preparation. Pipet 200 *u*L of 100 *ug*/L mercury primary daily standard (7.4.2) into a 300-mL BOD bottle and add 100 mL of reagent water. The concentration of the QL is 0.2 *ug*/L. Process as described in Sections 9.3.2 through 9.3.9.

9.5.4 QCS Preparation. Pipet 2.0 mL of 100 *ug*/L mercury secondary daily standard (7.4.4) into a 300-mL BOD bottle and add 98.0 mL of reagent water. The concentration of the QCS is 2.0 *ug*/L. Process as described in Sections 9.3.2 through 9.3.9.

9.5.5 LRB Preparation. Transfer 15 mL of reagent water to a 300-mL BOD bottle. Process as described in Sections 9.3.2 through 9.3.9.

9.5.6 LFB Preparation. Weigh 0.5 grams of LFB into a 300-mL BOD bottle. Record the sample weight in the preparation log. The concentration of the LFB is 12.3 mg/Kg. Process as described in Sections 9.3.2 through 9.3.9.

9.5.7 LFM Preparation. Weigh approximately 0.5 grams of a well-mixed sample designated as the QC sample to the 300-mL BOD bottle. Record the sample weight in the preparation log. Add 15 mL of reagent water. Swirl the bottle to mix. Pipet 2.0 mL of 100 *ug*/L mercury primary daily standard (7.4.2) into the sample. Mix well. Select a second QC sample for

LFM preparation if there are more than 20 samples in the batch. The concentration of the LFM is 2.0 *ug*/L. Process as described in Sections 9.3.2 through 9.3.9.

9.5.8 LFMD Preparation. Weigh approximately 0.5 grams of a well-mixed sample designated as the QC sample to the 300-mL BOD bottle. Record the sample weight in the preparation log. Pipet 2.0 mL of 100 *ug*/L mercury primary daily standard (7.4.2) into the sample. Mix well. Select a second QC sample for LFMD preparation if there are more than 20 samples in the batch. The concentration of the LFMD is 2.0 *ug*/L. Process as described in Sections 9.3.2 through 9.3.9.

9.6 Calibration and Standardization for the Leeman PS200 Automated Mercury Analyzer - 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. Typical operating parameters for the Leeman PS200 Automated Mercury Analyzer are as follows:

Parameter	Setting
Argon Flow Rate	0.30 LPM
Pump Rate	5.0 mL/min

9.7 Analytical Run Sequence (Leeman PS200 Automated Mercury Analyzer)

9.7.1 Set-up and configure the instrument and data system. The Leeman PS200 mercury analyzer will be operational from a cold start (i.e. Leeman PS200 turned off) after an approximate 2.5 hour warm-up period. Inspect the pump tubing for pinching. Replace the pump tubing if excessive wear is apparent. Clamp the pump tubings in the holder and snap to seal. Prepare a fresh magnesium perchlorate drying tube by inserting some glass or quartz wool into a clean, dry drying tube, and

adding magnesium perchlorate to fill the tube up to the neck. Tap the tube to allow magnesium perchlorate to settle (do not compact the magnesium perchlorate), plug the drying tube with some more glass or quartz wool and attach the drying-tube fittings so that they are finger-tight. Pour out the reservoir containing reagent water into

a waste container and add 10% hydrochloric acid (7.3.19) to a level approximately 1 inch from the top. Lightly oil the autosampler traverse arm and wipe clean.

9.7.2 After the 2.5 hour warm-up sequence has been completed, check the aperture reading by getting into the **Utility** menu and then into the **Diagnostics** menu. The aperture should be -100 to +100 (an ideal reading is zero); if not, take off the front panel of the PS200 and, using the hex wrench provided, gently adjust the bottom nut (if the value is negative) or the top nut (if the value is positive) so that the aperture reading is within the range and then replace the front panel. Use the **User Name** menu to enter analyst initials and then get back to the **Main Menu**. Select the **Protocol** (Mercury) and enter in a file name (for example, 20012061 which corresponds to instrument #2 (the Leeman PS200), the date (12/06/00), and the first run of the day(1)). Transfer the calibration standards (in order, 0, 0.2, 0.5, 1.0, 5.0 and 15.0 μg/L mercury) into the first 6 spots in the 50mL standards tube rack. Place the bottle of 10% $SnCl_2$ in 10% HCl onto a stirring plate, stir, and put the reductant tubing into the container.

9.7.3 Transfer the QA/QC standards and samples into clean autosampler vials and place into the 44-sample capacity rack.

9.7.4 Enter the autosampler loading list into data system using **Rack Entry** and **Setup**, including all required QC and routine samples. Print the autosampler entries by pressing the F3 key.

9.7.5 Calibrate the instrument using the six standards. After calibration, get into **Calibration** on the **Main Menu** and then get into the **Line Calibration** menu. The current curve will be highlighted on the graph. Check the correlation coefficient (r); the correlation coefficient of the curve must be $\geq$0.995 or the instrument must be re-calibrated. If the correlation coefficient meets the 0.995 requirement, press the **A** key to Accept the curve and press the F3 key to print the curve. All six standards must be used to determine the correlation coefficient. The Leeman PS200 software allows you to delete a standard from the calibration. **Deletion of standards must never be performed!**

9.7.6 Start autosampler analysis sequence and analyze samples. Review results for QC compliance and off-scale results. Identify samples which must be re-analyzed in a different analytical run. Samples having analytes at concentrations greater than 15 μg/L must be diluted into calibration range and re-analyzed.

