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Response Action Contract IX

QUALITY ASSURANCE PROJECT PLAN
OMEGA CHEMICAL SUPERFUND SITE OPERABLE UNIT 2
REMEDIAL INVESTIGATION/FEASIBILITY STUDY

MONTEBELLO FOREBAY
LOS ANGELES, CALIFORNIA

U.S. Environmental Protection Agency
Contract No. 68-W-98-225

CH2M HILL, Inc.
and Team Subcontractors:
URS Group, Inc.
E2 Consulting Engineers, Inc.

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OMEGA CHEMICAL SUPERFUND SITE OPERABLE UNIT 2
REMEDIAL INVESTIGATION/FEASIBILITY STUDY

MONTEBELLO FOREBAY
LOS ANGELES, CALIFORNIA

EPA CONTRACT NO. 68-W-98-225
EPA WORK ASSIGNMENT NO. 175-RICO-09BC
CH2M HILL PROJECT NO. 183122

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

Prepared by
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April 2004

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April 27, 2004

183122.pp.01

Christopher Lichens
U.S. EPA Region IX
Superfund Project Manager
75 Hawthorne Street
San Francisco, CA 94105

Subject: Revised FSP and QAPP for Omega Chemical Superfund Site Remedial Investigation/Feasibility Study for OU-2

Dear Mr. Lichens:

Please find enclosed copies of the subject documents.

Please contact me at 909/890-9857 if you have questions regarding the enclosed documents.

Sincerely,

CH2M HILL

Tom Perina

Tom Perina
Site Manager

Enclosures
c: David Taylor, U.S. EPA Region IX Quality Assurance Manager

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U.S. ENVIRONMENTAL PROTECTION AGENCY REGION IX

Plan Title:	Quality Assurance Project Plan Omega Chemical Superfund Site Operable Unit 2 Remedial Investigation/Feasibility Study
Site Name:	Omega Chemical Superfund Site
Site Location:	Whittier
City/State/Zip:	Los Angeles County, California
Site EPA ID#:	09BC
Anticipated Sampling Dates:	2004 to 2005
Prepared By:	Tom Perina
Date:	April 2004
Agency or Firm:	CH2M HILL, Inc.
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* *

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Approved: Artemis Antipas, Ph.D. [signature] Date: April 2004
CH2M HILL Quality Assurance Officer

Approved: Christopher Lichens Date: ________
EPA Work Assignment Manager

Approved: ________ Date: ________
EPA Quality Assurance Officer

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_____ CH2M HILL Field Team Leader

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Contents

Section **Page**

Acronyms ..... **iii**

Introduction **1**

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-3
- A.3 Project Description and Schedule A-3
  - A.3.1 Description of Work to be Performed A-3
  - A.3.2 Schedule of Activities A-5
- A.4 Data Quality Objectives A-5
  - A.4.1 Project Quality Objectives A-5
  - A.4.2 Measurement Performance Criteria A-5
- A.5 Special Training Requirements/Certification (A8) A-6
- A.6 Documentation and Records A-6

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-1
- B.2 Sampling Method Requirements B-1
- B.3 Sample Handling and Custody Requirements B-1
  - B.3.1 Chain-of-Custody B-2
  - B.3.2 Custody Seals B-4
  - B.3.3 Field Notebooks B-4
  - B.3.4 Corrections to Documentation B-4
- B.4 Analytical Methods Requirements B-4
- B.5 Quality Control Requirements B-5
  - B.5.1 Field QC Procedures B-5
  - B.5.2 Laboratory Procedures B-5
- B.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements B-5
- B.7 Instrument Calibration and Frequency B-6
  - B.7.1 Field Calibration Procedures B-6
  - B.7.2 Laboratory Calibration Procedures B-7
- B.8 Data Acquisition Requirements (Nondirect Measurements) B-7

B.9 Data Management B-7

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-2
D.3 Reconciliation with Data Quality Objectives D-2
D.3.1 Precision D-2
D.3.2 Accuracy D-2
D.3.3 Completeness (Statistical) D-3

References R-1

Appendixes

A Data Quality Objectives

B Analytical Specifications

Tables

A-1 Data Needs and Uses

A-2 Measurement Performance Criteria

Figures

A-1 Project Organization

A-2 Data Users/Recipients

A-3 Site Map

Acronyms

AL	action level
AN	analytical support and data validation
AOC	administrative order on consent
ARAR	Applicable or Relevant and Appropriate Requirements
BOD	biological oxygen demand
CCR	California Code of Regulations
CFR	Code of Federal Regulations
cis-1,2-DCE	cis-1,2-dichloroethene
CLP	Contract Laboratory Program
COC	chain-of-custody
COD	chemical oxygen demand
Cr (VI)	hexavalent chromium
CRDL	contract-required detection levels
1,1-DCE	1,1-dichloroethene
DE	data evaluation
DHS	Department of Health Services
DQO	data quality objective
EC	electrical conductivity
EE/CA	engineering evaluation/corrective action
EPA	United States Environmental Protection Agency
ERA	ecological risk assessment
FAR	Federal Acquisition Regulations
Freon 11	trichlorofluoromethane
Freon 113	trichlorotrifluoroethane
FSP	field sampling plan
GAC	granular activated carbon
GC	gas chromatography
GIS	geographic information system

HHRA	human health risk assessment
HSP	health and safety plan
IDW	investigation-derived waste
LOE	level of effort
MAU	middle alluvial unit
MCL	maximum contaminant level
MDL	method detection limit
μg/L	micrograms per liter
MNA	monitored natural attenuation
MP	multiport
MS/MSD	matrix spike/matrix spike duplicate
msl	mean sea level
MTBE	methyl tert-butyl ether
NDMA	n-nitrosodimethylamine
NPDES	National Pollutant Discharge Elimination System
NPL	National Priorities List
OEHHA	Office of Environmental Health Hazard Assessment
OPOG	Omega Chemical Site Potentially Responsible Party Organized Group
OU	operable unit
PARCC	precision, accuracy, representativeness, comparability, and completeness
PCB	polychlorinated biphenyl
PCE	perchloroethene (tetrachloroethene)
PHG	public health goal
ppb	parts per billion
ppm	parts per million
PRP	potentially responsible party
QA/QC	quality assurance/quality control
QAO	quality assurance officer
QAPP	quality assurance project plan
RA	remedial action
RAC	response action contract

RCRA	Resource Conservation and Recovery Act
RD	remedial design
RFA	request for analyses
RI/FS	remedial investigation/feasibility study
ROD	record of decision
RPD	relative percent difference
RPM	remedial project manager
RSCC	Regional Sample Control Center
RSD	relative standard deviation
RTL	review team leader
SM	site manager
SOW	statement of work
SRM	standard reference material
SSC	site safety coordinator
STL	sampling team leader
SVOC	semivolatile organic compound
1,2,3-TCP	1,2,3-trichloropropane
TAL	Target Analyte List
TCA	1,1,1-trichloroethane
TCE	trichloroethene
TCL	target compound list
TDS	total dissolved solids
TKN	total Kjeldahl nitrogen
TOC	total organic carbon
TPH	total petroleum hydrocarbons
TSDF	treatment, storage, and disposal facility
UAU	upper alluvial unit
VOC	volatile organic compound
WA	work assignment
WAM	work assignment manager

Introduction

This Quality Assurance Project Plan (QAPP) follows United States Environmental Protection Agency (EPA) guidelines contained in *EPA Guidance for Quality Assurance Project Plans* (EPA, 2002), and *EPA Requirements for Quality Assurance Project Plans* (EPA, 2001). Thus, the following section headings correlate with the subtitles found in the EPA guidelines.

Section A
Project Management/Data Quality Objectives

A.1 Project Organization

This work assignment issued under EPA Response Action Contract (RAC) Assignment No. 174-RSBD-09BC has a site manager (SM) who works directly with the EPA work assignment manager (WAM) to accomplish the work assignment. 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), senior reviewer/review team leader (RTL), and individual task managers for field sampling (sampling team leader, or STL).

The primary responsibility for project quality rests with the SM. Independent quality control (QC) 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 QAPP/field sampling plan (FSP)/health and 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 STL.

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 analyses, depending on EPA regional laboratory availability.

Where quality assurance (QA) problems or deficiencies requiring special action are uncovered, the SM, RTL, and QAO will identify the appropriate corrective action to be initiated by the STL 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 QA personnel are shown.

The organizational functions noted above are consistent with the overall RAC IX Program Plan; 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/analysis and construction activities at Omega Chemical Superfund Site and accompanies the data quality objectives (DQOs), which can be found in Appendix A (EPA, 1994 and 2000).

This QAPP follows EPA guidelines contained in *EPA Guidance for Quality Assurance Project Plans* (EPA, 1998 and 2002), and *EPA Requirements for Quality Assurance Project Plans* (EPA, 2001). Thus, the following section headings correlate with the subtitles found in the EPA guidelines.

A.2.2 Problem Statement

Existing groundwater and soil data indicate that elevated concentrations of volatile organic compounds (VOCs) and other compounds are present in the soil and groundwater beneath the former Omega Chemical Facility (Operable Unit 1 [OU-1]) and up to 2 miles downgradient in shallow groundwater. A series of soil gas, soil, and groundwater investigations has been performed at OU-1 by a variety of consultants beginning in 1985. Chlorinated hydrocarbons (primarily perchloroethene [PCE], trichloroethene [TCE], 1,1-dichloroethene [1,1-DCE], cis-1,2-dichloroethene [cis-1,2-DCE], and chloroform) and Freons (trichlorofluoromethane [Freon 11] and trichlorotrifluoroethane [Freon 113]) were identified as the primary chemicals of concern directly beneath the site. Elevated total chromium also was reported in groundwater beneath the Omega site. Perchlorate contamination is suspected. Other contaminants of concern (detected or suspected at the site) include cyanides, n-nitrosodimethylamine (NDMA), pesticides and polychlorinated biphenyls (PCBs), dissolved metals, and 1,4-dioxane. Elevated concentrations of chemicals of concern were also reported west and southwest of the Omega facility, suggesting that a downgradient migration of the contaminant plume from the site has occurred.

OU-2 generally includes the groundwater-contaminated areas encompassing the Omega Chemical Facility and extends approximately 2.2 miles to the southwest. The vadose zone contamination at the Omega site and the highly contaminated portion of the aquifer in the immediate site vicinity are addressed as OU-1 under a separate effort. The primary objective of this investigation is to conduct a remedial investigation/feasibility study (RI/FS) to estimate the vertical and lateral extent of groundwater contamination within OU-2. An investigation of potential source areas other than the Omega facility is not included in this QAPP, and will be addressed by an addendum to this document after additional information (records search) becomes available. It is anticipated that this future investigation will include soil gas and soil sampling, well installation, and aquifer testing.

A.2.3 Background

The Omega Chemical Corporation (Omega) is a former refrigerant/solvent recycling operation located in Whittier, California, a community of approximately 85,000 people. The facility is located across the street from a residential neighborhood and within 1 mile of several schools, including three elementary schools and two high schools. The facility operated as a Resource Conservation and Recovery Act (RCRA) solvent and refrigerant recycling and treatment facility from approximately 1976 to 1991, handling primarily chlorinated hydrocarbons and chlorofluorocarbons. Drums and bulk loads of waste solvents and chemicals from various industrial activities were processed at Omega to form commercial products. Chemical, thermal, and physical treatment processes were reportedly used to recycle the waste materials. Wastes generated from these treatment and recycling activities included distillation column (still) bottoms, aqueous fractions, and non-recoverable solvents. Additional data regarding site history, past investigations, and remediation activities are discussed in detail in the *Final On-Site Soils RI/FS Work Plan*

(Camp Dresser & McKee [CDM], 2003) and the *Omega Chemical Superfund Site; Whittier, California; Phase 2 Groundwater Characterization Study Report* (Weston Solutions, Inc. [Weston], 2002).

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 Table A-1 at the end of this section. Table A-1 lists the analytes of concern and presents regulatory criteria/action level requirements for organics and inorganics. The table presents a listing of applicable regulations and identifies the lowest regulatory criteria where there are multiple regulatory criteria/action levels for a given analyte. Table A-2 lists the analytical methods and laboratory reporting limits selected to meet these criteria.

A.3 Project Description and Schedule

A.3.1 Description of Work to be Performed

A summary of the work to be performed relating to sample collection, analysis, and interpretation is provided below.

Field Investigation

CH2M HILL will conduct the RI/FS field investigation at OU-2. Samples will include surface and subsurface soil samples, soil gas samples, groundwater samples, and associated field duplicates.

Sample Analysis

Sample analyses will be carried out by the EPA Contract Laboratory Program (CLP), Regional Laboratory, and Contract Laboratories as needed.

Analytical Support and Data Validation

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 QA management section or their designee.

Data Evaluation

CH2M HILL will organize and evaluate existing data and data gathered from this investigation. The data evaluation activities will include:

- Data usability evaluation and field QA/QC
- Data reduction, tabulation, and evaluation
- Preparing a data evaluation report

A brief data evaluation report will be prepared after each sampling event. The data reports will include sampling location maps and results tables for each medium sampled (soil, soil gas, and groundwater) and provide prior sampling results where appropriate for comparison and evaluation. The results and findings from data validation and data usability review will be summarized and incorporated into each data report. The validated

concentration data will be used in numerical modeling of the fate and transport of the contaminants dissolved in groundwater at the site.

Assessment of Risk

CH2M HILL will provide an evaluation and assessment of risk to human health and the environment posed by site contaminants. The risk assessment will account for both OU-1 and OU-2 and will include the following:

- Determination of the current or potential risk to human health and the environment posed by site contaminants in the absence of any remedial action
- Contaminant identification, exposure assessment, toxicity assessment, and risk characterization
- Determination of the necessity of a remedial action at the site, justification for performing remedial action, and determination of exposure pathways that need to be removed

CH2M HILL will prepare a Human Health Risk Assessment report that includes the following:

- Hazard identification (sources)
- Dose-response assessment
- Conceptual exposure/pathway analysis
- Characterization of site and potential receptors
- Exposure assessment
- Risk characterization
- Identification of limitations/uncertainties
- Site conceptual model

CH2M HILL will prepare an Ecological Risk Assessment report that includes the following:

- Hazard identification (sources)
- Dose-response assessment
- Conceptual exposure/pathway analysis
- Critical exposure pathways (e.g., surface water)
- Characterization of site and potential receptors
- Select chemicals, indicator species, and end points
- Exposure assessment
- Toxicity assessment/ecological effects assessment
- Risk characterization
- Identification of limitations/uncertainties
- Site conceptual model

Remedial Investigation Report

CH2M HILL will prepare a Remedial Investigation Report that establishes the site characteristics such as media contaminated, extent of contamination, and the physical boundaries of the contamination, and will assess the fate and transport of the contamination.

A.3.2 Schedule of Activities

The field investigation is expected to start in mid-2004 and will last approximately 2 years.

A.4 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 remedial investigation are optimally achieved. Specific DQOs were considered independently through the DQO process (EPA, 1994 and 2000) to meet the data user's needs for each activity. Appendix A presents the DQO decision-making process for the remedial field activities.

A.4.2 Measurement Performance Criteria

The 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 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-2.

Reporting detection levels/target detection limits listed in Table A-2 are per-method reporting limits, 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. Laboratory-specific method detection limits (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. This is not expected to impact 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-handling 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. The level of effort (LOE) for accuracy measurements will be a minimum frequency of 1 in 20 samples analyzed.

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

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 will be health and safety trained, and will follow requirements specified in the Health and Safety Plan (HSP) for the project, which can be found in the companion FSP (EPA, 2004). 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. Laboratory documentation will be per: (1) methods and QA protocols listed in Section B, and (2) EPA Regional Laboratory specific standard operating procedures. Overall project documentation will be per the EPA Region IX RAC Program Plan.

TABLE A-1
Data Needs and Uses – Regulatory Limits for Organic Parameters and Emergent Compounds
Quality Assurance Project Plan, Omega OU-2

Organic Compound	Uses/Decisions	Applicable Regulatory Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [2]	Additional Regulatory Limits (µg/L)
TCL Volatile Organic Compounds					
Acetone	Exceedances with respect to federal and state drinking water standards, and state action levels.				
Benzene		1	CA Primary MCL [A]	0.5	0.15 [E]
Bromodichloromethane		100	USEPA Primary MCL [C]	0.5	2.5 [I] ; 100-proposed [A]
Bromoform	Evaluate water treatment system design.	100	USEPA Primary MCL [C]	0.5	45 [I] ; 100-proposed [A]
Bromomethane		500	CA Proposition 65 Regulatory Level [I]	0.5	
n-Butylbenzene	Evaluate remedial action performance.	260	CA DHS State Action Level [F]		
sec-Butylbenzene		260	CA DHS State Action Level [F]		
Carbon disulfide		160	CA DHS State Action Level [F]		
Carbon tetrachloride		0.5	CA Primary MCL [A]	0.5	0.1 [E]
Chlorobenzene		100	USEPA Primary MCL [C]		50 [H]
Chloroethane		16	Other Taste and Odor [H]	0.5	100 [I]
Chloroform					
Chloromethane			No Applicable ARAR		
2-Chlorotoluene		140	CA DHS State Action Level [F]		
4-Chlorotoluene		140	CA DHS State Action Level [F]		
Cyclohexane					
Dibromomethane					
Dibromochloromethane					
Dibromochloropropane (DBCP)		0.2	USEPA Primary MCL [C]		0.05 [I]
1,2-Dibromoethane		0.05			0.1 [I]
1,2-Dichlorobenzene		600	CA DHS State Action Level [G]	0.5	600 [E]
1,3-Dichlorobenzene		600	CA DHS State Action Level [G]	0.5	600 [F]
1,4-Dichlorobenzene		5	CA Primary MCL [A]	0.5	6 [E]
Dichlorodifluoromethane		1,000	CA DHS State Action Level [F]		

TABLE A-1
Data Needs and Uses – Regulatory Limits for Organic Parameters and Emergent Compounds
Quality Assurance Project Plan, Omega OU-2

Organic Compound	Uses/Decisions	Applicable Regulatory Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [2]	Additional Regulatory Limits (µg/L)
1,1-Dichloroethane	Exceedances with respect to federal and state drinking water standards, and state action levels.	5	CA Primary MCL [A]	0.5	3 [E]
1,2-Dichloroethane		0.5	CA Primary MCL [A]	0.5	0.4 [E]
1,1-Dichloroethylene		6	CA Primary MCL [A]	0.5	7 [C]; 10 [E]
cis-1,2-Dichloroethylene	Evaluate water treatment system design.	6	CA Primary MCL [A]	0.5	70 [C]
trans-1,2-Dichloroethylene		10	CA Primary MCL [A]	0.5	100 [C]
Dichloromethane (Methylene Chloride)	Evaluate remedial action performance.	5	CA/USEPA Primary MCL [A] [C]	0.5	4 [E]
1,2-Dichloropropane		5	CA/USEPA Primary MCL [A] [C]	0.5	0.5 [E]
2,2-Dichloropropane					
1,1-Dichloropropene					
1,3-Dichloropropene		0.5	CA Primary MCL [A]		
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]
Ethane					
Ethene					
Ethybenzene		300	CA Primary MCL [A])	0.5	700 [C]; 300 [E]; 29 [H]
Hexachlorobutadiene					
2-Hexanone					
Isopropylbenzene (Cumene)		770	CA DHS State Action Level [F]	0.5	
Methane					
Methyl acetate					
Methyl ethyl ketone		8,400	Other Taste and Odor [H]	5	
Methyl isobutyl ketone (MIBK)		120	CA DHS State Action Level [F]		1300 [H]
Methylcyclohexane					
Napthalene		170	CA DHS State Action Level [F]		
n-Propylbenzene		260	CA DHS State Action Level [F]		

TABLE A-1
Data Needs and Uses – Regulatory Limits for Organic Parameters and Emergent Compounds
Quality Assurance Project Plan, Omega OU-2

Organic Compound	Uses/Decisions	Applicable Regulatory Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [2]	Additional Regulatory Limits (µg/L)
Styrene	Exceedances with respect to federal and state drinking water standards, and state action levels.	100	CA/USEPA Primary MCL [A] [C]	0.5	11 [H]
1,1,2,2-Tetrachloroethane		1	CA Primary MCL [A]	0.1	0.5 [E];1.5 [I]
Tetrachloroethylene (PCE)		5	CA/USEPA Primary MCL [A] [C]	0.5	0.06 [E]
Toluene	Evaluate water treatment system design.	150	CA Primary MCL [A]/CA PHG [E]	0.5	42 [H]; 1,000 [C]
1,2,3-Trichlorobenzene					
1,2,4-Trichlorobenzene	Evaluate remedial action performance.	5	CA Primary MCL [A]/CA PHG [E]	0.5	70 [C]
1,1,1-Trichloroethane (1,1,1-TCA)		200	CA/USEPA Primary MCL [A] [C]	0.5	
1,1,2-Trichloroethane		5	CA/USEPA Primary MCL [A] [C]	0.5	5 [I]
Trichloroethylene (TCE)		5	CA/USEPA Primary MCL [A] [C]	0.5	0.8 [E]
Trichlorofluoromethane		150	CA Primary MCL [A]	5	700 [E]
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)		1,200	CA Primary MCL [A]	10	4,000 [E]
1,2,4-Trimethylbenzene		330	CA DHS State Action Level [F]		
1,3,5-Trimethylbenzene		330	CA DHS State Action Level [F]		
Vinyl chloride		0.5	CA Primary MCL [A]	0.5	0.05 [E]; 2 [C]
Xylene(s)		1,750	CA Primary MCL [A]	1,800	17 [H]; 10,000 [C]
Additional Volatiles					
Methyl tert-butyl ether (MTBE)	Exceedances with respect to federal and state drinking water standards, and state action levels	`13	CA Secondary MCL [B]	3	13 [E]

TABLE A-1
Data Needs and Uses – Regulatory Limits for Organic Parameters and Emergent Compounds
Quality Assurance Project Plan, Omega OU-2

Organic Compound	Uses/Decisions	Applicable Regulatory Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [2]	Additional Regulatory Limits (µg/L)
TCL Semivolatile Organic Compounds					
Acenaphthene	Exceedances with respect to federal and state drinking water standards, and state action levels.				
Acenaphthylene					
Acetophenone					
Aniline (Phenylamine) (Aminobenzene)	Evaluate water treatment system design.				
Anthracene.	Evaluate remedial action performance.				
Benzaldehyde					
Benzoic Acid (Carboxybenzene)					
Benzo(a)anthracene					
Benzo(a)pyrene		0.2	CA/USEPA Primary MCL [A,] [C]	0.1	0.004 [E]
Benzo(b)fluoranthene					
Benzo(g,h,i)perylene					
Benzo(k)fluoranthene					
Benzyl Alcohol (Phenylmethanol)					
1,1'-Biphenyl					
Bis(2-chloroethoxy)methane					
Bis(2-chloroethyl)ether					
Bis(2-chloroisopropyl)ether					
4-Bromophenyl-phenyl ether					
Butylbenzyl phthalate (BBP)					
Caprolactam					
Carbazole					
4-Chloro-3-methylphenol					
4-Chloroaniline					

TABLE A-1
Data Needs and Uses – Regulatory Limits for Organic Parameters and Emergent Compounds
Quality Assurance Project Plan, Omega OU-2

Organic Compound	Uses/Decisions	Applicable Regulatory Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [2]	Additional Regulatory Limits (µg/L)
2-Chloronaphthalene	Exceedances with respect to federal and state drinking water standards, and state action levels.				
2-Chlorophenol					
4-Chlorophenyl-phenyl ether					
Chrysene	Evaluate water treatment system design.				
Di(2-ethylhexyl)adipate		400	CA/USEPA Primary MCL [A] [C]	5	200 [E]
Di(2-ethylhexyl)phthalate	Evaluate remedial action performance.	4	CA Primary MCL [A]	3	6 [C]; 12 [E]
Dibenz(a,h)anthracene					
Dibenzofuran (Diphenylene oxide)					
3,3'-Dichlorobenzidine					
2,4-Dichlorophenol					
Diethyl phthalate (DEP)					
Dimethyl phthalate					
2,4-Dimethylphenol		100	CA DHS State Action Level [F]		
4,6-Dinitro-2-methylphenol					
2,4-Dinitrophenol					
2,4-Dinitrotoluene					
2,6-Dinitrotoluene					
Di-n-butylphthalate (Dibutyl phthalate)					
Di-n-octylphthalate(Dioctyl phthalate)					
Endothall		100	CA/USEPA Primary MCL [A] [C]	45	580 [E]
Fluoranthene (Idryl)					
Fluorene					
Glyphosate		700	CA/USEPA Primary MCL [A] [C]	25	1,000 [E]
Hexachlorobenzene		1	CA/USEPA Primary MCL [A] [C]	0.5	0.03 [E]

TABLE A-1
Data Needs and Uses – Regulatory Limits for Organic Parameters and Emergent Compounds
Quality Assurance Project Plan, Omega OU-2

Organic Compound	Uses/Decisions	Applicable Regulatory Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [2]	Additional Regulatory Limits (µg/L)
Hexachlorocyclopentadiene	Exceedances with respect to federal and state drinking water standards, and state action levels.	50	CA/USEPA Primary MCL [A] [C]	1	50 [E]
Hexachloroethane					
Indeno(1,2,3-cd)pyrene					
Isophorone	Evaluate water treatment system design.				
2-Methylnaphthalene					
2-Methylphenol	Evaluate remedial action performance.				
4-Methylphenol					
3,4-Methylphenol					
2-Nitroaniline					
3-Nitroaniline					
2-Nitrophenol					
4-Nitroaniline					
4-Nitrophenol					
Pentachlorophenol		1	CA/USEPA Primary MCL [A] [C]	0.2	0.4 [E]
Phenanthrene					
Phenol		4,200	CA DHS State Action Level [F]		
Pyrene					
Pyridine					
2,4,6-Trichlorophenol					
2,4,5-Trichlorophenol					
Emergent Compounds	Exceedances with respect to federal and state drinking water standards, and state action levels.				
1,4-Dioxane		3	CA DHS State Action Level [F]		15 [I]
N-Nitrosodimethylamine (NDMA)		0.01	CA DHS State Action Level [F]		0.02 [I]
1,2,3-Trichloropropane (1,2,3-TCP)	Evaluate water treatment system design.	0.005	CA DHS State Action Level [F]		

TABLE A-1
Data Needs and Uses – Regulatory Limits for Organic Parameters and Emergent Compounds
Quality Assurance Project Plan, Omega OU-2

Organic Compound	Uses/Decisions	Applicable Regulatory Limit (µg/L)	Applicable ARAR (1)	California DHS DLR (µg/L) (2)	Additional Regulatory Limits (µg/L)
Treatment/Discharge Parameters					
Total Organic Parameters	Evaluate groundwater treatment alternatives.				
Total Organic Carbon					
Biological Oxygen Demand	Evaluate treated groundwater discharge alternatives.				
Chemical Oxygen Demand					

Notes:

(1) ARARs from June 2003 California EPA Compilation of Water Quality Goals and Updates through September 2003.

(2) California Department of Health Services required Detection limit for Purposes of Reporting (DLR).

(3) Calculated ARAR based on hardness = 120 mg/L as $CaCO_3$.

(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-1
Data Needs and Uses – Regulatory Limits for Organic Parameters and Emergent Compounds
Quality Assurance Project Plan, Omega OU-2

Inorganic Parameter	Uses/Decisions	Applicable Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [3]	Additional ARARs (µg/L)
Emergent Compounds					
Chromium (VI)	Exceedances with respect to federal and state drinking water standards, and state action levels.	11 (0.2) [4]	California Toxics Rule for Aquatic Life Protection [H]	1	
Perchlorate		4	CA DHS State Action Level [F]	4 (preliminary)	
	Evaluate water treatment system design.				
TAL Inorganics					
Aluminum	Exceedances with respect to federal and state drinking water standards, and state action levels.	50	USEPA Secondary MCL [D]11	50	200 [B]; 600 [E]
Antimony		6	CA/USEPA Primary MCL [A] [C]	6	20 [E]
Arsenic		10	USEPA Primary MCL [C]	2	50 [A]; 0.004 [E]
Barium	Evaluate groundwater treatment alternatives and treated groundwater discharge options.	1,000	CA Primary MCL [A]	100	2,000 [C] [E]
Beryllium		4	CA/USEPA Primary MCL [A] [C]	1	1 [E]
Cadmium		5	CA/USEPA Primary MCL [A] [C]	1	0.07 [E]; 2.6 [3] [H]
Calcium					
Chromium (total)		50	CA Primary MCL [A]	10	100 [C]
Cobalt					
Copper		11 [2]	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	California Toxics Rule for Aquatic Life Protection [H]	5	15 [F]; 2 [E]; 0.25 [G]
Magnesium					
Manganese		50	CA/USEPA Secondary MCL [B] [D]	20	
Mercury		2	CA/USEPA Primary MCL [A] [C]	1	1.2 [E]
Molybdenum					
Nickel		61	California Toxics Rule for Aquatic Life Protection [H]	10	100 [A];12 [E]
Potassium					
Selenium		5	California Toxics Rule for Aquatic Life Protection [H]	5	50 [A] [C]

TABLE A-1
Data Needs and Uses – Regulatory Limits for Organic Parameters and Emergent Compounds
Quality Assurance Project Plan, Omega OU-2

Inorganic Parameter	Uses/Decisions	Applicable Limit (µg/L)	Applicable ARAR [1]	California DHS DLR (µg/L) [3]	Additional ARARs (µg/L)
Silver	Exceedances with respect to federal and state drinking water standards, and state action levels.	4.7 [2]	California Toxics Rule for Aquatic Life Protection [I]	10	100 [B] [D]
Sodium					
Thallium		2.0	CA/USEPA Primary MCL [A] [C]	1	0.1 [E]
Vanadium	Evaluate groundwater treatment alternatives and treated groundwater discharge options.	50	CA DHS State Action Level [F]	3 (preliminary)	
Zinc		140 [2]	California Toxics Rule for Aquatic Life Protection [H]	50	5,000 [B] [D]
Cyanide		5.2	California Toxics Rule for Aquatic Life Protection [H]	100	200 [C];150 [E]
Additional Inorganics					
Boron	Evaluate groundwater treatment alternatives and treated groundwater discharge options	1,000	CA DHS State Action Level [F]		
Silicon					
Treatment/Discharge Parameters					
pH	Evaluate groundwater treatment alternatives and treated groundwater discharge options	6.5 to 8.5	USEPA Secondary MCL [D]		
Alkalinity					
Ammonia		500	Other Tastes and Odors [J]		
Bicarbonate	Exceedances with respect to federal and state drinking water standards, and state action levels				
Bromide					
Chloride		250,000	CA/USEPA Secondary MCL [B,D]		
Fluoride		1,000	CA PHG [E]	100	2,000 [A] [D]
Nitrate (as N)		10,000	USEPA Primary MCL [C]		10,000 [E]
Nitrite (as N)		1,000	CA/USEPA Primary MCL [A] [C]	400	1,000 [E]
Phosphorus (orthophosphate, total phosphorus)					
Sulfate		250,000	CA Secondary MCL [B]	500	250,000 [D]

TABLE A-1
Data Needs and Uses – Regulatory Limits for Organic Parameters and Emergent Compounds
Quality Assurance Project Plan, Omega OU-2

Inorganic Parameter	Uses/Decisions	Applicable Limit (µg/L)	Applicable ARAR (1)	California DHS DLR (µg/L) (3)	Additional ARARs (µg/L)
Total dissolved solids (TDS)	Evaluate groundwater treatment alternatives and treated groundwater discharge options Exceedances with respect to federal and state drinking water standards, and state action levels	250,000	CA/USEPA Secondary MCL (B,D)		

NOTES:

(1) ARARs from June 2003 California EPA Compilation of Water Quality Goals and Updates through September 2003.

(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.

(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-2
Measurement Performance Criteria
Quality Assurance Project Plan for Omega OU-2

Parameter	Method	Target Detection Limit[h]	Analytical Accuracy (% Recovery)	Analytical Precision (Relative % Deviation)	Overall Completeness (%)
Volatile Organic Compounds					
TCL Volatile Organic Compounds (VOCs) plus MTBE [a]	EPA 524.2/CLP [b]	(c)	70-130/CLP	±30/CLP	90
TCL[a] Semivolatile Organic Compounds (SVOCs)	CLP [b]	(c)	CLP		
Emergent Compounds					
1,4-Dioxane	EPA 8270 [b]	1 µg/L	40-130	±30	90
NDMA	Modified EPA Method 1625 [b]	0.02 µg/L	50-125	±30	90
Perchlorate	EPA 314 [b,d,]	5 µg/L	50-150	±50	90
Hexavalent Chromium	EPA 218.6 [b, d]	0.2 µg/L	70-140	±30	90
1,2,3 TCP	(i)	0.005 µg/L	(i)	(i)	90
Groundwater Treatment and Discharge Parameters					
TAL [a] Metals (field-filtered) plus Boron, Silicon	EPA 200.7[d,b] EPA 200.8[d,b] EPA 245.1/CLP	(g)	70-130	±30	90
Cyanide	EPA 335.4[d,b]	10 mg/L	75-125	±25	90
Bromide	EPA 300.0[d,b]	1.0 mg/L	75-125	±25	90
Chloride	EPA 300.0[d,b]	1.0 mg/L	75-125	±25	90
Fluoride	EPA 300.0[d,b]	0.1 mg/L	75-125	±25	90
Nitrate-N	EPA 300.0[d,b]	0.1 mg/L	75-125	±25	90
Nitrite-N	EPA 300.0[d,b]	0.1 mg/L	75-125	±25	90
Orthophosphate-P	EPA 300.0[d,b]	1.0 mg/L	75-125	±25	90
Total Sulfate	EPA 300.0[d,b]	1.0 mg/L	75-125	±25	90
Total Kjeldahl Nitrogen (TKN)	EPA 351.2[d,b]	0.3 mg/L	75-125	±25	90
Ammonia	EPA 350.2[d,b]	0.3 mg/L	75-125	±25	90
Total Phosphorus	EPA 365.4[d,b]	0.3 mg/L	75-125	±25	90
Total Dissolved Solids (TDS)	EPA 160.1[d,b]	20 mg/L	75-125	±25	90
Alkalinity	SM 2320B [b, e]	20 mg/L	75-125	±25	90
Total Organic Carbon	EPA 415.1[d]	2.0 mg/L	75-125	±30	90

TABLE A-2
Measurement Performance Criteria
Quality Assurance Project Plan for Omega OU-2

Parameter	Method	Target Detection Limit[h]	Analytical Accuracy (% Recovery)	Analytical Precision (Relative % Deviation)	Overall Completeness (%)
BOD	SM 5210B[e]	3 mg/L	75-125	±25	90
COD	SM5220D[e]	5.0 mg/L	75-125	±30	90
Field Analyses for Volatile Organics	(j)	(j)	(j)	(j)	90

[a] Target Compound List (TCL) and Target Analyte List (TAL) as shown in Table A-1 and Appendix B. MTBE: methyl tert-butyl ether.

[b] Volatile organics, semivolatile organics, metals and cyanide may be analyzed by the EPA Contract Laboratory Program (CLP) Statement of Work or the equivalent EPA Regional Laboratory Standard Operating Procedures shown in Appendix B, depending on availability. For other analytes, the analyses will be carried out by EPA Regional Laboratory or a Contract Laboratory. EPA Regional Laboratory specifications or data quality indicator specifications have been provided in Appendix B.

[c] For volatile organics, detection limits will be at 1 part per billion (ppb) for all except 0.5 ppb for vinyl chloride, carbon tetrachloride, 1,2 dichlorethane, cis and trans-1,3-dichloropropene, and 2 ppb for 1,2-dibromo-3-chloropropene. CLP detection limits are shown in Appendix B.

[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. Silicon to be determined as silica by EPA 200.7 and will have a detection level < 0.1 part per million (ppm).

[h] Target detection level is reporting level, see text for explanation.

[i] The method and QA/QC will follow California State guidance to achieve the needed low regulatory limit. Laboratory-specific standard operating procedures will be defined prior to start of work, and subsequent to selection of laboratory.

[j] Volatile organics to be analyzed in the field will be the same list as the offsite laboratory analyses (a), target detection levels will also be equivalent to the offsite laboratory analyses. Method will be based on 8260/GC/MS. Method and field laboratory-specific standard operating procedures will be defined prior to start of work.