9.7.7 An example of a loading list for an analytical run sequence is listed in the table below.

Seq.	Desc.	Seq.	Desc.	Seq.	Desc.
1	IPC	13	IPC	25	IPC
2	CB	14	CB	26	CB
3	QCS	15	S5	27	S15
4	QL	16	S6	28	S16
5	LRB	17	S7	29	S17
6	LFB	18	S8	30	S18
7	S1	19	S9	31	S19
8	S1-LFM	20	S10	32	S20
9	S1-LFMD	21	S11	33	IPC
10	S2	22	S12	34	CB
11	S3	23	S13	35	
12	S4	24	S14	36	

9.8 Data Reduction and Reporting - After set-up and calibration the Leeman PS200 software reports results for the analyzed solution in units of μg/L. Solid samples should be reported using the following equation:

$$R = \frac{Mx(0.1L)x(1mg/1000ug)xD}{(W)x(1Kg/1000g)x(\%solids/100)}$$

where:

R	=	final reported concentration, in mg/Kg.
M	=	measured concentration reported by instrument, in μg/L.
D	=	dilution factor, to account for dilution performed after sample preparation.
W	=	Weight of sample, in grams.

The concentrations reported by the instrument must be corrected for any dilutions performed as part of the sample preparation or analysis process. 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 ½ the QL. Values between ½ 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.

10 DOCUMENTATION

10.1 Mercury Digestion Log - Entries are made for the case number, SDG number, date of preparation, electronic file ID, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, sample aliquots, volume of acids added, volume of reagents added, final volume of digestate and comments, if any. A copy of the mercury digestion log must be submitted with the raw data. The Leeman PS200 digestion log is maintained in Room 302.

10.2 Standards Documentation - Copies of all standard solution preparation entries (CAL, IPC, QL, LFB, LFM, LFMD, QCS, etc.) must be submitted with each raw data package.

10.3 Leeman PS200 Mercury Run Log - Entries are made for the case number, SDG number, date of analysis, site name, file name, analyst initials, lab sample IDs, client sample IDs, standard IDs and comments, if any. The run log is maintained in Room 302.

10.4 Report Narrative and Deliverable

The data package consists of the report narrative, reports and data, as listed in the table below.

Data Package Contents
Report Narrative: Discusses any problems encountered, both technical and administrative, the corrective action taken, and the resolution. All universal analytical flags should also be discussed in the report narrative.
Tabulated sample results on an analytical spreadsheet, with units, sample collection dates, client sample IDs, laboratory IDs and station locations. (Attachment E)
Method blank data included on the analytical spreadsheet. (Attachment E)

LFM and LFMD results on a QC summary report with calculated relative percent difference (RPD). (Attachment F)

LFM and LFB results on a QC summary report with calculated percent recoveries (%R). (Attachment F)

Raw sample, standard and QC data, including run logs and any work sheets, if applicable. (Attachments B, C and D)

11 REFERENCES

11.1 U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Method 7471b, Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique), Revision 2, January 1998.

11.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed.; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1996; SW-846.

11.3 Region 9 SOP 110, *Sample Receipt, Log-in and Storage.*

11.4 Region 9 SOP 125, *Sample Disposal.*

11.5 Region 9 SOP 130, *Glassware Cleaning Procedures.*

11.6 Region 9 SOP 840, *Notebook Documentation and Control.*

11.7 Region 9 SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency.*

Attachment A
Deviations From Reference Method (EPA 7471B)

A.1 This SOP uses the Leeman PS200 Automated Mercury Analyzer which requires only a small digested sample aliquot (approximately 5 mL) to perform the mercury analysis. Method 7471B requires purging of the headspace in the digestion vessel, the addition of stannous sulfate 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 which 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.

A.2 The calibration curve generated by the Leeman PS200 Automated Mercury Analyzer used in this SOP is generated electronically and gives results in units of *ug*/L. The calibration is performed assuming that the volume of sample (or standard) + reagent is constant (approximately 136.5 mL).

A.3 Potassium persulfate is added to all standards and samples to eliminate the interferences caused by high concentrations of oxidizable organic materials which can cause low recoveries of organic mercury.

Appendix C
U.S. EPA Region IX Instructions for Sample Shipping and Documentation

INSTRUCTIONS FOR

SAMPLE SHIPPING

AND DOCUMENTATION

November 1997

Quality Assurance Management Section
U. S. EPA Region 9
San Francisco, CA

TABLE OF CONTENTS

1.0 GENERAL 1
1.3 DISTRIBUTION OF COPIES 1

2.0 SAMPLE SHIPMENTS 2

3.0 CLP ANALYTICAL SERVICES (CLPAS) TRAFFIC REPORT/CHAIN-OF-CUSTODY FORMS FOR ORGANIC AND INORGANIC ANALYSES 3
3.1 CASE DOCUMENTATION 3
3.2 HEADER INFORMATION 4
3.3 SAMPLE DOCUMENTATION 5
3.4 "SHIPMENT FOR CASE COMPLETE (Y/N)" 7
3.5 "PAGE 1 OF __" 7
3.6 "SAMPLE USED FOR SPIKE AND/OR DUPLICATE" 7
3.7 "ADDITIONAL SAMPLER SIGNATURES" 7
3.8 "CHAIN OF CUSTODY SEAL NUMBER" 7

4.0 REGIONAL ANALYTICAL PROGRAM (RAP) CHAIN-OF-CUSTODY FORMS 7
4.1 CASE DOCUMENTATION 7
4.2 SAMPLE DOCUMENTATION 8
4.3 AIRBILL NUMBER 9
4.4 "REMARKS" BOX 9

5.0 SAMPLE BOTTLES 9

6.0 FIELD QA/QC SUMMARY FORM 10

FIGURES

TYPE OF ACTIVITY ..... Appendix A
CLP SAMPLE NUMBERS ..... Appendix B
ORGANIC TRAFFIC REPORT & CHAIN OF CUSTODY RECORD ..... Attachment 1
INORGANIC TRAFFIC REPORT & CHAIN OF CUSTODY RECORD ..... Attachment 2
(REGIONAL) CHAIN OF CUSTODY RECORD ..... Attachment 3
FIELD QA/QC SUMMARY FORM ..... Attachment 4
SAMPLE SHIPMENT INFORMATION ..... Attachment 5

1.0 GENERAL

1.1 When all paperwork has been completed by the sampler and samples are ready to be shipped, place the laboratories' copies in a plastic bag and tape it to the inside of the lid of the cooler(s). For CLP Analytical Services, Contract Laboratory Analytical Services Support's (CLASS) copies must be submitted within 5 days of sampling. The Region's copies may be submitted at that time or at the end of the sampling event. If the sampling event covers an extended length of time, the Region's copies must be submitted weekly. (Note: The RSCC coordinator will not forward CLASS's copies. They will be returned to the sampler.)

QAMS address:

U.S. EPA Region 9
Quality Assurance Program (PMD-3)
75 Hawthorne Street
San Francisco, CA 94105
Attn.: RSCC Coordinator

CLASS address:

Contract Laboratory Analytical Services Support
DynCorp
2000 Edmund Halley Dr.
Reston, VA 20191-3436
Attn.: Region 9 Coordinator

1.2 For analyses performed by the Regional Laboratory, DO NOT send any copies of the paperwork to the Contract Laboratory Analytical Services Support (CLASS).

1.3 DISTRIBUTION OF COPIES

1.3.1 CLP ANALYTICAL SERVICES

1.3.1.1 ORGANIC TRAFFIC REPORT/CHAIN-OF-CUSTODY FORM

a. Blue (original) copy to QAMS, Region 9
b. Pink (second) copy to CLASS
c. White (third) and Yellow (fourth) copies accompany samples to laboratory
d. Photocopy for sampler's files

1.3.1.2 INORGANIC TRAFFIC REPORT/CHAIN-OF-CUSTODY FORM

a. Green (original) copy to QAMS, Region 9
b. Pink (second) copy to CLASS
c. White (third) and Yellow (fourth) copies accompany samples to laboratory
d. Photocopy for sampler's files

1.3.2 REGIONAL ANALYTICAL PROGRAM (RAP):

1.3.2.1 RAP CHAIN-OF-CUSTODY FORM

a. White (original) copy to laboratory with samples

b. Pink copy to QAMS, Region 9
c. Photocopy for sampler's file

1.3.3 FIELD QA/QC SUMMARY FORM

a. Original to QAMS, Region 9
b. Photocopy for sampler's files

2.0 SAMPLE SHIPMENTS

2.1 Calling in shipments to the RSCC coordinator

2.1.1 Call the EPA Regional Sample Control Center (RSCC) coordinator on a daily basis, even if no shipments were made. The RSCC coordinator may be reached at (415) 744-1498.

2.1.2 Try to stick to the sampling schedule. If this is not possible, let the RSCC coordinator know immediately so other arrangements can be made.

2.1.3 Notify the RSCC coordinator within 12 hours of sample shipments. Calling in sample shipments to the RSCC coordinator is MANDATORY. Provide the following information to the RSCC coordinator:

1. Case number
2. Name of Laboratory
3. Date of shipment
4. Carrier and airbill number
5. Number of samples shipped by matrix and analysis type
6. Number of coolers shipped
7. Information on completions, changes, delays, etc.

2.2 Special shipments (i.e., Saturday delivery/pickup)

2.2.1 General - Friday shipments for Saturday delivery/pickup must be called in by noon (12:00 pm) Friday. This is to enable the RSCC coordinator to pass the information on to CLASS or to the laboratories. Samplers may not contact the laboratories directly. (Laboratories do not have to accept notification of delivery of samples from sources other than CLASS or RSCC.)

2.2.2 Regional Laboratory - The Regional Laboratory is located within a gated compound that is closed on weekends and holidays. Designated laboratory personnel will pickup the samples at the Federal Express office, take them to the laboratory and place them inside the refrigerators. If the following shipping instructions are not followed, an unsuccessful delivery attempt will be made to the Regional Laboratory. In addition, the staff member on call will not be able to pickup the samples, since they will not be at the Federal Express office.

To ensure that samples are held at the Federal Express office, please be sure to complete the following items:

1. On the lower left side of the Federal Express airbill, "For HOLD at FedEx Location check here," mark the box for "Hold Saturday."

2. In Section 3 of the airbill, print the following Federal Express office address:

1600 63rd Street
Emeryville, CA 94608

Federal Express may affix stickers to the coolers. Be sure they read "SATURDAY FEDERAL EXPRESS CENTER HOLD" or something similar. Under no circumstances should a "SATURDAY DELIVERY" sticker be placed on the cooler.

If a carrier other than Federal Express is used, please call the RSCC coordinator (415-744-1498) to make special arrangements.

2.2.3 Most CLP laboratories and other commercial laboratories contracted by QAP are staffed on Saturdays. Therefore, coolers can be delivered directly to these laboratories. In this case, the "SATURDAY DELIVERY" sticker should be placed on the cooler.