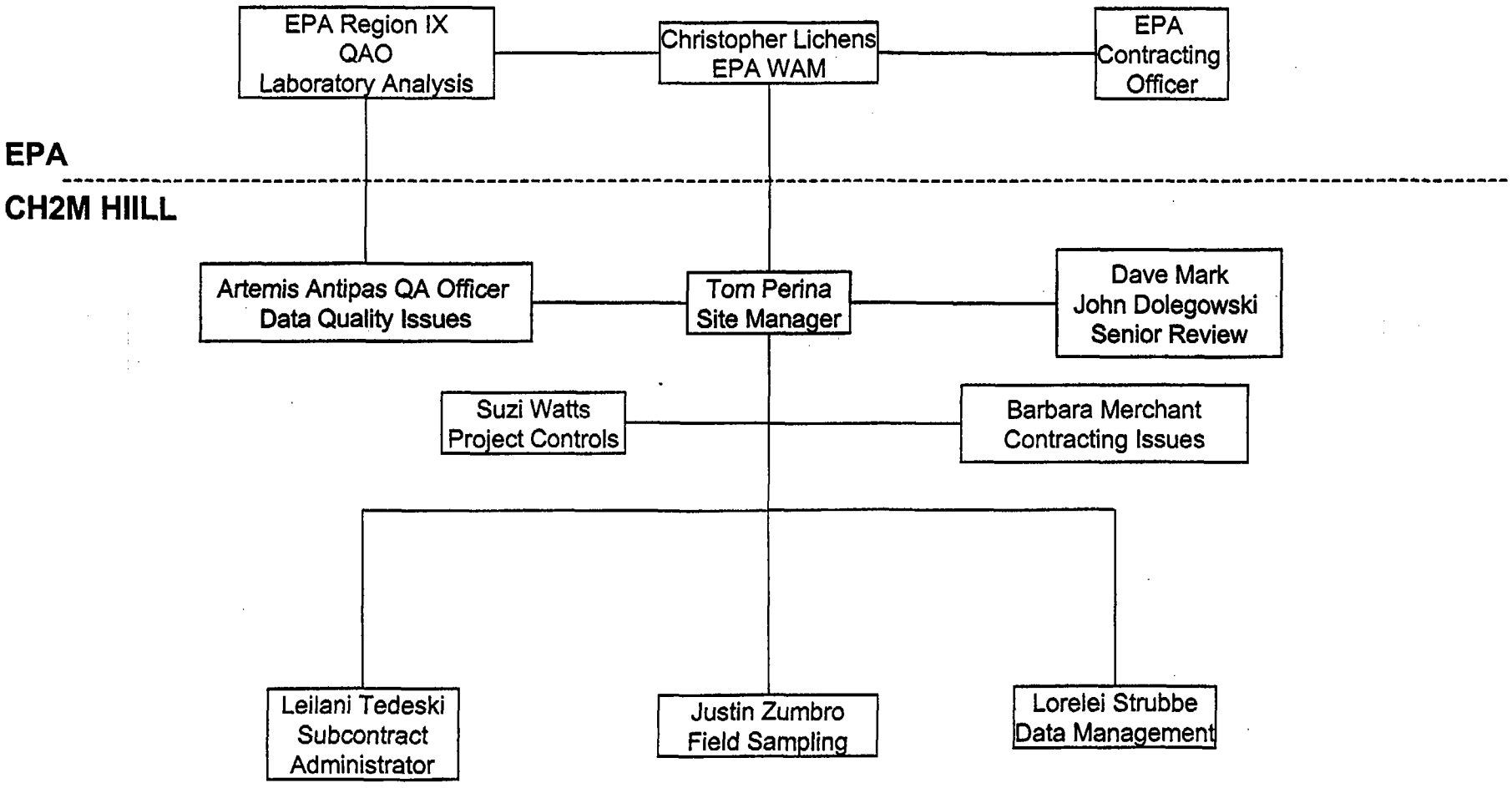

Figure A-1
Omega Chemical OU2 Project Organization
RI/FS Field Activities

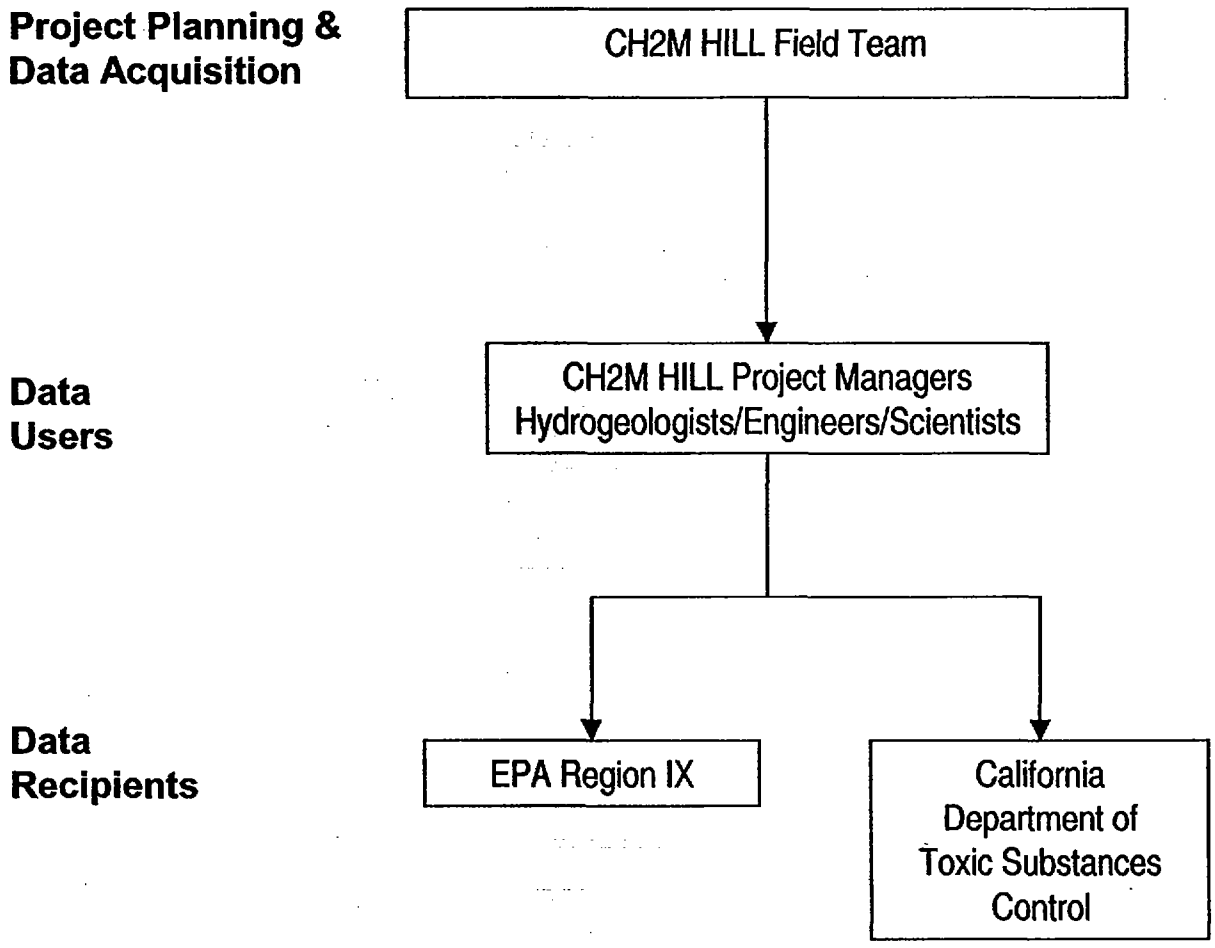

Figure A-2
Data Users/Recipients
RI/FS Field Activities

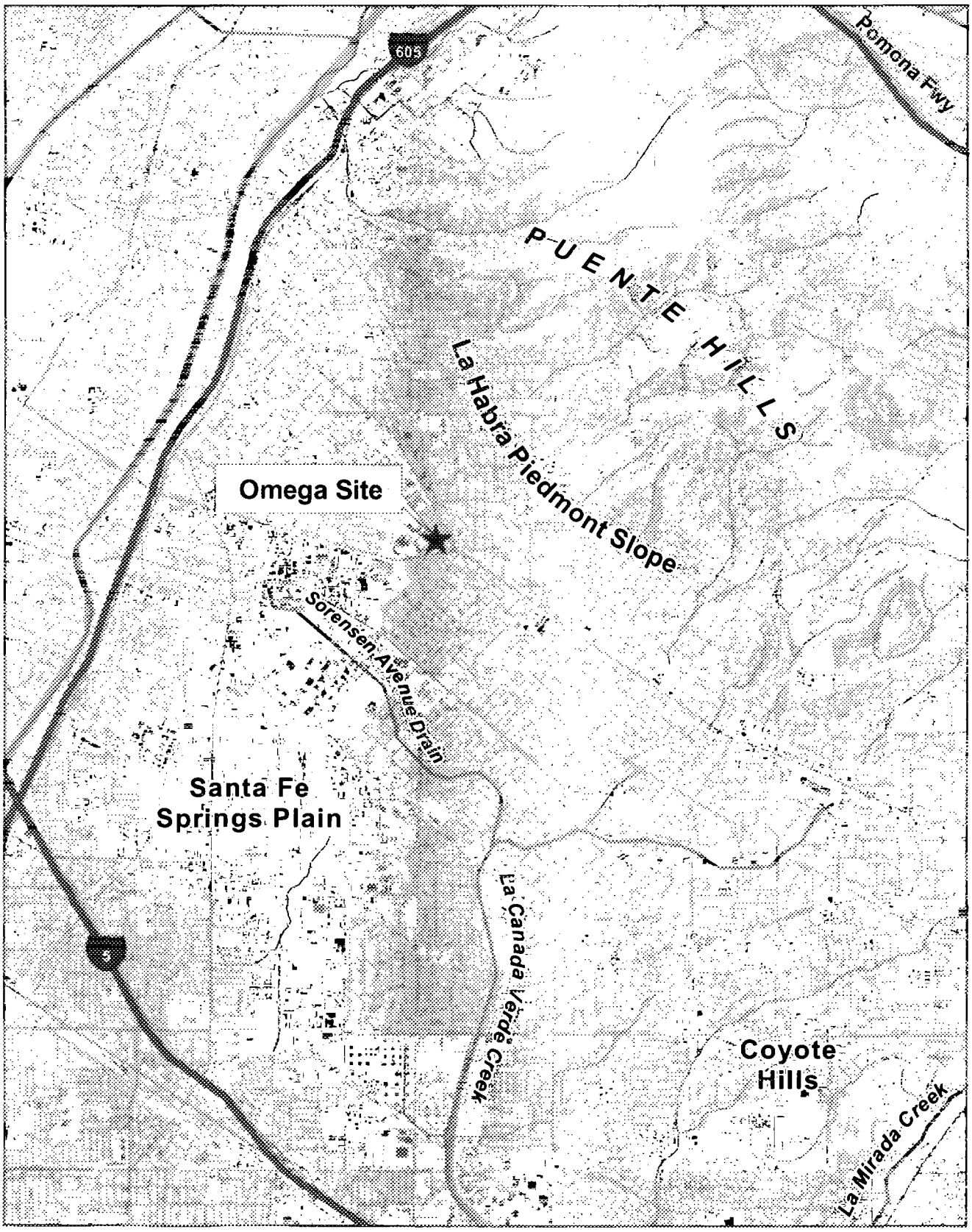

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Figure 1-1
Site Location Map
Omega Chemical Superfund Site

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SCO183122 PPC Site_Loc.ai 01/04

Section B
Measurement Data Acquisition

This section presents sampling process design and requirements for sampling methods, sample handling and custody, analytical methods, QC, and instrumentation for the sampling activities that will be conducted as a part of the RI/FS at the Omega Chemical Superfund site. Data acquisition requirements and data management for these sampling events are also addressed in this section.

B.1 Sampling Process Design

B.1.1 Background

Background information and objectives are presented in Section A. The primary objectives of this RI/FS are to delineate the vertical and lateral extent of groundwater contamination at the OU-2 site and investigate potential source areas other than the Omega facility.

B.1.2 Schedule of Analyses

The field investigation is expected to last approximately 2 years after mobilization.

B.1.3 Rationale for Sampling Design

Sampling Locations and Number of Samples

Soil, soil gas, and groundwater sample locations and number of samples are summarized in Section 3 of the accompanying FSP.

Laboratory Analyses

Samples will be analyzed at the EPA CLP laboratories, EPA Regional Laboratory and/or Contract Laboratories.

The analytical parameters for the individual samples are detailed in Table A-2 as well as the accompanying FSP in the request for analyses tables.

B.2 Sampling Method Requirements

Sampling method requirements have been detailed in the associated FSP in Section 5.

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 the Region IX Laboratory; this will be preceded with the RSCC request form. COC 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 and COC record
- Inorganic traffic report and COC record
- EPA Region IX COC 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 B of the FSP (EPA, 2004). Completed field QA/QC 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. COC 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 field work, 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.

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 Section 5.10 of the companion FSP (EPA, 2004). In addition to COC records, a bound field notebook must be maintained by each STL 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, methods, and required detection levels have been listed in Table A-2. The analyses for volatiles, semivolatiles, and metals will be per EPA CLP methodology and laboratories or the EPA Regional Laboratory depending on availability. As required, if detection limits and the analyte lists differ from the standard CLP lists, the analyses will be carried out per special services provisions currently available under the CLP. A low-level ICP/MS statement of work (ILM 5.1) may be used for metals. Similarly, a low-level organic statement of work (OLC 3.2) or larger sample volumes may be used to attain lower-level organic detection limits. Samples for VOCs in soil will be collected and preserved following EPA Method 5035. If the CLP is unavailable, the analyses can be carried out at the EPA Regional Laboratory using the laboratory's standard operating procedures and QA equivalent to the CLP per standard operating procedures in Appendix B.

The analyses for other analytes in Table A-2 will be per the EPA Regional Laboratory standard operating procedures or the data quality indicators provided in Appendix B. The

analyses may be carried out by the Regional Laboratory or Contract Laboratories, depending on availability.

For 1,2,3 TCP the method and QA/QC will follow California State guidance to achieve the needed low regulatory limit. Laboratory-specific standard operating procedures will be defined prior to start of work, and subsequent to selection of the laboratory.

Volatile organics to be analyzed in the field will be the same as those listed for the offsite laboratory analyses; target detection levels will also be equivalent to the offsite laboratory analyses. The method will be based on 8260/GC/MS. The method and field laboratory-specific standard operating procedures will be defined prior to start of work.

B.5 Quality Control Requirements

B.5.1 Field QC Procedures

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

Field QC samples include field duplicates, field blanks, and laboratory QC samples (for matrix spike/matrix spike duplicates [MS/MSDs]). QC samples will be collected immediately following collection of target samples, using the same procedures as those used for collection of the target sample. These procedures are presented in the accompanying FSP (EPA, 2004).

B.5.2 Laboratory Procedures

Laboratory QC procedures will include the following:

- Analytical methodology according to specific methods listed in Table A-2.
- Instrument calibrations and standards as defined in specific methods listed in the CLP statement of work.
- Laboratory blank measurements per CLP statement of work.
- Accuracy and precision measurements per CLP statement of work, at a minimum of 1 in 20, 1 per batch.
- Data reduction and reporting according to specific methods listed in Table A-2.
- Laboratory documentation equivalent to the CLP statement of work.

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 described 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 particular model's operation and maintenance handbook.

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: pH, electrical conductivity (EC), temperature, dissolved oxygen and oxidation/reduction potential 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 operations and maintenance manual for the particular instrument.

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 QA/QC reviewer will be notified.

B.7.2 Laboratory Calibration Procedures

Laboratory calibration procedures are specified in the referenced methods for all parameters listed in Table A-2.

B.8 Data Acquisition Requirements (Nondirect Measurements)

Previously collected data and other information will be used to assist decisionmaking during the RI/FS. These data will be in both hard copy and electronic format. Electronic data will be handled by the electronic data management system described below.

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 project database to facilitate database inquiries 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 assignments (WAs) 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 or others at EPA's request. Major components for complete data management will be as follows:

- **Data Conversion/Manipulation/Review.** Reports of data from sampling are received from the 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 the database.

- **Preparation of Tables.** Data tables will be prepared following receipt of validated data from the QAO following each sample event of the WA. Queries will be created for the database to generate updated tables.

- **Database Documentation.** An update of the database and complete documentation will be performed at the end of the project. The commands, file names, and general operating procedures for all the data queries will be documented 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 Statement 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) the 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 are expected to be performed by the EPA CLP Laboratories, the EPA Regional Laboratory, and/or Contract Laboratories. The distribution of analyses may change at the time of analyses depending on availability. The QA of the CLP is centrally managed by EPA. The QA of the Regional Laboratory is managed by the EPA QAO. Laboratories subcontracted to CH2M HILL, if any, will be selected based on prior performance on Regional Superfund projects. Additionally, onsite audits or performance evaluation samples will be administered by the project QAO, as necessary.

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. Analyses carried out by CLP laboratories will be reviewed by the EPA Quality Assurance Management Section or their designee. Analyses carried out by the EPA Regional Laboratory will be reviewed by the contractor independent of the laboratory.

Data will be reviewed outside the laboratory at the following level of effort:

1. For sampling episodes where few samples are analyzed (one to two batches) data will be reviewed at Tier 3 as defined by the regional QAO guidance.

2. For sampling episodes where there are more than two batches, data will be reviewed at Tier 2 and Tier 3. 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 will be 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 laboratory 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; this scope is covered under the current Regional Tier 2 review.

The level of effort detailed above is based on the objectives of this project and deal with quantitative evaluation of samples at trace levels for all analytes. The full database requires consistent flags for comparable and reproducible data, which should be met with this level of effort. 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, TCE may be detected more frequently than other analytes. Establishing the validity of nondetect results is as important as the detected results for monitoring, thus 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 performed 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, 1994, 1999, and 2002) 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-2 of this QAPP. Assessment of data for precision, accuracy, and completeness will be per the following quantitative definitions.

D.3.1 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 deviation (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:

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

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

D.3.2 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

D.3.3 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

Camp Dresser & McKee (CDM). 2003. *Final On-Site Soils Remedial Investigation/Feasibility Study Work Plan.*

U.S. Environmental Protection Agency (EPA). 1994, 1999, and 2002. *Contract Laboratory Program National Functional Guidelines for Inorganic/ Organic Data Review.* February.

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————. 2004. *Field Sampling Plan for Omega Chemical Superfund Site Operable Unit 2, Remedial Investigation/Feasibility Study Oversight.* Prepared by CH2M HILL. February.

Weston Solutions, Inc. (Weston). 2002. Omega Chemical Superfund Site; Whittier, California; Phase 2 Groundwater Characterization Study Report. June.

Appendix A
Data Quality Objectives

Data Quality Objectives (DQOs)
Well Construction, Aquifer Testing, and Groundwater Sampling
Remedial Investigation/Feasibility Study
Omega Chemical Superfund Site Operable Unit 2

Step 1. State the Problem

(1) *Identify members of the planning team* – The members of the planning team are the Environmental Protection Agency (EPA) Work Assignment Manager (WAM), CH2M HILL Site Manager (SM), CH2M HILL Staff Hydrogeologists, and CH2M HILL Quality Assurance Officer (QAO).

(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 Omega Chemical Corporation (Omega) is a former refrigerant/solvent recycling operation located in Whittier, California, a community of approximately 85,000 people. Existing groundwater and soil data indicate that elevated concentrations of volatile organic compounds (VOCs) and other compounds are present the soil and groundwater beneath the former Omega Chemical Facility (Operable Unit 1 [OU-1]) and up to 2 miles downgradient in shallow groundwater. A series of soil gas, soil, and groundwater investigations have been performed at OU-1 by a variety of consultants beginning in 1985. Chlorinated hydrocarbons (primarily PCE, TCE, 1,1-DCE, cis-1,2-DCE, and chloroform) and Freons (Freon 11 and Freon 113) were identified as the primary chemicals of concern directly beneath the site. Elevated total chromium also was reported in groundwater beneath the Omega site. Perchlorate contamination is suspected. Other contaminants of concern (detected or suspected at the site) include cyanides, NDMA, pesticides and PCBs, dissolved metals, and 1,4-dioxane. Elevated concentrations of chemicals of concern were also reported west and southwest of the Omega facility, suggesting that a downgradient migration of the contaminant plume from the site has occurred.

Operable Unit 2 (OU-2) generally includes the groundwater-contaminated areas encompassing the Omega Chemical Facility and extends approximately 2.2 miles to the southwest. The vadose zone contamination at the Omega site and the highly contaminated portion of the aquifer in the immediate site vicinity are addressed as OU-1 under a separate effort. The primary objective of this investigation is to conduct an RI/FS to estimate the vertical and lateral extent of groundwater contamination within OU-2.

EPA has conducted a record search that indicated industrial facilities other than Omega Chemical likely contributed to groundwater contamination within OU-2. The current understanding is that the groundwater contamination present at OU-2 is a continuous, co-mingled plume originating from multiple source areas. This investigation will assess the continuity of groundwater contamination at OU-2 and characterize the main source

areas of the contamination. Many of these facilities are currently under a regulatory oversight and the extent of contamination has been addressed by remedial investigation. As part of the Omega investigation, reports on these sites maintained at the Los Angeles Regional Water Quality Control Board (LA RWQCB) and Department of Toxic Substances Control (DTSC) will be reviewed and the information compiled and evaluated.

It is possible that characterization of some of the potential sources has not been completed and will need to be addressed under this investigation. Because the extent of such effort is unknown at this time, it is not included in this QAPP and will be addressed by an addendum to this document after additional information becomes available. It is anticipated that such future investigation, if necessary, will include soil gas and soil sampling, well installation, and aquifer testing.

The problem is summarized as follows:

(a) The vertical and lateral extent, as well as the nature of contamination in groundwater beneath OU-2 needs to be determined. The trend in contaminant concentrations in groundwater needs to be evaluated.

(b) The risk to human health and the environment from contaminants present at OU-2 needs to be assessed.

(c) The presence, extent, and concentrations of emergent contaminants (1,4-dioxane, perchlorate, NDMA, hexavalent chromium, and 1,2,3-trichloropropane [1,2,3-TCP]) in groundwater surrounding and downgradient of the Omega site need to be determined.

(d) The remedial action best suited to site conditions needs to be selected to restore the aquifer, prevent the contamination of nearby drinking water wells, prevent ongoing contamination migration, and prevent exposure to humans and the environment.

(e) Investigation-derived waste (IDW) generated during field activities (e.g., drill cuttings, well development water, well purge water, and aquifer testing water) will need to be properly disposed in accordance with state, federal, and local regulations.

(4) Specify available resources and relevant deadlines for the study –

Although not complete, investigations have been performed previously at the Omega site. The site history, past investigations, and remediation activities are discussed in detail in the *Final On-Site Soils RI/FS Work Plan* (Camp Dresser & McKee [CDM], 2003) and the *Omega Chemical Superfund Site; Whittier, California; Phase 2 Groundwater Characterization Study Report* (Weston Solutions, Inc. [Weston], 2002).

Data obtained in 1988 from site assessment activities, including groundwater and soil sampling conducted by the site owner/operator, Dennis O'Meara, and data from a preliminary assessment conducted by EPA in January 1995, indicated the presence of hazardous substances in subsurface soil and groundwater at the site, including methylene chloride, PCE, and TCE. The presence of these substances and deteriorated underground storage tanks at Omega lead EPA to determine that an imminent and

substantial endangerment requiring a removal action existed at Omega. On May 3, 1995, EPA issued an Action Memorandum authorizing a Removal Action involving the following response actions:

- Securing the site
- Sampling and categorizing hazardous materials
- Removing hazardous substances and grossly contaminated equipment, structures, and debris
- Sampling surface and subsurface soils and groundwater to determine the nature and extent of contamination
- Disposing, stabilizing, or treating grossly contaminated soils
- Grading, capping, and fencing contaminated soil areas

EPA has divided the Omega Chemical Superfund Site into two Operable Units: OU-1 and OU-2. OU-1 includes the Omega Chemical Facility property and extends a short distance west-southwest to Putnam Street (Weston, 2003). OU-2 surrounds the Omega Chemical Facility and extends offsite approximately 2.2 miles to the southwest. This DQO describes work to be completed within OU-2.

As part of the OU-1 effort, EPA entered into a Partial Consent Decree with the potentially responsible parties (PRPs) who had agreed to complete work at the site. This group is known as Omega Chemical Site PRP Organized Group (OPOG). This Partial Consent Decree was entered into the District Court on February 23, 2001. OPOG agreed to perform an RI/FS, conduct a Non-Time Critical Removal Action, perform a risk assessment, and install groundwater monitoring wells at OU-1, also referred to as the Phase 1A area.

As part of the OU-2 effort, EPA issued an order to another group of PRPs to complete work at OU-2 and initiated settlement negotiations with the remaining PRPs. The resolutions of these actions are pending. In the meantime, EPA authorized its consultant, CH2M HILL, to initiate the RI/FS at OU-2.

Record search conducted by EPA revealed on-going remedial activities at multiple facilities within OU-2. Relevant reports and other documents are available at LA RWQCB and DTSC.

A local water supply well is impacted and continues to be threatened, although it is not known at this time whether the contamination originated at Omega. If no action is taken, drinking water aquifers may become impaired by contamination from Omega and potentially also from other sources within OU-2. The OU-2 RI/FS is scheduled to be competed in 2006. For cost-estimating purposes in support of settlement negotiations, the duration of remedial action (RA) was assumed to be between 2006 and 2038 (remedial system construction between 2006 and 2008, and operation between 2009 and 2038). The time required to achieve aquifer restoration at OU-2 is necessarily longer; but the sense of urgency is nevertheless underscored by the need for taking action.

Step 2. Identify the Decision

(1) *Identify the principal study question –*

The apparent problem at the site is the migration to groundwater of chlorinated solvents and associated attenuation products, and potentially of other compounds. The current decision requires adequate data for use in plume delineation, contamination forensic evaluation, assessment of human health and ecological risk, and recommending a remedial action. The concentrations of these VOC and attenuation compounds are greater than background levels for the area and exceed health-based benchmarks in the vicinity of the site. The principal goals for CH2M HILL are to develop a sufficient amount of data to support selection of an appropriate approach for the site remediation and develop a well-supported Record of Decision (ROD). Achieving these goals includes answering the following study questions:

(a) What is the vertical and lateral extent and nature of contamination in groundwater beneath OU-2, and what is the trend in groundwater concentrations?

(b) Do contaminants pose an unacceptable potential risk to human health and the environment?

(c) Are emergent contaminants (1,4-dioxane, perchlorate, NDMA, hexavalent chromium, and 1,2,3-TCP) present in groundwater surrounding and downgradient of the Omega site?

(d) What remedial action will best suit the site conditions to restore the aquifer, prevent the contamination of nearby drinking water wells, prevent ongoing contamination migration, and prevent exposure to humans and the environment?

(e) How can IDW (e.g., drill cuttings, well development water, well purge water, and aquifer testing water) be properly disposed in accordance with state, federal, and local regulations?

(2) *Define alternate actions that could result from resolution of the principal study question* – The alternate actions for goals defined in (1) above will be, respectively:

(a) (1) The nature and extent of groundwater contamination will be based on existing information, including groundwater samples from past cone penetrometer test (CPT) investigations and a limited number of existing monitoring wells. Uncertainties regarding the extent of the plume will remain and changes in concentrations within areas previously characterized by in-situ samples will not be assessed.

(2) Additional well clusters will be installed and monitored at locations within the plume with no permanent monitoring wells at downgradient and lateral edges of the plume to characterize the lateral and vertical extent of contamination. These wells will be available for future monitoring to evaluate changes in contaminant concentrations in groundwater.

(b) (1)Additional data collection indicates that there is a risk to human health, (2) no risk, or (3) insufficient data.

(c) (1) If emergent chemicals are not present in groundwater, then commonly used technologies for groundwater treatment will be utilized. (2) If emergent chemicals are present, then additional groundwater treatment will be required.

(d) Remedial actions that may be considered include no action, natural attenuation, groundwater extraction and treatment system. The site conditions and treatment requirements may require collection of additional data or information to select a remedial action that will best suit the site conditions.

(e) Drill cuttings may be disposed as (1) nonhazardous soil in a Class II landfill, or (2) hazardous waste in a Class I landfill. IDW water can be disposed as clean water to a storm drain if no contaminants exceeding maximum contaminant levels (MCLs) or Action Levels (ALs) are present. Wastewater containing contaminants above ALs or MCLs must be treated onsite or disposed at a treatment, storage, and disposal facility (TSDF).

(3) *Combine the principal study question and the alternative actions into a decision statement* –

(a) If the new understanding of the nature and extent of groundwater contamination is shown to be significantly different than the current understanding, then a different remedial approach may need to be considered. If the new data are not sufficient to adequately characterize the nature and extent of the contamination, then additional wells will be installed and/or the duration of monitoring extended.

(b) If the contaminants at OU-2 pose an unacceptable potential risk to human health and the environment, a remedial action will be recommended. No action will be recommended otherwise. A recommendation for collection of additional data will be made if the risk cannot be fully assessed based on the data collected.

(c) If emergent contaminants are present, additional treatment technologies for groundwater may be required.

(d) If the selection of a remedial action that will best suit the site conditions cannot be made based on the data available, additional data or information will be collected.

(e) IDW water will be treated onsite and discharged as clean if onsite treatment is feasible. If IDW water cannot be treated onsite, it will be disposed at a TSDF. If drill cuttings have not met nonhazardous waste criteria, they will need to be placed in a Class I landfill. If drill cuttings have met nonhazardous waste criteria, they will be placed in a Class II landfill.

(4) *Organize multiple decisions* – Based on the answers to the principal study questions, decisions about alternate actions and additional phases of RI/FS activities will be made during the progress of the RI/FS. The resolution of 3(b) and 3(c) may impact 3(a) by requiring that additional data or information be collected.

(a) The updated assessment of the nature and extent of contamination may indicate that the VOC plume has migrated further downgradient or to a greater depth than is currently expected. If so, it may result in the need for additional monitoring wells and extended groundwater monitoring.

(b) If a risk of exposure is determined to exceed human health or ecological criteria, then a remedial action to reduce that risk to an acceptable level will be recommended.

(c) The presence of emerging contaminants in groundwater may necessitate additional site characterization and groundwater treatment technology.

(d) If IDW water can be treated onsite, it will be discharged as clean. If IDW water cannot be treated onsite, it will be disposed at a TSDF. If drill cuttings have not met nonhazardous waste criteria, they will need to be placed in a Class I landfill. If drill cuttings have met nonhazardous waste criteria, they will be placed in a Class II landfill. The range of IDW disposal options was presented and the associated waste profiling specified; evaluation of other disposal options is not required.

Step 3. Identify Inputs to the Decision

The purpose of this step is to identify the information and measurements needed to support the decision statement. The data will be evaluated with regard to the four principal questions of the RI/FS.

(1) *Identify the information that will be required to resolve the decision statement* – Based on data uses and availability, the following data are needed:

(a) To resolve the decision statement, the planning team will need contaminant concentration data for groundwater samples from new and existing monitoring wells, and hydrogeological data (including historical) from existing wells, as well as applicable regulatory criteria for the following constituents: VOCs, semivolatile organic compounds (SVOCs), metals, perchlorate, and hexavalent chromium.

(b) To resolve the decision statement (b), the planning team will need groundwater and soil concentrations of contaminants listed under (a) and (c), appropriate human health risk and ecological risk criteria, information on exposure pathways, and exposure information.

(c) To resolve the decision statement (c), the planning team will need the analytical results for emerging contaminants (1,4-dioxane; perchlorate; NDMA; 1,2,3-TCP; hexavalent chromium) from site monitoring wells as well as applicable regulatory criteria.

(d) To resolve the decision statement (d), aquifer hydraulic characteristics derived from aquifer testing will be used to provide information critical to assess contaminant fate and transport and evaluate remediation alternatives. Groundwater elevations and contaminant concentrations in groundwater will be measured to define groundwater flow direction, allow plume tracking over time, and provide calibration data for the numerical model to assess contaminant fate and transport and evaluate remedial alternatives. Analytical results for groundwater samples, including compounds listed under (a) and (c), and additional compounds (nitrate, sulfate, methane, total dissolved solids [TDS], biological oxygen demand [BOD], chemical oxygen demand [COD], pH) will be used to select the treatment technology. Hydraulic conductivity, soil moisture, redox potential, cation exchange

capacity, and total organic carbon (TOC) will be used to evaluate contaminant fate and transport.

(e) To resolve the decision statement (e), the planning team will need the analytical results for the IDW, both soil cuttings and groundwater, as well as applicable regulatory action levels and screening criteria.

(2) *Determine the sources for each item of information identified:* The results from this investigation will provide the necessary information to resolve the decision statement. Data from previous site investigations will be utilized as needed.

(a) Lithologic and laboratory analytical data from samples collected at new and existing monitoring wells.

(b) Soil and groundwater analytical data collected during this and previous investigations as well as information on exposure pathways.

(c) Laboratory analyses of emerging compounds from groundwater samples collected from the new and existing wells.

(d) Data collected under (a), (b), and (c), aquifer test results, regulatory requirements, cost analysis.

(e) Laboratory analysis results for samples of IDW water and soil.

(3) *Identify the information that is needed to establish the action level* – Action levels will be generated in the risk assessment using EPA guidance.

(a) The regulatory action levels include California and federal drinking water standards, ALs in California, and California Public Health Goals (PHGs) (Table A-1 in the main text of this QAPP). Method detection limits and historical concentrations, as appropriate, will be used for unregulated drinking water compounds.

(b) A risk assessor will evaluate human health and ecological risk; specific action levels will not be recommended.

(c) California ALs will be applied.

(d) If groundwater treatment is required, discharge options will be guided by MCLs, California ALs, California PHGs, Los Angeles Basin Plan Water Quality Objectives, National Pollutant Discharge Elimination System (NPDES) Permits, California Toxic Rules, and South Coast Air Quality Monitoring District Permits.

(e) For IDW soil: 40 Code of Federal Regulations (CFR) Section 261.24, 22 California Code of Regulations (CCR) Section 66261.24, and waste acceptance criteria for offsite nonhazardous waste TSDF. For IDW water: California Toxic Rules (40 CFR Section 131.38), 22 CCR Section 64431 (Drinking Water Standards); Department of Health Services (DHS); Office of Environmental Health Hazard Assessment (OEHHA); and best professional judgment.

(4) *Confirm that appropriate measurement methods exist to provide the necessary data* – The appropriate methods have been identified to meet project needs and are shown in the QAPP.

Step 4. Define the Boundaries for the Study

(1) *Specify the characteristics that define the population of interest* –

(a) Concentrations of chlorinated solvents and their degradation products, and other parameters, including VOCs, SVOCs, pesticides/PCBs, cyanide, perchlorate, and metals in groundwater within shallow unconsolidated sediments.

(b) Same as (a). The groundwater samples will be collected following a systematic rather than statistical sampling design.

(c) Concentrations of emerging contaminants in groundwater within shallow unconsolidated sediments.

(d) Impacted groundwater within shallow unconsolidated sediments.

(e) IDW soil and water containerized in roll-off bins, tanks, 55-gallon drums, and other storage containers.

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

(a) Define the geographical area to which the decision statement applies – The boundary of OU-2 is the extent of the contamination in groundwater. One objective of the RI/FS (principal study question a) is to determine the extent of the spatial boundary. This geographical area applies to all principal study questions.

(b) Divide the population into strata that have relatively homogeneous characteristics – For all the principal study questions, the contaminated aquifer may be considered one stratum.

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

(a) Determine the timeframe to which the decision statement applies – For principal study questions (a), (b), and (c), the timeframe is 2 years, the duration of the project. For principal study questions (d) and (e), the duration if indefinite because the liability associated with the remedy and IDW disposal extends into the future.

(b) Determine when to collect data - The anticipated duration of the RI/FS is 2 years (all principal study questions).

(4) *Define the scale of decisionmaking* – The scale of decisionmaking will be limited to the OU-2 area (the same geographic boundary).

(5) *Identify practical constraints on data collection* – The sampling locations and schedule may depend on site access, permitting, and right-of-way constraints. For all principal study questions, there are practical funding limitations imposed by Congressional appropriations. The decisions and professional practices will be based on the current scientific understanding of contaminant fate and transport, adverse effects of

contaminants on human health and environment, and treatment of contaminated media.

Step 5. Develop a Decision Rule

(1) *Specify the statistical parameter that characterizes the population of interest*

(a) Sample analysis reports will be compared to action levels. Each value, not a statistical parameter such as mean concentration, will be evaluated against the action levels.

(b) Sample analysis reports will be compared to action levels on a point-by-point basis.

(c) Sample analysis reports will be compared to action levels. Each value, not a statistical parameter such as mean concentration, will be evaluated against the action levels.

(d) The full range of concentrations will be used semi-quantitatively in the evaluation of remedial alternatives.

(e) Sample analysis reports will be compared to applicable criteria on a point-by-point basis to characterize IDW soil for disposal and IDW water for treatment and discharge.

(2) *Specify the action level for the study –See Step 3, Item (3).*

(3) *Develop a decision rule (an "if...then..." statement) –*

(a) If an analytical result is greater than an action limit, then the sampling location can be included in OU-2 and may warrant further investigation.

(b) If the assessment of risk concludes the contamination at OU-2 poses an unacceptable risk to human health and/or the environment, a remedial action will be recommended.

(c) If emerging contaminants are detected, remedial alternative selection will include appropriate treatment technologies.

(d) If the collected data allow for clear identification of remedial alternatives, the alternative selection will be developed; otherwise, additional data or information will be collected.

(e) If waste soil profiling indicates the results meet nonhazardous waste criteria, the IDW soil will be shipped to a Class II landfill; otherwise, it will be transported to a Class I landfill. If waste profiling for IDW water indicates it meets regulatory requirements, it will be treated and discharged onsite; otherwise, it will be send to a TSDF.

Step 6. Specify Tolerable Limits on Decision Errors

Tolerable limits on decision errors, which are used to establish performance goals for the data collection design, are specified in this step.

(1) *Determine the range of the parameters of interest* – The available historical range of the parameters of interest (for principal study questions a, b, c, and d) is known for a portion of OU-2 only. Concentrations of chlorinated hydrocarbons in groundwater ranged from nondetect to tens of thousands of micrograms per liter ($\mu g/L$). Concentrations of perchlorate were less than 7 $\mu g/L$. Part of principal study question (a) is to determine the range of contaminant concentrations. The historical range of contaminant concentrations in IDW (principal study question e) was not known at the time of preparation of this document.

(2) *Identify the decision errors and choose a null hypothesis* – For principal study questions a through d: The DQO guidance prescribes the identification of the null hypothesis and associated decision errors for determining the number of random samples and the locations to attain a given level of confidence with the spatial distribution. Because samples will be collected at systematically selected locations, statistical decision errors cannot be defined. However, project error tolerances are defined in terms of precision, accuracy, representativeness, comparability, and completeness (PARCC) parameters in Section A.4 of this QAPP. Analyte-specific accuracy and precision ranges are shown in Table A-2 of this QAPP. The project completeness goal is set at 90 percent. The laboratory data will be evaluated against PARCC requirements as outlined in the QAPP. Possible decision errors will be considered tolerable when data meet stated PARCC goals.

For principal study question e, for IDW soil, guidance published in EPA Publication SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, will be followed (see Step 7, Item 3). For IDW water, mixing is expected to occur while each Baker tank is being filled, thus providing a well-mixed, homogeneous condition for sample collection.

(4) *Specify a range of possible values of the parameter of interest where the consequences of decision error are relatively minor* – Not applicable.

(5) *Assign probability values to points above and below the action level that reflect the tolerable probability for the occurrence of decision errors* – Applies to all principal study questions: Because sample locations are predetermined, probability values cannot be assigned. Instead, error tolerances are defined in terms of the PARCC parameters and are explained in Section A.4 of the QAPP. Needed project accuracy and precision ranges are shown in Table A-2 of the QAPP for the individual analytes. The completeness goal for the project is set at 90 percent.

Step 7. Optimize the Design

(1) *Review the data quality objective (DQO) outputs and existing data*

(a) The results will also be compared to historical data and to regulatory action levels (e.g., state and federal MCLs, California ALs, PHGs) as per the objectives described above. Discrete groundwater sampling and screening-level laboratory analysis of the discrete samples will be used to select the screen depth intervals of the new monitoring wells.

(b) Existing (i.e., historical) data will also be included in the risk assessment. The analytical results for the discrete-depth groundwater samples and IDW samples will not be used in the risk assessment.

(c) The results will also be compared to historical data and to regulatory action levels (e.g., California ALs) as per the objectives described above.

(d) Areally averaged concentrations in groundwater will be used to estimate the average influent concentrations, which then can be used for the feasibility evaluation and treatment unit process design.

(e) The waste profiling results will not be compared to past IDW results. For proper disposal, the waste profiling results will be compared to applicable screening criteria, federal and California hazardous waste action levels, and facility-specific waste acceptance criteria.

(2) *Develop general data collection design alternatives* –

(a) None anticipated. Sampling will be done from fixed well locations, which are based on professional judgment, so there are no alternatives.

(b) None anticipated. Samples will be collected at locations selected as part of principal study questions a and c.

(c) None anticipated. Sampling will be done from fixed well locations, which are based on professional judgment, so there are no alternatives.

(d) None anticipated. The feasibility study will use areally averaged results from samples collected at fixed well locations, which are based on professional judgment, so there are no alternatives.

(e) Representative sampling of IDW soil can be achieved either by averaging the results of separate samples collected, or by collecting the samples, compositing first, and then analyzing the composited sample. The IDW water is expected to be relatively well-mixed as holding containers are filled. Given that the constituents are expected to be in the dissolved phase (not in nonaqueous phase), a single sample per container should be representative of the wastewater.

(3) *For each data collection design alternative, select the optimal sample size that satisfies the objectives* - None anticipated for principal study questions a through d; the sample size is based on professional judgment.

For DQO e, for IDW soil, the optimal sample size (see table below) is based on the requirements listed in EPA Publication SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*.

Volume (CY)	Minimum No. of Subsamples/Aliquots	Comments
<10	2	1 sample from each half
10 to 20	3	1 sample from each third
20 to 100	4	1 sample from each quarter
>100	1 per 25 CY	1 sample from each 25-CY portion

Note that roll-off bins are each 10-cubic yard (CY) bins and more than one roll-off bin may be grouped together for composite sampling.

For IDW water, one sample per 20,000-gallon tank is expected to be adequate.

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

(a) The proposed groundwater monitoring well locations were selected to fill data gaps in areas where the extent of the groundwater contamination is not known. Discrete groundwater sampling will be used to select a representative well screen depth and minimize the number of wells necessary.

(b) All historical and new data will be used.

(c) Same as (a).

(d) Same as (b).

(e) Attempts will be made to separate relatively clean IDW from contaminated IDW. Compositing of samples from segregated IDW will minimize the number of laboratory analyses.

(5) *Document the operational details and theoretical assumptions of the selected design in sampling and analysis plan* – The data collection program, including sampling rationale, is presented in the FSP (EPA, 2004).

Appendix B
Analytical Technical Specifications

Appendix B
Analytical Technical Specifications

Contents

B-1	TCL Volatile Organic Compounds (VOCs) plus MTBE
B-2	1,4-Dioxane
B-3	NDMA
B-4	Perchlorate
B-5	Hexavalent Chromium
B-6	TAL Metals (field filtered) plus Boron, Silicon, and Cyanide
B-7	Anions: Bromide, Chloride, Fluoride, Nitrate-N, Nitrite-N, Orthophosphate-P, Sulfate
B-8	Total Kjeldahl Nitrogen (TKN)
B-9	Ammonia
B-10	Total Phosphorus
B-11	Total Dissolved Solids (TDS)
B-12	Total Organic Carbon (TOC)
B-13	Alkalinity
B-14	Biological Oxygen Demand (BOD)
B-15	Chemical Oxygen Demand (COD)

Attachment 1: CLP Analytes and Limits

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: _____ _____
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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).

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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 μg/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

System Name	HP5973J	HP5973H	HP5973K
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(μg/L) = SD $\times$ 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.

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

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:

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

where:

A_x	= area of the characteristic ion of the compound
AMT_{IS}	= amount of internal standard in $\mu g/L$ (5 $\mu g/L$)
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 μg/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: _____ _____
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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
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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:

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

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
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 $\mu g/L$ 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)
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 $\mu g/mL$ (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
			Low	Med.	On

Semivolatiles	CAS Number	Water µg/L	Soil µg/Kg	Soil µg/Kg	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)

MWH LABORATORIES

Standard Operating Procedure
for

NDMA by GCMS

Modified EPA Method 625/1625

Approved:

(1) Group Leader:_____Date_____

(2) QA Officer:_____Date_____

(3) Technical Director/:_____Date_____
Laboratory Director

ACCREDITED IN ACCORDANCE WITH
nelac
01114CA

Controlled Copy____
of _____ copies
MWH Laboratories
Initials_____Date_____

TABLE of CONTENTS

I. TITLE
II. SCOPE and APPLICATION
III. METHOD SUMMARY
IV. INTERFERENCES
V. SAFETY CONSIDERATIONS
VI. INSTRUMENTATION/APPARATUS
VII. REAGENTS & STANDARDS
VIII. SAMPLE COLLECTION, PRESERVATION and HANDLING
IX. CALIBRATION PROCEDURE
X. ANALYTICAL PROCEDURE
XI. QUALITY CONTROL REQUIREMENTS
XII. CALCULATIONS
XIII. METHOD PERFORMANCE
XIV. REFERENCES
XV. DEVIATIONS from REFERENCED METHODOLOGY
XVI. METHOD DETECTION LIMIT
XVII. DEFINITIONS
XVIII. POLLUTION PREVENTION
XIX. WASTE MANAGEMENT
XX. REVISIONS
XXI. ATTACHMENTS

I. TITLE

NDMA (N-nitrosodimethylamine) by GCMS (Based on EPA Method 1625/625 Mod)

II. SCOPE and APPLICATION

A. This standard operating procedure describes the qualitative and quantitative analysis of organic compounds in water using gas chromatograph/mass spectrometry as described in EPA Method 1625/625 Modified. SIM is used to reach a detection limit of 1ppt (2ppt MRL).

B. The above method reporting limits (MRL) are based on extracting an 1 liter aliquot of aqueous sample, adding NDMA-d6 and NDPA-d14 as internal standards and/or surrogates for isotope dilution, and concentrating it down to a final volume of 1.0 ml.

C. See Attachment III, Quantitation and Confirmation Ion Table for additional information.

III. METHOD SUMMARY

A. A 1-liter aliquot of the sample is extracted with methylene chloride at a pH of 11 using a continuous extractor. Neutral organics may be removed prior to extraction using a C-18 disk.

B. The methylene chloride extract is dried and concentrated down to a final volume of 1mL before being analyzed by GC/MS.

C. Qualitative identification of target analytes is achieved by monitoring quantitation and secondary ions and comparing relative retention times of reference standards.

D. Target analyte concentrations are then determined by the use of internal standard calculations. Analyte recovery is monitored against N-Nitroso-di-npropyl amine-d14.

IV. INTERFERENCES

A. Extracts with high concentration of carboxylic acid or compounds of high basicity can be detrimental to the GC column.

B. To minimize contamination, all glassware should be washed and baked at 400 °C in a muffle furnace.

C. Sodium sulfate and glasswool used in extraction should also be baked and solvent rinsed before use.

D. Only high quality reagent grade solvents should be used for extraction and the preparation of standards and extracts.

V. SAFETY CONSIDERATIONS

A. Methylene chloride is a suspected carcinogen as is NDMA. Each chemical should be treated as potential health hazard.

B. Use a fume hood when working with all standards and extracts

C. Materials Safety Data Sheets (MSDS) for chemicals used in GCMS are available in the department and in central files located in the date entry room on the second floor.

D. Analysts should be familiar with the MSDS information BEFORE working with the chemicals, especially neat compounds and stock solutions in high concentration.

E. Refer to the MWH Laboratories SOP "Hazardous Waste Management and Sample Disposal Procedures" and OSHA Standard 29 CFR 1910.1450 Occupational Exposure to Hazardous Chemicals in Laboratories; Final Rule for additional safety information.

VI. INSTRUMENTATION/APPARATUS

A. Positive Ion EI

1. Finnigan TRACE mass spectrometer with Finnigan TRACE 2000 GC and CTC AS200 autosampler.
2. Fused silica capillary column 30 meter x 0.25 mm I.D. and 1 micron film thickness (Restek DB5-Amine or equivalent)

B. Positive ION CI

1. Finnigan Polaris-Q Ion Trap with EI, CI and MS/MS capabilities. Trace 2000 GC and CTC AS-200 Autosampler.
2. Fused silica capillary column. J&W Scientific DB626. 60Mx0.32mmx1.8u.
3. Injector speed 1 uL/sec. (PTV-LV injection)Instrument parameters may be modified to maximize chromatographic separations and quantitation reliability.

C. See Attachment VII for Instrument Parameters.

D. Instrument parameters may be modified to maximize chromatographic separations and quantitation reliability.

VII. REAGENTS & STANDARDS

Material Safety Data Sheets for the chemicals listed in this document may be found in files located in the laboratory or on the World Wide Web at the Cornell University MSDS database search page, "http://msds.pdc.cornell.edu/msdssrch.asp".

A. Solvent - Methylene chloride, reagent grade.

B. Standards

1. DFTPP at 5 ng/ul in methylene chloride (MeCl2). For EI analysis only.
2. NDMA/NDPA-d14 standard at 1 pg/ul, 2pg/ul, 5pg/ul, 10pg/ul, 20pg/ul, 40 pg/ul, 100, and 250 pg/ul in MeCl2. Each standard level should contain 20 pg/ul NDMA-d6 as an internal standard

C. Refer to Attachment IV for the preparation of standards and storage conditions. Standards should be discarded if the expiration date on the ampule has passed.

VIII. SAMPLE COLLECTION, PRESERVATION and HANDLING

A. Grab samples should be collected in a minimum of two separate 1-Liter amber glass bottles (3 bottles required for LFM/LFMD studies), fitted with a screw cap lined with teflon. Note that 3 bottles does not allow for any back-up in the event of QC failure. Preferably request 5 bottles when a client has a specific sample for LFM/LFMD so adequate backup is available.

B. Conventional sampling practices should be followed except that the bottle must not be pre-rinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. All samples must be iced or refrigerated at 4 C from the date of collection until extraction.

C. If residual chlorine is present, add 80mg of sodium thiosulfate per liter of sample and mix well.

D. All samples must be extracted within 7 days of collection and completely analyzed within 30 days of extraction.

IX. CALIBRATION PROCEDURE

A. Laboratory Performance Check (LPC) - 5 ng of DFTPP (Only for EI analysis) should be analyzed at the beginning of every 12 hours that samples are analyzed. The ion abundance criteria in Table 2 must be met before any analysis can take place.

B. See Attachment V for DFTPP tuning criteria

C. Injector inertness

1. For EI analysis, verify injector condition DDT and ENDRIN are injected with DFTPP. Neither compound should degrade more than 20% on injection
2. For CI analysis verify peak symmetry, with minimal asymmetry.

D. Initial Calibration (IC)

1. This should be analyzed when the continuing calibration standard fails.
2. Analyze after a successful DFTPP (for EI analysis only).
3. The %RSD for each analyte must not exceed 20.
4. Alternatively, construct a calibration curve that introduces the linear or quadratic least error fit with the correlation coefficient no less than 0.995. A minimum of 5 standards are required. When using quadratic fit, the curve must be verified at, at least 2 calibration levels.
5. Failure to meet the required RSD and or correlation coefficient require the system be inspected for integrity and corrective action taken. Suggested actions include but are not limited to, injector and column maintenance, GC/MS interface maintenance, prepare new standard solutions as necessary.
6. The eight concentrations for the initial calibration standards are in the range from 1 pg/ul to 250 pg/ul. A minimum of five point calibration is required in the method. The lowest point should be at a concentration near the MDL and the other concentrations should correspond to the expected range of concentration found in real samples or should define the working range of the GC/MS system.
7. Note at analyte levels lower than 40 pg/ul, system response may be rather noisy. Manual integration may be necessary to establish a proper baseline and integrate the peak area. This applies to standards and unknown samples. When manual integrations is needed, print the QEDIT report from Chemstation before re-integrating and after re-integrating a peak. Annotate the report as necessary.

E. Continuing Calibration Verification Standard (CCV at 2 or 5 pg/ul)

1. The working curve or response factors (RF) is verified by a mid-level continuing calibration verification standard.
2. The response should agree within +/- 20% of the initial calibration response factor.

3. If linear regression is used, drift must be within +/- 20%.
4. Bracket every 10 sample injections with a suitable standard. Rotate between 5, 10 and 20 pg/ul standards. Be sure to end the analysis batch with a closing standard.
5. After 12 hours has elapsed since DFTPP injection (EI mode only), verify tune by analyzing another DFTPP injection and verify calibration with another CC standard injection before analyzing more samples.

X. ANALYTICAL PROCEDURE

A. Analysts should keep track of the operating conditions of the instrument such as MS manifold temp, GC head pressure, split rate, tune, GC and acquisition parameter.

B. Verify source performance by injecting DFTPP daily.

C. Document all instrument/software problems and maintenance in the instrument logbook.

D. If necessary, perform column maintenance (this may include replacing septum, injector liner, ferrules and trimming column or cleaning the inside of the injector port).

E. If DFTPP in EI mode passes, inject 2 to 10 ul of a 2 or 5 pg/ul NDMA standard for either mode of analysis.

F. If the standard meets the QC criteria stated in this SOP, prepare the extraction batch assigned that day which may include LRB, LFB and samples for analysis.

G. With a syringe or pasteur pipette, pull out sufficient NDMA extract for at least 2 10 ul injections and place it into an CDC AS200 conical vial. Cap the vial with a crimper.

H. Place the vial on the auto-sampler in numerical order and set up the sample sequence on the data system for analysis.

I. Record sample sequence in instrument run log.

J. Bracket every 10 sample injections with a suitable standard. Rotate between 5, 10 and 20 pg/ul standards. Be sure to end the analysis batch with a closing standard.

H. After 12 hours has elapsed since DFTPP injection (EI mode only), verify tune by analyzing another DFTPP injection and verify calibration with another CC standard injection before analyzing more samples.

I. Qualitative analysis of target compounds

1. NDMA and its deuterated analog yield simple spectra.
2. To enhance sensitivity the EI Quadrapole MS is run in SIM mode and full scan mass spectral data is not available.
3. A second ion for NDMA and NDMA-d6 is monitored in the run. Qualitative identification may be made on the basis of GC RT.
4. The mass ratio for NDMA (74/42) should range between 1.2 and 6.1. NDMA-d6 mass ratios (80/46) should range between 1 and 4.8. GC retention time should be within 5 seconds of the injected standard.
5. Using Positive ion CI the spectra is even simpler; however, the reagent gas should never be adjusted to a level that the molecular ion +1 is not seen. Reagent gas pressure affects adduct/molecular ion. Adduct/molecular ion ratios should be similar to those observed in the CCV's. Analyte training and experience is essential I n proper ID. MS/MS experiments may be run to confirm analyte identity if needed.

J. Resolution of interference or co-elution - Should there be evidence of an interfering or co-eluting peak, samples in question should be reanalyzed on a second GC column of differing polarity, such as a DB-1701 or DB-VRX.

K. Quantitate target analytes and surrogate recoveries with the average RF in the initial calibration.

L. ALL data should go through peer review before they can be entered into the MWH Labs data system.

XI. QUALITY CONTROL REQUIREMENTS

A. DFTPP (for EI only.) must pass the ion abundance criteria listed in Attachment V.

B. The initial and CCV standards must meet the QC requirements listed in the calibration section in this SOP.

C. The LRB should be included with each extraction batch or every 20 samples, whichever is more frequent, and should not have any target analytes above 0.5 ppt.

D. An LFB/LFBD pair spiked at 10 ppt and an LFB and an LFM/LFMD at 2 ppt (spike level is variable depending on expected NDMA concentration in the sample) are included with each extraction batch or every 20 samples, whichever is more frequent. Precision is monitored with the LFM/LFMD pair. Should the sample not be spiked at a meaningful level, precision may be monitored with the LFB/LFBD pair. All target analytes are included in the LFBs and LFM/LFMD. If a sample is subjected to follow-up monitoring as a result of detection of NDMA, the

LFM/LFMD level on the batch that includes the follow up sample should be adjusted to a level approximately equivalent to the prior detected level. This information must be conveyed by the client to the project manager and from the project manager to sample preparation when the sample is submitted. To ensure that the sample is spiked appropriately it must be logged into the LIMS system as requiring a spike and is typically considered a billable sample.

E. Precision as measured by the RPD between the LFM and LFMD should be < 27% (equivalent to RSD < 20 %). If insufficient sample is received to prepare duplicate spiked samples, the high level LFB/LFBD samples will be used to measure precision using the same criteria. Accuracy as measured by % recovery should be 80 to 120 % as a warning limit and 70 to 130% as a control limit for LFM/LFMD and LFBs.

F. The areas of the internal standard in the sample must be within -50 to +150% of those in the initial calibration or > 70% of continuing calibration standard.

G. The retention time of the internal standard must be within +/-5 seconds of the last calibration check standard.

H. The surrogate, NDPA-d14 must recover within 70 to 130%. The acceptance criteria is an internal guideline and is not specified in EPA Method 625, 1625, or the DHS memorandum on NDMA dated Nov 15, 1999.

I. If any of the above QC criteria are not met, re-inject the extract. Should the parameters be met, report the data as is; otherwise, document the failures in a Quality Investigation Report (QIR) and annotate the data as necessary.

J. Contingencies for handling out of control data.

1. Submit a Quality Investigation Report (QIR) with any data associated with failed batch or instrument QC.
2. Details regarding use of the QIR can be found in the MWH Laboratories Comprehensive Quality Assurance Plan, Chapter 11, Section 11.2.1.6 and Chapter 13, Sections 13.3, 13.4 and 13.5.
3. See the MWH Laboratories Comprehensive Quality Assurance Plan, Chapter 13, Section 13.5 for a list of data qualifiers and a discussion of report comments.

XII. CALCULATIONS

See Attachment VI for calculations.

XIII. METHOD PERFORMANCE

A. Attachment I, Documentation of Continuing Demonstration of Precision and Accuracy.

B. Attachment II, Documentation of Method Detection Limit Study

XIV. REFERENCES

A. EPA method 625, 40 CFR Ch. 1(7-1-95 Edition)

B. EPA method 1625, 40 CFR Part 136, Appendix A (revised July 1, 1995)

C. DOHS January 14, 2000 "General Considerations Acceptable Analytical Approaches Laboratories Capable of Low-Level Analysis for NDMA"

XV. DEVIATIONS from REFERENCED METHODOLOGY

A. Tuning criteria is taken from EPA Method 525.2 rather than EPA Method 625

B. System performance is monitored with EPA Method 525.2 compounds, endrin and DDT

D. CI may be used to monitor NDMA. EI tuning and system performance criteria meaningless for CI.

E. NDMA-d6 used as internal standard, at 1 concentration. Concentration in calibration standard not the same as NDMA.

XVI. METHOD DETECTION LIMIT

A. Method Detection Limits (MDLs) will be determined as per 40CFR, part 136, Appendix B. Essentially, this requires that an estimate of the detection limit be determined for each target analyte based on analytical experience or published references. Seven replicates of DI water or Ottawa sand must then be spiked at this estimated MDL for each method analyte carried through the entire procedure. The MDL is then calculated as the standard deviation of the 7 replicates multiplied by the statistical "t-value" associated with the actual number of replicates analyzed assuming N-1 degrees of freedom (for exactly 7 replicates, the t-value is 3.143; 40 CFR, Part 136). The extractions/digestions/analyses must be performed over a period of at least three days to provide a more reasonable MDL.

B. An MDL study must be repeated for each new analyst trained in a particular method, or if there is a change in the instrumentation that is used for the analysis in question.

C. Select a fortifying concentration that provides an instrument signal 2 to 5 times above the noise level.

D. The spike concentration must not exceed 10x the calculated MDL or the process must be repeated at a lower spike concentration. The recovery of spiked analyte should be at least 50%-150% (when the spike level is at the MRL level) or ±3 standard deviations, whichever is greater.

E. If there is a significant blank level, the spike level for the MDL determination must be at least three times greater than the blank concentration.

XVII. DEFINITIONS

A. LFB (Laboratory Fortified Blank), LCS, LCS1 (Laboratory Control Sample), QCS (Quality Control Standard) – All of these terms are synonymous as follows: An aliquot of LRB to which known quantities of the method analytes from an external source are added in the laboratory. The LFB/LCS/LCS1/QCS 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.

B. LFBD (Laboratory Fortified Blank Duplicate), LCSD, LCS2 (Laboratory Control Sample Duplicate) – All of these terms are synonymous as follows: An aliquot of LRB to which known quantities of the method analytes from an external source are added in the laboratory. The LFBD/LCSD/LCS2 is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control with regard to precision.

C. LFM (Laboratory Fortified Matrix), MS (Matrix Spike), FS (Fortified Spike) – All of these terms are synonymous as follows: An aliquot of an environmental sample to which known quantities of the method analytes from an external source are added in the laboratory. The LFM/MS/FS 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/MS/FS corrected for background concentrations.

D. LFMD (Laboratory Fortified Matrix Duplicate), MSD (Matrix Spike Duplicate), FSD (Fortified Spike Duplicate) – All of these terms are synonymous as follows: An additional aliquot of the same parent environmental sample of the LFM/MS/FS to which known quantities of the method analytes from an external source are added in the laboratory. The LFMD/MSD/FSD is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control with regard to precision. The background concentrations of the analytes in the sample matrix must

be determined in a separate aliquot and the measured values in the LFMD/MSD/FSD corrected for background concentrations.

E. LRB (Laboratory Reagent Blank), MB (Method Blank) – All of these terms are synonymous as follows: An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB/MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

F. Refer to the MWH Laboratories Comprehensive Quality Assurance Plan Glossary for a complete list of terms and definitions.

XVIII. POLLUTION PREVENTION

A. Because this analysis is performed to meet United States Government and/or local regulatory requirements, reduction in volume of samples, reagents or standards is not possible. Practice pollution prevention by implementing the suggestions listed below and by carefully following the instructions in the Waste Management Section of this document.

B. Reduce disposal costs by ordering quantities of reagents and standards that will be approximately consumed by the expiration date.

C. Practice spill prevention by storing chemicals in secondary containment. Do not store incompatible chemicals in close proximity.

D. Reuse solvents for the first step in glassware cleaning if possible.

XIX. WASTE MANAGEMENT

A. It is the responsibility of the laboratory to determine whether its wastes are hazardous and to assure safe handling and disposal. The laboratory works closely with the Treatment, Storage, Disposal Facility to ensure that certain wastes are recycled where possible, that the source of waste is reduced to the lowest possible level and that stringent land disposal restrictions are followed.

B. Refer to the following documents for additional information regarding waste management:

1. Hazardous Waste Management and Sample Disposal Procedures
2. Resource Conservation and Recovery Act (RCRA)-Title 40 of the Code of Federal Regulations, Parts 260 through 270 (40 CFR 260-270)

3. California Hazardous Waste Control Law (HWCL)-CCR Title 22 where 40 CFR was duplicated into CCR Title 22, Parts 66260-66270.

XX. REVISIONS

A. Revision 1.1 (02/02/00)

1. Quantitation procedure modified to use isotope dilution for analyte quantitation as in method 1625.
2. Qualitative analysis RT window tightened to 0.03 minutes.
3. Initial calibration range modified to include 100 pg/ul standard.

B. Revision 1.2 (03/01/00)

1. Method reference updated to 1625
2. Adjusted preservation to include thiosulfate.
3. Surrogate amount adjusted to 20 ppt equivalent from 10 ppt equivalent
4. Wastewater samples surrogate amount adjusted to 100 ppt equivalent

C. Revision 2.0 (03/09/00)

1. Definitions section added
2. Safety section expanded to included references to additional resources.
3. Pollution Prevention section added.
4. Waste Management section added.
5. Method Performance section added

D. Revision 3.0 (05/04/00)

1. Corrected typographical errors.
2. Added specific acceptance criteria for mass ratio of the primary to secondary ion for NDMA and NDMA-d6.
3. Added discussion of interferences.
4. Removed references to the use of dichlorobenzene-d4 as an internal standard.

D. Revision 4.0 (05/18/00)

1. Corrected typographical errors.
2. Corrected volume of sample required for LFM/LFMD
3. Added criteria for when to do LFM/LFMD at alternative concentrations
4. Made retention time criteria consistent in sections XI and XII.
5. Added storage conditions for standards.

E. Revision 5.0 (06/09/00)

1. Section VI modified to allow optimizing instrument parameters
2. Removed 50 to 150% recovery requirement for MDL study in section XVI.

G. Revision 6.0 (07/11/00)

1. Quality Control section revised to include frequency of LRB analysis
2. Quality Control section revised to include the provision for using LFB/LFBD to measure precision if necessary.
3. Method Summary section revised to state that: "Solute recovery will be monitored by an additional internal standard when a suitable compound is found."
4. Revision section updated to show that tuning criteria is taken from EPA Method 525.2 rather than EPA Method 625 and that endrin and DDT are used to monitor system performance
5. Quality Control section revised to allow RPD criteria for measuring precision rather than RSD.
6. Quality Control section revised to allow measurement of precision with the LFB/LFBD pair if the LFM/LFMD pair is not spiked at a meaningful level.

H. Revision 7.0 (10/24/00)

1. Section XVII, Definitions – Added definitions for LFB, LCS, QCS, LFBD, LCSD, LFM, MS, FS, LFMD, MSD, FSD, and LRB.
2. Section XI, Quality Control – Added warning limits for LFBs and LFMs (80%-120%)

I. Revision 8.0 (01/25/02)

1. Modified Attachment III, Quantitation and Confirmation Ion Table for positive ion ammonia CI.
2. Modified Section VI to allow use of Finnigan Polaris-Q ion trap.
3. Added Attachment VII, Instrument parameters for ION trap. Note as with EI, parameters may be adjusted to maximize sensitivity and analytical selectivity.
4. Modified Attachment IV to reflect the current calibration practice.
5. Section XI.H: Added "The surrogate, NDPA-d14 must recover within 70 to 130%. The acceptance criteria is not specified in method 625, 1625, or the DHS memorandum on NDMA dated Nov 15, 1999."
6.Section II, Scope and Application - Moved Ion Table to Attachment III
7. Section VI, Instrumentation/Apparatus – deleted the GC and MS conditions as they are included in attachment VII, Instrument parameters.
8. Section XII, Calculations - moved discussion of "qualitative analysis of target compounds" and "resolution of interference or co-elution" to Section X, Analytical Procedure. Moved "Quantitate target analytes and surrogate

recoveries with the average RF in the initial calibration" to Section X, Analytical Procedure. Moved calculations to Attachment VI
9. Section XIII and XXI: Deleted Attachment III, Summary of Ongoing Control C.
10. Section XVI, Method Detection Limit - added the following - " The recovery of spiked analyte should be at least 50%-150% (when the spike level is at the MRL level) or ±3 standard deviations, whichever is greater."
11. Corporate name change implemented.
12. Standardized entire document on MWH Labs current template.
13. All sections formatted for web display.
14. Added Table of Contents page.
15. Section XXI, Added Attachments III through VII
16. Section IX.D.6, Added 8th standard to Initial calibration (250 pg/ul).
17. Section IX.E, Added 4 (CCV every 10 samples) and 5 (closing CCV)

XXI. ATTACHMENTS

A. Attachment I, Documentation of Continuing Demonstration of Precision and Accuracy

B. Attachment II, Documentation of Method Detection Limit Study

C. Attachment III, Quantitation and Confirmation Ion Table

D. Attachment IV, Preparation of Standards

E. Attachment V, DFTPP Tuning Criteria

F. Attachment VI, Calculations

G. Attachment VII, Instrument Parameters

Attachment I, Documnetation of Continuing Demonstration of Precision and Accuracy

N-Nitroso dimethylamine (NDMA)
Date Reported: 10/19/01
Analyzed By: col
Prepared by: lib
Units: ng/l

Assignment: col
Method/FOT(s): EPA 625 - 111.120
Group#: 81018

	Actual	DOC1	DOC2	DOC3	DOC4	Avg	%Rcvy	Stdv	%RSD
Preparation Date		08/01	08/01	08/06	08/06				
Analytical Date		08/07	08/07	08/07	08/07				
N-Nitroso dimethylamine	10	9.0	10.2	9.0	9.6	9.450	94.5	0.574	6.1

Attachment II, Documentation of Method Detection Limit Study)

N-Nitroso dimethylamine (NDMA)
Date Reported: 10/19/01
Analyzed By: col
Prepared by: lib
Units: ng/l

Assignment: col
Method/FOT(s): EPA 625 - 111.120
Group#: 81017

	Actual	MDL1	MDL2	MDL3	MDL4	MDL5	MDL6	MDL7	Avg	%Rcvy	Stdv	%RSD	MDL	MRL	Actual/MDL	MRL-MDL
Preparation Date		08/01	08/06	08/15	08/20	09/05	08/27	09/24								
Analytical Date		08/07	08/07	08/20	08/21	09/07	09/01	10/01								
N-Nitroso dimethylamine	2	2.0	1.8	2.2	2.0	1.4	2.4	1.6	1.914	95.7	0.3436	18.0	1.079	2.0000	1.9	0.921

Attachment III, Quantitation and Confirmation Ion Table

Positive ion EI with SIM

Internal Standard	Quantitation Ion	Additional ions monitored
NDMA-d6	80	46
NDMA	**Quantitation Ions**	**Additional ions monitored**
NDMA	74	42

Positive ion CI (NH_3)

Internal Standard	Quantitation Ion	Additional ions monitored
NDMA-d6	98	81
Surrogate	**Quantitation Ion**	**Additional ions monitored**
NDPA-d14	162	148
Target Analytes	**Quantitation Ion**	**Additional ions monitored**
NDMA	92	75

Attachment IV, Preparation of Standards

A. Preparation of 2000 ul of 5.0 ng DFTPP solution

10.0 ul of 1mg/ml DFTPP/DDT/ENDRIN stock solution
dilute to 2ml with $MeCl_2$

B. Preparation of NDMA Calibration Standards

Supplies

Methylene Chloride Residue Grade
Methanol Residue Grade or better.
1000 ppm NDMA-d6 (CIL DLM-2130-S)
1000 ppm NDPA-d14 (CIL DLM-2131-S)
5000 ppm NDMA (Supelco 40059)

Note other sources or concentrations may be used as long as final concentrations are not affected.

Record all dilution information in standard preparation log book!

1 ppm NDMA-d6, NDPA-d14 Surrogate fortification mixture 1 ppm NDMA-d6 and 1 ppm NDPA-d14

10µL of 1000 ppm NDMA-d6 + 10µL 1000 ppm NDPA-d14, dilute to 10 mL with methanol Bottle in 8 mL amber bottles. Label with all information and store refrigerated <5°C.

5 ppm NDMA intermediate in methanol

10µL 5000 ppm NDMA solution diluted to 10 mL in methanol.

1 ppm NDMA LCS fortification standard

1mL of 5 ppm NDMA intermediate. Dilute to 5 mL in methanol. Bottle in 8 mL amber bottle. Label with all information and store refrigerated <5°C.

1 ppm NDMA-d6 intermediate in methylene chloride

10µL OF 1000 ppm NDMA-d6 solution. Dilute to 10 mL with methylene Chloride. Bottle in 8 mL amber bottle. Label with all information and store refrigerated <5°C.

1 ppm NDMA and 1 ppm NDPA-d14 intermediate in methylene chloride.

2µL of 5000 ppm NDMA solution + 10µL 1000 ppm NDPA-d14 solution. Dilute to 10ml with methylene chloride. Bottle in 8 mL amber bottle. Label with all information and store refrigerated <5°C.

NDMA working standard.

Add indicated volumes of NDMA-d6 and NDMA+NDPA-d14 intermediates and methylene chloride from the following table. Bottle in 2 ml amber bottles. Label with all information and store refrigerated <5°C.

Attachment IV, Preparation of Standards

Table 1

Working standard preparation

uL 1 ppm NDMA-d6	uL 1ppm NDMA, NDPA-d14	uL MeCl2	final concentration (ppt)
20	1	979	1
20	2	978	2
20	5	975	5
20	10	970	10
20	20	960	20
20	40	940	40
20	100	880	100
20	250	730	250

1.

Attachment V, DFTPP Tuning Criteria

Tuning Criteria for Decafluorotriphenylphosphine(DFTPP)

Mass	Ion Abundance Criteria
51	10 to 80% of mass 198
68	less than 2% of mass 69
70	less than 2% of mass 69
127	10 to 80% of mass 198
197	less than 1% of mass 198
198	base peak, or >50% of 442
199	5 to 9% of mass 198
275	10 to 60% of mass 198
365	greater than 1% of mass 198
441	present but less than mass 443
442	greater than 50% of mass 198
443	15 to 24% of mass 442

Tune Ion trap to instrument manfufacturer's EI specifications with the auto tune. Replace the EI ion volume with a CI ion volume. Adjust ammonia to a level where the ammonia adduct is observed (m35), but peak shape is still symmetric with minimal fronting.

Attachment VI, Calculations

Concentration

Concentration (ug/L) = $$\frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where :

A_s = Area of the characteristic m/z for the parameter or surrogate standard to be measured.

A_{is} = Area of the characteristic m/z for the internal standard (NDMA-d6).

I_s = Amount of internal standard added to each extract(ug) (NDMA-d6).

V_o = Volume of water extracted (L).

Attachment VII, Instrument Parameters

Instrument Method: NDMA_CI_mini_PTV110702

AS200S Autosampler Method

Before Injection

Solvent washes:	4
Sample cleans:	0
Sample pullups:	0
Hold time:	2.0 seconds

Sample

Injection speed	1 µL/sec
Sample volume:	8.0 µL
Air volume:	1.0 µL

After Injection

Pull-out delay:	2.0 seconds
Solvent washes:	5

Attachment VII, Instrument Parameters

Instrument Method: NDMA_CI_mini_PTV110702

MS Method

Acquisition Time:	GC Run Time
Cal Gas:	Off
Reagent Gas:	On
Reagent Gas Type:	Ammonia
Acquire Profile:	No
Acq Threshold:	0
Source Temp:	150 C

Segment 1

Start Time:	9.30 minutes
Polarity:	POS
Mult Offset:	+50 volts
Tune File:	ci_100801
Reagent Gas Flow:	1.0 mL/Min

Scan Event 1

Micro Scans:	3
Max Ion Time:	70
Mass Defect:	0.00
Scan Mode:	Full Scan
First Mass:	41.0
Last Mass:	165.0

Segment 2

Start Time:	13.00 minutes
Polarity:	POS
Mult Offset:	-100 volts
Tune File:	ci_100801-ndep
Reagent Gas Flow:	1.0 mL/Min

Scan Event 1

Micro Scans:	5
Max Ion Time:	25
Mass Defect:	0.00
Scan Mode:	Full Scan
First Mass:	50.0
Last Mass:	165.0

SIM Parameters
For all ions, use mass ±0.2 amu

	Primary Ion	Secondary Ion
NDMA	92	75
NDMA-d6	98	81
NDPA-d14	162	145

Attachment VII, Instrument Parameters

Instrument Method: NDMA_CI_mini_PTV110702

TRACE GC 2000 Method

Oven Method

Initial Temperature (C):	35
Initial Time (min):	2.00
Number of Ramps:	3
Rate #1 (deg/min):	20.0
Final Temperature #1:	40
Hold Time #1:	2.00
Rate #2 (deg/min):	20.0
Final Temperature #2:	180
Hold Time #2:	0.00
Rate #3 (deg/min):	35.0
Final Temperature #3:	235
Hold Time #3:	3.00
Post Run Temperature:	Off
Enable Cryogenics:	Off
Maximum Temperature (C):	999.00
Prep Run Timeout (min):	0.05

Right PTV Method

Base Temperature:	On
Base Temperature (C):	35
Mode:	PTV Large Volume
Split Flow:	On
Split Flow Flow (ml/min):	30
Splitless Time (min):	0.70
Solvent Valve Temperature:	On
Solvent Valve Temperature (C):	125
Surge Pressure (psi):	0.50
Surge Duration (min):	0.00
Constant Purge:	On
Stop Purge At: (min):	0.00
Evaporation Phase:	On
Cleaning Phase:	On
Ramped Pressure:	Off
Sub-ambient:	Off
Backflush:	Off
Inject Time (min):	0.0
Vent Flow (ml/min):	30
Evaporation Rate (deg/sec):	14.5
Evaporation Temperature (C):	40
Evaporation Time (min):	1.0
Transfer Rate (deg/sec):	14.5
Transfer Temperature (C):	250
Transfer Time (min):	0.7
Clean Rate (deg/sec):	14.5
Clean Temperature (C):	250
Clean Time (min):	14.0

Attachment VII, Instrument Parameters

Instrument Method: NDMA_CI_mini_PTV110702

TRACE GC 2000 Method

Clean Flow (ml/min):	30
Right Carrier Method	
Mode:	Constant Flow
Initial Value:	On
Initial Value (ml/min):	2.00
Gas Saver:	1.00
Gas Saver Flow (ml/min):	Off
Gas Saver Time:	20
Vacuum Compensation:	On

Aux Zones	
Aux Temperature 0:	On
Aux Temperature 0 (C):	235
Aux Temperature 1:	Off
Aux Temperature 1 (C):	0
Aux Pressure 0:	Off
Aux Pressure 0 (psi):	0.00
Aux Pressure 1:	Off
Aux Pressure 1 (psi):	0.00
Aux Pressure 2:	Off
Aux Pressure 2 (psi):	0.00

Run Table	
External Event #1 Prep-Run Default:	Off
External Event #2 Prep-Run Default:	Off
External Event #3 Prep-Run Default:	Off
External Event #4 Prep-Run Default:	Off
External Event #5 Prep-Run Default:	Off
External Event #6 Prep-Run Default:	Off
External Event #7 Prep-Run Default:	Off
External Event #8 Prep-Run Default:	Off

Appendix B-4
Perchlorate

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 531

ANALYSIS OF PERCHLORATE BY ION CHROMATOGRAPHY

Prepared by:

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_____ _____
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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:

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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 19

10 DOCUMENTATION 24

11 REFERENCES 24

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 *ug*/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 μg/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 *u*g/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 *ug*/L perchlorate standard to each 25 mL volumetric flask and dilute to volume with reagent water to yield a final perchlorate concentration of 25 *ug*/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 ≥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, *ug*/L.
T = true concentration of perchlorate in the IPC/QCS/LFB or IPC, *ug*/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 *ug*/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, *ug*/L.
T = true concentration of perchlorate in the QL, *ug*/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 $\leq$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, μg/L.
C	=	measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions, μg/L.
s	=	expected analyte concentration in the LFM, corrected for sample preparation and any dilutions, μg/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, μg/L.
C_{lfmd}	=	measured concentration in the LFMD corrected for sample preparation and any dilutions, μg/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 *ug/L* using the following calculation:

$$C = M \times D$$

where:

C	=	final reported concentration, in *ug/L*.
M	=	measured concentration reported by software, in *ug/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 precolumn (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

Parameter/Method	Analyte	Water			
		RL	Unit		
Hexavalent Chromium/218.6	Hexavalent Chromium	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
		MS/MSD or Dup/MS	Every 20 samples	70-140%recovery 30%RPD	Find problem, repeat or explain
		MDL Study	Every 12 months	None (1ug/l needed)	None

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

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Approved by:

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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:

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CONTENTS

1 SCOPE AND APPLICATION 5

2 METHOD SUMMARY 6

3 DEFINITIONS 7

4 HEALTH AND SAFETY 9

5 SAMPLE HANDLING AND PRESERVATION 10

6 INTERFERENCES 10

7 APPARATUS AND MATERIALS 12

8 QUALITY CONTROL PROCEDURES 14

9 ANALYTICAL PROCEDURES 20

10 DOCUMENTATION 22

11 REFERENCES 23

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 ≥ 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-μm 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-μm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid contamination). The laboratory must perform filtration immediately if the step was not performed in the field. Acidify the filtrate 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 μL, 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 μg/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 μg/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 μg/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:

$$\%R = \frac{Clfm - C}{s} \times 100$$

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 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 ± 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 μg/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 μg/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				[illegible]				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
[illegible]													
Arsenic (200.8)	20				20	U			20	U			5
[illegible]													
Beryllium (200.7)	1	U			1	U			1	U			1
[illegible]													
Cadmium (200.8)	5	U			5	U			5	U			1
[illegible]													
Chromium (200.7)	10	U			10	U			10	U			10
[illegible]													
Copper (200.8)	4				4	U			4	U			1
[illegible]													
Iron (200.7)	5	U			5	U			5	U			1
[illegible]													
Manganese (200.8)	3				3	U			3	U			1
[illegible]													
Molybdenum (200.8)	5	U			5	U			5	U			1
[illegible]													
Potassium (200.7)	5000				5000	U			5000	U			5000
[illegible]													
Silver (200.8)	5	U			5	U			5	U			1
[illegible]													
Thallium (200.8)	5	U			5	U			5	U			1
[illegible]													
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:

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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:

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ESAT Document Control Number: B0101029-0485

CONTENTS

1 SCOPE AND APPLICATION 4

2 METHOD SUMMARY 5

3 DEFINITIONS 6

4 HEALTH AND SAFETY 8

6 INTERFERENCES 10

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-μm 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-μm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid contamination). The laboratory must perform filtration immediately if the step was not performed in the field. Acidify the filtrate with (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 μL, 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 μg/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 μg/L, with the exceptions of selenium at 250 μg/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 μg/mL stock standards to contain 500 μg/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 μg/L of each analyte, except for selenium. Selenium is fortified at 500 μg/L. Prepare the LFM by fortifying an aliquot of the QC sample with the calibration stock standards to contain 100 μg/L of each analyte, except for selenium. Selenium is fortified at 500 μg/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 μg/L of each analyte, except for selenium which will be fortified at 125 μg/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 μg/mL stock standards to contain 500 μg/L of barium and cerium and 10 μg/L each of beryllium, magnesium, cobalt, indium, lead, and uranium.