2.2.4 Laboratories may request advance notification of the arrival of certain types of samples, such as samples with very short holding times (e.g., Cr +6) that will be hand delivered to the laboratory. Required deadlines for notification of sample shipments in these special cases will be determined on a case by case basis. The RSCC coordinator will inform the samplers as to when notification of sample delivery is required (e.g., by noon on the day samples will be delivered). This is to facilitate the laboratory(ies) having personnel available to analyze the samples as soon as they arrive.

2.3 Cooler Return

Samplers are responsible for providing laboratories with a means to return coolers to their place of origin. The easiest way is to enclose an airbill with return shipping instructions (i.e., the address filled in as to where the coolers are to be returned to) and an account number to charge shipping costs to.

Samplers using EMFAC coolers should refer to Section 7 of the EMFAC Users Guide for cooler return instructions. EPA contractors should contact their EPA Project Officer for details on acceptable modes of cooler return and shipping cost reimbursement.

3.0 CLP ANALYTICAL SERVICES (CLPAS) TRAFFIC REPORT/CHAIN-OF-CUSTODY FORMS FOR ORGANIC AND INORGANIC ANALYSES

3.1 CASE DOCUMENTATION

Complete this form when collecting CLPAS samples. See Attachments 1 through 3 for examples.

Enter the CLPAS case number in the box(es) located in the upper right corner of the form. CLPAS case numbers have the format "xxxxx" (e.g., 18123).

3.2 HEADER INFORMATION

3.2.1 Box 1 - PROJECT CODE/SITE INFORMATION

Enter the Project Code (i.e., $F), Site Name, City, State, Site Spill ID. **(Note: the information entered here does not go through to the laboratory's copies.)**

If sampling is not under the Superfund program, enter the Account code (account to be billed), any Regional Information and the name of the program (e.g., RCRA) in the box titled "Non-Superfund program."

3.2.2 Box 2 - REGIONAL INFORMATION

Enter the Region number, the name of your sampling company, and your name and signature in the designated spaces.

3.2.3 Box 3 - TYPE OF ACTIVITY

Check the appropriate box(es) for the type of activity for this sampling event. See Appendix A for acronym definitions.

3.2.4 Box 4 - SHIPPING INFORMATION

Enter the date shipped, the carrier (e.g., Federal Express, Airbourne, etc.) and the air bill number in the appropriate spaces.

3.2.5 Box 5 - SHIP TO

Enter the laboratory name, full address and laboratory contact (e.g., Sample Custodian).

3.2.6 Box 6 - PRESERVATIVE

This box provides a list of commonly used preservatives. Enter the appropriate preservative in Column D. If you enter "5" on the Organic Traffic Report or "7" on the Inorganic Traffic Report indicating "Other", specify the preservative used at the bottom of the "Sample Documentation" area.

If you are using more than one type of preservative, you may either note the preservatives in the box specifically under the requested analyses (e.g., in the Cyanide box enter "2") or list them, separated by commas, in the same order as the checked sample analyses. (Alternatively, the analyses may be listed on separate lines.)

3.2.7 Box 7 - SAMPLE DESCRIPTION

This box provides a list of the description/matrices of the samples that are collected. Enter the appropriate description in Column A.

3.3 SAMPLE DOCUMENTATION

3.3.1 SAMPLE NUMBERS

Carefully transcribe the CLPAS sample numbers from the printed labels onto the Organic or Inorganic Traffic Report/Chain-of-Custody forms in the column labeled "CLP Sample Numbers".

CLPAS sample numbers have the following formats: YX123 for organic and MYX123 for inorganic samples. See Appendix B for examples.

3.3.2 Column A - SAMPLE DESCRIPTION

Enter the appropriate sample description code from Box 7.

Note: Item #6 "Oil" and Item #7 "Waste" are for RAP projects only. Do not ship oily samples or waste samples without making prior arrangements with the EPA.

3.3.3 Column B - CONCENTRATION

Enter "L" for low and "M" for medium concentration samples. (Prior arrangements must have been made with the ESAT RSCC coordinator, CLASS and the laboratories accepting the samples before shipping medium concentration samples. At this time, high concentration samples must be scheduled through the RAP system.)

NOTE: Medium concentration samples must be shipped in metal cans.

3.3.4 Column C - SAMPLE TYPE COMPOSITE/GRAB

Enter the type of sample you collected. A composite is a sample composed of more than one discrete sample. A grab is a discrete sample.

3.3.5 Column D - PRESERVATIVE USED

Enter the preservative used from Box 6.

3.3.6 Column E - CLPAS ANALYSIS

Check the analytical fractions requested for each sample, for example, VOAs, BNAs and Pesticides/PCBs are for low/medium concentration organics. Total metals and cyanide are for low/medium concentration inorganics.

NOTE: If dissolved metals are requested, a note must be added indicating that the samples have been field filtered and that digestion is required. See Attachment 2 for an example.

3.3.7 Column F - REGIONAL SPECIFIC TRACKING NUMBERS OR TAG NUMBERS

Region 9 does not issue tracking numbers or tag numbers. Samplers may use this column for sampler specific tracking numbers or for "Special Instructions". If you choose to use this as "Special Instructions", be sure to note, at the bottom of the "Sample Documentation" area, what the special

handling is. The number and type of containers could be entered here. (e.g., 3-40 mL, 6-1L)

3.3.8 Column G - STATION LOCATION NUMBER

Enter the station location in the space provided.

3.3.9 Column H - MO/DAY/YEAR/TIME OF SAMPLE COLLECTION

Record the month, day, year and time (use military time, e.g., 1600 = 4:00 pm) of sample collection.

3.3.10 Column I - SAMPLER INITIALS

Enter your initials.

3.3.11 Column J - CORRESPONDING CLP ORGANIC/INORGANIC SAMPLE NUMBER

Enter the corresponding CLP sample number for organic or inorganic CLPAS analysis.

3.3.12 Column K - DESIGNATED FIELD QC

NOTE: This column is NOT to be used for the designated laboratory QC samples. **Information entered here is not reproduced onto the laboratories' copies.**

Enter the appropriate qualifier as listed below for "Blind" Field QC samples in this column. (NOTE: All samples must have a qualifier.)

Blind Field QC	Qualifier
Blind Blanks (field, etc.)	B
Blind Field Duplicates	D
Blind Field Spikes	S
Blind PE Samples	PE
All other field samples	--

"B" = These are blanks and include trip blanks (T), field blanks (F) and equipment blanks (E). Blanks may be further identified by the letter in parenthesis. For example, B(T) indicates that the sample is a trip blank.

"D" = These are field duplicates. Do not include samples designated as laboratory duplicates. The primary sample is identified with "--" and the duplicate is given "D" in column K. In addition, the station locations should also identify the primary and duplicate samples. For example, MW-1 is the primary sample and MW-1B is the duplicate sample.

"S" = These are spiked field samples and are generated by field personnel

"PE" = These are performance evaluation samples. They are spiked samples but are not field samples. They are usually prepared by other than field personnel.

"--" = All other samples not designated as blind field QC samples are given this qualifier.

3.4 "SHIPMENT FOR CASE COMPLETE (Y/N)"

This should reflect the status of the samples scheduled to be shipped to a laboratory for a specific case. Only when ALL samples scheduled for shipment to a laboratory for a specific case have been shipped is the case complete.

3.5 "PAGE 1 OF __"

Enter the number of Traffic Report/Chain-of-Custody Record form(s) enclosed in each cooler. The form(s) accompanying each cooler must list only those samples contained in that cooler.

3.6 "SAMPLE USED FOR SPIKE AND/OR DUPLICATE"

Enter the sample number of the sample designated for laboratory spike and/or duplicate analysis. This is also known as the Laboratory QC sample. This sample should be included in the first shipment to the laboratory and in the first shipment for each subsequent sample delivery group (SDG).

DO NOT enter samples designated as blind field duplicates in this block.

3.7 "ADDITIONAL SAMPLER SIGNATURES"

Record additional sampler signatures that are different from that in Box 2.

3.8 "CHAIN OF CUSTODY SEAL NUMBER"

Enter the Chain of Custody Seal Number used to seal the cooler, if applicable.

3.9 Instructions summarizing CLP sample volumes, packaging and shipment reporting requirements are printed on the back of the Traffic Reports.

4.0 REGIONAL ANALYTICAL PROGRAM (RAP) CHAIN-OF-CUSTODY FORMS

4.1 CASE DOCUMENTATION

Complete this form when collecting RAP samples. See Attachment 4 for an example.

4.1.1 PROJECT NUMBER

Enter the RAP case number in this box.

4.1.2 PROJECT NAME

Leave this space blank.

4.1.3 SAMPLERS (Signature)

Record all sampler signatures in this box.

4.2 SAMPLE DOCUMENTATION

4.2.1 SAMPLE NUMBERS

No sample numbers are provided. Samplers should designate their own numbers and enter them in the space labeled STA.NO.

4.2.2 DATE

Enter the month, day and year the sample was collected in the "DATE" column.

4.2.3 TIME

Enter the time (using military time) in the "TIME" column.

4.2.4 COMP/GRAB

Check the kind of sample collected in the composite or grab column.

4.2.5 STATION LOCATION

Enter the sample site location in the space provided.

4.2.6 SAMPLE MATRIX

For each sample, enter the appropriate sample matrix description in the right third portion of the "STATION LOCATION" column.

4.2.7 NO. OF CONTAINERS

Enter the total number of sample containers collected for each matrix at each station location.

4.2.8 SAMPLE ANALYSES

There are six slanted columns to be used to specify the kind of analysis to be performed by the laboratory. Enter the appropriate analysis in each column. Mark the box of the appropriate analysis for each sample collected.

4.2.9 REMARKS

The items listed below are to be included in this area on the appropriate sample line.

4.2.9.1 CONCENTRATION

Enter "L" for low concentration, "M" for medium concentration and "H" for high concentration.

NOTE: Medium and high concentration samples must be shipped in metal cans.

4.2.9.2 PRESERVATIVE USED

Enter the preservative used.

If more than one type of preservative is used for a sample, separate the preservative references with commas. The sequence of the reference numbers must follow the sequence of the requested "RAP Analysis" parameters that are recorded in the analysis columns.

4.2.9.3 SAMPLE USED FOR SPIKE AND/OR DUPLICATE

Enter the sample number designated for spike and/or duplicate analysis. This is also known as the Laboratory QC sample. This sample should be included in the first shipment to the laboratory and in the first shipment for each subsequent sample delivery group (SDG).

4.3 AIRBILL NUMBER

The airbill number should be entered on the first signature line, in the box marked "Received by: (Signature)".

4.4 "REMARKS" BOX

Located in the lower right hand corner of the Chain of Custody is a box labeled "Remarks". The following items should be entered there.

4.4.1 CHAIN OF CUSTODY SEAL NUMBER

Enter the Chain of Custody Seal Number used to seal the coolers, if applicable, in the box labeled "Remarks", in the lower right-hand corner.

4.4.2 LABORATORY NAME

Enter the Laboratory name in the box labeled "Remarks", in the lower right-hand corner.