7.2.16 Quality Control Sample (QCS) - Prepare a multi-element standard from 1000 μg/mL stock standards to contain 100 μg/L of each analyte, except for selenium at 500 μg/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 μg/mL stock standards to contain 1 μg/L of each analyte, except for arsenic, selenium and zinc at 5 μg/L, aluminum at 20 ug/L and vanadium at 10 μg/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, μg/L.
s	=	expected analyte concentration in the IPC, μg/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, μg/L.
s	=	expected analyte concentration in the LFB, μg/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, μg/L.

C = measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions, μg/L.

s = expected analyte concentration in the LFM, corrected for sample preparation and any dilutions, μg/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.

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 μg/L for all analytes and 125 μg/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 μg/L for all analytes and 125 μg/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 μg/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 μg/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 μg/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 μg/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 μg/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 μg/L using the following calculation:

$$C = M \times \frac{V_f}{V_i} \times D$$

where:

C	=	final reported concentration, in μg/L.
M	=	measured concentration reported by instrument, in μg/L.
V_f	=	final volume of sample solution after sample preparation, in mL.
V_i	=	initial volume of sample used in sample preparation, in mL.
D	=	sample analysis dilution factor, to account for any dilution performed after sample preparation.

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*

Table 1: Internal Standards And Limitations of Use

Internal standard	Mass	Possible Limitation
^{6}Lithium	6	a
Scandium	45	polyatomic ion interference
Yttrium	89	a,b
Rhodium	103	
Indium	115	isobaric interference by Sn
Terbium	159	
Holmium	165	
Lutetium	175	
Bismuth	209	a

a May be present in environmental samples

b In some instruments Yttrium may form measurable amounts of YO^+ (105 amu) and YOH^+ (106 amu). If this is the case, care should be taken in the use of the cadmium elemental correction equation.

Internal standards recommended for use with this method are underlined.
Internal standards currently used by R9 Lab are in bold.

Table 2: Recommended Elemental Equations for Data Calculations

Element	Elemental Equation	Note
Al	$(1.000)(^{27}C)$	
Sb	$(1.000)(^{123}C)$	
As	$1.000(^{75}C)-(3.1278)[(^{77}C)-(0.3254)(^{78}C)]$	1
Ba	$1.000(^{137}C)$	
Be	$1.000(^{9}C)$	
Cd	$1.000(^{111}C)-(1.073)[(^{108}C)-(0.712)(^{106}C)]$	2
Cr	$1.000(^{52}C)$	3
Co	$1.000(^{59}C)$	
Cu	$1.000(^{63}C)$	
Pb	$1.000(^{206}C)+1.000(^{207}C)+1.000(^{208}C)$	4
Mn	$1.000(^{55}C)$	
Mo	$1.000(^{98}C)-0.146(^{99}C)$	5
Ni	$1.000(^{60}C)$	
Se	$1.000(^{82}C)$	6
Ag	$1.000(^{107}C)$	
Tl	$1.000(^{205}C)$	
Th	$1.000(^{232}C)$	
U	$1.000(^{238}C)$	
V	$1.000(^{51}C)-(3.127)[(^{53}C)-(0.113)(^{52}C)]$	7
Zn	$1.000(^{66}C)$	
Bi	$1.000(^{209}C)$	
In	$1.000(^{115}C)-0.016(^{118}C)$	8
Li	$1.000(^{6}C)-0.0813(^{7}C)$	9
Sc	$1.000(^{45}C)$	
Tb	$1.000(^{159}C)$	
Y	$1.000(^{89}C)$	

C Calibration blank subtracted counts at specified mass.

1 Correction equation for As taken from EPA method 6020. Isobaric correction for ArCl,Se. (See Reference 5 of Section 11).

2 Correction for MoO, Sn.

3 The background for ClOH will normally be small and can be estimated from the reagent blank.

4 Allowance for isobaric variability of lead isotopes.

5 Isobaric elemental correction for Ru.

6 Some Ar supplies contain Kr as an impurity. Se is corrected for ^{82}Kr by background subtraction.

7 Correction for chloride interference with adjustment for ^{53}Cr. ClO 51/53 ratio may be determined from the reagent blank. Isobaric mass 52 must be from Cr only, not ArC^{+}.

8 Isobaric correction for Sn

9 Isobaric correction for Li natural.

Table 3: Recommended Analytical Isotopes and Additional Masses Which Must Be Monitored

Element of Interest	Isotope
Aluminum	27
Antimony	121,123
Arsenic	75
Barium	135,137
Beryllium	9
Cadmium	106,108,111,114
Chromium	52,53
Cobalt	59
Copper	63,65
Lead	206,207,208
Manganese	55
Molybdenum	95,97,98
Nickel	60,62
Selenium	77,82
Silver	107,109
Thallium	203,205
Thorium	232
Uranium	238
Vanadium	51
Zinc	66,67,68
Ruthenium	99
Palladium	105
Tin	118

NOTE: Isotopes recommended for analytical determination are underlined.

Attachment A
Deviations From Reference Method

A.1 Mercury is not included in the analyte list due to excessive carryover which was not resolved using gold as a matrix modifier.

A.2 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.3 The Region 9 Laboratory do not perform total suspended solids on samples which have no visible undissolved solids.

A.4 Aqueous samples with less than 1% undissolved solids are brought up to a final volume of 100 mL (no preparation step is performed at the instrument).

A.5 The scope of this SOP does not include the digestion of water samples and the digestion or analysis of solid samples. Refer to Region 9 Laboratory SOP 403 for the digestion procedure of water samples.

A.6 The Region 9 Laboratory do not blank subtract the LRB results from the LFB results for calculation of LFB recoveries.

A.7 The arsenic interference equation used was taken from EPA SW846 Method 6020.

A.8 Laboratory duplicate (LD) sample is not analyzed in this method, instead LFMD is analyzed for precision calculation.

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

ICP/MS RUN LOG

Date:_____ File Name:_____ Analyst:_____

H.T. _____ In_____ Pb_____

Case #:_____ SDG:_____ MATRIX:_____

Site ID:_____ Page _____ of _____

	STD/ Sample ID	EPA/STD#	Comments		STD/ Sample ID	EPA/STD#	Comments
1				26			
2				27			
3				28			
4				29			
5				30			
6				31			
7				32			
8				33			
9				34			
10				35			
11				36			
12				37			
13				38			
14				39			
15				40			
16				41			
17				42			
18				43			
19				44			
20				45			
21				46			
22				47			
23				48			
24				49			
25				50			

Reviewed by:_____ Date:_____

ICP/MS.wk4 REVIEWED: 7/97 REVISED: 8/97

ICP/MS Run Log

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				01/23/01				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
Arsenic (200.8)	20				20	U			20	U			5
Beryllium (200.7)	1	U			1	U			1	U			1
Cadmium (200.8)	5	U			5	U			5	U			1
Chromium (200.7)	10	U			10	U			10	U			10
Copper (200.8)	5				5	U			5	U			1
Iron (200.7)	5	U			5	U			5	U			1
Manganese (200.7)	4		J	A	4	U			5	U			1
Molybdenum (200.7)	5	U			5	U			5	U			1
Potassium (200.7)	5000				5000	U			5000	U			5000
Silver (200.8)	5	U			5	U			5	U			5
Thallium (200.8)	5	U			5	U			5	U			1
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 (Analyst)	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)			??	

Appendix B-6
TAL Metals (field filtered) plus Boron, Silicon, and Cyanide

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 515

DETERMINATION OF MERCURY IN WATER BY COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY

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 515

DETERMINATION OF MERCURY IN WATER BY COLD VAPOR ATOMIC ABSORPTION 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: B0101029-0400

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 8

9 ANALYTICAL PROCEDURES 12

10 DOCUMENTATION 16

11 REFERENCES 16

Attachment A - Deviations from Reference Method

Attachment B - Inorganic Standards and Reagents Preparation Log Book

Attachment C - Leeman PS200 Mercury Run Log

Attachment D - CETAC M6000A Automated Mercury Analyzer Run Log

Attachment E - Analytical Spreadsheet

1 SCOPE AND APPLICATION

1.1 This SOP describes the instrumental analytical procedures for mercury by cold vapor atomic absorption (CVAA). This method is applicable for drinking, ground, surface, sea and brackish water, domestic and industrial wastes. This method applies to the determination of total mercury (organic + inorganic) by EPA Method 245.1 using the Leeman PS200 Mercury Analyzer for high level samples and the CETAC M6000A Mercury Analyzer for drinking water samples. Sample and standard preparation procedures for both mercury analyzers are described in Region 9 Laboratory SOP 415.

1.2 The quantitation limit (QL) is 0.2 μg/L for total mercury analyzed using the Leeman PS200; the QL is 30 ng/L for total mercury analyzed using the CETAC M6000A.

2 METHOD SUMMARY

2.1 An aliquot of a water sample is transferred to a BOD bottle or equivalent closed-system container. The sample is digested with a dilute potassium permanganate-potassium persulfate solution for two hours at 95°C. The digestion oxidizes all forms of mercury to Hg(II). The Hg(II) in the digested water sample is reduced with stannous chloride to elemental mercury which is sparged from the sample and detected by atomic absorption. The measurement step is performed using an automated mercury analyzer.

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 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 standard containing the analytes of interest which is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout an analysis sequence.

3.7 Laboratory Fortified Blank (LFB) - An aliquot of reagent water or other blank matrix to which known quantities of the method analyte is 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.

3.8 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.

3.9 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.

3.10 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 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.

3.12 Performance Evaluation Sample (PE) - A solution of method analyte(s) obtained from a second-source (Environmental Resource Associates, AccuStandard, SPEX 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.

3.13 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. Region 9 laboratory currently has a QL of 0.2 μg/L for total mercury analyzed using the Leeman PS200 Mercury Analyzer and a QL of 30 ng/L for total mercury analyzed using the CETAC M6000A Mercury Analyzer.

3.14 Quality Control Sample (QCS) - An independent solution of the method analyte 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.

3.15 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. Refer to the Material Safety Data Sheets located in the library and Room 413 for additional information.

4.2 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 and 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 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.

4.4 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.

4.5 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 ensure a representative sample, allow for replicate analysis and minimize waste disposal. A 500 mL sample volume should be sufficient to meet these objectives.

5.2 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 Samples must be received preserved with HNO_3 to pH<2. Any deviations from the preservation must be noted in the report narrative.

5.5 The maximum sample holding time for mercury is 28 days from the time of collection.

6 INTERFERENCES

6.1 Interferences have been reported for water samples 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 interfering compounds 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).

7 APPARATUS AND MATERIALS

7.1 Apparatus

7.1.1 Leeman PS200 Mercury Analyzer - includes optical cell, mercury lamp, peristaltic pump, drying tube, sample and reagent tubing and Leeman PS200 software.
7.1.2 CETAC M6000A Mercury Analyzer - includes optical cell, mercury lamp, peristaltic pump, drying tube, sample and reagent tubing, ASX-500 autosampler and CETAC M6000A software.
7.1.3 Stirrer plate and stirring bars.
7.1.4 50-mL plastic standard cups (Leeman P/N 116-2102) or 50-mL centrifuge tubes.
7.1.5 Disposable plastic or borosilicate autosampler vials, 16x100 mm.
7.1.6 Class "S" weights.
7.1.7 Analytical balance capable of weighing to the nearest 0.01 g.

7.1.8 Drying tubes.

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 Glass or quartz wool.

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, trace metals grade or better.

7.3.3 Stannous chloride ($SnCl_2$), ACS Reagent Grade or better, suitable for mercury determination.

7.3.4 10% $SnCl_2$ in 10% HCl. Dissolve 100 g of stannous chloride (7.3.3) in 100 mL HCl (7.3.2) and dilute to 1L with reagent water. Place a stirring bar into the solution. Prepare fresh monthly.

7.3.5 Argon gas, ICP grade.

7.3.7 Magnesium perchlorate, powder or granular.

7.3.8 10% HCl. Add 200 mL HCl (7.3.2) to approximately 1.5 liters reagent water and dilute to 2L with reagent 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, 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 Region 9 Laboratory SOP 415. Check the correlation coefficient (r); the correlation coefficient of the curve must be $\geq$0.995 or the instrument must be re-calibrated.

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 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 the analyte, μg/L or ng/L.
T	=	true concentration of the analyte in the IPC, μg/L or ng/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 concentration in a QCS sample must be measured once per analytical run to verify the calibration standards and acceptable instrument performance. The concentration of analyte in the QCS should be in the upper half of the calibrated range. The recoveries must be within 90-110% or the samples in the batch must be re-analyzed:

$$\%R = \frac{C_m}{C_t} \times 100$$

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.

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 532

CYANIDE ANALYSIS

Prepared by:

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STANDARD OPERATING PROCEDURE 532

CYANIDE 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).

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ESAT Document Control Number: B0101029-0501

CONTENTS

1 SCOPE AND APPLICATION 4

2 METHOD SUMMARY 4

3 DEFINITIONS 4

4 HEALTH & SAFETY 6

5 SAMPLE HANDLING AND PRESERVATION 6

6 INTERFERENCES 7

7 APPARATUS AND MATERIALS 7

8 QUALITY CONTROL PROCEDURES 10

9 ANALYTICAL PROCEDURES 13

10 DOCUMENTATION 18

11 REFERENCE 19

Attachment A - Deviations from Reference Method

Attachment B - Inorganic Standards and Reagents Preparation Log Book

Attachment C - Cyanide Analysis by Lachat Run Log

Attachment D - Analytical Spreadsheet

Attachment E - QC Summary Report

1 SCOPE AND APPLICATION

1.1 This procedure is for the determination of cyanide in drinking, ground, surface, and saline waters as well as domestic and industrial waste for use in the USEPA Region 9 Laboratory, Richmond, CA. This SOP is based on EPA Method 335.4, Rev. 1.0 (August 1993).

1.2 The applicable range is 10 to 100 $\mu g/L$ cyanide. The calibration range can be extended for high level samples through dilution either before or after the distillation procedure.

2 METHOD SUMMARY

2.1 This procedure is based upon a modification of EPA Method 335.4, in which sample and reagent volumes are reduced to 12% of the method volumes as allowed by Method 335.4, Section 2.2. The volume reduction has several advantages, including the generation of significantly less waste and reducing the space and labor required for the distillation process.

2.2 Samples are preserved to pH 12 in the field. Inside a micro-distillation apparatus, the basic samples are acidified, which converts free cyanide and most cyanide complexes to hydrogen cyanide (HCN). The HCN is distilled from the sample and trapped in a 0.25M NaOH scrubber solution. The solution is analyzed for cyanide colorimetrically by flow injection analysis. The colorimetric determination is based upon the reaction of cyanide with chloramine-T at pH<8 to form cyanogen chloride, which subsequently reacts with a pyridine-barbituric acid reagent to form a red-blue dye. The absorbance of the dye is monitored at 570nm and is directly proportional to the concentration of cyanide in the scrubber solution. The system is calibrated by analyzing cyanide calibration standards.

3 DEFINITIONS

3.1 Analytical Sample - Any sample in which cyanide 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 by diluting the primary 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 purpose of the FRB is to determine if contamination is

occurring in the field environment. Note: Field reagent blanks cannot be used for LFM or LFMD analyses.

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 Instrument Performance Check Solution (IPC) - A standard containing the analyte of interest which is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout an analysis sequence.

3.7 Laboratory Fortified Blank (LFB) - An aliquot of reagent water or other blank matrix to which known quantities of the method analyte is added in the laboratory. The source of the LFB must be independent of the calibration standards. 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. For cyanide, two LFB samples are prepared; one at a low concentration (LFB-L) and one at a high concentration (LFB-H).

3.8 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 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 Fortified Sample Matrix Duplicate (LFMD) - An 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. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFMD corrected for background concentrations.

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 Linear Calibration Range (LCR) - The concentration range over which the instrument response is linear.

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 standard containing cyanide which is used to verify the accuracy of the analysis. For this procedure, the QCS has been combined with the IPC and analyzed as a single solution.

3.14 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.

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

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

4 HEALTH & 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. 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 The following chemicals are toxic or hazardous; hydrochloric acid, pyridine, barbituric acid, potassium cyanide, and sulfuric acid. The analyst should consult the MSDS for each chemical for specific information regarding the potential hazards and safe handling. Refer to the Material Safety Data Sheets located in the Library and Room 413 for additional information.

4.3 The distillation step should be performed in a well ventilated hood due to the generation of HCN gas.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Samples should be collected in precleaned plastic or glass bottles. Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis and minimize waste disposal. A 100 mL sample volume should be sufficient to meet these objectives.

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. Samples must be preserved

at the time of collection with sodium hydroxide to pH ≥ 12. 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 sample must be analyzed within 14 days of the sample collection date.

5.5 If oxidizing agents (such as chlorine) or sulfide are present in the sample immediate steps are required to properly preserve the sample. Refer to Sections 6.3 and 6.4.

6 INTERFERENCES

6.1 Several interferences are encountered with this method. Some of the known interferences are aldehydes, nitrate-nitrite and oxidizing agents such as chlorine, thiocyanate, thiosulfate and sulfide. Multiple interferences may require the analysis of a series of laboratory fortified matrices (LFM) to verify the suitability of the chosen treatment. Some interferences are eliminated or reduced by the distillation.

6.2 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation nitrate and nitrite will form nitrous acid that will react with some organic compounds to form oximes. These oximes will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid (Sect. 9.1).

6.3 Oxidizing agents, such as chlorine, decompose most cyanides. All samples must be tested at the time of collection by placing a drop of sample on a strip of potassium iodide-starch paper. If a bluish discoloration is noted, add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper; then add an additional 0.06 g of ascorbic acid for each liter of sample volume. See Section 9.1.

6.4 Oxidized products of sulfide convert CN^- to SCN^- rapidly, especially at high pH. Samples suspected of containing sulfide must be tested at the time of collection for S^{2-} by placing a drop of sample on lead acetate test paper. Darkening of the paper indicates presence of S^{2-}. If S^{2-} is present, add powdered cadmium carbonate ($Cd(CO_3)_2$) to avoid significantly reducing pH. Filter sample before raising pH for stabilization. When particulate metal cyanide complexes are suspected, filter solution before removing S^{2-}. Alternatively, the test for sulfide may be performed at the laboratory; the laboratory must be informed of the possible presence of sulfide and the samples must be received unpreserved. Performance of this test at the laboratory is less desirable since cyanide may be lost from the unpreserved sample.

7 APPARATUS AND MATERIALS

7.1 Instrumentation

7.1.1 Analytical balance capable of accurately weighing to the nearest 0.1 mg.
7.1.2 Neoprene heat-resistant gloves.
7.1.3 Blue Sample tube rack.
7.1.4 Micro-Distillation Heating Block, capable of heating up to 120°C.
7.1.5 Micro-Distillation Tubes, 6.0-mL sample capacity.
7.1.6 Red Micro-Distillation assembly press.
7.1.7 Collector tube rack.
7.1.8 Lachat QuikChem AE automated flow injection analyzer.

7.2 Glassware and Incidentals

7.2.1 Autosampler glass tubes, 13×100mm, KIMAX or equivalent.
7.2.2 Glass scintillation vials, 20 mL.
7.2.3 Volumetric flasks, type A, 1000-mL, 250-mL, 100-mL, 50-mL.
7.2.4 Volumetric pipet, type A, 6-mL.
7.2.5 Re-pipet Reagent Bottles, 500-mL.
7.2.6 Microliter pipets, 10-5000 μL.
7.2.7 Lead Acetate test paper.
7.2.8 Potassium Iodide test paper.

7.3 Reagents and Standards

7.3.1 Reagent water - All references to water in this procedure refer to ASTM Type II grade water.
7.3.2 Ascorbic acid, crystal, reagent grade.
7.3.3 Sulfamic acid, reagent grade.

7.3.4 Cyanide Standard Stock Solution, 1000 mg/L cyanide - Purchase from a reputable supplier such as ERA, Spex or Inorganic Ventures. The stability of the commercially-acquired 1000 mg/L cyanide stock standard solution is usually one year from the date of purchase.

7.3.5 Cyanide Standard Working Solution, 10 mg/L cyanide - Dilute 1.0 mL of the 1000 mg/L cyanide standard stock solution (7.3.4) with 0.25M NaOH solution to 100 mL. This standard must be prepared fresh daily. Record the preparation of this standard in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.3.6 Cyanide Calibration and IPC/QCS Standards - The calibration and IPC/QCS standards are prepared daily by appropriate dilution of the 10 mg/L Cyanide Standard Working Solution with 0.25M NaOH, as listed in the following table.

Type	Cyanide (μg/L)	mL 10 mg/L Standard Working Solution	Final volume (mL)

S1	100	0.5	50
S2	75	0.375	50
S3, IPC/QCS	50	0.25	50
S4	25	0.125	50
S5, QL	10	0.05	50

7.3.7 Cyanide QCS Solution - A solution obtained from a commercial vendor (SPEX, ERA or Inorganic Ventures) with a known concentration of cyanide. Region 9 laboratory currently uses a cyanide QCS solution with approximately 330 μg/L cyanide. This solution is usually stable for 1 year from the date of purchase.

7.3.8 Magnesium Chloride/Sulfuric Acid Solution - Dissolve 16.1 g magnesium chloride hexahydrate in 55.4 g reagent water. Slowly add 69.5g of concentrated sulfuric acid in increments of 20g to the solution, swirling between additions. Allow to cool to room temperature. Transfer to a Re-pipet reagent bottle (the reagent can be made directly in the Re-pipet reagent bottle). This reagent must be prepared fresh every 6 months. Record the preparation of this reagent in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.3.9 Potassium dihydrogen phosphate buffer, 0.71 M - In a 1-L volumetric flask, dissolve 97g anhydrous potassium dihydrogen phosphate in approximately 800 mL reagent water. Dilute to volume with reagent water and mix well. This reagent must be prepared fresh every 6 months. Record the preparation of this reagent in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.3.10 Pyridine Barbituric Acid Reagent - Working in a fume hood, add 15.0g barbituric acid to a 1-L volumetric flask. Add 100 mL reagent water, ensuring that all of the barbituric acid is rinsed into the bottom of the flask. Add 75 mL of pyridine and mix until the barbituric acid dissolves. Add 15 mL concentrated hydrochloric acid and mix. Dilute to volume with reagent water and mix well. This reagent must be prepared fresh every 6 months. Record the preparation of this reagent in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.3.11 Sodium Hydroxide Solution, 0.25 M - In a 1-L volumetric flask dissolve 10g NaOH in about 100 mL reagent water. Dilute to volume with reagent water and mix well. This reagent must be prepared fresh every month. Record the preparation of this reagent in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.3.12 Chloramine-T Solution - Dissolve 1.0 g of chloramine-T in 250 mL reagent water. This reagent must be prepared fresh daily. Record the preparation of this reagent in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.3.13 Sodium Hydroxide Distillation Tube Filling Solution, 0.95M - Dissolve 9.5 g sodium hydroxide pellets in a 250-mL volumetric flask and bring to volume with reagent water. Caution: Very exothermic reaction will generate considerable heat.

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 - Each analyst must complete an initial demonstration of proficiency following EPA Region 9 Laboratory SOP 880 prior to analyzing samples following this method.

8.2.1 LCR - The absorbance response vs. Cyanide concentration is generally a linear function over a limited concentration range. The LCR is not determined in this procedure, but any sample with concentration greater than the highest calibration standard must be diluted.

8.2.2 MDL - A method detection limit must be confirmed every year and must be <½ QL or corrective action must be initiated.

8.3 Routine Analytical Quality Control - The various routine QC samples analyzed during each analytical run are specified in this section. Some are treated like samples and undergo distillation before analysis, while some are not distilled. The following table lists the QC samples and indicates whether sample distillation is required prior to analysis:

QC Sample ID	Distillation Required ?	QC Sample ID	Distillation Required ?
Calibration Standards S1, S2, S3, S4 and S5	N	IPC/QCS	N
QL	N	CB	N
LFB-H, LFB-L	Y	LFM/LFMD	Y
LRB	Y		

8.3.1 The instrument must be calibrated with a blank and 5 standards. The correlation coefficient of the calibration curve must be $\geq$0.995 or the instrument must be recalibrated.

8.3.2 IPC /QCS- The accuracy and stability of the calibration shall be verified by the periodic analysis of an IPC/QCS 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 IPC /QCS is at a concentration of 50 μg/L cyanide and is not distilled. The recovery of cyanide in the IPC is calculated as follows:

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

Where

%R = percent recovery
M = measured concentration of cyanide, μg/L
T = true concentration of cyanide in the IPC

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.

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 QL, the result is acceptable. If the absolute value of the CB result equals or 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 reanalyzed.

8.3.4 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. The QL is at a concentration of 10 μg/L cyanide and is not distilled. The recovery of the analyte in the QL is calculated as follows:

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

Where

%R = percent recovery
M = measured concentration of the analyte, μg/L
T = true concentration in the QL

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 reanalyzed. If, after recalibration, the

QL recovery still exceeds the 50-150% limits, the calibration standards must be reprepared and the instrument recalibrated.

8.3.5 LRB - The laboratory must analyze at least one LRB daily with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the QL indicate laboratory contamination. The LRB must be re-prepared along with the affected samples, and re-analyzed. Note: Samples must be re-prepared and re-analyzed if the LRB analyte concentration is

8.3.6 LFB - High - One high-level LFB must be prepared, distilled and analyzed with each analytical run. The LFB-H is also used to fulfill the method requirements of a high standard that insures that the distillation technique is reliable. The recovery of cyanide in the LFB-H is calculated as follows:

$$\%R = \frac{LFB}{s} \times 100$$

Where

$\%R$ = percent recovery.
LFB = measured concentration of cyanide in the LFB-H in μg/L.
s = cyanide concentration in the LFB-H in μg/L.

The recovery of cyanide in the LFB-H must be within the 90-110% limits. If the recovery exceeds the limits, the distillation and/or 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 LFB-Low - One LFB-L must be prepared, distilled and analyzed with each analytical run. The LFB-L is also used to fulfill the method requirements of a low standard that insures that the distillation technique is reliable. The recovery of cyanide in the LFB-L is calculated as follows:

$$\%R = \frac{LFB}{s} \times 100$$

Where

$\%R$ = percent recovery
LFB = measured concentration of cyanide in the LFB-L in μg/L.
s = cyanide concentration in the LFB-L in μg/L.

The recovery of cyanide in the LFB-L must be within the 90-110% limits. If the recovery exceeds the limits, the distillation and/or analysis system is judged to be out-of-control, and the source of the problem must be identified and resolved before continuing analyses.

8.3.8 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. Samples identified as field blanks cannot be used for LFM sample analysis. The recovery of cyanide 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 = analyte concentration in the LFM, corrected for sample preparation and any dilutions.

If the value of C is less than 4 times the value of s, 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. The problem should be discussed in the reporte 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. Document actions in the report narrative.

8.3.9 LFMD - The LFMD is designed to provide information about the effect of sample matrix on the measurement system, it can also be used to assess sample homogeneity. One LFMD must be prepared for every 10 routine samples of the same matrix in a sample batch. Samples identified as field blanks cannot be used for LFMD sample analysis. The recovery of cyanide in the LFMD is calculated as in Section 8.3.8 and 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 cyanide in the LFMD.

C = measured cyanide in the LFM.

The relative percent difference (RPD) must be $\leq$20%. If the control limits are exceeded, flag all associated analyte results. Document actions in the report narrative.

9 ANALYTICAL PROCEDURES

9.1 Sample Preparation - All samples must be tested for oxidizing agents at the time of collection; if the samples have NOT been tested at the time of collection, the samples must be tested by the Region 9 Laboratory prior to distillation (Sect. 6.3). Document actions in the Cyanide Distillation Run Log and in the report narrative. Samples are distilled using the Micro-Dist Heater Block. The procedure is outlined in the following steps.

1) Turn on the power switch on the Micro-Dist Heater Block. It takes at least 30 minutes for the heater block to heat up to the distillation temperature of 120°C.

2) Measure a 6.0 mL aliquot of an analytical or quality control sample into a sample tube. The preparation of quality control samples is summarized in the following tables:

QC Sample	Sample Volume	Volume of 330 μg/L cyanide QCS solution (mL)	Concentration of Cyanide (μg/L)
LRB	6 mL reagent water	0	0
LFB-H	4.64 mL reagent water	1.36	75
LFB-L	5.55 mL reagent water	0.45	25

QC Sample	Sample Volume	Volume of 10 mg/L cyanide Standard Working Solution (μL)	Concentration of Cyanide (μg/L)
LFM/LFMD	6 mL designated analytical sample	15	25

3) Approximately 0.024g sulfamic acid is added to all samples with the exception of drinking waters to counteract interferences caused by NO_3 and/or NO_2.

4) The collector tube must first be filled with 1.58 mL of 0.95 M NaOH then add 0.75 mL $MgCl_2$ / H_2SO_4 solution to the first sample tube. Using the Red Micro-Dist assembly press, immediately push the uncapped bottom end of the Cyanide-collector tube over the end of the sample tube until the stop ring on the sample tube hits the bottom of the collector tube.

5) Place the sealed sample tube / collector tube assembly into the Micro-Dist Heating Block (at this point, the heating block must be at 120°C).

6) Repeat steps 4 and 5 for each sample until all samples have been placed in the Micro-Dist Heating Block. Distill in the Micro-Dist Heating Block for 30 minutes.

7) When 30 minutes is up, put on the heat-resistant gloves. Remove the first collector tube from the block and immediately pull off its sample tube by twisting it back and forth while pulling down on it. Place the sample tube in the blue rack. Repeat the same procedure for the rest of the tubes in the heater block. The hot solution in the sample tube is allowed to cool to room temperature and disposed of in the cyanide analysis waste container. The sample tube is disposed of in the solid waste container. The power switch on the Micro-Dist Heating Block can be turned off.

8) Allow the collector tubes to cool for at least 10 minutes in the white rack. Then, for each collector tube, hold the tube horizontally and rinse its walls with the distillate in order to homogenize it. Then slowly roll the distillate around in the tube to gather all droplets clinging to its walls into the bulk of the distillate. Slowly return the collector tube to an upright position. Break away the top section of the collector tube and tear it off. Discard the top section of the collector tube. Dilute the distillate in the bottom section of the collector tube with reagent water to the 6 mL mark. Place the cap onto the top of this section and shake the tube with a gentle whipping motion to mix. Place the tube into the white rack and repeat the same procedure for the rest of the tubes. It is best to analyze the distilled samples as soon as possible. If they cannot be analyzed within the same day they are distilled, seal both ends of the collector tube with parafilm.

9.2 CALIBRATION AND STANDARDIZATION - Cyanide is determined colorimetrically using the Lachat Automated Ion 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.

9.2.1 Instrument Set-up

1) Turn on the Lachat QuikChem AE analyzer and allow the heater module to heat up to 60°C for about 15 minutes. Degas each reagent with helium gas for at least 3 minutes.

2) Connect the cyanide manifold, sample loop and the interference filter to the module. Place the waste lines into the cyanide analysis waste container and place a tube cartridge to support each reagent line onto the pump. Place each reagent line into the appropriate reagent solution. Turn on the pump and set the speed to 35 RPM. Download the cyanide method. Allow the reagents to flow through the manifold until the air bubbles disappear into the waste container.

9.2.2 Calibration and Sample Analysis

1) Pour the five calibration standards and the blank (0.25 M NaOH, Sect. 7.3.11) into 20-mL scintillation vials. Place the calibration standards in decreasing concentration - starting from position A - into the calibration tray, which is positioned on the right side of the autosampler tray. Place the IPC, CB and QL in positions J, K and I, respectively, in the calibration tray.

2) Load the analytical and QC samples into the sample trays using the 13×100mm autosampler tubes. The usual sample loading sequence is listed in the following table:

Seq.	Desc.	Seq.	Desc.	Seq.	Desc.	Seq.	Desc.
A	S1, 100 ug/L	3	LFB-H	11	S5	J	IPC
B	S2, 75 ug/L	4	LFB-L	12	S6	K	CB
C	S3, 50 ug/L	5	S1	13	S7	21	S13
D	S4, 25 ug/L	6	S1-LFM	14	S8	22	S14
E	S5, 10 ug/L	7	S1-LFMD	15	S9	23	S15
F	S6, 0 ug/L	8	S2	16	S10	24	S16
J	IPC/QCS	9	S3	17	S11	25	S17
K	CB	10	S4	18	S11-LFM	26	S18
I (1)	QL	J	IPC	19	S11-LFMD	J	IPC
2	LRB	K	CB	20	S12	K	CB

3) Select *File* from the *Sample Identification & Tray Submission Menu.* Highlight *Template Read (Public)* and press *Enter*. Select *QC_Sched*, press *Enter*, highlight *Identification* and press *Enter*. Next, enter each check standard and all samples that are to be analyzed in the same order as in the table above. The calibration standards, the IPC/QCS, the QL and the CBs that are positioned in cups A through K are not entered into the sample tray. They are automatically analyzed during the sample tray analysis. The IPC and the CB will be analyzed automatically after every 10 samples and at the end of the analytical run. Type in *(..)* after the last sample in the tray to mark the end of the sample tray.

4) Select *Submit current tray* under *Sample Identification & Tray Submission Menu.* Answer *Yes* to *Submit tray now*?

5) The system will analyze the calibration standards and calculate a calibration curve prior to analyzing any of the samples. The system will emit a beeping sound when the calibration is complete. The calibration data may be viewed by selecting *Results/Approval, View Calibration and Sample Reports, Tray Selection, Calibration Trays*, and *tentative calibration*. Press *Enter* until the plotted calibration curve appears

on the screen. A correlation coefficient of at least 0.995 is the requirement for the calibration to pass. It is approved by selecting *Approval* on the menu bar. The system will now automatically analyze the samples loaded in the sample tray.

9.2.3 Post-analysis Review

1) QC Sample Results - Review the results for all QC samples for compliance with the criteria specified in Section 8. If results are not acceptable, take appropriate corrective action.

2) Off-scale Results - Review results for samples that exceed the calibration range. Samples having cyanide at concentrations greater than 100 μg/L must be diluted into range with 0.25 M NaOH and re-analyzed. Only 2 mL of sample is used per analysis; there is sufficient volume for dilution and reanalysis.

9.2.4 Instrument Shutdown

1) With the pump still turned on, remove each reagent line from the reagent and place into a container of reagent water. Allow the reagent water to flush through the reagent lines for at least 15 minutes.

2) After the 15 minute period, remove the reagent lines from the reagent water and allow the reagent lines to be purged of the reagent water. Observe the tubing on the manifold - when no liquid is apparent in the tubing the pump can be turned off. Cap all reagents, discard all samples and standards into the appropriate waste containers and turn the power off at the power strip behind the autosampler.

9.3 Data Reduction - After set-up and calibration the instrument software analyzes sample absorbances and calculates the cyanide concentration in the samples based upon the current calibration. The concentrations reported by the instrument must be corrected for any dilutions performed and not accounted for by the instrument software. The additional calculations can be performed by the analyst or instrument. Data for aqueous samples should be reported in units of μg/L using the following calculation:

$$C = M \times D$$

Where

C = final reported concentration, in μg/L
M = measured concentration reported by instrument, in μg/L
D = sample analysis dilution factor

9.4 Rounding and Reporting - 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:

1) If the number following those to be retained is less than 5, round down;
2) If the number following those to be retained is greater than 5, round up; or
3) 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 The Inorganic Standards and Reagents Preparation Log Book is maintained in room 207. Each reagent and standard that is prepared for the analysis is entered in the Inorganic Standards and Reagents Preparation Log Book. Copies of the appropriate page(s) is (are) included in the data package (Attachment B).

10.2 The Cyanide Distillation Run Log Book is maintained in room 207. Each QC sample and sample that is distilled is documented in the log book. The amount and sample identification (from the Inorganic Reagents and Standards Preparation Log Book) of the spiking solution used in the distillation process is also noted in the Cyanide Distillation Log Book. Copies of the appropriate page(s) is (are) included in the data package.

10.3 The Cyanide Analysis by Lachat Run Log must be filled out for each sample batch that is analyzed. The sample identification of each standard, analytical sample, and QC sample are entered into the Cyanide Run Log. Copies of the appropriate page(s) is(are) included in the data package (Attachment C).

10.4 An analytical spreadsheet, with the cyanide results in μg/L, sample collection date(s), client sample ID's, lab ID's, and station locations must be included with the data package (Attachment D).

10.5 QC summary reports with LFB, LFM and LFMD results must be prepared and included in the data package (Attachment E).

10.6 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.

Method blank: Data included on the analytical spreadsheet.

LFM and LFMD: On a QC summary report with calculated relative percent difference (RPD).

LFM, LFMD and LFB results: On a QC summary report with calculated percent recoveries (%R).

Raw sample, standard and QC data, including distillation logs, run logs and any work sheets, if applicable.

11 REFERENCE

11.1 EPA Method 335.4, *Determination of Total Cyanide by Semi-Automated Colorimetry*, Revision 1.0, Environmental Monitoring Systems Laboratory, August 1993.

11.2 Micro-Dist Distillation System Reference and Methods Manual, Lachat Instruments, 22 May 1991.

11.3 QuikChem Cyanide (Micro-Dist) Method, Lachat Instruments, 24 June 1993.

11.4 Method 4500-CN^-, Standard Methods For the Examination of Water and Wastewater, 18th Edition, 1992.

11.5 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 The EPA Region 9 Laboratory procedure utilize the volume reductions allowed in Section 2.2 of the reference method. A 6 mL sample volume is distilled in place of the 50 mL used in the method and all reagent volumes are adjusted.

A.2 LCR is not determined in this procedure, but any sample with a concentration greater than the highest calibration standard must be diluted.

A.3 A laboratory duplicate (LD) sample is not analyzed in this procedure, instead a LFMD is analyzed to calculate for precision.

A.4 In this procedure, the IPC and QCS standards are analyzed as one solution.

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
Cyanide Analysis by Lachat Run Log

CYANIDE ANALYSIS BY LACHAT RUN LOG

File Name : _____ Analysis Date : _____

Case Number : _____ Distillation Date : _____

SDG Number : _____ QCS Source : _____

Analyst : _____ Calib. Std. , IPC Source : _____

CUP #	CALIBRATION STD.	CUP #	LAB ID / EPA ID
A	100 ug/L	11	
B	75 ug/L	12	
C	50 ug/L	13	
D	25 ug/L	14	
E	10 ug/L	15	
F	Blank	16	
G	IPC/QCS	17	
H	CB	18	
I	QL	19	
J	IPC	20	
K	CB		IPC
	LAB ID / CLIENT ID		CB
1	LRB	21	
2	LFB-H	22	
3	LFB-L	23	
4		24	
5		25	
6		26	
7		27	
8		28	
9		29	
10		30	
	IPC		IPC
	CB		CB

US EPA REGION 9 LABORATORY

COMMENTS :

Filename:CNRUNLOG.WK4 REVIEWED:_____ REVISED: 01/99

Attachment D
Analytical Spreadsheet

EPA REGION 9 LABORATORY-RICHMOND, CA
SUMMARY OF ANALYTICAL RESULTS

Case Number:	R01SXX	**Analysis:**	Fluoride, Chloride, Nitrite-N, Bromide, Nitrate-N, Orthophosphate, Sulfate, TDS, Cyanide
Site:	DUMMY		
SDG:	01LSIA	**Matrix:**	Water
Date:	06/28/01		

Sample No.	8			9			10			11			Reagent			Quantitation
Sample I.D.	DUMMY			DUMMY			DUMMY			DUMMY			Blank			Limit
Lab Sample I.D.	AB001122			AB001122			AB001122			AB001122			N/A			N/A
Date of Collection	05/30/01			05/30/01			05/30/01			05/30/01			N/A			N/A
Units	mg/L			mg/L			mg/L			mg/L			mg/L			mg/L
Analyte	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result
Chloride	40			0.1	J	A	57			96			1	U		1
Bromide	0.1			0.1	U		0.1			0.1			0.1	U		0.1
Orthophosphate-P	1	U		1	U		1	U		1	U		1	U		1
Total Dissolved Solids	508			20	U		500			500			20	U		20
					U									U		

Com - Comments refer to the corresponding section in the report section 6 for each letter.

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 E
QC Summary Report

US E.P.A.
REGION 9 LABORATORY
June 14, 2001
Case Number: R01SXX
SDG: 01130A

Laboratory Fortified Matrix (AA-BBCC)

Analyzed Date	Analyte	Sample Result (ug/L)	LFM Added (ug/L)	LFM Result (ug/L)	% Recovery	Q
05/22/01	Cyanide	0.16	2	2.334	109	

Laboratory Fortified Matrix Duplicate (AA-BBCC)

Analyzed Date	Analyte	Sample Result (ug/L)	LFM Added (ug/L)	LFM Result (ug/L)	% Recovery	Q
05/22/01	Cyanide	0.16	2	2.374	111	

Laboratory Fortified Matrix and Laboratory Fortified Matrix Duplicate (AA-BBCC)

Analyzed Date	Analyte	LFM Result (ug/L)	LFMD Result (ug/L)	RPD	Q
05/22/01	Cyanide	2.334	2.374	2	

Appendix B-7
Anions: Bromide, Chloride, Fluoride, Nitrate-N, Nitrite-N, Orthophosphate-P, Sulfate

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 530

ANALYSIS OF ANIONS BY ION CHROMATOGRAPHY

Prepared by: _____ _____
Christina Navarro-Dizon, 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 530

ANALYSIS OF ANIONS 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
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ESAT Document Control Number: B0101029-0530

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 10

9 ANALYTICAL PROCEDURES 14

10 DOCUMENTATION 19

11 REFERENCES 20

Attachment A - Deviations from Reference Method

Attachment B - Inorganic Standards and Reagents Preparation Log Book

Attachment C - Ion Chromatography Run Log

Attachment D - Analytical Spreadsheet

Attachment E - QC Summary Report

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 Ion Chromatography for use in the USEPA Region 9 Laboratory, Richmond, CA. This SOP is based on EPA Method 300.0, revision 2.1, August 1993.

1.3 The quantitation limit (QL) is 0.1 mg/L for fluoride, nitrite (reported as mg/L N), bromide, and nitrate (reported as mg/L N), and 1.0 mg/L for chloride, 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. A quadratic calibration is used to determine concentrations in environmental samples for fluoride, nitrite, bromide, chloride, ortho-phosphate, and sulfate. For nitrate quantitation, an exponential calibration is used.

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 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 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.

3.5 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 purposes of the FRB is to determine if contamination is occurring in the field environment. Note: Field reagent blanks cannot be used for LFM or LFMD analyses.

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 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 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.

3.9 Laboratory Fortified Sample Matrix (LFM/LFMD) - 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.

3.10 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 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.

3.12 Quality Control Sample (QCS) - A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

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 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.

3.16 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 Safety precautions must be taken when handling solutions and samples. Protective clothing including lab coats, safety glasses and gloves must always be worn. Contact lenses must not be worn. If solutions come into contact with your eyes, flush with water continuously for 15 minutes. If solutions come in contact with your skin, wash thoroughly with soap and water. ESAT personnel should contact the Group Leader or Health and Safety and 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. Refer to the Material Safety Data Sheets located in the library and Room 413 for additional information.

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 100 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. 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 Times For IC Analytes - The maximum sample holding time for nitrite-N, nitrate-N and ortho-phosphate-P is 48 hours from the time of sample collection. For fluoride, chloride, bromide, and sulfate, the holding time is 28 days from the time of sample collection.

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. See Section 9.5.3 for procedures employed to prevent reporting false negative results for nitrite in the presence of chloride.

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

1) Dionex Ion Chromatograph Model DX-120 System - Includes the Advance Chromatography Module, pump, Conductivity Cell Detector, Dionex Advance Computer Interface and Dionex PeakNet 6/Chromeleon 6 Data System.

7.1.2 Dionex AS40 Autosampler.

7.1.3 Anion Guard Column - AG14-4mm from Dionex or equivalent.

7.1.4 Anion Separator Column - AS14-4mm from Dionex or equivalent.

7.1.5 Anion Suppressor device - Anion Self-Regenerating Suppressor ASRS-Ultra 4mm 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 and Incidentals

7.2.1 Volumetric Class "A" Flasks - 2000 mL, 500 mL, 100 mL, 50mL, 25ml, 10mL and 5mL.
7.2.2 Volumetric Class "A" Pipettes - 10 mL, 5 mL, and 4 mL.
7.2.3 100-mL beakers or Erlenmyer flasks.
7.2.4 Drying oven, capable of being controlled at 105 ± 5°C.
7.2.5 Desiccator.
7.2.6 Plastic or Teflon spray bottle.

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 Sodium Bicarbonate ($NaHCO_3$), ACS reagent grade.
7.3.4 Sodium Carbonate (Na_2CO_3), ACS reagent grade.
7.3.5 Sodium Chloride (NaCl), ACS reagent grade.
7.3.6 Sodium Fluoride (NaF), ACS reagent grade.
7.3.7 Sodium Nitrate ($NaNO_3$), ACS reagent grade.
7.3.8 Sodium Nitrite ($NaNO_2$), ACS reagent grade.
7.3.9 Sodium Bromide (NaBr), ACS reagent grade.
7.3.10 Potassium Phosphate (KH_2PO_4), ACS reagent grade.
7.3.11 Potassium Sulfate (K_2SO_4), ACS reagent grade.
7.3.12 Helium, 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 8.40 g of sodium bicarbonate in 100 mL of reagent water and diluting to final volume of 200 mL.

7.4.1.2 The working eluent solution is prepared by pipetting 14.0 mL of 0.5 M Na_2CO_3 plus 4.0 mL of 0.5 M $NaHCO_3$ into a 2-L volumetric flask and diluting to volume with degassed reagent water.

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 Mixed Stock Standard 1: 1000 mg/L fluoride, nitrite-N, bromide, and nitrate-N standard - Prepared by dissolving 1.106 g NaF, 2.462 g $NaNO_2$, 0.6505 g NaBr, and 3.0115 g $NaNO_3$ in reagent water and diluting to volume in a 500-mL volumetric flask.

7.4.2.2 Mixed Stock Standard 2: 1000 mg/L chloride, ortho-phosphate-P, and sulfate - Prepared by dissolving 0.824 g of NaCl, 2.2028 g of KH_2PO_4, and 0.9075 g of K_2SO_4 in reagent water and diluting to volume in a 500-ml volumetric flask.

7.4.2.3 Working Standard: 25 mg/L fluoride, nitrite-N, bromide, and nitrate-N - Prepared by pipeting 1.25 mL of Mixed Stock Standard 1 (7.4.2.1) in reagent water and diluting to volume in a 50-mL volumetric flask

7.4.3 Calibration Standard 5 (**std5**): **25 mg/L** fluoride, nitrite-N, bromide, and nitrate-N standard and **50 mg/L** chloride, ortho-phosphate-P, and sulfate standard - Pipet 2.5 mL of Mixed Stock Standard 1 (7.4.2.1) and 5.0 mL of Mixed Stock Standard 2 (7.4.2.2) into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily.

7.4.4 Calibration Standard 4 (**std4**): **10 mg/L** fluoride, nitrite-N, bromide, and nitrate-N standard and **25 mg/L** chloride, ortho-phosphate-P, and sulfate standard - Pipet 1.0 mL of Mixed Stock Standard 1 (7.4.2.1) and 2.5 mL of Mixed Stock Standard 2 (7.4.2.2) into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily. This calibration standard is also used as the IPC.

7.4.5 Calibration Standard 3 (**std3**): **5 mg/L** fluoride, nitrite-N, bromide, and nitrate-N standard and **10.0 mg/L** chloride, ortho-phosphate-P, and sulfate standard - Pipet 0.5 mL of Mixed

Stock Standard 1 (7.4.2.1) and 1.0 mL of Mixed Stock Standard 2 (7.4.2.2) into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily.

7.4.6 Calibration Standard 2 (**std2**): **1.0 mg/L** fluoride, nitrite-N, bromide, and nitrate-N standard and **5.0 mg/L** chloride, ortho-phosphate-P, and sulfate standard - Pipet 0.1 mL of Mixed Stock Standard 1 (7.4.2.1) and 0.5 mL of Mixed Stock Standard 2 (7.4.2.2) into a 100-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily.

7.4.7 Calibration Standard 1 (**std1**): **0.1 mg/L** fluoride, nitrite-N, bromide, and nitrate-N and **1.0 mg/L** chloride, ortho-phosphate-P, and sulfate standard - Pipet 0.4 mL of Working Standard (7.4.2.3) and 0.1 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. This calibration standard is also used as the QL standard for fluoride, nitrite-N, bromide, and nitrate-N, chloride, orthophosphate-P, and sulfate.

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 the calibration standards. It is used to check laboratory performance with externally prepared test materials. The Region 9 Laboratory uses a Custom Multi-Anion solution from Alltech as the QCS containing approximately 30 mg/L sulfate, 20 mg/L each bromide and chloride, 10 mg/L each fluoride and ortho-phosphate-P, 6 mg/L nitrite-N, and 4.5 mg/L nitrate-N.

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 listed in Section 7.4.3 thru 7.4.7. Check the correlation coefficient (r); the correlation coefficient of the curve must be $\geq$0.995 or the instrument must be re-calibrated.

8.3.2 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. (Note: If it is suspected that the IPC was prepared incorrectly, the IPC may be re-prepared and reanalyzed. If it passes, the analysis may continue without re-calibration). The instrument must be re-calibrated and all samples not bracketed by acceptable IPC results must be re-analyzed. The IPC analyzed immediately after calibration is also a QCS/LFB (30 mg/L sulfate, 20 mg/L each bromide and chloride, 10 mg/L each fluoride and ortho-phosphate-P, 6 mg/L nitrite-N, 4.5 mg/L nitrate-N); both have recovery limits of 90-110%. All subsequent IPCs have analyte concentrations at 10 mg/L for fluoride, nitrite-N, bromide, and nitrate-N and 25 mg/L for chloride, ortho-phosphate-P, and sulfate (7.4.4).

8.3.3 CB - The stability of the baseline must be monitored by analyzing a CB immediately after every IPC standard. If the absolute value of the CB result is less than the QL, the result is acceptable. If the absolute value of the CB result equals or exceeds the QL, the analysis must be terminated. The cause of the high CB result must be determined and the problem corrected. All samples not bracketed by acceptable CB results must be re-analyzed. If there was no sample preparation required, the CB analyzed immediately before the first of the analytical samples can also be used as the LRB (8.3.6).

8.3.4 QCS/LFB Analysis - The anion concentrations in a QCS/LFB sample must be measured daily or once per batch of 20 samples, whichever is more frequent. The first QCS/LFB analyzed is also the initial IPC (30 mg/L for sulfate, 20 mg/L for bromide and chloride, 10 mg/L for fluoride and ortho-phosphate-P, 6 mg/L for nitrite-N, 4.5 mg/L for nitrate-N). The recoveries must be within 90-110% or the samples in the batch must be re-analyzed.

$$\%R = \frac{Cm}{Ct} \times 100$$

Where

$\%R$ = percent recovery.
C_m = measured analyte concentration in the QCS/LFB.
C_t = true analyte concentration in the QCS/LFB.

8.3.5 Quantitation Limit (QL) - To verify the ability to detect target analytes near the QL, QL standards must be analyzed at the QL level (Section 1.3) at the beginning of the analytical run but not before the initial IPC. The Region 9 Laboratory analyzes one QL standard with analyte concentrations at 0.1 mg/L (for fluoride, nitrite-N, bromide, and nitrate-N) and 1 mg/L (for chloride, ortho-phosphate-P, and sulfate). 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 re-calibrated if it is determined that the difference in responses are not due to standard prepared incorrectly 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. If that does not work, prepare new stock standards and re-calibrate.

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, the following statements describe when samples must be re-prepared and re-analyzed:

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.

If there was no sample preparation required, the CB analyzed immediately before the first of the analytical samples can also be used as the LRB (8.3.3).

8.3.7 Laboratory Duplicate (LD) - Sample homogeneity can affect the quality and interpretation of the data. LD results can be used to assess sample homogeneity.

A laboratory duplicate is analyzed only if the original sample concentration is more than 4x the LFM spike level. The sample is diluted appropriately so that the concentration falls within the calibration curve. A sample and a laboratory duplicate are diluted appropriately and analyzed for every LFM and LFM duplicate that fall outside the calibration range.

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, corrected for sample preparation and any dilutions.
C	=	measured analyte in the routine sample, corrected for sample preparation and any dilutions.

The relative percent difference (RPD) for any analyte must be ≤20 for samples with analyte levels greater than or equal to 1 mg/L for fluoride, nitrite-N, bromide and nitrate-N and 10 mg/L for chloride, ortho-phosphate-P and sulfate. The absolute difference between duplicate results must be less than the QL for samples containing less than 1 mg/L for fluoride, nitrite-N, bromide and nitrate-N and 10 mg/L for chloride, ortho-phosphate-P and sulfate. If the control limits are exceeded, flag all associated analyte results as estimated (J flag). Document actions in the report narrative.

8.3.9 LFM and LFM duplicate- The LFM and LFMD are designed to provide information about the effect of sample matrix on the measurement system. A set of LFM and LFM duplicate must be prepared for every 10 routine samples of the same matrix in a sample batch. No LFM and LFM duplicate dilution is necessary for an analyte if the QC sample concentration for that analyte is more than 4x the spike level. The sample and duplicate of the sample for

that analyte are diluted appropriately and analyzed, instead. Samples identified as field blanks cannot be used for LFM and LFMD sample analysis. The recovery of analyte in the LFM/LFMD 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 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 and QCS/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 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. Flag any out-of-control results as estimated (J). The spiking levels for the LFM are as follows:

Parameter	Recommended LFM Spiking Level (mg/L)
Fluoride	5
Chloride	10
Nitrite-N	5
Bromide	5
Nitrate-N	5
Ortho-Phosphate-P	10
Sulfate	10

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 DX-120 are as follows:

DX-120 Detector Parameters

Detector Type: DX-120
Data Collection time (minutes): 12.00
Data Collection Rate: 5.00 Hz
Real time plot scale maximum (us): 100.000
Real time plot scale minimum (us): -10.000

DX-120 Integration Parameters

Peak detection algorithm: Standard
Starting peak width (seconds):10.00
Hit threshold: 950
Minimum area: 0.001 us/min

DX-120 Integration Data Events

Time	Description
0.00	Min. Area 0.001 [signal]*min
0.00	inhibit integration ON
0.00	Peak Slice 0.50s
2.1	inhibit integration OFF
2.25	Valley to Valley

DX-120 Calibration Parameters

External or internal calibration: EXTERNAL
Number of replicates for calibration:1
Rejection: Manual
Level Weighting: Equal
Calibration standard volume: 25 uL
Sample volume: 25 uL
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: 1.2 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, 1.0/5.0, 5.0/10, 10/25, and 25/50 mg/L for all analytes). Calibration for all analytes are calculated using quadratic fit, except for nitrate, for which exponential fit is used. The initial calibration is considered valid as long as the instrument performance check (IPC/QCS/LFB) 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 Preparation

9.3.1 Fill a 5-mL 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 5-mL disposable syringe; pull out the plunger and pour approximately 5 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 5-mL polyvial and repeat the procedure until the polyvial is filled close to the 5-mL mark (discard the remaining sample into the waste container and the syringe assembly into a solid waste container). Attach a filter cap to the 5-mL 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 Instrument Start-up Procedure

9.4.1 Turn on the DX-120 eluent pressure by pressing the "eluent pressure" button and the pump by pressing the "pump" button on the front panel of the instrument. Turn on the suppressor "SRS" button and allow the system to equilibrate for about 15 minutes. The pressure in the system should be approximately 1997 psi, the baseline conductivity should be around 17.88 uS, and the flow should be 1.2 mL/min when the system is ready to analyze samples. Push the "system/control" button until the word "remote" appears on the screen on the front panel of the DX-120.

9.4.2 Turn on the computer system and the printer connected to the DX-120. Log into the network. Double click on the "server monitor" icon and click on the "start" button to turn on the Peaknet server. This will allow the instrument to transfer data into the computer. When the server is running, the message in the status box on the computer monitor should say "Peaknet Server is running idle".

9.4.3 Double click on the "PeakNet" icon to get into the "Browser" section of the software. Set up a sequence by clicking on a sequence file that contains the last calibration performed on the DX-120.The sequence files are located in: C:\USEnvironmental_local\DX120\Data_anions\sequence#. The sequence number is a seven digit number containing the year, the month, the day, and the run number (1), ex. 0109131. Re-save the accessed file and save it as today's sequence file. Ensure that the small box "save raw data" is checked on prior to clicking the save button. Under the "status" column for each position in the sequence to be analyze, change "finished" to "single". This will enable the computer system to acquire the data for the standards and samples to their designated position in the sequence file. Ensure that the "status" column for the calibration standards (std1 thru std5) says "finished", which will prevent the computer from writing over the calibration data. If a new calibration is to be analyzed with the QC standards and samples, every entry in the "status" column should be "single". Check for errors within the sequence file by clicking on "Batch", "Edit", "Add", click on the sequence file you wish to run, click "open", click on the data file that was just added, click on "ready check", when it says "OK", click on the "OK" box.

9.4.4 Load the standards and samples to be analyzed according to their designated position in the sequence file. Start the autosampler (Dionex AS40) by pressing the "Hold/Run" button until the light on the side of the word "Run" is lighted.

9.4.5 The analysis is started by clicking on the "start" button in the Batch list section of the software. The analysis will stop automatically by inserting a "sample" positioned at the end of the sequence file and changing the Program name (AnionsProgram) under the "Program" column to DX120Stop, and re-saving the edited sequence file.

9.4.6 For each sample injected through the autosampler, the sample loop is flushed with the sample for approximately 1 minute prior to sample analysis/data acquisition.

9.4.7 The width of the retention time window used to make identifications is based upon ±10% of the retention times acquired for the highest calibration standard. 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. The retention time for each analyte is determined by the retention times acquired for the highest calibration standard.

All chromatograms are reviewed to ensure that the correct peaks are integrated. The retention time windows used on the DX-120 are listed in the following table:

Parameter	Retention Time (min)	Retention Time Window (min)
Fluoride	2.42	2.18 - 2.66
Chloride	3.32	2.99 - 3.65
Nitrite-N	3.90	3.51 - 4.29
Bromide	4.77	4.29 - 5.25
Nitrate-N	5.40	4.86 - 5.94
O-Phosphate-P	6.71	6.04 - 7.38
Sulfate	8.00	7.20 - 8.80

9.4.8 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.

9.4.9 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	S5	25	S13	37	QCS/LFB
2	CB	14	S6	26	S14	38	QL
3	QL	15	S7	27	S15	39	LRB
4	IPC	16	IPC	28	IPC	40	S21
5	CB	17	CB	29	CB	41	S22
6	LRB	18	S8	30	S16	42	S23
7	S1	19	S9	31	S17	43	S24
8	S1-LFM	20	S10	32	S18	44	S25
9	S1-LFMD	21	S11	33	S19	45	S25-LFM
10	S2	22	S11-LFM	34	S20	46	S25-LFMD
11	S3	23	S11-LFMD	35	IPC	47	IPC
12	S4	24	S12	36	CB	48	CB

9.5 Data Reduction - After set-up and calibration the software reports results for the analyzed solution in units of mg/L and aqueous samples should be reported using the following equation:

$$C = M \times D$$

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.

9.5.1 Reporting - 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.

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 initialled and dated by the analyst, noted in the run log and approved by the ESAT Task Leader, ESAT QA Task Manager or ESAT Program Manager the same day the manual integration was performed (Reference 11.6).

9.5.2 Solid Samples - Data for solid samples should be reported in units of mg/Kg using the following calculation:

$$C = M \times \frac{V_f}{V_i} \times D \times 100/S$$

Where

C	=	final reported concentration, in mg/Kg.
M	=	measured concentration reported by software, in 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.
S	=	Percent of solids in the sample used

Solid samples are prepared by adding reagent water equal to ten times the weight of solid material taken as sample. The slurry is mixed together with a magnetic stirrer for ten minutes. The resulting mixture is then filtered with a 0.45 micron type of filter prior to analysis. For the LFM and LFMD sample, the mixture is spiked with the spiking standards prior to mixing with magnetic stirring device.

9.5.3 Nitrite results in the presence of chloride

Based on a study done at the USEPA Region 9 Laboratory on the effect of chloride on the nitrite peak, it was concluded that nitrite quantitation may be affected by the chloride concentration. Therefore, the following rule applies:

1) If chloride concentration ≤15 mg/L, nitrite QL = 0.1 mg/L.
2) If chloride concentration >15 mg/L and <50 mg/L, nitrite QL = 0.5 mg/L.
3) If chloride concentration >50 mg/L, sample must be diluted. Apply #1 and #2 to the diluted run but the QL must be multiplied by the dilution factor.

However, if nitrite is present in the undiluted sample, then it must be reported regardless of the presence of chloride. If nitrite is present and chloride is ≥15 mg/L, the nitrite result is "J" flagged as quantitatively uncertain due to interference from chloride.

10 DOCUMENTATION

10.1 Inorganic Standards and Reagents Preparation Log Book - Copies of all standard solution preparation entries (CAL, IPC, QL, QCS/LFB, LFM, etc.) must be submitted with each data package. (Attachment B)

10.2 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. (Attachment C)

10.3 Chromatograms and Quantitation Reports - The chromatograms must be scaled such that the baseline used for measuring the peak is visible. For most samples, re-scale the chromatograms from -1.0 to 2.0 *u*S.

10.4 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, LFMD or Duplicate 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). (Attachment E)
Raw sample, standard and QC data, including run logs and any work sheets, if applicable. (Attachments B and C)

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 Laboratory SOP 125, *Sample Disposal.*

11.4 Region 9 Laboratory SOP 110, *Sample Receipt, Log-in and Storage.*

11.5 Region 9 Laboratory SOP 835, *Chromatographic Integration Procedures.*

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

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

11.8 Region 9 Laboratory SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency.*

Attachment A
Deviations From Reference Method

A.1 This SOP specifies the use of quadratic and exponential calibration. Review of instrument response using various calibration protocols demonstrates that instrument response is not linear at low concentrations. The use of quadratic calibration for fluoride, chloride, nitrite, bromide, ortho-phosphate, and sulfate and exponential calibration for nitrate 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 chlorite, and sulfite.

A.3 LRB values should be less than the QL.

A.4 This SOP specifies a recovery limit of 70-130% for LFM and LFMD.

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
Ion Chromatography Run Log

ION CHROMATOGRAPHY RUN LOG FOR DIONEX 120

SCHEDULE FILE : I:\Peaknet\Schedule\ _____.Sch

FILE NAME : I:\Data\Room 207\ DX120_____

ANALYSIS DATE : _____

ANALYST : _____

QCS Source:_____

IPC Source:_____

QL Source:_____

LFM Source:_____

ELUENT Source:_____

INJ. #	CASE NUMBER	SDG NUMBER	CALIBRATION STANDARD	LAB ID / CLIENT ID	DIL'N	COMMENTS	M
1							
2							
3							
4							
5							
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7							
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9							
10							
11							
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USEPA REGION 9 LABORATORY

Filename:ICRUNLOG.WK4 Reviewed:_____ Date:_____

Attachment D
Analytical Spreadsheet

EPA REGION 9 LABORATORY-RICHMOND, CA
SUMMARY OF ANALYTICAL RESULTS

Case Number:	R91SXX	Analysis:	Fluoride, Chloride, Nitrite-N, Bromide, Nitrate-N, Orthophosphate, Sulfate, TDS, Cyanide
Site:	DUMMY		
SDG:	01151A	Matrix:	Water
Date:	06/28/01		

Sample No.	8			9			10			11			Reagent			Quantitation
Sample I.D.	DUMMY			DUMMY			DUMMY			DUMMY			Blank			Limit
Lab Sample I.D.	AB001122			AB001122			AB001155			AB001122			N/A			N/A
Date of Collection	05/30/01			05/30/01			05/30/01			05/30/01			N/A			N/A
Units	mg/L			mg/L			mg/L			mg/L			mg/L			mg/L
Analyte	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result
Chloride	60			0.5	J	A	[illegible]			56			1 U			1
Bromide	0.1			0.1 U			[illegible]			0.1			0.1 U			0.1
Orthophosphate	1 U			1 U			[illegible]			1 U			1 U			1
Total Dissolved Solids	599			20 U			[illegible]			100			20 U			20
				U									U			

Com - Comments refer to the corresponding section in the report narrative for each letter.
NR - 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 E
QC Summary Report

US E.P.A.
REGION 9 LABORATORY
September 5, 2001
Case Number: R01SXX
SDG: 01ZZ0A

Laboratory Fortified Matrix (DUMMY)

Analyzed Date	Analyte	Sample Result (mg/L)	LFM Added (mg/L)	LFM Result (mg/L)	% Recovery	Q
08/08/01	Fluoride	0.226	5	5.002	96	
08/08/01	Nitrite-N	0	5	4.724	94	
08/08/01	Bromide	3.394	5	8.537	103	
08/08/01	Nitrate-N	0.042	5	5.005	99	
08/08/01	Orthophosphate-P	0	10	9.969	100	
08/08/01	Sulfate	19.997	10	30.671	107	

Laboratory Fortified Matrix Duplicate (DUMMY)

Analyzed Date	Analyte	Sample Result (mg/L)	LFM Added (mg/L)	LFMD Result (mg/L)	% Recovery	Q
08/08/01	Fluoride	0.226	5	5.29	101	
08/08/01	Nitrite-N	0	5	4.741	95	
08/08/01	Bromide	3.394	5	8.551	103	
08/08/01	Nitrate-N	0.042	5	4.907	97	
08/08/01	Orthophosphate-P	0	10	9.994	100	
08/08/01	Sulfate	19.997	10	29.715	97	

Appendix B-8
Total Kjeldahl Nitrogen (TKN)

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 592

ANALYSIS OF TOTAL KJELDAHL NITROGEN IN WATER

Prepared by:

Christina Navarro-Dizon, ESAT Region 9, Lockheed Martin	Date

Review by:

Richard Bauer, ChemistryTeam Leader	Date

Approved by:

Brenda Bettencourt, Laboratory Director	Date

Periodic Review:

Signature	Title	Date

STANDARD OPERATING PROCEDURE 592

ANALYSIS OF TOTAL KJELDAHL NITROGEN IN WATER

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
Kathy O'Brien, QA/QC Coordinator,Lockheed Martin	Date
Jack Berges, ESAT Team Manager, Lockheed Martin	Date

ESAT Document Control Number: ESAT-9B-2043

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 9

9 ANALYTICAL PROCEDURES 13

10 DOCUMENTATION 17

11 REFERENCES 18

Attachment A - Deviations From Reference Method

Attachment B - Inorganic Standards and Reagents Preparation Log Book

Attachment C - TKN and Total Phosphorus Digestion Run Log

Attachment D - TKN Analysis by Lachat Run Log

Attachment E - Analytical Spreadsheet

Attachment F - QC Summary Report

1 SCOPE AND APPLICATION

1.1 This method is for the determination of total Kjeldahl nitrogen (TKN) in drinking and surface waters, domestic and industrial wastes. This SOP is based on EPA Method 351.2, Revision 2.0.

1.2 The colorimetric method is based on reactions that are specific for the ammonia ion. The digestion converts organic forms of nitrogen to ammonium sulfate. Nitrate and some amines, nitro compounds, oximes, semicarbazones and some refractory tertiary amines are not converted to ammonium sulfate during digestion.

1.3 The applicable range is 0.3 to 10 mg/L. The range can be extended for high level samples through dilution either before or after the digestion procedure.

1.4 The quantitation limit for total Kjeldahl nitrogen is 0.3 mg/L.

2 METHOD SUMMARY

2.1 During the digestion procedure, the sample is heated in the presence of sulfuric acid, K_2SO_4, and $HgSO_4$ for two and a half hours. This converts free ammonia, ammonium-nitrogen, and nitrogen components of biological origin such as amino acids, proteins and peptides to ammonium sulfate $(NH_4)_2SO_4$. The residue is cooled, diluted with water and analyzed for ammonia. (This digested sample may also be used for total phosphorus determination). In-line neutralization of the digested sample with concentrated buffer on the chemistry manifold of the Lachat QuikChem AE converts the ammonium cation to ammonia, and also prevents undue influence of the sulfuric acid matrix on the pH-sensitive color reaction which follows. The ammonia that is produced is heated at 60°C with salicylate and hypochlorite to produce a dark blue-green color, which is proportional to the ammonia concentration. The absorbance is read at 660nm.

2.2 Total Kjeldahl nitrogen is the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate during the digestion process. Organic Kjeldahl nitrogen is the difference obtained by subtracting the free-ammonia value from the total Kjeldahl nitrogen value.

3 DEFINITIONS

3.1 Analytical Sample - Any sample in which TKN 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 analyte.

3.3 Calibration Standard (CAL) - A solution prepared by diluting the primary 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 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.

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 the sample collection and storage as well as the laboratory procedures.

3.6 Instrument Performance Check Solution (IPC) - A standard containing the analyte of interest which is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout an analysis sequence.

3.7 Laboratory Fortified Blank (LFB) - An aliquot of reagent water or other blank matrix to which known quantities of the method analyte is added in the laboratory. The source of the LFB must be independent of the calibration standards. 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. The LFB also fulfills the requirements of the QCS (3.13).

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 marix 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 Linear Calibration Range (LCR) - The concentration range over which the instrument response is linear.

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 standard containing TKN which is used to verify the accuracy of the analysis. The method requires that the source of the QCS must be independent of the calibration standards and that the QCS be analyzed quarterly. The Region 9 Laboratory exceeds this requirement through the daily analysis of the LFB.

3.14 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 0.3 mg/L.

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

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

4 HEALTH & 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.

4.2 The following chemicals are toxic or hazardous: hydrochloric acid, mercury, sodium nitroprusside, sodium potassium tartrate and sulfuric acid.

4.3 Since small amounts of sulfuric acid fumes and aerosol are released to the room during the Kjeldahl digestion, the BD-46 block digestor should be operated in a laboratory fume hood.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Samples should be collected in precleaned plastic or glass bottles. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis and minimize waste disposal. A 100 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. Sample IDs and dates of collection are verified against the chain-of-custody form. Samples must be preserved at the time of collection with sulfuric acid to pH ≤ 2. 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 samples must be analyzed within 28 days of the sample collection date.

6 INTERFERENCES

6.1 During Kjeldahl digestion, nitrate in excess of 10 mg/L can oxidize a portion of the ammonia released from the digested organic nitrogen, producing N_2O and resulting in a negative interference. If interference is suspected, samples should be diluted and reanalyzed.

6.2 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that bias analyte response.

7 APPARATUS AND MATERIALS

7.1 Instrumentation

7.1.1 Analytical balance capable of accurately weighing to the nearest 0.1 mg.
7.1.2 A ventilated oven capable of heating up to 110 ±5°C, or equivalent.
7.1.3 BD-46 Block Digestor (capable of heating up to 380°C), or equivalent.
7.1.4 Lachat QuikChem AE automated flow injection analyzer, total Kjeldahl nitrogen manifold, Lachat Quikchem AE software and a personal computer.

7.2 Glassware and Incidentals

7.2.1 Autosampler glass tubes, 13×100 mm (KIMAX) or equivalent.
7.2.2 Coldfingers for the digestion tubes.
7.2.3 Digestion tubes, 20- to 75-mL digestion volume capacity.
7.2.4 Eppendorf pipeter and pipet tips, 100- to 1000-μL or equivalent.
7.2.5 Glass scintillation vials, 20-mL (KIMAX) or equivalent.
7.2.6 25-mL graduated cylinders.
7.2.7 Magnetic stirrers and magnetic stirrer plate.

7.2.8 A pair of heat-resistant gloves.
7.2.9 5-mL and 20-mL repipet dispensers.
7.2.10 Hengar granules, plain, or teflon boiling chips, or equivalent.
7.2.11 Volumetric flasks, Class A, 1000-mL, 250-mL, 100-mL, 50-mL.
7.2.12 Volumetric pipets, Class A, 25-mL, 10-mL, 5-mL.

7.3 Reagents and Standards

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 water in this method refer to ASTM Type II grade water.

7.3.2 Mercuric Sulfate Solution: To a 100-mL volumetric flask, add approximately 40 mL of reagent water and 10 mL concentrated sulfuric acid (H_2SO_4). Then add 8.0 g red mercuric oxide (HgO). Stir at low heat on a hot plate until dissolved. Allow to cool, dilute to the mark and invert to mix. Prepare fresh annually.

7.3.3 Digestion solution: In a 1-L volumetric flask, add 133.0 g potassium sulfate (K_2SO_4) and 200 mL concentrated sulfuric acid (H_2SO_4) to approximately 700 mL reagent water. Add 25 mL of mercuric sulfate solution. Allow to cool, dilute to the mark with reagent water and invert to mix. Prepare fresh annually.

7.3.4 TKN Stock Standard, 2000 mg/L N: In a 250-mL volumetric flask, dissolve 1.9095 g ammonium chloride (NH_4Cl) that has been dried for at least two hours at 110°C in about 150 mL reagent water. Add 0.5 mL of concentrated sulfuric acid, dilute to the 250 mL mark, and invert to mix. Prepare fresh annually.

7.3.5 TKN Working Standard, 20 mg/L N: In a 100-mL volumetric flask, add 1.0 mL of the TKN Stock Standard (7.3.4) to about 75 mL reagent water. Add 0.2 mL H_2SO_4, dilute to the mark and invert to mix. Prepare this standard fresh daily.