4.4.3 SHIPPING COMPLETE?

Enter "yes, shipping is complete" or "No, shipping is not complete" in the box labeled "Remarks", in the lower right-hand corner.

4.4.4 CARRIER

Enter the carrier (e.g., "Fed Ex") in the box labeled "Remarks", in the lower right-hand corner.

5.0 SAMPLE BOTTLES

5.1 Sample bottles be labeled with the following information:

a. Case number
b. Date/Time of collection
c. Matrix/Concentration
d. Station Location
e. Sample number (CLP or sampler designated)
f. Analysis
g. Preservative

5.2 Pre-printed, self-adhesive labels are provided for CLPAS Organic, CLPAS Inorganic and RAP samples.

5.2.1 Transcribe the appropriate sample number onto the corresponding bottle label and/or affix the sample number label onto the bottle.

5.2.2 Destroy all unused labels or return them to the ESAT RSCC coordinator. DO NOT use them for future samplings. New sample numbers will be assigned.

6.0 FIELD QA/QC SUMMARY FORM

6.1 Complete one form per laboratory per matrix for each sampling event. For long term projects, complete a form(s) after each week of sampling. Complete the header portion even if no QA/QC samples were provided.

6.2 Complete all applicable entries. Please use the appropriate sample numbers for each laboratory. (e.g., for the laboratory performing CLPAS organics, use the CLP organic sample numbers, YX123, etc. For the laboratory performing RAP analyses, use the RAP sample numbers, SY0123, etc.) Please do not use station locations. If a laboratory is performing more than one type of analysis, list all applicable sample numbers.

6.3 This form is very important for validation purposes. The validators will compare the results of duplicates and assess the quality of blanks, if they know which samples they are. Failure to provide this information will delay the completion of validation.

Appendix A

TYPE OF ACTIVITY

Check the box which describes the funding lead for this sampling event:

Funding Lead

SF = Superfund
PRP = Potentially Responsible Party
ST = State
FED = Federal

Check one or more boxes, as appropriate, which describe the task of this sampling event:

Pre-Remedial

PA = Preliminary Assessment
SSI = Screening Site Investigation
LSI = Listing Site Investigation

Remedial

RIFS = Remedial Investigation Feasibility Study
RD = Remedial Design
O&M = Operations and Maintenance
NPLD = National Priorities List

Removal

CLEM = Classic Emergency
REMA = Removal Assessment
REM = Removal
OIL = Oil Response
UST = Underground Storage Tank Response

Appendix B

CLP SAMPLE NUMBERS

Each sample is assigned a unique sample number. A "sample" is defined as follows:

- one matrix, e.g., water, soil/sediment, fish, etc.
- one station location
- one analytical program, e.g., CLPAS organics, CLPAS inorganics or a RAP analysis
- one laboratory

Sample numbers for CLPAS analyses:

- CLPAS Organic sample numbers consist of five alpha-numerics, always beginning with "Y"

  Example - YJ386

- CLPAS Inorganic sample numbers consist of six alpha-numerics, always beginning with "MY"

  Example - MYG528

Examples for assigning sample numbers:

- CLPAS Volatiles & CLPAS Pesticides/PCBs receive the **SAME SAMPLE NUMBER**, if the samples are:
  - the same matrix
  - part of the same analytical program, e.g., CLPAS organics
  - from the same station location
  - going to the same laboratory

- CLPAS Volatiles & CLPAS Pesticides/PCBs receive **DIFFERENT SAMPLE NUMBERS**, if the samples are:
  - the same matrix
  - part of the same analytical program, e.g., CLPAS organics
  - from the same station location
  - going to different laboratories

- CLPAS Volatiles & CLPAS Metals receive **DIFFERENT SAMPLE NUMBERS**, if the samples are:
  - the same matrix
  - part of different analytical programs, e.g., CLPAS organics & CLPAS inorganics
  - from the same station location
  - going to the same laboratory

Organic Traffic Report & Chain of Custody Record

(For Organic CLP Analysis)

EPA — United States Environmental Protection Agency
Contract Laboratory Program Sample Management Office
PO Box 818 Alexandria, VA 22313
703-557-2490 FTS 557-2490

SAS No. (If applicable):

Case No.: 17235

1. Project Code: SF | Account Code:

2. Region No.: 9 | Sampling Co.: Ace

4. Date Shipped: 1-7-94 | Carrier: Fed. Express

Airbill Number: 091234567 8

Regional Information:

Sampler (Name): Gail Jones

Non-Superfund Program:

Sampler Signature: Gail Jones

5. Ship To: Alpha Lab
123 Pine Ave.
NY, NY 10001
ATTN: John Doe

Site Name: Toxic Dump

3. Type of Activity — Lead / Pre-Remedial / Remedial / Removal

	Lead	Pre-Remedial	Remedial	Removal
SF	X	PA	RIFS X	CLEM
PRP		SSI	RD	REMA
ST		LSI	RA	REM
FED			O&M	DIL
			NPLD	UST

City, State: Smallville CA | Site Split ID: 99

6. Preservative (Enter in Column D)
1. HCl
2. HNO_3
3. $NaHSO_4$
4. H_2SO_4
5. Other (Specify)
6. Ice only
N. Not preserved

7. Sample Description (Enter in Column A)
1. Surface Water
2. Ground Water
3. Leachate
4. Rinsate
5. Soil/Sediment
6. Oil (High only)
7. Waste (High only)
8. Other (Specify)