The following five calibration standards, QL and IPC are prepared using the 20 mg/L N working standard and diluted with reagent water:

Calibration Standard	Vol. of 20 mg/L N	Vol. of digestion solution	Final volume
10 mg/L	25 mL	12.5 mL	50 mL
5.0 mg/L, IPC	12.5 mL	12.5 mL	50 mL
2.0 mg/L	5.0 mL	12.5 mL	50 mL

1.0 mg/L	2.5 mL	12.5 mL	50 mL
0.3 mg/L, QL	0.75 mL	12.5 mL	50 mL
Blank	0 mL	12.5 mL	50 mL

7.3.6 Buffer: In a 1-L volumetric flask containing 900 mL reagent water, completely dissolve 35.0 g sodium phosphate dibasic heptahydrate ($Na_2HPO_4 \cdot 7H_2O$). Next, add 20 g disodium EDTA (ethylenediaminetetracetic acid disodium salt). Finally, add 65 g sodium hydroxide (NaOH). Stir until dissolved, allow to cool, dilute to the mark, and degas weekly with helium before use. Prepare fresh annually.

7.3.7 Salicylate Nitroprusside: In a 1-L volumetric flask, dissolve 150.0 g sodium salicylate [salicylic acid sodium salt, $C_6H_4(OH)(COO)Na$], and 1.00 g sodium nitroprusside [sodium nitroferricyanide dihydrate, $Na_2Fe(CN)_5NO \cdot 2H_2O$] in about 800 mL reagent water. Dilute to the mark and invert to mix. Store in a dark bottle. Degas with helium prior to using it. Prepare fresh annually.

7.3.8 Hypochlorite solution: In a 250-mL volumetric flask, dilute 15.0 mL Regular Clorox Bleach (5.25% sodium hypochlorite, The Clorox Company, Oakland, CA) to the mark with reagent water, and invert to mix. Prepare fresh daily. Degas with helium prior to use.

7.3.9 Total Kjeldahl Nitrogen QCS Solution - A solution obtained from a commercial vendor (SPEX, CPI or Inorganic Ventures) with a known concentration of total Kjeldahl nitrogen. Region 9 laboratory currently uses a solution with approximately 3.0 mg/L total Kjeldahl nitrogen as the QCS. The QCS must be prepared fresh daily.

7.3.10 5% Hydrochloric Acid: Add 50 mL of concentrated hydrochloric acid to 950 mL reagent water. This solution is used to soak the digestion coldfingers and digestion tubes prior to use.

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 - Each analyst must complete an initial demonstration of proficiency prior to analyzing samples following this method.

8.2.1 LCR - The absorbance response vs. total Kjeldahl nitrogen concentration is generally a linear function over a limited concentration range. The LCR must be determined prior to using this method for routine analysis and confirmed annually.

8.2.2 MDL - A method detection limit must be confirmed annually and must be <1/2 QL or corrective action must be initiated.

8.2.3 QCS - A QCS standard must be prepared and analyzed when beginning the use of this method, on a quarterly basis or as required to meet data-quality needs. The source of the QCS must be independent of the calibration standards. The QCS verifies the calibration standards.

8.3 Routine Analytical Quality Control - The various routine QC samples analyzed during each analytical run are specified in this section. Some are treated like samples and undergo digestion before analysis, while some are not digested. The following table lists the QC samples and indicates whether sample digestion is required prior to analysis:

QC Sample ID	Digestion Required?	QC Sample ID	Digestion Required?
Calibration Standards: Blank, S1, S2, S3, S4, and S5.	N	Instrument performance check (IPC)	N
Quantitation Limit (QL)	N	Calibration Blank (CB)	N
Laboratory Fortified Blank (LFB)	Y	Laboratory Duplicate (LD)	Y
Laboratory Reagent Blank (LRB)	Y	Laboratory Fortified Matrix (LFM)	Y
Quality Control Sample (QCS)	Y		

8.3.1 The instrument must be calibrated daily with a blank and 5 standards. The correlation coefficient of the calibration curve must be $\geq$0.995 or the instrument must be recalibrated.

8.3.2 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 TKN in the IPC is calculated as follows:

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

Where

%R = percent recovery of the standard
M = measured concentration of total Kjeldahl nitrogen, mg/L
T = true concentration of TKN 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 is at a concentration of 5.0 mg/L total Kjeldahl nitrogen.

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 the QL, the result is acceptable. If the absolute value of the CB result equals or 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 reanalyzed.

8.3.4 QL - The accuracy of the calibration at the reporting 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 CB of the QCS. The recovery of the analyte in the QL is calculated as follows:

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

Where
%R = percent recovery
M = measured concentration of the analyte, mg/L
T = true concentration 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 re-calibrated and all affected samples must be reanalyzed. If, after recalibration, the QL recovery still exceeds the 50-150% limits, the calibration standards must be reprepared and the instrument recalibrated.

8.3.5 LRB - The laboratory must analyze at least one LRB daily with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the QL indicate laboratory contamination. The LRB must be re-prepared along with the affected samples, and re-analyzed.

8.3.6 LFB - A LFB must be prepared, digested and analyzed with each analytical run. The LFB is also used to fulfill the method requirements that ensures that the digestion method is reliable and the calibration standards used to calibrate are accurate. The LFB is the QCS. The recovery of total Kjeldahl nitrogen in the LFB is calculated as follows:

$$\%R = \frac{LFB}{s} \times 100$$

Where

%R = percent recovery
LFB= measured concentration of TKN in the LFB in mg/L.
s = TKN concentration in the LFB in mg/L.

The recovery of TKN in the LFB must be within the 90-110% limits. If the recovery exceeds the limits, the digestion and/or 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 LD - Sample homogeneity can affect the quality and interpretation of the data. LD results can be used to assess sample homogeneity. One LD must be prepared for every 10 routine samples of the same matrix in a sample batch. Samples identified as field blanks cannot be used for duplicate sample analysis. 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 TKN in the LD, mg/L
C = measured TKN in the routine sample, mg/L

The relative percent difference (RPD) must be $\leq$20% for samples with TKN levels greater than or equal to 5 times the QL. For other samples, the absolute difference between duplicate results must be less than the QL. If the control limits are exceeded, flag all associated analyte results. Document actions in the report 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 LFM is prepared by spiking 20 μL of the 2000 mg/L TKN Stock solution (7.3.4) into

20 mL of an analytical sample. The resulting concentration of TKN in the LFM will be 2.0 mg/L. The recovery of TKN 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, mg/L
- C = measured concentration of analyte in the routine sample, mg/L corrected for the 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 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, QL, 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 report 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. Document actions in the report narrative.

9 ANALYTICAL PROCEDURES

9.1 Sample Digestion

1) Initiate a TKN and Total Phosphorus Digestion Run Log, one for each batch of samples to be digested, before beginning with any preparations. Complete the TKN and Total Phosphorus Digestion Run Log as given in Sections 7.3.5, 9.4.6, 9.4.7, 9.4.8 and Attachment C.

2) Gather all the digestion tubes and coldfingers, scintillation vials and caps, autosampler sample tubes, and graduated cylinders that are to be used in preparation for the total Kjeldahl nitrogen analysis. They need to be pre-soaked in a 5% hydrochloric acid bath (7.3.10) for at least half a day. They are then thoroughly rinsed with reagent water. The scintillation vials and caps and the autosampler tubes must be dried before they are used, but the digestion tubes may

be used right after they are rinsed with reagent water. Excess reagent water needs to be shaken off the sample tubes.

3) The LFM is prepared by spiking 20 μL of the 2000 mg/L TKN Stock solution into 20 mL of an analytical sample. The resulting concentration of TKN in the LFM will be 2.0 mg/L. The following samples and check standards are carried through the digestion procedure:

QCS	Sample A	Sample B
LFB	LD (Sample A)	Sample C
LRB	LFM (Sample A)	Sample D

4) Using 25-mL graduated cylinders, measure 20 mL of each sample to be digested into a digestion tube, and place the tubes in the digestion tube rack. Add 5.0 mL of digestion solution (section 7.3.3), mix, and add 3 to 4 teflon boiling chips to each sample. Place the digestion tube rack with the samples on the BD-46 block digestor.

5) Ensure that the **Temp1** and the **Time1** setting on the **controller panel** are set at 160°C and 60 minutes, respectively. Also make sure that the **Temp2** and the **Time2** setting on the controller are set at 380°C and 150 minutes, respectively. Then turn on the main switch on the right rear panel of the digestor. Also turn on the toggle switch on the temperature **controller panel** (the **yellow light** should illuminate if the block digestor is operating normally), and allow the temperature to go up to 160°C, which will take about 20 to 25 minutes. When the temperature on the controller panel indicates that the digestion block is at **(Temp1)** 160°C ± 5 (and the first **red light** will be on), push the green **start button** on the controller panel. The first **green light** will turn on and the digestor block will then hold the **160°C (Temp1)** temperature for **60 minutes (Time1)**, which is the amount of time required to boil off the water in the samples.

6) After 60 minutes, the coldfingers should be placed on the sample tubes and the green **start button** on the **controller panel** should be pressed again **(Time2** starts here), which will cause the next **yellow light** to illuminate. The temperature of the block digestor will then start to go up to 380°C, which will take about an hour. The second **green light** will turn on when **380°C (Temp2)** is reached, and the temperature will be held for another hour and a half. When the **Time2 (150 minutes)** has elapsed, the last **red light** will light. The temperature of the digestion block will then start to go down and only the first **yellow** and the last **red light** will remain lit. Put on a pair of heat resistant gloves and take the sample tube rack out of the digestor block while the block temperature is still hot. Otherwise, it will be

harder to take the sample tubes out of the block digestor.

7) Set the sample tube rack on its rack base in the fume hood and allow the samples to cool for about 10 minutes. Then add 19.5 mL of reagent water to each of the samples in the sample tubes, swirl several times to mix, and transfer each sample to an acid rinsed scintillation vial and cap each sample tightly. Each scintillation vial should be labeled according to its contents. The digested samples are good for one week, although it is best to analyze the sample as soon as they are digested.

9.2 CALIBRATION AND STANDARDIZATION - Total Kjeldahl nitrogen is determined colorimetrically using the Lachat Automated Ion 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.

9.2.1 Instrument Set-up

1) Turn on the Lachat QuikChem AE analyzer and allow the heater module to heat up to 60°C for about 15 minutes. Degas each reagent with helium gas for at least 3 minutes.

2) Connect the total Kjeldahl nitrogen manifold, sample loop and the wavelength filter to the module. Place the waste lines into the TKN analysis waste container and place a tube cartridge to support each reagent line onto the pump. Place each reagent line into the appropriate reagent solution. Turn on the pump and set the speed to 35 RPM, download the TKN method, and allow the reagents to flow through the manifold until the air bubbles disappear into the waste container.

9.2.2 Calibration and Sample Analysis

1) Pour the five calibration standards, the blank, IPC, CB and QL, into 20 mL scintillation vials. Place the calibration standards in decreasing order - starting from position A- in the calibration tray, which is positioned on the right side of the autosampler tray. Place the IPC, CB and QL in positions J, K and I, respectively, in the calibration tray.

2) Load the analytical and QC samples into the sample trays using the 13×100mm autosampler tubes. The usual sample loading sequence is listed in the following table:

Seq.#	Cup #	Desc.	Seq.	Cup #	Desc.	Seq.	Cup #	Desc.
1	A	10 mg/L	15	7	S2	29	19	S12
2	B	5.0 mg/L	16	8	S3	30	20	S13
3	C	2.0 mg/L	17	9	S4	31	J	IPC
4	D	1.0 mg/L	18	10	S5	32	K	CB
5	E	0.3 mg/L	19	J	IPC	33	21	S14
6	F	0 mg/L	20	K	CB	34	22	S15
7	J	IPC	21	11	S6	35	23	S16
8	K	CB	22	12	S7	36	24	S17
9	I (1)	QL	23	13	S8	37	25	S18
10	2	LRB	24	14	S9	38	26	S19
11	3	LFB	25	15	S10	39	27	S20
12	4	S1	26	16	S11	40	J	IPC
13	5	S1-LD	27	17	S11-LD	41	K	CB
14	6	S1-LFM	28	18	S11-LFM	42		

3) Select ***File*** from the ***Sample Identification & Tray Submission Menu.*** Highlight ***Template Read (Public)*** and press ***Enter***. Select ***QC_Sched***, press ***Enter***, highlight ***Identification*** and press ***Enter***. Next, enter each check standard and all samples that are to be analyzed in the same order as in the table above. The calibration standards, the IPC/QCS, the QL and the CBs that are positioned in cups A through K are not entered into the sample tray. They are automatically analyzed during the sample tray analysis. The IPC and the CB will be analyzed automatically after every 10 samples and at the end of the analytical run. Type in *(..)* after the last sample in the tray to mark the end of the sample tray.

4) Select ***Submit current tray*** under ***Sample Identification & Tray Submission Menu***. Answer ***Yes*** to ***Submit tray now?***

5) The system will analyze the calibration standards and calculate a calibration curve prior to analyzing any of the samples. The system will emit a beeping sound when the calibration is complete. The calibration data may be viewed by selecting ***Results/Approval, View Calibration and Sample Reports, Tray Selection, Calibration Trays***, and ***tentative calibration***. Press ***Enter*** until the plotted calibration curve appears on the screen. A correlation coefficient of at least 0.995 is the requirement for the calibration to pass. It is approved by selecting ***Approval*** on the menu bar. The system will now automatically analyze the samples loaded in the sample tray.

9.2.3 Post-analysis Review

1) QC Sample Results - Review the results for all QC samples for compliance with the criteria specified in Section 8. If results are not acceptable, take appropriate corrective action.

2) Off-scale Results - Review results for samples that exceed the calibration range. Samples having total Kjeldahl nitrogen at concentrations greater than 10 mg/L must be diluted into range with the calibration blank and re-analyzed. Only 2 mL of sample is used per analysis; there is sufficient volume for dilution and reanalysis.

9.2.4 Instrument Shutdown

1) With the pump still turned on, remove each reagent line from the reagent and place into a container of reagent water. Allow the reagent water to flush through the reagent lines for at least 15 minutes.

2) After the 15 minute period, remove the reagent lines from the reagent water and allow the reagent lines to be purged of the reagent water. Observe the tubing on the manifold - when no liquid is apparent in the tubing the pump can be turned off. Cap all reagents, discard all samples and standards into the appropriate waste containers and turn the power off at the power strip behind the autosampler.

10 DOCUMENTATION

10.1 The Inorganic Standards and Reagents Preparation Log Book is maintained in room 207. Each reagent and standard that is prepared for the analysis is entered in the Inorganic Standards and Reagents Preparation Log Book. Copies of the appropriate page(s) is (are) included in the data package (Attachment B).

10.2 The TKN and Total Phosphorus Digestion Run Log is maintained in room 207. Each QC sample and sample that is digested is documented in the log book. The amount and sample identification (from the Inorganic Reagents and Standards Preparation Log Book) of the spiking solution used in the digestion process is also noted in the TKN and Total Phosphorus Digestion Run Log. Copies of the appropriate page(s) is (are) included in the data package (Attachment C).

10.3 The TKN Analysis by Lachat Run Log must be filled out for each sample batch that is analyzed. The sample identification of each standard, analytical sample, and QC sample are entered into the TKN Analysis by Lachat Run Log. Copies of the appropriate page(s) is(are) included in the data package (Attachment D).

10.4 An analytical spreadsheet, with the total Kjeldahl nitrogen results in mg/L, sample collection date(s), client sample ID's, lab ID's, and station locations must be included with the data package (Attachment E).

10.5 QC summary reports with LFB, LD and LFM results must be prepared and included in the data package (Attachment F).

10.6 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)
Duplicate 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 digestion logs, run logs and any work sheets, if applicable. (Attachments B, C and D)

11 REFERENCE

11.1 EPA Method 351.2 *Determination of Total Kjeldahl Nitrogen By Semi-Automated Colorimetry*, Revision 2.0, August 1993.
11.2 BD-46 Block Digestor Installation & User Guide, Lachat Instruments, 16 April 1993.
11.3 QuikChem Method 10-107-06-2-E, *Determination of Total Kjeldahl Nitrogen by Flow Injection Analysis Colorimetry (Block Digestor Method)*, Lachat Instruments, 17 June 1994.
11.4 Method 4500-N_{org}, Standard Methods For the Examination of Water and Wastewater, 18th Edition, 1992.
11.5 Region 9 SOP 840, *Notebook Documentation and Control.*
11.6 Region 9 SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency.*

Attachment A
Deviations From Reference Method

A.1 1.00 g of sodium nitroprusside is used instead of 0.3 g.

A.2 One buffer solution containing sodium phosphate dibasic heptahydrate ($Na_2HPO_4 \cdot 7H_2O$), disodium EDTA (ethylenediaminetetracetic acid disodium salt) and sodium hydroxide (NaOH) is prepared rather than a mixture of three separate solutions.

A.3 This SOP includes routine quality control procedures based on EPA Region 9 Laboratory policy which are in addition to those listed in EPA Method 351.2. These include the analysis of a QL standard and laboratory duplicate.

Appendix B-9
Ammonia

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 590

AMMONIA ANALYSIS

Prepared by:

Eddie Rankin, ESAT Region 9, Lockheed Martin — Date

Review by:

Richard Bauer, ChemistryTeam Leader — Date

Approved by:

Brenda Bettencourt, Laboratory Director — Date

Periodic Review:

Signature	Title	Date

STANDARD OPERATING PROCEDURE 590

AMMONIA 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:

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ESAT Document Control Number: ESAT-9B-2674

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 6

8 QUALITY CONTROL PROCEDURES 8

9 ANALYTICAL PROCEDURES 12

10 DOCUMENTATION 15

11 REFERENCES 16

Attachment A - Deviations From Reference Method

Attachment B - Inorganic Standards and Reagents Preparation Log Book

Attachment C - Ammonia Analysis by Lachat Run Log

Attachment D - Analytical Spreadsheet

Attachment E - QC Summary Report

1 SCOPE AND APPLICATION

1.1 This method is for the determination of ammonia in drinking, surface, and saline waters, domestic and industrial waste.

1.2 The colorimetric method is based on reactions which are the same as those in SOP #592, "Analysis of Total Kjeldahl Nitrogen in Water," EPA Method 351.2.

1.3 The applicable range is 0.3 to 10 mg/L. The range can be extended for high level samples through dilution.

1.4 The quantitation limit for ammonia is 0.3 mg/L

2 METHOD SUMMARY

2.1 During the analytical procedure, the sample is neutralized in-line with concentrated buffer on the chemistry manifold of the Lachat QuikChem AE and the ammonium cation is converted to ammonia. The ammonia that is produced is heated at 60°C with salicylate and hypochlorite to produce dark blue-green color, which is proportional to the ammonia concentration. The absorbance is read at 660nm.

3 DEFINITIONS

3.1 Analytical Sample - Any sample in which ammonia 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 analyte.

3.3 Calibration Standard (CAL) - A solution prepared by diluting the primary 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 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.

3.5 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 the sample collection and storage as well as the laboratory procedures.

3.6 Instrument Performance Check Solution (IPC) - A standard containing the analyte of interest which is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout an analysis sequence.

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 source of the LFB must be independent of the calibration standards. 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. The LFB also fulfills the requirements of the QCS (3.13)

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 marix 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 Linear Calibration Range (LCR) - The concentration range over which the instrument response is linear.

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 standard containing ammonia which is used to verify the accuracy of the analysis. The method requires that the source of the QCS must be independent of the calibration standards and that the QCS be analyzed quarterly. The Region 9 Laboratory exceeds this requirement through the daily analysis of the LFB.

3.14 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 0.3 mg/L.

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

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

4 HEALTH & 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.

4.2 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS: sodium phosphate dibasic heptahydrate, sodium salicylate, sodium nitroprusside, disodium EDTA, sodium hypochlorite, ammonium chloride, sodium hydroxide and sulfuric acid.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Samples should be collected in precleaned plastic or glass bottles. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis and minimize waste disposal. A 100 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. Sample IDs and dates of collection are verified against the chain-of-custody form. Samples must be preserved at the time of collection with sulfuric acid to pH ≤ 2. 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 samples must be analyzed within 28 days of the sample collection date.

6 INTERFERENCES

6.1 Calcium and magnesium ions may be present in concentration sufficent to cause precipitation probelms during analysis. A 5% EDTA solution is used to prevent the precipitation of calcium and magnesium ions from river water and industrial waste.

7 APPARATUS AND MATERIALS

7.1 Instrumentation

7.1.1 Analytical balance capable of accurately weighing to the nearest 0.1 mg.
7.1.2 A ventilated oven capable of heating up to 110°C, or equivalent.
7.1.3 Lachat QuikChem AE, an automated flow injection analyzer, ammonia manifold and a Lachat AE data system with software.

7.2 Glassware and Incidentals

7.2.1 Eppendorf pipeter and pipet tips, 100- to 1000-μL.
7.2.2 25-mL graduated cylinders.
7.2.3 Magnetic stirrers and magnetic stirrer plate.
7.2.4 5-mL and 20-mL repipet dispensers.
7.2.5 Volumetric flasks, Class A, 1000-mL, 250-mL, 100-mL, 50-mL.
7.2.6 Volumetric pipets, Class A, 25-mL, 10-mL, 5-mL.

7.3 Standards 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, ASTM D1193.

7.3.2 Degassed reagent water - Reagent water that has been purged with helium for 5 minutes.

7.3.3 Ammonia Stock Standard, 2000 mg/L: In a 250-mL volumetric flask, dissolve 1.9095 g ammonium chloride (NH_4Cl) that has been dried for at least two hours at 110°C in about 150 mL reagent water. Add 0.5 mL of concentrated sulfuric acid, dilute to the mark, and invert to mix. Prepare fresh annually.

7.3.4 Ammonia Working Standard, 20 mg/L: In a 100-mL volumetric flask add 1.00 mL of the ammonia stock standard (7.3.3) to about 75 mL reagent water, 0.20 mL H_2SO_4, and dilute to the mark. The following five calibration standards, QL and IPC are prepared using the 20 mg/L ammonia working standard and diluting with reagent water:

Calibration Standard	Vol. of 20 mg/L Ammonia Working Standard	Final volume
10.0 mg/L	25 mL	50 mL
5.0 mg/L, IPC	12.5 mL	50 mL
2.0 mg/L	5.0 mL	50 mL
1.0 mg/L	2.5 mL	50 mL
0.3 mg/L, QL	0.75 mL	50 mL
Blank	0 mL	50 mL

7.3.5 Ammonia QCS Solution - A solution obtained from a commercial vendor (SPEX, CPI or Inorganic Ventures) with a known concentration of ammonia. Region 9 laboratory currently uses an ammonia QCS solution with approximately 1.0 mg/L ammonia. This solution must be prepared fresh every 6 months.

7.3.6 Buffer: In a 1-L volumetric flask containing 900 mL reagent water, completely dissolve 67.0 g sodium phosphate dibasic heptahydrate ($Na_2HPO_4 \cdot 7H_2O$). Next, add 25.0 g disodium EDTA (ethylenediaminetetracetic acid disodium salt). Finally, add 30.0 g sodium hydroxide (NaOH). Stir until dissolved, allow to cool, dilute to the mark, and degas with helium prior to use. Prepare fresh annually.

7.3.7 Salicylate Nitroprusside: In a 1-L volumetric flask, dissolve 144.0 g sodium salicylate [salicylic acid sodium salt, $C_6H_4(OH)(COO)Na$], and 3.5 g sodium nitroprusside [sodium nitroferricyanide dihydrate, $Na_2Fe(CN)_5NO \cdot 2H_2O$] in about 800 mL reagent water. Dilute to the mark and invert to mix. Store in a dark bottle. Degas with helium prior to use.

7.3.8 Hypochlorite solution: In a 250-ml volumetric flask, dilute 15.0 mL Regular Clorox Bleach (5.25% sodium hypochlorite, The Clorox Company, Oakland, CA) to the mark with reagent water, and invert to mix. Prepare daily and degas with helium prior to use.

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 - Each analyst must complete an initial demonstration of proficiency prior to analyzing samples following this method.

8.2.1 LCR - The absorbance response vs. ammonia concentration is generally a linear function over a limited concentration range. The LCR must be determined prior to using this

method for routine analysis and confirmed annually.

8.2.2 MDL - A method detection limit must be confirmed annually and must be <1/2 QL or corrective action must be initiated.

8.2.3 QCS - A QCS standard must be prepared and analyzed when beginning the use of this method, on a quarterly basis or as required to meet data-quality needs. The source of the QCS must be independent of the calibration standards. The QCS verifies the calibration standards. The Region 9 Laboratory fulfills the requirements of the QCS with analysis of the LFB.

8.3 Routine Analytical Quality Control - The various routine QC samples analyzed during each analytical run are specified in this section. The following table lists the QC samples.

QC Sample ID	QC Sample ID
Calibration Standards: Blank, S1, S2, S3, S4, and S5.	Instrument performance check (IPC)
Quantitaion Limit (QL)	Calibration Blank (CB)
Laboratory Fortified Blank (LFB)	Laboratory Duplicate (LD)
Laboratory Reagent Blank (LRB)	Laboratory Fortified Matrix (LFM)
Quality Control Sample (QCS)	

8.3.1 The instrument must be calibrated daily with a blank and 5 standards. The correlation coefficient of the calibration curve must be ≥0.995 or the instrument must be recalibrated.

8.3.2 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 ammonia in the IPC is calculated as follows:

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

Where

$\%R$ =percent recovery of the standard.
M =measured concentration of ammonia, mg/L.
T =true concentration of ammonia 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 IPCs are at a concentration of 5.0 mg/L ammonia.

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 the QL, the result is acceptable. If the absolute value of the CB result equals or 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 reanalyzed.

8.3.4 QL - The accuracy of the calibration at the reporting 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 CB of the QCS. The recovery of the ammonia in the QL is calculated as follows:

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

Where
$\%R$ =percent recovery
M =measured concentration of the analyte, mg/L
T =true concentration 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 re-calibrated and all affected samples must be reanalyzed. If, after recalibration, the QL recovery still exceeds the 50-150% limits, the calibration standards must be reprepared and the instrument recalibrated.

8.3.5 LRB - The laboratory must analyze at least one LRB daily with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the QL indicate laboratory contamination. The LRB must be re-prepared along with the affected samples, and re-analyzed.

8.3.6 LFB - A LFB must be prepared and analyzed with each analytical run. The LFB is also used to fulfill the method requirements that ensures that the method is reliable and the calibration standards used to calibrate are accurate. The LFB is a QCS. The recovery of ammonia in the LFB is calculated as follows:

$$\%R = \frac{LFB}{s} \times 100$$

Where
$\%R$ = percent recovery
LFB = measured concentration of ammonia in the LFB in mg/L.
s = ammonia concentration in the LFB in mg/L.

The recovery of ammonia 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 LD - Sample homogeneity can affect the quality and interpretation of the data. LD results can be used to assess sample homogeneity. One LD must be prepared for every 10 routine samples of the same matrix in a sample batch. Samples identified as field blanks cannot be used for duplicate sample analysis. Homogenize the routine sample selected as the LD, obtain a representative aliquot, and proceed with sample 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 ammonia in the LD, mg/L
C = measured ammonia in the routine sample, mg/L

The relative percent difference (RPD) must be $\leq$20% for samples with ammonia levels greater than or equal to 5 times the QL. For other samples, the absolute difference between duplicate results must be less than the QL. If the control limits are exceeded, flag all associated analyte results. Document actions in the report 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 LFM is prepared by spiking 20 mL of an analytical sample with 20 μL of the 2000 mg/L ammonia stock standard (7.3.3). The resulting concentration of ammonia in the LFM will be 2.0 mg/L. The recovery of ammonia in the LFM is calculated as follows:

$$\%R = \frac{C_{lfm} - C}{s} \times 100$$

Where

$\%R$ = percent recovery

C_{lfm} = measured concentration of ammonia in the LFM, corrected for any dilutions, mg/L

C = measured concentration of ammonia in the routine sample, corrected for any dilutions, mg/L

s = ammonia concentration in the LFM, corrected for 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 falls outside the acceptance window other QC data must be examined to determine if a matrix problem exists. If the laboratory performance for ammonia is in control (i.e., the IPC, QL, 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 report narrative and the data user informed that the result for ammonia in the unfortified sample is suspect due either to heterogeneous nature of the sample or a matrix effect. Flag any out-of-control results. Document actions in the report narrative.

9 ANALYTICAL PROCEDURES

9.1 CALIBRATION AND STANDARDIZATION - Ammonia is determined colorimetrically using the Lachat Automated Ion 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.

9.1.1 Instrument Set-up

1) Turn on the Lachat QuikChem AE analyzer, set the heater module to 60°C and allow it to heat up to 60°C for about 15 minutes. Degas each reagent with helium gas for at least 5 minutes.

2) Connect the ammonia manifold, sample loop and the wavelength filter to the module. The wavelength is set at 660 nm. Place the waste lines into the ammonia analysis waste container and place a tube cartridge to support each reagent line onto the pump. Place each reagent line into the appropriate reagent solution. Turn on the pump and set the speed to 35 RPM, download the ammonia method, and allow the reagents to flow through the manifold until the air bubbles disappear into the waste container.

9.2.2 Calibration and Sample Analysis

1) Pour the five calibration standards, the blank, IPC, CB and QL into 20-mL scintillation vials. Place the calibration standards in decreasing order - starting from position A- in the calibration tray, which is positioned on the right side of the autosampler tray. Place the IPC, CB and QL in positions J, K and I, respectively, in the calibration tray.

2) Load the analytical and QC samples into the sample trays using the 13×100mm autosampler tubes. The usual sample loading sequence is listed in the following table:

Seq.#	Cup #	Desc.	Seq.	Cup #	Desc.	Seq.	Cup #	Desc.
1	A	10 mg/L	15	7	S2	29	19	S12
2	B	5.0 mg/L	16	8	S3	30	20	S13
3	C	2.0 mg/L	17	9	S4	31	J	IPC
4	D	1.0 mg/L	18	10	S5	32	K	CB
5	E	0.3 mg/L	19	J	IPC	33	21	S14
6	F	0 mg/L	20	K	CB	34	22	S15
7	J	IPC	21	11	S6	35	23	S16
8	K	CB	22	12	S7	36	24	S17
9	I (1)	QL	23	13	S8	37	25	S18
10	2	LRB	24	14	S9	38	26	S19
11	3	LFB	25	15	S10	39	27	S20
12	4	S1	26	16	S11	40	J	IPC
13	5	S1-LD	27	17	S11-LD	41	K	CB
14	6	S1-LFM	28	18	S11-LFM	42		

3) Select ***File*** from the ***Sample Identification & Tray Submission Menu.*** Highlight ***Template Read (Public)*** and press ***Enter***. Select ***QC_Sched***, press ***Enter***, highlight ***Identification*** and press ***Enter***. Next, enter each check standard and all samples that are to be analyzed in the same order as in the table above. The calibration standards, the IPC/QCS, the QL and the CBs that are positioned in cups A through K are not entered into the sample tray. They are automatically analyzed during the sample tray analysis. The IPC and the CB will be analyzed automatically after every 10 samples and at the end of the analytical run. Type in *(..)* after the last sample in the tray to mark the end of the sample tray.

4) Select ***Submit current tray*** under ***Sample Identification & Tray Submission***

Menu. Answer ***Yes*** to ***Submit tray now?***

5) The system will analyze the calibration standards and calculate a calibration curve prior to analyzing any of the samples. The system will emit a beeping sound when the calibration is complete. The calibration data may be viewed by selecting ***Results/Approval, View Calibration and Sample Reports, Tray Selection, Calibration Trays***, and ***tentative calibration***. Press ***Enter*** until the plotted calibration curve appears on the screen. A correlation coefficient of at least 0.995 is the requirement for the calibration to pass. It is approved by selecting ***Approval*** on the menu bar. The system will now automatically analyze the samples loaded in the sample tray.

9.2.3 Post-analysis Review

1) QC Sample Results - Review the results for all QC samples for compliance with the criteria specified in Section 8. If results are not acceptable, take appropriate corrective action.

2) Off-scale Results - Review results for samples that exceed the calibration range. Samples having ammonia at concentrations larger than 10 mg/L must be diluted into range with the calibration blank and re-analyzed.

9.2.4 Instrument Shutdown

1) With the pump still turned on, remove each reagent line from the reagent and place into a container of reagent water. Allow the reagent water to flush through the reagent lines for at least 15 minutes.

2) After the 15 minute period, remove the reagent lines from the reagent water and allow the reagent lines to be purged of the reagent water. Observe the tubing on the manifold - when no liquid is apparent in the tubing the pump can be turned off. Cap all reagents, discard all samples and standards into the appropriate waste containers and turn the power off at the power strip behind the autosampler.

9.3 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 two significant figures; however, no values of less significance than the MDL may be reported (values near the MDL 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).

9.3.1 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

9.3.2 Reporting - 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 The Inorganic Standards and Reagents Preparation Log Book is maintained in room 207. Each reagent and standard that is prepared for the analysis is entered in the Inorganic Standards and Reagents Preparation Log Book. Copies of the appropriate page(s) is (are) included in the data package (Attachment B).

10.2 The Ammonia Analysis by Lachat Run Log must be filled out for each sample batch that is analyzed. The sample identification of each standard, analytical sample, and QC sample are entered into the Ammonia Analysis by Lachat Run Log. Copies of the appropriate page(s) is(are) included in the data package (Attachment C).

10.3 An analytical spreadsheet, with the ammonia results in mg/L, sample collection date(s), client sample ID's, lab ID's, and station locations must be included with the data package (Attachment D).

10.4 QC summary reports with LFB, LD and LFM results must be prepared and included in the data package (Attachment E).

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 D)
LRB data included on the analytical spreadsheet. (Attachment D)
Duplicate results on a QC summary report with calculated relative percent difference (RPD). (Attachment E)
LFM and LFB 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 REFERENCE

11.1 *EPA Method 350.1 "Determination of Ammonia Nitrogen by Semi-Automated Colorimetry"*, Revision 2.0, August 1993.

11.2 *EPA Method 351.2 "Determination of Total Kjeldahl Nitrogen by Semi-Automated Colorimetry"*, Revision 2.0, August 1993.

11.3 QuikChem Method 10-107-06-2-A, *Ammonia in Surface Water, Wastewater*, Lachat Instruments, 29 August 1992.

11.4 Method 4500-N_{org}, Standard Methods For the Examination of Water and Wastewater, 20th Edition, 1998.

11.5 R9 SOP 592 "*Analysis of Total Kjeldahl Nitrogen in Water.*"

Attachment A
Deviations From Reference Method

A.1 The procedures used follow SOP 592, "Analysis of Total Kjeldahl Nitrogen in Water."

A.2 This SOP includes routine quality control procedures based on EPA Region 9 Laboratory policy which are in addition to those listed in EPA Method 350.1. These include the analysis of a QL standard and laboratory duplicate.

Appendix B-10
Total Phosphorus

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 596

ANALYSIS OF TOTAL PHOSPHORUS IN WATER

Prepared by:

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Approved by:

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Periodic Review:

Signature	Title	Date

STANDARD OPERATING PROCEDURE 596

ANALYSIS OF TOTAL PHOSPHORUS IN WATER

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
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ESAT Document Control Number: ESAT-9B-1959

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 18

11 REFERENCES 19

Attachment A - Deviations From Reference Method

Attachment B - Inorganic Standards and Reagents Preparation Log Book

Attachment C - TKN and Total Phosphorus Digestion Run Log

Attachment D - Total Phosphorus Analysis by Lachat Run Log

Attachment E - Analytical Spreadsheet

Attachment F - QC Summary Report

1 SCOPE AND APPLICATION

1.1 This method is for the determination of total phosphorus in drinking and surface waters, domestic and industrial wastes, which are digested by the Kjeldahl digestion method. This SOP is based on EPA Method 365.4, issued 1974.

1.2 The colorimetric method is based on reactions that are specific for the orthophosphate ion. The digestion converts the phosphorus in the sample to the orthophosphate ion.

1.3 The application of these procedures to samples with ferric iron concentrations in excess of 50 mg/L is not recommended due to a negative interference.

1.4 The applicable range is 0.3 to 10 mg/L total phosphorus. The range can be extended for high level samples through dilution either before or after the digestion procedure.

1.5 The quantitation limit for total phosphorus is 0.3 mg/L.

2 METHOD SUMMARY

2.1 During the digestion procedure, the sample is heated in the presence of sulfuric acid, K_2SO_4, and $HgSO_4$ for two and a half hours. With mercuric oxide as a catalyst, the phosphorus in the sample is converted to the orthophosphate ion. Potassium sulfate is also added to raise the boiling temperature of the digestion and speed the conversion to orthophosphate.

2.2 The orthophosphate ion (PO_4^{3-}) in the digested sample reacts with ammonium molybdate and antimony potassium tartrate to form an antimony-phosphomolybdate complex. This complex is reduced with ascorbic acid to form an intense blue color, which is read at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

3 DEFINITIONS

3.1 Analytical Sample - Any sample in which total phosphorus 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 by diluting the primary 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.

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 the sample collection and storage as well as the laboratory procedures.

3.6 Instrument Performance Check Solution (IPC) - A standard containing the analytes of interest which is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout an analysis sequence.

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 source of the LFB must be independent of the calibration standards. 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. The LFB also fulfills the requirements of the QCS (3.13).

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 Linear Calibration Range (LCR) - The concentration range over which the instrument response is linear.

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 standard containing total phosphorus which is used to verify the accuracy of the analysis. The method requires that the source of the QCS must be independent of the calibration standards and that the QCS be analyzed quarterly. The Region 9 Laboratory exceeds this requirement through the daily analysis of the LFB.

3.14 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 total phosphorus QL of 0.3 mg/L.

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.

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

4 HEALTH & 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.

4.2 The following chemicals are toxic or hazardous: antimony potassium tartrate, ammonium molybdate, mercury, hydrochloric acid and sulfuric acid. The analyst should consult the MSDS for each chemical for specific information regarding the potential hazards and safe handling.

4.3 Since small amounts of sulfuric acid fumes and aerosol are released to the room during the Kjeldahl digestion, the BD-46 block digestor should be operated in a laboratory fume hood.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Samples should be collected in precleaned plastic or glass bottles. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis and minimize waste disposal. A 100 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. Sample IDs and dates of collection are verified against the chain-of-custody form. Samples must be preserved at the time of collection with sulfuric acid to pH ≤ 2. 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 samples must be analyzed within 28 days of the sample collection date.

5.5 Digested samples should be analyzed within one week of the date of digestion.

6 INTERFERENCES

6.1 Silica forms a pale blue complex which also absorbs at 880 nm. This interference is generally insignificant as a silica concentration of approximately 4000 mg/L would be required to produce a 1 mg/L positive error in orthophosphate.

6.2 Concentrations of ferric iron (Fe^{3+}) greater than 50 mg/L will cause a negative error due to competition with the complex for the reducing agent, ascorbic acid. The iron content in the corresponding metals samples (if applicable) should be noted, and any high (greater than 50 mg/L iron) iron results should be noted in the report narrative.

7 APPARATUS AND MATERIALS

7.1 Instrumentation

7.1.1 Analytical balance capable of accurately weighing to the nearest 0.1mg.
7.1.2 A ventilated oven capable of heating up to 110 ±5°C, or equivalent.
7.1.3 BD-46 Block Digestor (capable of heating up to 380°C), or equivalent.
7.1.4 Lachat QuikChem AE automated flow injection analyzer, total P manifold and the Lachat QuikChem data system.

7.2 Glassware and Incidentals

7.2.1 Autosampler glass tubes, 13×100 mm (KIMAX), or equivalent.
7.2.2 Coldfingers for the digestion tubes.
7.2.3 Digestion tubes, 20- to 75-mL digestion volume capacity.
7.2.4 Eppendorf pipeter and pipet tips, 100- to 1000-μL, or equivalent.
7.2.5 Glass scintillation vials, 20-mL (KIMAX), or equivalent.
7.2.6 25-mL graduated cylinders.
7.2.7 Magnetic stirrers and magnetic stirrer plate.
7.2.8 A pair of heat-resistant gloves.
7.2.9 5-mL and 20-mL repipet dispensers.
7.2.10 Hengar granules, plain, or Teflon boiling chips, or equivalent.
7.2.11 Volumetric flasks, type A, 1000-mL, 250-mL, 100-mL, 50-mL.
7.2.12 Volumetric pipet, type A, 25-mL, 10-mL, 5-mL.

7.3 Reagents and Standards

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 water in this method refer to ASTM Type II grade water.

7.3.2 Mercuric Sulfate Solution: To a 100-mL volumetric flask, add approximately 40 mL of reagent water and 10 mL concentrated sulfuric acid (H_2SO_4). Then add 8.0 g red mercuric oxide (HgO). Stir at low heat on a hot plate until dissolved. Allow to cool, dilute to the mark and invert to mix. Prepare fresh annually.

7.3.3 Digestion solution: In a 1-L volumetric flask, add 133.0 g potassium sulfate (K_2SO_4) and 200 mL concentrated sulfuric acid (H_2SO_4) to approximately 700 mL reagent water. Add 25.0 mL of mercuric sulfate solution (7.3.2). Allow to cool, dilute to the mark with reagent water and invert to mix. Prepare fresh annually.

7.3.4 Total Phosphorus Stock Standard, 1000 mg/L phosphorus: In a 250-mL volumetric flask, dissolve 1.099 g of primary standard grade anhydrous potassium dihydrogen phosphate (KH_2PO_4) that has been dried for two hours at 110°C in about 150 mL reagent water. Add 0.5 mL of concentrated sulfuric acid, dilute to the 250 mL mark, and invert to mix. Prepare fresh annually. Alternatively, a commercially-prepared standard can be obtained from a reputable supplier such as CPI, SPEX or Inorganic Ventures.

7.3.5 The 20 mg/L phosphorus working standard is prepared in a 100 mL volumetric flask by

adding 2.0 mL of the total phosphorus stock standard (7.3.4) to about 75 mL reagent water; add 0.20 mL H_2SO_4, dilute to the mark and invert to mix. Prepare this standard fresh daily.

The following five calibration standards, QL and IPC are prepared using the 20 mg/L phosphorus working standard and diluted with reagent water:

Calibration Standard	Vol. of 20 mg/L phosphorus	Vol. of digestion solution	Final volume
10 mg/L	25 mL	12.5 mL	50 mL
5.0 mg/L, IPC	12.5 mL	12.5 mL	50 mL
2.0 mg/L	5.0 mL	12.5 mL	50 mL
1.0 mg/L	2.5 mL	12.5 mL	50 mL
0.3 mg/L, QL	0.75 mL	12.5 mL	50 mL
Blank	0 mL	12.5 mL	50 mL

7.3.6 Stock Ammonium Molybdate Solution: In a 1-L volumetric flask dissolve 40.0 g ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] in approximately 800 mL reagent water. Dilute to the mark and mix with a magnetic stirrer until dissolved. Store in a plastic bottle and refrigerate. Prepare fresh annually.

7.3.7 Stock Antimony Potassium Tartrate Solution: In a 1-L volumetric flask, dissolve 1.5 g antimony potassium tartrate (potassium antimonyl tartrate trihydrate $C_8H_4K_2O_{12}Sb_2 \cdot 3H_2O$) in approximately 400 mL reagent water. Dilute to the mark and mix with a magnetic stirrer on a stirrer plate until dissolved. Store in a dark bottle and refrigerate. Prepare fresh annually.

7.3.8 Molybdate Color Reagent: To a 1-L volumetric flask, add about 500 mL reagent water, and then add 213 mL Stock Ammonium Molybdate Solution (7.3.6) and 72 mL Stock Antimony Potassium Tartrate Solution (7.3.7). Dilute to the mark and shake to mix. Degas this solution with helium prior to use. Prepare fresh annually.

7.3.9 Ascorbic Acid Reducing Solution: In a 250-mL volumetric flask, dissolve 15.0 g ascorbic acid in about 150 mL reagent water. Dilute to the mark and mix with a magnetic stirrer on a stirrer plate. Degas this solution with helium prior to use. Then add 0.25 g SDS (sodium dodecyl sulfate). Mix with a magnetic stirrer on a stirrer plate. Prepare fresh

every two days.

7.3.10 Sodium Chloride/Sodium Hydroxide Solution: In a 1-L volumetric flask, dissolve 160 g sodium chloride and 20 g sodium hydroxide in about 600 mL reagent water. Dilute to the mark and mix with a magnetic stirrer. Degas this solution with helium prior to use. Prepare fresh annually.

7.3.11 Sulfuric Acid/Potassium Sulfate solution (carrier): In a 1-L volumetric flask, add about 600 mL reagent water, then add 40 mL concentrated sulfuric acid (Caution: The solution will get hot!). When it can be comfortably handled, add 31.7 g potassium sulfate (K_2SO_4). Dilute to the mark and mix with a magnetic stirrer until dissolved. Degas this solution with helium prior to use. Prepare fresh annually.

7.3.12 Total Phosphorus QCS Solution - A solution obtained from a commercial vendor (SPEX, CPI or Inorganic Ventures) with a known concentration of total phosphorus. Region 9 laboratory currently uses a solution with approximately 3.0 mg/L total phosphorus as the QCS. The QCS must be prepared fresh daily.

7.3.13 5% Hydrochloric Acid: Add 50 mL of concentrated hydrochloric acid to 950 mL reagent water. This solution is used to soak the digestion coldfingers and digestion tubes prior to use.

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 - Each analyst must complete an initial demonstration of proficiency prior to analyzing samples following this method.

8.2.1 LCR - The absorbance response vs. total phosphorus concentration is generally a linear function over a limited concentration range. The LCR must be determined prior to using this method for routine analysis and confirmed annually.

8.2.2 MDL - A method detection limit must be confirmed annually and must be <1/2 QL or corrective action must be initiated.

8.2.3 QCS - A QCS standard must be prepared and analyzed when beginning the use of this method, on a quarterly basis or as required to meet data-quality needs. The source of the QCS must be independent of the calibration standards. The QCS verifies the calibration standards. The Region 9 Laboratory fulfills the requirements of the QCS with analysis of the LFB.

8.3 Routine Analytical Quality Control - The various routine QC samples analyzed during each analytical run are specified in this section. Some are treated like samples and undergo digestion before analysis, while some are not digested. The following table lists the QC samples and indicates whether sample digestion is required prior to analysis:

QC Sample ID	Digestion Required?	QC Sample ID	Digestion Required ?
Calibration Standards: Blank, S1, S2, S3, S4, and S5.	N	Instrument performance check (IPC)	N
Quantitation Limit (QL)	N	Calibration Blank (CB)	N
Laboratory Fortified Blank (LFB)	Y	Laboratory Duplicate (LD)	Y
Laboratory Reagent Blank (LRB)	Y	Laboratory Fortified Matrix (LFM)	Y
Quality Control Sample (QCS)	Y		

8.3.1 The instrument must be calibrated with a blank and 5 standards. The correlation coefficient of the calibration curve must be ≥ 0.995 or the instrument must be recalibrated.

8.3.2 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 total phosphorus in the IPC is calculated as follows:

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

Where

%R = percent recovery of the standard.
M = measured concentration of total phosphorus, mg/L.
T = true concentration of total phosphorus 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 IPCs are at a concentration of 5.0 mg/L total phosphorus.

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 the QL, the result is acceptable. If the absolute value of the CB result equals or 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 reanalyzed.

8.3.4 QL - The accuracy of the calibration at the reporting 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 CB of the QCS. The recovery of the analyte 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 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 re-calibrated and all affected samples must be reanalyzed. If, after recalibration, the QL recovery still exceeds the 50-150% limits, the calibration standards must be reprepared and the instrument recalibrated.

8.3.5 LRB - The laboratory must analyze at least one LRB daily with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the QL indicate laboratory contamination. The LRB must be re-prepared along with the affected samples, and re-analyzed.

8.3.6 LFB - A LFB must be prepared, digested and analyzed with each batch of 20 or fewer samples. The LFB assures that the digestion method is reliable and the calibration standards used to calibrate are accurate. The LFB is the QCS. The recovery of total phosphorus in the LFB is calculated as follows:

$$\%R = \frac{LFB}{s} \times 100$$

Where

%R = percent recovery
LFB= measured concentration of total phosphorus in the LFB in mg/L.
s = Total phosphorus concentration in the LFB in mg/L.

The recovery of total phosphorus in the LFB must be within the 90-110% limits. If the recovery exceeds the limits, the digestion and/or 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 LD - Sample homogeneity can affect the quality and interpretation of the data. LD results can be used to assess sample homogeneity. One LD must be prepared for every 10 routine samples of the same matrix in a sample batch. Samples identified as field blanks cannot be used for duplicate sample analysis. 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 total phosphorus in the LD, mg/L
C = measured total phosphorus in the routine sample, mg/L

The relative percent difference (RPD) must be $\leq$20% for samples with total phosphorus levels greater than or equal to 5 times the QL. For other samples, the absolute difference between duplicate results must be less than the QL. If the control limits are exceeded, flag all associated analyte results. Document actions in the report 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 LFM is prepared by spiking 40 μL of the 1000 mg/L Total Phosphorus Stock solution into 20 mL of an analytical sample. The resulting concentration of total phosphorus in the LFM will be 2.0 mg/L. The recovery of total phosphorus 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, 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 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, QL, 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 report 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. Document actions in the report narrative.

9 ANALYTICAL PROCEDURES

9.1 Sample Digestion

1) Gather all the digestion tubes and coldfingers, scintillation vials and caps, autosampler sample tubes, and graduated cylinders that are to be used in preparation for the total phosphorus analysis. They need to be pre-soaked in a 5% hydrochloric acid bath (7.3.13) for at least half a day. They are then thoroughly rinsed with reagent water. The scintillation vials and caps and the autosampler tubes must be dried before they are used, but the digestion tubes may be used right after they are rinsed with reagent water. Excess reagent water needs to be shaken off the sample tubes.

2) The LFM is prepared by spiking a 20 mL aliquot of the QC sample with 1.0 mL of the 20 mg/L phosphorus working standard. The following quality control samples are carried through the digestion procedure:

QCS	Sample A
LFB	LD (Sample A)
LRB	LFM (Sample A)

3) Using 25-mL graduated cylinders, measure 20 mL of each sample to be digested into a digestion tube, label each tube with the sample/standard ID using a Sharpie pen and place the tubes in the digestion tube rack. Add 5.0 mL of digestion solution (section 7.3.3), mix, and add 3 to 4 Teflon boiling chips to each sample. Place the digestion tube rack with the samples on the BD-46 block digestor.

4) Ensure that the **Temp1** and the **Time1** setting on the **controller panel** are set at 160°C and 60 minutes, respectively. Also make sure that the **Temp2** and the **Time2** setting on the controller are set at 380°C and 150 minutes, respectively. Then turn on the main switch on the right rear panel of the digestor. Also turn on the toggle switch on the temperature **controller panel** (the **yellow light** should illuminate if the block digestor is operating normally), and allow the temperature to go up to 160°C, which will take about 20 to 25 minutes. When the temperature on the controller panel indicates that the digestion block is at **(Temp1)** 160°C ± 5 (and the first **red light** will be on), push the green **start button** on the controller panel. The first **green light** will turn on and the digestor block will then hold the **160°C (Temp1)** temperature for **60 minutes (Time1)**, which is the amount of time required to boil off the water in the samples.

5) After 60 minutes, the coldfingers should be placed on the sample tubes and the green **start button on the controller panel** should be pressed again **(Time2** starts here), which will cause the next **yellow light** to illuminate. The temperature of the block digestor will then start to go up to 380°C, which will take about an hour. The second **green light** will turn on when **380°C (Temp2)** is reached, and the temperature will be held for another hour and a half. When the **Time2 (150 minutes)** has elapsed, the last **red light** will light. The temperature of the digestion block will then start to go down and only the first **yellow** and the last **red light** will remain lit. Put on a pair of heat resistant gloves and take the sample tube rack out of the digestor block while the block temperature is still hot. Otherwise, it will be harder to take the sample tubes out of the block digestor.

6) Set the sample tube rack on its rack base in the fume hood and allow the samples to cool for about 10 minutes. Then add 19.5 mL of reagent water to each of the samples in the sample tubes, swirl several times to mix, and transfer each sample

to an acid rinsed scintillation vial and cap each sample tightly. Each scintillation vial should be labeled according to its contents. It is best to analyze the samples as soon as possible after digestion, although they are good for one week after digestion.

9.2 CALIBRATION AND STANDARDIZATION - Total phosphorus is determined colorimetrically using the Lachat Automated Ion 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.

9.2.1 Instrument Set-up

1) Turn on the Lachat QuikChem AE analyzer and allow the heater module to heat up to 37°C for about 15 minutes. Degas each reagent with helium gas for at least 5 minutes.

2) Connect the total phosphorus manifold, sample loop and the wavelength filter to the module. The wavelength is set at 880 nm. Place the waste lines into the total phosphorus analysis waste container and place a tube cartridge to support each reagent line onto the pump. Place each reagent line into the appropriate reagent solution. Turn on the pump and set the speed to 35 RPM, download the total phosphorus method, and allow the reagents to flow through the manifold until the air bubbles disappear into the waste container.

9.2.2 Calibration and Sample Analysis

1) Pour the five calibration standards, the blank, IPC, CB and the QL into 20-mL scintillation vials. Place the calibration standards in decreasing order - starting from position A to F - in the calibration tray, which is positioned on the right side of the autosampler tray. Place the IPC, CB and QL in positions J, K and I, respectively, in the calibration tray.

2) Load the analytical and QC samples into the sample trays using the 13×100mm autosampler tubes. The usual sample loading sequence is listed in the following table:

Seq.#	Cup #	Desc.	Seq.	Cup #	Desc.	Seq.	Cup #	Desc.
1	A	10 mg/L	15	7	S2	29	19	S12
2	B	5.0 mg/L	16	8	S3	30	20	S13

3	C	2.0 mg/L	17	9	S4	31	J	IPC
4	D	1.0 mg/L	18	10	S5	32	K	CB
5	E	0.3 mg/L	19	J	IPC	33	21	S14
6	F	0 mg/L	20	K	CB	34	22	S15
7	J	IPC	21	11	S6	35	23	S16
8	K	CB	22	12	S7	36	24	S17
9	I (1)	QL	23	13	S8	37	25	S18
10	2	LRB	24	14	S9	38	26	S19
11	3	LFB	25	15	S10	39	27	S20
12	4	S1	26	16	S11	40	J	IPC
13	5	S1-LD	27	17	S11-LD	41	K	CB
14	6	S1-LFM	28	18	S11-LFM	42		

3) Select ***File*** from the ***Sample Identification & Tray Submission Menu.*** Highlight ***Template Read (Public)*** and press ***Enter***. Select ***QC_Sched***, press ***Enter***, highlight ***Identification*** and press ***Enter***. Next, enter each check standard and all samples that are to be analyzed in the same order as in the table above. The calibration standards, the IPC, the CB and the QL that are positioned in cups A through K are not entered into the sample tray. They are automatically analyzed during the sample tray analysis. The IPC and the CB will be analyzed automatically after every 10 samples and at the end of the analytical run. Type in *(..)* after the last sample in the tray to mark the end of the sample tray.

4) Select ***Submit current tray*** under ***Sample Identification & Tray Submission Menu***. Answer ***Yes*** to ***Submit tray now?***

5) The system will analyze the calibration standards and calculate a calibration curve prior to analyzing any of the samples. The system will emit a beeping sound when the calibration is complete. The calibration data may be viewed by selecting ***Results/Approval, View Calibration and Sample Reports, Tray Selection, Calibration Trays***, and ***tentative calibration***. Press ***Enter*** until the plotted calibration curve appears on the screen. A correlation coefficient of at least 0.995 is the requirement for the calibration to pass. It is approved by selecting ***Approval*** on the menu bar. The system will now automatically analyze the samples loaded in the sample tray.

9.2.3 Post-analysis Review

1) QC Sample Results - Review the results for all QC samples for compliance with the

criteria specified in Section 8. If results are not acceptable, take appropriate corrective action.

2) Off-scale Results - Review results for samples that exceed the calibration range. Samples having total phosphorus at concentrations larger than 10 mg/L must be diluted into range with the calibration blank and re-analyzed. Only 2 mL of sample is used per analysis; there is sufficient volume for dilution and reanalysis.

9.2.4 Instrument Shutdown

1) With the pump still turned on, remove each reagent line from the reagent and place into a container of reagent water. Allow the reagent water to flush through the reagent lines for at least 15 minutes.

2) After the 15 minute period, remove the reagent lines from the reagent water and allow the reagent lines to be purged of the reagent water. Observe the tubing on the manifold - when no liquid is apparent in the tubing the pump can be turned off. Cap all reagents, discard all samples and standards into the appropriate waste containers and turn the power off at the power strip behind the autosampler.

9.3 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 two significant figures; however, no values of less significance than the MDL may be reported (values near the MDL 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).

9.3.1 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.

9.3.2 Reporting - 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 The Inorganic Standards and Reagents Preparation Log Book is maintained in room 207. Each reagent and standard that is prepared for the analysis is entered in the Inorganic Standards and Reagents Preparation Log Book. Copies of the appropriate page(s) is (are) included in the data package (Attachment B).

10.2 The TKN and Total Phosphorus Digestion Run Log is maintained in room 207. Each QC sample and sample that is digested is documented in the log book. The amount and sample identification (from the Inorganic Reagents and Standards Preparation Log Book) of the spiking solution used in the digestion process is also noted in the TKN and Total Phosphorus Digestion Run Log. Copies of the appropriate page(s) is (are) included in the data package (Attachment C).

10.3 The Total Phosphorus Analysis by Lachat Run Log must be filled out for each sample batch that is analyzed. The sample identification of each standard, analytical sample, and QC sample are entered into the Total Phosphorus Analysis by Lachat Run Log. Copies of the appropriate page(s) is(are) included in the data package (Attachment D).

10.4 An analytical spreadsheet, with the total phosphorus results in mg/L, sample collection date(s), client sample ID's, lab ID's, and station locations must be included with the data package (Attachment E).

10.5 QC summary reports with LFB, LD and LFM results must be prepared and included in the data package (Attachment F).

10.6 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)

Duplicate 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 digestion logs, run logs and any work sheets, if applicable. (Attachments B, C and D)

11 REFERENCE

11.1 *EPA Method 365.4 (Colorimetric, Automated Block Digestor, AAII)*, Storet No. 00665, 1974.

11.2 BD-46 Block Digestor Installation & User Guide, Lachat Instruments, 16 April 1993.

11.3 QuikChem Total Phosphorus in Kjeldahl Digests Method 10-115-01-1-C, Lachat Instruments, 30 May 1995.

11.4 Method 4500-P, Standard Methods For the Examination of Water and Wastewater, 20th Edition, 1998.

Attachment A
Deviations From Reference Method

A.1 A wavelength of 880 nm is used for sample analyses.

A.2 Stock Ammonium Molybdate and Stock Antimony Potassium Tartrate solutions are prepared separately and combined to form the Molybdate Color Reagent.

A.3 Sodium dodecyl sulfate (SDS) is used in the Ascorbic Acid reducing solution instead of acetone.

A.4 Sulfuric Acid/Potassium Sulfate solution is used as the carrier in place of the dilute Sulfuric Acid solution.

A.5 Sodium Chloride/Sodium Hydroxide solution is used in place of the dilute water (sodium chloride) solution.

A.6 EPA Method 365.4 does not include quality control procedures. This SOP includes routine quality control procedures based on EPA Region 9 Laboratory policy.

Appendix B-11
Total Dissolved Solids (TDS)

ESAT REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 461

ANALYSIS OF TOTAL DISSOLVED SOLIDS

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 461

ANALYSIS OF TOTAL DISSOLVED SOLIDS

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
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ESAT Document Control Number: B0101029-0433

CONTENTS

1 SCOPE AND APPLICATION 4

METHOD SUMMARY 4

DEFINITIONS 4

HEALTH AND SAFETY 5

SAMPLE HANDLING AND PRESERVATION 6

INTERFERENCES 6

APPARATUS AND MATERIALS 6

QUALITY CONTROL PROCEDURES 7

ANALYTICAL PROCEDURES 9

DOCUMENTATION 13

REFERENCES 14

Attachment A - Deviations from Reference Method

Attachment B - Inorganic Standards and Reagents Preparation Log Book

Attachment C - TDS Reporting Benchsheet

Attachment D - Analytical Spreadsheet

Attachment E - QC Summary Page

Attachment F - Balance Calibration Logbook Page

1 SCOPE AND APPLICATION

1.1 This method is applicable for drinking, ground, surface, and saline waters, domestic and industrial wastes. This SOP is based on EPA Method 160.1.

1.2 The range of the determination is from 20 to 20,000 mg/L. The quantitation limit is 20 mg/L total dissolved solids (TDS).

2 METHOD SUMMARY

2.1 A well-mixed sample aliquot is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.

2.2 If total suspended solids is also being determined, the filtrate from that method may be used to determine total dissolved solids.

3 DEFINITIONS

3.1 Analytical Sample - Any sample in which TDS is being determined, excluding method blanks or QC reference samples.

3.2 Conductivity Standard - A commercially purchased potassium chloride solution used to calibrate a conductivity meter. Sample conductivity is used to select a sample volume for analysis.

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 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 TDS contamination is occurring in the field environment. Note: Field reagent blanks cannot be used for LD analyses.

3.5 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.

3.6 Laboratory Reagent Blank (LRB) - An aliquot of reagent water that is treated exactly as a sample. The LRB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment.

3.7 Method Detection Limit (MDL) - The minimum TDS in an environmental sample that can be measured and reported with 99% confidence that the TDS concentration is greater than zero.

3.8 Quality Control Sample (QCS) - A solution containing a known TDS concentration. The QCS may be prepared internally or obtained from a commercial source. It is used to check laboratory performance.

3.9 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.

3.10 Total Dissolved Solids (TDS) - The residue from an aqueous sample which is passed through a glass fiber filter and dried to constant weight at 180°C. TDS is often referred to as filterable residue.

3.11 Total Suspended Solids (TSS) - TSS is defined as the solids incapable of passing through a glass fiber filter and dried to constant weight at 103-105°C. TSS is often referred to as non-filterable residue.

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

3.13 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 Safety precautions must be taken when handling solutions and samples. Protective clothing including lab coats, safety glasses and gloves must always be worn. Contact lenses must not be worn. If solutions come into contact with your eyes, flush with water continuously for 15 minutes. If solutions come in contact with your skin, wash thoroughly with soap and water. ESAT personnel should contact the Group Leader or Health and Safety and Env. Compliance Task Manager and EPA staff should see the Team Leader or Laboratory Safety, Health and Environmental Compliance Manager to determine if additional treatment is required.

4.2 Refer to Material Safety Data Sheets (MSDSs) for information on a specific chemical hazard.

4.3 Since samples are of an unknown nature, the drying of the samples should be done in an oven that is ventilated into a fume hood to prevent possible noxious fumes.

4.4 All sample dish transfers to and from the oven should be performed using tongs or heat-resistant gloves.

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 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 within 7 days from the date of collection.

6 INTERFERENCES

6.1 TDS residue from highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation, and rapid weighing.

6.2 Samples containing high concentrations of bicarbonate will require careful and possible prolonged drying at 180°C to ensure that all the bicarbonate is converted to carbonate.

6.3 The sample size for samples containing high TDS must be selected such that the total residue does not exceed 200 mg. Too much residue in the evaporating dish will interfere with evaporation of water during the drying step. A crust may form on the residue which can trap sample moisture, and lead to long drying times and incomplete drying.

7 APPARATUS AND MATERIALS

7.1 Apparatus

7.1.1 Drying oven, capable of being controlled at 180 ± 2 °C and 104 ± 1 °C.
7.1.2 Filter holder or membrane filter funnel.
7.1.3 Glass fiber filter discs, without organic binder, Reeve Angel type 934-AH, Whatman Catalog No. 1827-047, or equivalent.
7.1.4 Suction flask, 250- to 500-mL capacity.
7.1.5 Evaporating dishes, porcelain, 150-mL volume.

7.1.6 Desiccator.
7.1.7 Vacuum pump or in-house vacuum source.
7.1.8 Analytical balance, capable of weighing to 0.1 mg.
7.1.9 Plastic or Teflon spray bottle.
7.1.10 Conductivity meter.
7.1.11 Graduated cylinder, 100-mL.
7.1.12 Volumetric flasks, 1000-mL.
7.1.13 Class "S" weights.
7.1.14 Volumetric Class "A" Pipets, 5.0- to 10.0-mL.

7.2 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. If the purity of a reagent is in question, analyze for contamination. Record the preparation of standards and reagents in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.2.1 Conductivity standard - A commercially purchased potassium chloride solution with known conductivity (1000 μmhos/cm) is used for conductivity measurement. Alternatively, prepare 0.01 M potassium chloride (KCl) by dissolving 0.7456 grams of anhydrous KCl in 1000 mL of reagent water. At 25°C this standard should have a conductivity of 1413 μmhos/cm.

7.2.2 Quality Control Sample (QCS) - One TDS QCS solution is required per batch of 20 or fewer samples. The QCS solution may be prepared by dissolving the appropriate amount of KCl in reagent water or it may be obtained from a commercial vendor such as E.R.A. or Inorganic Ventures.

7.2.3 Quantitation Limit Standard - The QL standard must be prepared by diluting an aliquot of QCS solution so that the concentration will be approximately 20 mg/L TDS. The solution should be prepared fresh every three months.

7.2.4 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, 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 SOP #880.

8.3 Routine Analytical Quality Control - The various routine QC samples analyzed during each analytical run are specified in this section.

8.3.1 LRB - The laboratory must analyze at least one LRB daily with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the QL indicate laboratory contamination. The LRB must be re-prepared along with the affected samples, and re-analyzed.

8.3.2 QCS Analysis - The TDS in the QCS sample must be measured daily or once per batch of 20 samples or fewer samples, whichever is more frequent. The recoveries must be within 85-115% or the samples in the batch must be reanalyzed.

$$\%R = \frac{TDSm}{TDSt} \times 100$$

Where

$\%R$ = percent recovery.
$TDSm$ = measured TDS in the QCS.
$TDSt$ = expected TDS in the QCS.

8.3.3 QL - The accuracy of the batch at the quantitation limit shall be verified by the analysis of a QL standard. The QL must be analyzed at the beginning of each analytical batch. The QL standard has a true value of 20 mg/L. The recovery of the TDS in the QL is calculated as follows:

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

Where

%R = percent recovery of the standard.
M = calculated concentration of the QL, mg/L.
T = true concentration of the QL, mg/L.

If the QL recovery exceeds the limits of 50-150%, the analysis shall be terminated. The cause of the poor recovery must be determined and the problem corrected. All affected samples must be reanalyzed.

8.3.4 LD - Sample homogeneity can affect the quality and interpretation of the data. LD results can be used to assess sample homogeneity.

One LD must be prepared for every 20 routine samples of the same matrix in a sample batch (e.g., 1 LD for a batch containing 1-20 routine samples). Homogenize the routine sample selected as the LD, obtain a representative aliquot, and proceed with sample preparation and analysis, treating the LD sample as a routine sample.

Calculate the relative percent difference using the following equation:

$$RPD = \frac{|C_{ld} - C|}{(C_{ld} + C)/2} \times 100$$

Where

RPD = relative percent difference.
C_{ld} = measured TDS in the LD.
C = measured TDS in the routine sample.

The relative percent difference (RPD) must be $\leq$20 for samples with TDS greater than or equal to 100 mg/L. The absolute difference between duplicate results must be less than the quantitation limit (20 mg/L) for samples containing less than 100 mg/L TDS. If the control limits are exceeded, re-analyze the sample and duplicate once. If the control limits are exceeded again, flag the associated sample result in the spreadsheet. Document actions in the report narrative.

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.

9.2 Balance Calibration Verification - On a daily basis, prior to use for TDS measurements, check the analytical balance with Class S weights of 100 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 Conductivity Meter Verification - On a daily basis, prior to measuring sample conductivity, check the calibration of the conductivity meter by pouring out a portion of the commercially purchased potassium chloride solution (or 0.01 M KCl solution) into a container. Insert the conductivity probe into the KCl solution, stir it gently to loosen any air bubbles and allow it to sit for 15 seconds. Make sure that the meter is in the automatic temperature control (ATC) mode. The conductivity of the solution should be 1000 ± 50 μmhos/cm. If the control limits are exceeded, check the solution and/or meter and re-calibrate. Record the results in the conductivity meter logbook.

9.4 Drying Oven Verification (104°C temperature) - Set the oven temperature to 104°C. Prior to use and before removing samples, check the oven temperature. Each temperature measurement and the measurement time must be recorded in the oven temperature logbook. The measurement of oven temperature can be done manually or by remote control (e.g., with a temperature data logger). The oven temperature must be monitored to ensure that it is within the limits of 103-105°C. If the oven is not able to maintain a constant temperature, it cannot be used in the TDS analysis. If the temperature drifts excessively during an analysis, the samples must be re-dried when the oven is brought back into control.

9.5 Drying Oven Verification (180°C temperature) - Set the oven temperature to 180°C. Prior to use and before removing samples, check the oven temperature. Each temperature measurement and the measurement time must be recorded in the oven temperature logbook. The measurement of oven temperature can be done manually or by remote control (e.g., with a temperature data logger). The oven temperature must be monitored to ensure that it is within the limits of 180 ± 2°C. If the oven is not able to maintain a constant temperature, it cannot be used in the TDS analysis. If the temperature drifts excessively during an analysis, the samples must be re-dried when the oven is brought back into control.

9.6 Equipment Preparation

9.6.1 Preparation of evaporating dishes - Scrub dishes with a brush and tap water. Rinse with reagent water. Heat the clean dishes for one hour at 180°C. Cool in a desiccator to room temperature. Weigh each dish immediately before use to the nearest 0.1 mg and record the weight.

9.6.2 Determination of volume of sample to be filtered - Shake the sample and pour out an aliquot of the sample into a container. Insert the conductivity probe into the solution, stir it gently to loosen any air bubbles and allow it to sit for 15 seconds. Make sure that the

meter is in the automatic temperature control (ATC) mode. Record the sample conductivity. From the following table determine the correct volume to filter for TDS determination. Failure to check sample conductivity beforehand may cause technical holding times to be exceeded if samples are reanalyzed because of high TDS.

Sample Conductivity (μmhos/cm)	Volume to filter (mL)
0 - 3000	100
3000 - 6000	50
6000 - 12000	25

9.6.3 Preparation of glass fiber filter - Connect suction hose from filtration flask to in-house vacuum or vacuum pump. Place a filter on the filter assembly. Apply vacuum and wash filter with three successive 20 mL volumes of reagent water. Continue to apply vacuum until all traces of water are removed. Discard the washings and rinse the filter flask with reagent water.

9.7 Sample Analysis

9.7.1 Sample filtration - Shake the sample vigorously and rapidly transfer the appropriate volume to the pre-washed filter apparatus using a 100-mL graduated cylinder. Record the volume used on the benchsheet/logbook.

Apply vacuum and filter the sample. Rinse the graduated cylinder with three successive 10 mL portions of reagent water and continue to apply vacuum for about one minute to remove as much water as possible.

9.7.2 Sample evaporation and weighing - Transfer the filtrate to a pre-weighed evaporating dish and evaporate in the oven at 103-105°C to dryness.

Dry the evaporated sample for at least one hour at 180 ± 2°C. Cool in a desiccator to room temperature and weigh. Record the weight.

Repeat the drying, cooling and weighing cycle until the weights from two consecutive cycles differ by less than 0.5 mg. Use the smallest weight from the final two cycles for calculation purposes.

9.7.3 The usual sample analytical sequence is listed in the following table:

Seq.	Desc.	Seq.	Desc.	Seq.	Desc.
1	LRB	11	S7	21	S17
2	LFB-QCS	12	S8	22	S18
3	QL	13	S9	23	S19
4	S1	14	S10	24	S20
5	S1-LD	15	S11		
6	S2	16	S12		
7	S3	17	S13		
8	S4	18	S14		
9	S5	19	S15		
10	S6	20	S16		

9.8 Data Reduction and Reporting

9.8.1 Calculate TDS as follows:

$$TDS = \frac{(A - B)}{C} \times 1000$$

Where

TDS = Total Dissolved Solids in mg/L.
A = weight of residue + evaporating dish, mg.
B = tare weight of evaporating dish, mg.
C = sample volume, mL.

If the sample residue exceeds 200 mg (*A-B*), the sample must be re-analyzed using a smaller sample aliquot.

9.8.2 Sample results are reported in the concentration unit of mg/L. All results should be reported using no more than two significant figures; however, no values of less significance than the QL may be reported (values near the QL will be reported with only one significant figure). Report down to 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 The Inorganic Standards and Reagents Preparation Log Book is maintained in room 300. Each reagent and standard that is prepared for the analysis is entered in the Inorganic Standards and Reagents Preparation Log Book. Copies of the appropriate page(s) are included in the data package (Attachment B).

10.2 The TDS Reporting Benchsheet must be filled out for each sample batch that is analyzed. Entries are made for the case number, SDG number, date of analysis, QC solution ID, analyst initials, initial and final oven temperatures, lab sample IDs, client sample IDs, crucible number, sample volume in mL, weight of crucible + residue in grams, tare weight of the crucible in grams, weight of the residue in grams, total dissolved solids in mg/L, conductivity check in μmhos/cm and comments, if any. The logbook is maintained in Room 300. Copies of the appropriate page(s) are included in the data package (Attachment C).

10.3 An analytical spreadsheet, with the TDS results in mg/L, sample collection date(s), client sample ID's, lab ID's, and station locations must be included with the data package (Attachment D).

10.4 QC summary reports with QCS and LD results must be prepared and included in the data package (Attachment E).

10.5 Analytical Balance Calibration Logbook - An entry is made for each weight (100 mg, 1 g, 10 g and 100 g). The logbook is maintained in Room 300. Copies of the appropriate page(s) are included in the data package (Attachment F).

10.6 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)
Duplicate results on a QC summary form with calculated relative percent difference (RPD). (Attachment E)
QCS results on a QC summary form with calculated percent recoveries (%R). (Attachment E)
Raw sample, standard and QC data, including bench sheets and any work sheets, if applicable. (Attachments B, C) Balance calibration logbook sheets. (Attachment F)

11 REFERENCES

11.1 EPA Method 160.1, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, 1983.

11.2 *Method 2540-C Total Dissolved Solids Dried at 180°C*, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998.

11.3 Region 9 SOP 840, *Notebook Documentation and Control.*

11.4 Region 9 SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency.*

Attachment A
Deviations From Reference Method

A.1 This SOP includes routine quality control procedures based on EPA Region 9 Laboratory policy which are in addition to those listed in EPA Method 160.1. These include the analysis of a QL standard and laboratory duplicate.

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
TDS Reporting Benchsheet

EPA REGION 9 LABORATORY
TOTAL DISSOLVED SOLIDS (EPA 160.1)

Case No:_____ #1QC Source Solution: (low)_____ Analyst:_____

SDG No:_____ #2QC Source Solution: (high)_____ Oven Temperature, Initial:_____

Date:_____ Conductivity Check (Iv=_____)_____ Oven Temperature, Final:_____

LAB SAMPLE NUMBER	CLIENT SAMPLE NUMBER	CRUCIBLE #	SAMPLE VOL. VOL(mL)	WT. DRIED RES. + CRUCIBLE (g) (A)	WT. CRUCIBLE (g) (B)	WT RESIDUE (g) (A-B)	TDS (mg/L)	SAMPLE COND. (µmhos/cm)	COMMENTS
				1.					
				2.					
				3.					
				1.					
				2.					
				3.					
				1.					
				2.					
				3.					
				1.					
				2.					
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				2.					
				3.					

US EPA REGION 9 LABORATORY

Filename: TDSLOG.WK4 Reviewed by:_____ Date:_____

Attachment D
Analytical Spreadsheet

EPA REGION 9 LABORATORY-RICHMOND, CA
SUMMARY OF ANALYTICAL RESULTS

Case Number:	R01SXX	Analysis:	Fluoride, Chloride, Nitrite-N, Bromide, Nitrate-N, Orthophosphate, Sulfate, TDS, Cyanide
Site:	DUMMY		
SDG:	01151A	Matrix:	Water
Date:	06/28/01		

Sample No.	8				9				10				11				Reagent				Quantitation
Sample ID.	DUMMY				DUMMY				DUMMY				DUMMY				Blank				Limit
Lab Sample I.D.	A9001122				A9001122				A9001122				A9001122				N/A				N/A
Date of Collection	05/30/01				05/30/01				05/30/01				05/30/01				N/A				N/A
Unit	mg/L				mg/L				mg/L				mg/L				mg/L				mg/L
Analyte	Result	Q	Conc		Result	Q	Conc		Result	Q	Conc		Result	Q	Conc		Result	Q	Conc		Result
Chloride	40				0.5	J	A		37				36				1	U			1
Bromide	0.3				0.1	U			0.2				0.7				0.1	U			0.1
Orthophosphate-P	1	U			1	U			1	U			1	U			1	U			1
Total Dissolved Solids	300				20	U			300				300				20	U			20
						U												U			

Conc - Concentration refer to the corresponding section in the report narrative for each item.
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 E
QC Summary Page

US E.P.A.
REGION 9 LABORATORY
June 14, 2001
Case Number: R01SXX
SDG: 011ZZA

Laboratory Duplicate Sample (DUMMY)

Analyzed Date	Analyte	Sample Result (mg/L)	Duplicate Result (mg/L)	RPD
05/14/01	Total Dissolved Solids	155	156	1

Laboratory Fortified Blank (TDS)

Analyzed Date	Analyte	TrueValue (mg/L)	Result (mg/L)	% Recovery
05/14/01	QC	2969	2932	99

Attachment F
Balance Calibration Logbook Page

Balance Calibration and Maintenance

Manufacturer: OHAus
Model #: Analytical Plus
Serial #: 111511063
EPA Property #:

DATE	ANALYST	ZERO	0.1 g	0.5 g	1.0 g	10.0 g	100.0 g
8/03/01	RT	0.0000	0.1000	0.5000	1.0000	10.0000	100.0013
8/13/01	ER	0.0000	0.1000	0.5000	1.0000	10.0000	100.0011
8/14/01	RT	0.0000	0.1000	0.5000	1.0000	10.0000	100.0011
8/15/01	ER	0.0000	0.1000	0.5000	1.0000	10.0000	100.0010
8/16/01	ER	0.0000	0.1000	0.5000	1.0000	10.0000	100.0010
8/17/01	RT	0.0000	0.1000	0.5000	1.0000	10.0000	100.0013
		Reviewed by: [illegible]			8-3-01		

Comments:

Instructions: Balances must be verified each day of use, every time the power is turned off and on each day, and anytime they are moved. Complete the information at the top of each page prior to beginning that page. Select appropriate calibration verification weights and record their weight at the top of each column. At a minimum, balances are verified at the low end of the balance capability and in the range of use.