CLP Sample Numbers (from labels)	A Enter # from Box 7	B Conc. Low Med High	C Sample Type: Comp./ Grab	D Preservative from Box 6	E RAS Analysis: VOA	BNA	Pest/ PCB	High only ARO/ TOX	F Regional Specific Tracking Number or Tag Numbers	G Station Location Number	H Mo/Day/ Year/Time Sample Collection	I Sampler Initials	J Corresp. CLP Inorg. Samp. No.	K Enter Appropriate Qualifier for Designated Field QC (B = Blank, S = Spike, D = Duplicate, PE = Perform. Eval., — = Not a QC Sample)
YJ126	2	L	G			X				MW-1	1-6-94 0900	GJ	MYG00X	—
YJ127	2	L	G			X				MW-2	1-6-94 1000	GJ	MYG00Y	—
YJ128	2	L	G			X				MW-3	1-6-94 1100	GJ	MYG00Z	—

Shipment for Case complete? (Y/N): Y

Page 1 of 1

Sample used for a spike and/or duplicate: YJ127

Additional Sampler Signatures:

Chain of Custody Seal Number:

CHAIN OF CUSTODY RECORD

Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Gail Jones	1-7-94 1600	091234567 8
Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)

Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Remarks: Is custody seal intact? Y/N/none

Split Samples: ☐ Accepted ☐ Declined (Signature)

EPA Form 9110-2 (Rev. 8-91) Replaces EPA Form (2075-7), previous edition which may be used

ATTACHMENT 1

04/13/99 TUE 13:13 FAX 1 415 744 1476 EPA REG 9 002

Inorganic Traffic Report & Chain of Custody Record

(For Inorganic CLP Analysis)

United States Environmental Protection Agency
Contract Laboratory Program Sample Management Office
PO Box 818 Alexandria, VA 22313
703-557-2490 FTS 557-2490

SAS No. (if applicable):

Case No.: 17235

1. Project Code: SF | Account Code:
Regional Information:
Non-Superfund Program:
Site Name: Toxic Dump
City, State: Smallville CA | Site Spill ID: 99

2. Region No.: 9 | Sampling Co.: Ace
Sampler (Name): Gail Jones
Sampler Signature: Gail Jones

3. Type of Activity — Lead / Pre-Remedial / Remedial / Removal

	Lead	Pre-Remedial	Remedial	Removal
SF	X		RIFS X	CLEM
PRP		PA	RD	REMA
ST		SSI	RA	REM
FED		LSI	O&M	OIL
			NPLD	UST

4. Date Shipped: 1-7-94 | Carrier: Fed. Express
Airbill Number: 091234569 9

5. Ship To: Beta Labs, Inc.
455 Maple Ave.
Atlanta, GA 04507
ATTN: Mary Smith

6. Preservative (Enter in Column D): 1. HCl 2. HNO_3 3. NaOH 4. H_2SO_4 5. $K_2CR_2O_7$ 6. Ice only 7. Other (Specify) N. Not preserved

7. Sample Description (Enter in Column A): 1. Surface Water 2. Ground Water 3. Leachate 4. Rinsate 5. Soil/Sediment 6. Oil (High only) 7. Waste (High only) 8. Other (Specify)

CLP Sample Numbers (from labels)	A Enter # from Box 7	B Conc. Low Med High	C Sample Type: Comp./ Grab	D Preservative from Box 6	E - RAS Analysis: Metals: Total	Metals: Dissolved	Metals: Cyanide	Low Conc. only: Nitrate/ Nitrite	Low Conc. only: Fluoride	High only: pH	High only: Conductivity	F Regional Specific Tracking Number or Tag Numbers	G Station Location Number	H Mo/Day/ Year/Time Sample Collection	I Sampler Initials	J Corresp. CLP Org. Samp. No.	K Enter Appropriate Qualifier for Designated Field QC: B = Blank S = Spike D = Duplicate PE = Perform. Eval. — = Not a QC Sample
MVG001	2	L	G	23	X		X						MW-1	1-6-94 0900	JB	YJ126	—
MVG002	2	L	G	2		X						A	MW-1	1-6-94 0915	JB	YJ126	—
MVG003	2	L	G	23	X		X						MW-2	1-6-94 1000	JB	YJ127	—
MVG004	2	L	G	2		X						A	MW-2	1-6-94 1015	JB	YJ127	—

A = Field Filtered, 0.45 micron Digestion required for all dissolved samples

Shipment for Case complete? (Y/N): Y | Page 1 of 1 | Sample used for a spike and/or duplicate: MVG003 + MVG004

Additional Sampler Signatures: John Brown | Chain of Custody Seal Number:

CHAIN OF CUSTODY RECORD

Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Gail Jones	1-7-94 1600	091234569 9
Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)

Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Date / Time	Remarks	Is custody seal intact? Y/N/none

Split Samples: ☐ Accepted ☐ Declined (Signature)

EPA Form 9240.1 (Rev. 5-91) Replaces EPA Form (2075-6), previous edition which may be used

1-4pm

ATTACHMENT 2

EPA REG 9

04/13/99 TUE 13:13 FAX 1 415 744 1476

003

ENVIRONMENTAL PROTECTION AGENCY
Office of Enforcement

REGION
75 Hawthorne Street
San Francisco, California 94105

CHAIN OF CUSTODY RECORD

PROJ. NO.	PROJECT NAME
R94312	

SAMPLERS: (Signature)
K. Pettit

STA. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	MATRIX	NO. OF CONTAINERS	LOW LEVEL VOA	SULFIDE	NITRATE/NITRITE				REMARKS
SJD000	7/21/94	1000		✓	FRONT - MW	GW	4	X	X	X				VOA'S PRESERVED W/ HCL SULFIDE PRESERVED W/ NaOH + Zn ACETATE
SJD001	7/21/94	1030		✓	BACK - MW	GW	4	X	X	X				
SJD002	7/21/94	1300		✓	EAST - MW	GW	4	X	X	X				LABQC
SJD003	7/21/94	1320	✓		EAST - S	SOIL	1			X				LABQC
														ALL SOIL AND GW SAMPLES ARE LOW CONCENTRATION

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
K. Pettit	7/22/94 1600	1234567890			
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks LAB: REGION 9 SHIPPING IS COMPLETE CARRIER: FED EX, 7/22/94 CUSTODY SEAL #: 12345	

Distribution: Original Accompanies Shipment; Copy to Coordinator Field Files

04/13/99 TUE 13:14 FAX 1 415 744 1476 EPA REG 9 004

ATTACHMENT #3

ATTACHMENT 4

FIELD QA/QC SUMMARY FORM

Instructions: Complete one form per laboratory and per matrix for each sampling event

Date: 1-10-94
Sampler: Gail Jones
Office: ACE
Phone: (415) 456-7890

Site: Toxic Dump
Case/SAS #: 17235
Laboratory: Beta Labs, Inc

Matrix: (check one) X Groundwater ___ Surface Water ___ Surface Soil ___ Subsurface Soil ___ Air ___ Other

I. BLANKS

Sample #	Type (circle one)	Date Collected
MVG 021	(Equip) / Field / Travel	1-9-94
	Equip / Field / Travel	
	Equip / Field / Travel	
	Equip / Field / Travel	
	Equip / Field / Travel	
	Equip / Field / Travel	
	Equip / Field / Travel	
	Equip / Field / Travel	
	Equip / Field / Travel	
	Equip / Field / Travel	
	Equip / Field / Travel	

II. BACKGROUND SAMPLES

Sample #	Date Collect

III. LAB QC SAMPLES

Sample #	Date Collec
MVG 003	1-6-94
MVG 004	1-6-94

IV. DUPLICATES

Sample #	Matches Sample #	Date Collected	Type (circle one)
MVG 015	MVG 016	1-9-94	a / (b) / c / d
			a / b / c / d
			a / b / c / d
			a / b / c / d
			a / b / c / d
			a / b / c / d

a= composite sa
b= consecutive
c= colocated
d= consecutive soil sleeve

V. Checklist of Field Problems Encountered

Sample # / Date(s) of Occurrence / Comments

- X None
- ___ Pumping Equipment Problems
- ___ Sample Filtering Problems
- ___ Less Than Required Sample Volume
- ___ Low Flow/Recharge Rates
- ___ Preservation Problems
- ___ Samples Not Shipped in 24 hrs.
- ___ Federal Express Delay
- ___ Other

ATTACHMENT 5

SAMPLE SHIPMENT INFORMATION

DATE: _____ # OF PAGES: _____

TO: GAIL JONES, RSCC COORDINATOR FROM: _____

CO.: EPA REGION 9 (R-3-2) CO.: _____

PHONE #: (415) 744-1496 PHONE #: _____

FAX #: (415) 744-1476 FAX #: _____

//

CASE #: _____ LAB NAME: _____

COOLERS: _____ SHIPPING DATE: _____

CARRIER: _____ AIRBILL #: _____

# SAMPLES	CONC/MATRIX	ANALYSES

Is this sampling event complete with this shipment? Y N

COMMENTS: _____

//

CASE #: _____ LAB NAME: _____

COOLERS: _____ SHIPPING DATE: _____

CARRIER: _____ AIRBILL #: _____

# SAMPLES	CONC/MATRIX	ANALYSES

Is this sampling event complete with this shipment? Y N

COMMENTS: _____

Revised Daily Sample Shipment Notification Procedure (Effective 6/1/02)

This revision supercedes all previous sample shipment notification instructions. All Friday shipments should be called into the respective points of contact by 12:00 PM Friday.

For EPA Region 9 Laboratory:

Call in shipment information to the Sample Receiving Telephone at:
(510) 412-2377

If there is a sample shipment related question or emergency, then press 0 for the Region 9 Laboratory Receptionist.

For EPA Contract Laboratory Program:

If email is available send shipping information to Rich Freitas at:
freitas.richard@epa.gov
and cc to:
brickner.carl@epa.gov
holly.rogers@dyncorp.com

or call in shipment information to Rich Freitas at:
(415) 972-3804

If Rich is out or unavailable Carl Brickner is his designated back-up and can be reached at (415) 972-3814.

For EPA Regional Analytical Contract Laboratory - EMAX:

If email is available send shipping information to Carl Brickner at:
brickner.carl@epa.gov
and cc to:
freitas.richard@epa.gov
mezquita.marlon@epa.gov

or call in shipment information to Carl Brickner at:
(415) 972-3814

If Carl is out or unavailable Rich Freitas is his designated back-up and can be reached at (415) 972-3804.

For EPA Dioxin Contract Laboratory Program:

If email is available send shipping information to Steve Remaley at:
remaley.steve@epa.gov

or call in shipment information to Steve Remaley at:

(415) 972-3802

Sample shipment information that is to be provided should include the following:

- Site Name
- Case Number
- Laboratory Name
- Shipping Date
- Carrier
- Airbill/Tracking Number
- Number of Coolers
- Number of Samples
- Sample Concentration
- Matrix
- Analyses
- Is the sampling event complete with this shipment or is it to continue?
- Any additional comments that may be relevant to the analyses or transportation of the samples.
- Sampler mobile phone number, if available.