Appendix B-12
Total Organic Carbon (TOC)

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 550

ANALYSIS OF TOC IN WATER

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 550

ANALYSIS OF TOC IN WATER

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: B0101029-0536

TABLE OF 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 9

9 ANALYTICAL PROCEDURES 13

10 DOCUMENTATION 17

11 REFERENCES 18

Attachment A - Deviations From Reference Method

Attachment B - Inorganic Standards and Reagents Preparation Log Book

Attachment C - TOC Analysis Run Log

Attachment D - Analytical Spreadsheet

1 SCOPE AND APPLICATION

1.1 This method applies to the determination of total organic carbon (TOC) in all water samples, such as drinking water, ground water, reagent water, and waste water at the EPA Region 9 Laboratory in Richmond, California. This SOP is based on EPA Method 415.1.

1.2 The calibration range is from 2 to 100 mg/L. The range can be extended by diluting the sample prior to analysis.

1.3 The quantitation limit for total organic carbon is 2 mg/L.

2 METHOD SUMMARY

2.1 Total carbon (TC) in a sample is oxidized to carbon dioxide (CO_2) and water (H_2O) by catalytic combustion. The oxygen gas flow that is received in the platinum combustion tube (maintained at 700°C) sweeps the CO_2 containing stream through a condenser, into a gas/liquid separator, and through a dehumidifier to remove the H_2O completely. The dried CO_2 containing gas is then passed through a copper scrubber and to a CO_2 specific non-dispersive infrared detector (NDIR) for quantification. Inorganic carbon (IC) in the sample is determined immediately after the TC analysis. The sample is automatically introduced into the IC reactor, which contains an acidic water solution at room temperature. In this acidic environment, all forms of IC are purged out of the solution as CO_2 by the continuous flow of the carrier, oxygen gas. The CO_2 is dried in the dehumidifier and passes on through the NDIR for quantification. Total organic carbon (TOC) is determined by taking the TC result and subtracting the IC result from it.

3 DEFINITIONS

3.1 Analytical Sample - Any sample in which TOC 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 analyte.

3.3 Calibration Standard (CAL) - A solution prepared by diluting the primary 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 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.

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 the sample collection and storage as well as the laboratory procedures.

3.6 Instrument Performance Check Solution (IPC) - A standard containing the analyte of interest which is used to verify the accuracy of the analysis and monitor instrument drift. It is analyzed periodically throughout an analysis sequence.

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 source of the LFB must be independent of the calibration standards. 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. The LFB also fulfills the requirements of the QCS (3.13).

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 Fortified Sample Matrix Duplicate (LFMD) - Duplicate of LFM (section 3.8). Analysis of the LFM and LFMD indicates the 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 marix 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 Linear Calibration Range (LCR) - The concentration range over which the instrument response is linear.

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 standard containing TOC which is used to verify the accuracy of the analysis. The method requires that the source of the QCS must be independent of the calibration standards and that the QCS be analyzed quarterly. The Region 9 Laboratory exceeds this requirement through the daily analysis of the LFB.

3.14 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 TOC QL of 2 mg/L.

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

3.16 Sample Delivery Group (SDG) - A group of twenty samples or less from the same case 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. ESAT personnel should contact the Group Leader or Health ans 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 The following chemicals have the potential to be highly toxic or hazardous, consult laboratory MSDS: hydrochloric acid, phosphoric acid, potassium acid phthalate and oxygen. Refer to the material safety data sheets (MSDSs) in the library and room 413 or on the laboratory computer network for additional information on these and other chemicals employed in these procedures.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Samples should be collected in precleaned glass bottles or vials. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis and minimize waste disposal. A 100 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. Sample IDs and dates of collection are verified against the chain-of-custody form. Samples must be preserved at the time of collection with hydrochloric acid to pH ≤ 2. 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 samples must be analyzed within 28 days of the sample collection date.

6 INTERFERENCES

6.1 The presence of volatile organic compounds in the sample can result in analytical variability. Minimizing head space in the autosampler tubes and capping with aluminum foil can reduce losses of volatile organic carbon. Exposure to air should also be minimized.

6.2 Sample preservation with sulfuric acid causes the formation of mist in the water trap and the permeation dryer. This will cause the permeation dryer to lose its effectiveness in drying the sample prior to its introduction to the NDIR, which will result in a shifting baseline.

7 APPARATUS AND MATERIALS

7.1 Apparatus

7.1.1 Dohrman Total Organic Carbon Analyzer DC-190 (equipped with NDIR detector, oxygen carrier gas, computer data station with Dohrmann Data Talk II Version 1.3, Epson LQ-570 computer printer, and autosampler).
7.1.2 Analytical balance - capable of weighing accurately to ±0.1 mg.

7.2 Glassware and Incidentals

7.2.1 Pipet, 100-1000 μL, automatic.
7.2.2 Pipet tips, 100-1000μL.
7.2.3 Volumetric Flasks - 100-mL, and 50-mL.
7.2.4 Volumetric Pipets - 5-mL, 2-mL, and 0.5-mL.
7.2.5 Vials, autosampler, 10-mL.
7.2.6 Copper, granular, 20 mesh, 1.5 oz.
7.2.7 Quartz wool, 1 g.
7.2.8 Dohrman copper scrubber assembly.
7.2.9 Pyrex wool, 1 g.
7.2.10 Platinum catalyst, 15 g.
7.2.11 Platinum screen.

7.3 Standards 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 the preparation of standards and reagents in the Inorganic Standards and Reagents Preparation Log Book (Attachment B).

7.3.1 Reagent water, equivalent to ASTM Type II water, ASTM D1193.
7.3.2 Potassium hydrogen phthalate ($C_8H_5KO_4$), primary standard grade
7.3.3 Sodium carbonate (Na_2CO_3), primary standard grade
7.3.4 Hydrochloric acid (HCl), concentrated, reagent grade
7.3.5 Phosphoric acid (H_3PO_4), reagent grade
7.3.6 20% H_3PO_4 - Add 100 mL reagent water to a 250-mL volumetric flask. Slowly add 50 mL of concentrated H_3PO_4, swirl gently to mix, then dilute to the mark with reagent water. Invert several times to mix. Prepare fresh annually or as needed.

7.3.7 Total Organic Carbon (TOC) Stock Standard Solution, 10,000 mg/L - Dissolve 2.126 g $C_8H_5KO_4$ (dry at 104 °C for 1 hour immediately prior to use, store in dessicator) in ~50 mL reagent water, acidify with 0.2 mL concentrated H_3PO_4, and dilute to 100 mL in a volumetric flask with reagent water. The TOC stock standard must be prepared fresh every six months.

7.3.8 Inorganic Carbon (IC) Stock Standard Solution, 1000 mg/L - Dissolve 0.883 g Na_2CO_3 (dry at 104 °C for 1 hour immediately prior to use, store in dessicator) in ~ 50 mL reagent water and dilute to 100 mL in a volumetric flask with reagent water. The IC stock standard must be prepared fresh every six months.

7.3.9 Working TOC Stock Standard Solution, 1000 mg/L - Pipet 5.00 mL of 10,000 mg/L of TOC stock standard into a 50-mL volumetric flask and dilute to volume with reagent water. Prepare fresh every six months.

7.3.10 TOC Calibration Standards - An aliquot of 1000 mg/L working TOC stock standard solution is added to a 50-mL volumetric flask, 0.5 mL 20% H_3PO_4 is added, and the solution diluted to the mark with reagent water. Prepare fresh daily. The following table lists the required calibration standards, IPC, QL and the aliquot of working TOC stock standard required:

Standard Name	TOC (mg/L)	Vol. of 1000 mg/L Working TOC Stock Std. (mL)	Final Volume (mL)
S1, CB, LRB	0	0.00	50
S2, QL	2.0	0.10	50
S3	10	0.50	50
S4	25	1.25	50
S5, IPC	50	2.50	50
S6	100	5.00	50

7.3.11 TOC QCS Solution - A solution obtained from a commercial vendor (SPEX or Inorganic Ventures) with a known concentration of TOC. Region 9 laboratory uses a solution with

approximately 4500 mg/L TOC although other concentrations are acceptable. Follow the expiration date indicated on the certificate of analysis. The solution is transferred to a 40-mL vial when the ampule is opened. The label is also transferred.

7.3.12 LFB Solution - Dilute the TOC QCS solution with reagent water. The final concentration of this solution must be 50 mg/L TOC. Prepare in a 100 mL Class A volumetric flask. Use the following equation to calculate the amount of TOC QCS solution required for a 50 mg/L standard. Prepare fresh daily.

$$X \text{ mL} = \frac{50 \text{ mg/L (concentration of LFB)} * 100 \text{ mL (volume of LFB solution)}}{Y \text{ mg/L (concentration of TOC QCS)}}$$

Where Y = Concentration of QCS Std., mg/L
X = Volume of Std., mL

For example, if the TOC QCS concentration is 4500 mg/L then X is equal to 1.10 mL.. If the volume of LFB solution required is more or less than 100 mL substitute the volume for the 100 mL in the above equation and solve for X.

7.3.13 IPC-IC Solution, 50 mg/L IC - Pipet 2.5 mL of the 1000 mg/L IC stock standard solution to a 50-mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily and keep tightly stoppered.

7.3.14 Matrix Spike, 25 mg/L TOC - Pipet 0.625 mL of 1000 mg/L TOC working stock standard into a 25-mL volumetric flask and dilute to volume with the sample designated for use as the LFM and LFMD.

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 EPA Region 9 Lab SOP #880.

8.3 Routine Analytical Quality Control - The various routine QC samples analyzed during each analytical run are specified in this section.

8.3.1 The instrument must be calibrated with a blank and 5 standards. The correlation coefficient of the calibration curve must be ≥0.995 or the instrument must be recalibrated.

8.3.2 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 EPA Region 9 Laboratory uses an IPC with 50 mg/L TOC. The recovery of TOC in the IPC is calculated as follows;

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

Where
%R = percent recovery of the standard
M = calculated concentration of the analyte, mg/L
T = true concentration of the 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.

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 reanalyzed.

8.3.4 IC Reference Standard - A standard containing only inorganic carbon is analyzed once per analytical run immediately after the initial IPC and CB are analyzed. The recovery of analytes in the IC reference is calculated as follows:

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

Where
%R = percent recovery of the standard.
M = calculated concentration of the IC, mg/L.
T = true concentration of the analyte in the IC reference, mg/L.

If the IC reference 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.

8.3.5 QL - The accuracy of the calibration at the reporting 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 IC. The recovery of the analyte in the QL is calculated as follows:

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

Where

%R = percent recovery of the standard
M = calculated concentration of the QL, mg/L
T = true concentration of the QL, mg/L

If the QL recovery exceeds the limits of 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 reanalyzed. If, after recalibration, the QL recovery still exceeds the 50-150% limits, the calibration standards must be reprepared and the instrument recalibrated.

8.3.6 LRB - The laboratory must analyze at least one LRB daily with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the QL indicate laboratory contamination. The LRB must be re-prepared along with the affected samples, and re-analyzed.

8.3.7 LFB - One LFB must be prepared and analyzed with each analytical run. The LFB is the QCS. The recovery of TOC in the LFB is calculated as follows:

$$\%R = \frac{LFB}{s} \times 100$$

Where

%R = percent recovery
LFB = calculated concentration of TOC in the LFB, mg/L
s = expected TOC concentration in the LFB, mg/L

The recovery of TOC in the LFB must be within the 90-110% limits. If the recovery of TOC 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. The LFB must be re-prepared along with the affected samples, and re-analyzed.

8.3.8 LFM and LFMD- The LFM and LFMD are designed to provide information about the effect of sample matrix on the measurement system. One LFM/LFMD pair must be prepared for every 10 routine samples of the same matrix in a sample batch [e.g. one LFM/LFMD pair for 1 to 10 routine samples, two LFM/LFMD pairs for 11 to 20 routine

samples, etc.). Samples identified as field blanks cannot be used for LFM/LFMD sample analysis. The LFM and LFMD are prepared by spiking 0.625 mL of the 1000 mg/L Working TOC Stock solution into 25 mL of an analytical sample. The resulting concentration of TOC in the LFM and LFMD will be 25 mg/L plus the concentration in the unspiked sample. The recovery of TOC in the LFM or LFMD is calculated as follows:

$$\%R = \frac{C_{lfm} - C}{s} \times 100$$

Where

$\%R$= percent recovery
C_{lfm}= calculated concentration of TOC in the LFM or LFMD, corrected for any dilutions, mg/L
C= calculated concentration of TOC in the routine sample, corrected for any dilutions, mg/L
s= expected TOC concentration in the LFM, corrected for 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 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 and LFB results are acceptable), the poor LFM or LFMD 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 heterogeneous nature of the sample or a matrix effect. Flag any out-of-control analytes. Document actions in the report narrative.

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} = calculated TOC in the LFM, mg/L
C = calculated TOC in the LFMD, mg/L

The relative percent difference (RPD) must be $\leq$20. If the control limit is exceeded, flag all associated analyte results. Document actions in the report narrative.

9 ANALYTICAL PROCEDURES

9.1 TOC Routine Setup and Maintenance

9.1.1 Replacing and adding DI water in the IC chamber - Replace the water in the IC chamber with fresh reagent water weekly, or whenever the chamber is dirty. If chamber walls are dirty, clean the chamber with liquinox solution. Replace any worn or cracked septa.

1) Slip the IC chamber from its holder and disconnect the chamber from the injection valve by pulling it downwards. Also disconnect the acid line from the upper side port and the sparge loop from the lower side port of the IC chamber. Discard the liquid from the IC chamber well and fill it to the level of the side port with 20% phosphoric acid (section 7.3.6).
2) Re-connect the acid line to the upper side port and the sparge loop to the lower side port of the IC chamber. Insert the IC chamber through the top plate into the IC injection valve. Replace the IC chamber holder over the mounting rod so that it supports the IC chamber.
3) Acidify the IC chamber by using the acid priming method on the TOC analyzer user interface menu. This is done by pressing the following keypad: **main menu, 2, 5, 1**. The acid priming menu is now displayed. Press **1** to prime the acid line to the IC chamber.
4) The acid line is connected to a 100 mL amber bottle, containing 20% phosphoric acid, located on the right side of the TOC analyzer. The bottle must be at least half full at all times.

9.1.2 Packing and re-conditioning the combustion tube

Prior to performing maintenance on the combustion tube the analyst should refer to the user's manual for a thorough discussion of the process.

1) Remove the top cover and right side panel from the DC-190. Remove the two mounting screws and the TC valve. Extract the combustion tube from the furnace by pulling it straight up. Ensure that the combustion tube has no cracks.
2) If plugging is apparent, replace the platinum catalyst with fresh catalyst; if the current catalyst is still good, pour the catalyst out into a beaker and rinse it well with clean reagent grade water. Do not soak the catalyst in water for more than 5 minutes. Air dry the catalyst in a 104 °C oven for an hour before re-packing into the combustion tube. Rinse the combustion tube well with reagent grade water. Replace the quartz wool.
3) Insert 1 to 1.5 inch of loosely packed quartz wool into the tube to elevate the catalyst. Pour 15 g of the platinum catalyst on top of the quartz wool. Place the platinum screen directly on top of the catalyst. The combustion tube is now ready to be reinstalled.

9.2 Sample Analysis - 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. The process of performing an analysis, including calibration is summarized in the following sub-sections of 9.2.

1) TOC Operating Conditions - The TOC combustion tube is kept at 700°C. This temperature is to be maintained throughout the analysis. The oxygen carrier gas must be turned on during the instrument operation. It is turned on by pressing the **Carrier Gas** keypad on the front panel of the instrument. The acceptable flow rate is 200 ± 20 cc/min. The system gas flow rate may be checked by pressing the **main menu** keypad, then the number **1**. Check the plumbing for any leaks, if the flow rate is not within the required range. Also, check the regulator at the main gas tank for any gas flow problems.

2) Place one to four sample vials containing reagent water in the autosampler rack, starting on the first position in the rack. Running de-ionized water through the system cleans the combustion tube of any residue remaining in the system. The analysis is started by pressing the **start** keypad on the front panel of the TOC analyzer. The instrument reading on the reagent water should be less than ½ the QL, which is 1 mg/L. If the reagent water is still reading higher than ½ the QL after several injections, combustion tube reconditioning may be necessary.

3) The instrument calibration factor is set at 1.3. This number is verified by pressing the **calibrate** keypad on the upper right corner of the front panel of the TOC analyzer. If the calibration factor is not 1.3, change it to 1.3 by pressing **1, clear, 1.3** and **Enter**. This calibration factor ensures that the TOC analyzer readings are close to the true concentration of the standards.

4) Load up the autosampler with the six calibration standards in order of increasing concentration. Label each vial in accordance to what is contained in it. Next, load the autosampler as indicated in the following table.

Seq.#	Desc.	Seq.	Desc.	Seq.	Desc.
1	S1, 0 mg/L	16	S2	31	IPC
2	S2, 2 mg/L	17	S3	32	CB
3	S3, 10 mg/L	18	S4	33	S15
4	S4, 25 mg/L	19	IPC	34	S16
5	S5, 50 mg/L	20	CB	35	S17
6	S6, 100 mg/L	21	S5	36	S18

Seq.#	Desc.	Seq.	Desc.	Seq.	Desc.
7	IPC	22	S6	37	S19
8	CB	23	S7	38	S20
9	IC REF.	24	S8	39	IPC
10	QL	25	S9	40	CB
11	LRB	26	S10	41	
12	LFB/QCS	27	S11	42	
13	S1	28	S12	43	
14	S1-LFM	29	S13	44	
15	S1-LFMD	30	S14	45	

5) Place a peg in the peg hole behind the very first empty vial holder in the autosampler - immediately following the last IPC and CB, which will terminate the oxygen gas flow. To ensure that the instrument does so, press the **ASM** keypad on the front panel of the TOC instrument. Press **3**. The word "yes" should be present beside the last item on the list shown on the instrument display screen. If not, press the number **5**, then **Enter** until **yes** appears.

6) Turn on the computer and the monitor. Log into the network. Click on **Dohrmann Data Talk II** icon. Click on **Run, then TOC**. Or pull down on the **File** menu from the top of the work bench, and click on **Run**. Then click on **TOC**. This will open up the **Dohrmann Data Talk Worksheet**, in which the TOC raw data gets stored as the samples are analyzed. The worksheet is a spreadsheet with numbered rows and columns. The worksheet will have some data from the previous run, if that last run was not deleted. That data may be deleted by clicking on **Delete**, then **All**. This will clear all the data cells in the worksheet. Click on the cell to the right of the **OPERATOR** heading and type in the analyst's name. The **Date and Time** fields will be filled in automatically when the first raw data is sent from the TOC analyzer. Click on the cell to the right of **RUN#** and enter the run number for this analysis

7) Click on the first empty cell in the **SAMPLE ID** column, and begin entering the autosampler loading list. Make sure **ENTER** is pressed after each entry.
8) The actual analysis is started by pressing the **START** keypad on the front panel of the DC-190 TOC analyzer. The autosampler will automatically reset to the first position in the rack. The instrument is set to rinse the sample probe with reagent water once before each sample analysis. Make sure that the reagent water wash container by the autosampler contains enough water to run the samples. The sample probe is rinsed once with each sample to be analyzed prior to actual analysis. This is to ensure that there is no sample carry over from the previous run. Each sample is analyzed with duplicate

injections. Each sample reading and the average of these two injections is stored and used to calculate the final reported result.

9.2.1 Post-analysis Review

1) QC Sample Results - Review the results for all QC samples for compliance with the criteria specified in Section 8. If results are not acceptable, take appropriate corrective action.

2) Off-scale Results - Review results for samples that exceed the calibration range. Samples having TOC at concentrations larger than 100 mg/L must be diluted into range with the calibration blank and re-analyzed.

9.3 Data Reduction and Reporting - Upon completion of the analysis, the standard calibration curve is calculated by pulling down on **Graph** and clicking on **calculate**. The slope, y-intercept and the correlation coefficient (r) are calculated using linear regression, which is performed using the Dohrmann Data Talk software. The correlation coefficient (r) must be at least 0.995 for the analysis to continue. The reported sample concentration is calculated using the linear equation:

$$y = Ax + b$$

Where
y = calculated sample TOC concentration.
A = slope of the plotted calibration curve.
x = measured TOC value from the TOC analyzer
b = y-intercept.

Once A and b are known, y can be calculated by substituting the measured TOC result for x. The software will automatically calculate the calibration and calculate the sample concentrations using the raw data. When the computer is done calculating the data, the calibration curve can be accessed by clicking on the toolbar that shows a plotted curve. This curve may be printed by clicking on **print** at the top of the calibration curve. The final data report for the analytical run is generated by clicking on **Report List**. Then click on **Rep3**. Rep3 is the report used to calculate the raw data. The IC concentration may be calculated automatically by entering the slope and y-intercept values in the appropriate boxes in the upper right corner of the Dohrman Data Talk worksheet.

Sample results are reported in the concentration unit 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 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).

9.3.1 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 = calculated concentration reported by software, in mg/L.
D = sample analysis dilution factor, to account for any dilution.

9.3.2 Rounding - 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 The Inorganic Standards and Reagents Preparation Log Book is maintained in room 304. Each reagent and standard that is prepared for the analysis is entered in the Inorganic Standards and Reagents Preparation Log Book. Copies of the appropriate page(s) is (are) included in the data package (Attachment B).

10.2 The TOC Analysis Run Log must be filled out for each sample batch that is analyzed. The sample identification of each standard, analytical sample, and QC sample are entered into the TOC Analysis Run Log. Copies of the appropriate page(s) is(are) included in the data package (Attachment C).

10.3 An analytical spreadsheet, with the TOC results in mg/L, sample collection date(s), client sample ID's, lab ID's, and station locations must be included with the data package (Attachment D).

10.4 QC summary reports with LFB, LFM and LFMD results must be prepared and included in the 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 collection7dates, client sample IDs, laboratory IDs and station locations. (Attachment D)
LRB data included on the analytical spreadsheet. (Attachment D)
Duplicate 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. (Attachments B & C)

11 REFERENCES

11.1 *EPA Method 415.1 (Combustion or Oxidation)*, Storet No. 00680, 1974.
11.2 DC-190 High-Temperature TOC Analyzer Operation Manual, Rosemount Inc, 1991.
11.3 Dohrmann DataTalk II, Version 1.03 User's Manual, Fisher-Rosemount/Dohrmann, 1993.
11.4 *Method 5310-B Total Organic Carbon (TOC) High-Temperature Combustion Method*, Standard Methods For the Examination of Water and Wastewater, 20th Edition, 1998.
11.5 Region 9 SOP 840, *Notebook Documentation and Control.*
11.6 Region 9 SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency..*

Attachment A
Deviations From Reference Method

A.1 EPA Method 415.1 does not include quality control procedures. This SOP includes routine quality control procedures based on EPA Region 9 Laboratory policy.

A.2 The linear calibration range is not determined in this procedure. All samples with concentrations exceeding the highest calibration standard are diluted and reanalyzed.

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
TOC Analysis Run Log

TOC (EPA 415.1) RUN LOG

FILE NAME : _____ ICV Source: _____
ANALYSIS DATE : _____ CCV Source: _____
ANALYST : _____ SPIKE Source: _____

RUN #	VIAL #	CASE NUMBER	SDG NUMBER	CALIBRATION STANDARD	LAB ID / EPA ID	DIL'N	COMMENTS
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							
25							
26							
27							
28							
29							
30							

Filename:TOCRUN.WK4 REVIEWED:_____ REVISED: 04/97

Attachment D
Analytical Spreadsheet

EPA REGION 9 LABORATORY-RICHMOND, CA
SUMMARY OF ANALYTICAL RESULTS

Case Number:	R01SXX	Analysis:	Fluoride, Chloride, Sulfate, Nitrate-N + Nitrite-N, TKN TDS, TSS, Hardness, and Alkalinity
Site:	DUMMY		
SDG:	011CCA	Matrix:	Water
Date:	06/13/01		

Sample No.	N/A			N/A			N/A			N/A			05/15/01			Quantitation
Sample I.D.	DUMMY			DUMMY			DUMMY			DUMMY			Reagent Blank			Limit
Lab Sample I.D.	ABDDDDD			ABEEEEE			ABFFFFF			ABGGGGG			N/A			N/A
Date of Collection	05/10/01			05/10/01			05/11/01			05/11/01			N/A			N/A
Units	mg/L			mg/L			mg/L			mg/L			mg/L			mg/L
Analyte	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result
[illegible]	[illegible]			[illegible]			[illegible]			[illegible]			0.1	U		0.1
Chloride	3			4			6			6			1	U		1
[illegible]	[illegible]			[illegible]			[illegible]			[illegible]			[illegible]			[illegible]
Nitrate-N + Nitrite-N	0.3	U		0.3	U		0.3	U		0.3	U		0.3	U		0.3
[illegible]	[illegible]			[illegible]			[illegible]			[illegible]			[illegible]			[illegible]
Total Dissolved Solids	740			250			1600			1700			20	U		20
[illegible]	[illegible]			[illegible]			[illegible]			[illegible]			[illegible]			[illegible]
Hardness	510			210			350			440			5	U		5
[illegible]	[illegible]			[illegible]			[illegible]			[illegible]			[illegible]			[illegible]
Bicarbonate Alkalinity	170			190			60	U		50	U		50	U		50
[illegible]	[illegible]			[illegible]			[illegible]			[illegible]			[illegible]			[illegible]
TOC	10			10			2	U		11			2	U		2

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.

Appendix B-13
Alkalinity

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 560

TOTAL ALKALINITY, TITRIMETRIC METHOD

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 560

TOTAL ALKALINITY, TITRIMETRIC METHOD

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: B0101029-0537

CONTENTS

1 SCOPE AND APPLICATION 4

2 METHOD SUMMARY 4

3 DEFINITIONS 4

4 HEALTH AND SAFETY 5

5 SAMPLE HANDLING AND PRESERVATION 6

6 INTERFERENCES 6

7 APPARATUS AND MATERIALS 6

8 QUALITY CONTROL PROCEDURES 8

9 ANALYTICAL PROCEDURES 9

10 DOCUMENTATION 13

11 REFERENCES 14

Attachment A - Deviations From Reference Method

Attachment B - Inorganic Standards and Reagents Preparation Log Book

Attachment C - Alkalinity Worksheet Log Book

Attachment D - Analytical Spreadsheet

Attachment E - QC Summary Report

1 SCOPE AND APPLICATION

1.1 This method describes the standard and sample analysis of waters for total alkalinity by titration for use in the USEPA Region 9 Laboratory, Richmond, CA. This method is applicable to drinking, ground, surface, and saline waters that can be characterized as carbonate systems. It is suitable for all concentration ranges of alkalinity. This method is based on Standard Method 2320, Alkalinity.

2 METHOD SUMMARY

2.1 Total alkalinity in drinking, surface, saline, and ground water samples is a function of the carbonate, bicarbonate, and hydroxyl ion concentrations. A representative sample aliquot is titrated with standardized sulfuric acid to an electrometrically determined end-point of pH 4.5. For low alkalinity samples, the titration is continued to reach a second end-point 0.3 pH-units below the initial end-point. Based upon the volume of acid used, the alkalinity in the sample is calculated and reported in units of mg/L $CaCO_3$.

2.2 For total alkalinity measurements, the sample must not be filtered, diluted, concentrated, or altered prior to titration. If the sample is altered, then the results must be qualified accordingly. For example, if the sample is filtered, the results might be considered as "dissolved" alkalinity.

3 DEFINITIONS

3.1 Analytical Sample - Any sample in which alkalinity 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 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 analyses.

3.5 Instrument Performance Check (IPC) - Periodic analysis of the pH-meter calibration standards performed to monitor calibration drift.

3.6 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.

3.7 Laboratory Fortified Blank (LFB) - An aliquot of reagent water or other blank matrix to which known quantities of the method analyte is 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.

3.8 Laboratory Reagent Blank (LRB) - An aliquot of reagent water that is treated exactly as a sample. The LRB is used to detect sample contamination resulting from the procedures used to prepare and analyze the samples in the laboratory environment.

3.9 Quality Control Sample (QCS) - A solution containing a known alkalinity. The QCS may be prepared from a concentrated solution or purchased at the appropriate concentration from a commercial source. It is used to check laboratory performance.

3.10 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 has an alkalinity QL of 10 mg/L.

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

3.12 Water Sample - For the purpose of this method, a sample taken from matrices classified as drinking, surface, ground, or storm runoff water.

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. 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 Since samples are of an unknown nature, the analysis of the samples must be done in a fume hood to prevent possible noxious gases.

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 within 14 days from the date of collection.

6 INTERFERENCES

6.1 The electrode, in general, is not subject to solution interferences from color, turbidity, oxidants, reductants, or high salinity.

6.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode. The EPA Region 9 Laboratory does not utilize such an electrode for these procedures.

6.3 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.

6.4 The sample temperature affects pH measurement in two manners.
1) The electrode response will vary with changes in temperature. The pH meter uses ATC to 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.

6.5 Because alkalinity is a conservative parameter, it is stable and not impacted unless that sample is physically altered. Alkalinity is not affected by exchange of CO_2 with the air.

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 ATC probe, Epoxy Body, Beckman No. 592373 or equivalent.

7.1.4 Analytical balance, capable of weighing to the nearest 0.001 g.

7.2 Glassware and Incidentals

7.2.1 Magnetic Stirrer and Teflon-coated stir bars.
7.2.2 Beakers - 50-mL, 250-mL.
7.2.3 Buret, 25-mL, 50-mL.
7.2.4 Volumetric pipettes, 50-mL, 25-mL, 10-mL, 4-mL.
7.2.5 Volumetric flasks, 1000-mL, 500-mL, 100-mL.
7.2.6 LDPE bottles, 1000-mL, 100-mL.

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.
7.3.2 pH Buffers - pH buffers at 4, 7 and 10 pH units.
7.3.3 Sodium Carbonate (Na_2CO_3), primary standard grade.
7.3.4 0.05N Na_2CO_3 Solution - Place 2.5 ± 0.2 g (to the nearest mg) of Na_2CO_3 (dried at 180°C for 4 hours and cooled in desiccator) into a 1-L volumetric flask and dilute to mark with reagent water. The solution contains approximately 2500 mg/L $CaCO_3$. Prepare fresh monthly. Calculate the exact normality as follows:

$$N\,(eq\,/\,L) = \frac{w}{V} \times \frac{1\,eq}{53.00\,g\,Na2CO3}$$

Where:

N = normality of Na_2CO_3 solution in units of equivalents per liter, eq/L.
w = weight of Na_2CO_3 in g.
V = final volume of solution (1.000 L).

7.3.5 Sulfuric Acid (H_2SO_4), concentrated, ACS reagent grade.
7.3.6 5N H_2SO_4 - Add 50 mL reagent water to a 100-mL volumetric flask. Slowly add 14 mL concentrated H_2SO_4 and mix. **Caution: The mixture will be hot.** Cool the mixture and dilute to the mark with reagent water and mix. Prepare fresh monthly.
7.3.7 0.02N H_2SO_4 - Add 500 mL reagent water to a 1-L volumetric flask. Add 4 mL 5N H_2SO_4 and dilute to the mark with reagent water. Standardize with 0.05N Na_2CO_3 solution prior to use as described in Section 9. Prepare fresh monthly.

7.3.8 QCS High - A reference sample obtained commercially with a certified alkalinity at approximately 100 mg/L $CaCO_3$.

7.3.9 QCS Low - A reference sample obtained commercially or prepared from a concentrated solution with alkalinity at approximately 10 mg/L $CaCO_3$.

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 IPC - Measure the pH of the pH calibration standards after the initial calibration, every 10 samples and at the end of the run. If the measured concentrations are not within ± 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.

8.3.2 QCS High and QCS Low - The QCS solutions are analyzed to verify the accuracy of the titration process, including the acid titer of H_2SO_4 titrant. Each QCS must be analyzed once per day or every 20 samples, whichever is more frequent. The QCS solutions must be analyzed prior to the analytical samples following the procedure in Section 9. After analysis, a percent recovery is calculated as follows:

$$\%R = \frac{C_m}{C_t} \times 100$$

Where

$\%R$	=	percent recovery.
C_m	=	measured analyte concentration in the QCS, mg/L.
C_t	=	true analyte concentration in the QCS, mg/L.

The recoveries must be within 85-115% or the samples in the batch must be re-analyzed.

8.3.3 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. The LRB must be re-prepared along with the affected samples, and the affected analytes re-analyzed.

8.3.4 LD - Sample homogeneity can affect the quality and interpretation of the data. LD results can be used to assess sample homogeneity. One LD must be prepared for every 20 routine samples of the same matrix in a sample batch (e.g., 1 LD for a batch containing 1-20 routine samples). Homogenize the routine sample selected as the LD, obtain a representative aliquot, and proceed with sample 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 alkalinity in the LD, mg/L.
C	=	measured alkalinity in the routine sample, mg/L.

The relative percent difference (RPD) must be less than or equal to 20 or the absolute difference must be less than the QL. If the control limits are exceeded, re-analyze the sample and duplicate once. If the control limits are exceeded again, flag the sample result as estimated ("J"). Document actions in the report narrative.

9 ANALYTICAL PROCEDURES

9.1 pH Meter Calibration and Standardization - 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.

9.1.1 Place a clean magnetic stirrer bar into a clean 50-mL beaker and add about 30-40 mL of the pH 4 calibration buffer. Immerse the ATC probe and the pH electrode into the buffer. 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. Insert a NIST-traceable thermometer into the buffer. The ATC probe temperature reading of the buffer will appear on the screen. The temperature measured by the ATC probe and the

NIST thermometer should agree within ±0.5 °C. Press **yes** if the temperature reading is correct. If it is incorrect, punch in the correct temperature. Record the buffer temperatures measured by the ATC probe and the NIST thermometer in the alkalinity log book.

9.1.2 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 (3). Press the ***yes*** button to do automatic calibration, and ***yes*** again to indicate that the electrode is in buffer 1. 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***. Next, wash the pH electrode and the ATC probe with reagent water and blot them dry with Kimwipes. Place a magnetic stirrer bar into a 50-mL beaker and pour approximately 30-40 mL of pH 7 calibration buffer. Calibrate with the second buffer by pressing ***yes*** to "ELECTRODE IN BUFFER 2?". Press ***yes*** again to calibrate with the number the pH meter determines the reading should be. Calibrate with the third buffer by pressing ***yes*** to "ELECTRODE IN BUFFER 3?". Press ***yes*** again to calibrate with the number the pH meter determines the reading should be. The determined slope will appear and press ***yes*** to continue.

9.1.3 Review the calibration slope results. The calibration slope must be within 95 - 105%. If the slope is acceptable, proceed with the sample analysis. If the slope is not acceptable, troubleshoot the system and re-calibrate. An acceptable calibration must be obtained before samples can be analyzed.

9.2 Standardization of H_2SO_4 Titrant - Pipet 10.00 mL 0.05N Na_2CO_3, into a 50-mL beaker. Add a stir-bar and place on the stir-plate. Stir gently (no visible vortex). Insert the pH electrode and titrate potentiometrically with the 0.02 N H_2SO_4 titrant to pH 4.50 ± 0.05. Record the volume of H_2SO_4 added. Perform the standardization two additional times. Calculate the H_2SO_4 titer as follows:

$$N_{H_2SO_4} = \frac{V_{Na_2CO_3} \times N_{Na_2CO_3}}{V_{H_2SO_4}}$$

Where:

N_{H2SO4} = normality of H_2SO_4 titrant, eq/L.
V_{Na2CO3} = volume of sodium carbonate primary standard solution, mL.
N_{Na2CO3} = normality of sodium carbonate primary standard solution, eq/L.
V_{H2SO4} = volume of H_2SO_4 titrant, mL.

Average the readings of the three measurements. Use the calculated H_2SO_4 normality to calculate alkalinity in the samples.

9.3 Sample Analysis - Allow samples to come to room temperature before analysis. Analyze the samples in the sequence listed in the following table.

Seq.	Desc.	Seq.	Desc.	Seq.	Desc.	Seq.	Desc.
1	IPC - pH 4	11	S5	21	S11	31	S18
2	IPC - pH 7	12	S6	22	S12	32	S19
3	IPC - pH 10	13	S6-LD	23	S13	33	S20
4	QCS High	14	IPC - pH 4	24	S14	34	IPC - pH 4
5	QCS Low	15	IPC - pH 7	25	S15	35	IPC - pH 7
6	LRB	16	IPC - pH 10	26	S16	36	IPC - pH 10
7	S1	17	S7	27	IPC - pH 4	37	
8	S2	18	S8	28	IPC - pH 7	38	
9	S3	19	S9	29	IPC - pH 10	39	
10	S4	20	S10	30	S17	40	

Measure 100 mL of sample into a 250-mL Erlenmeyer flask or beaker, add a stir bar, and stir on the magnetic stirrer. Immerse the pH electrode and allow to stabilize. Record the sample volume and initial pH. Based upon the initial pH, titrate the sample as indicated in the following table:

Initial Sample pH	H_2SO_4 Titrant N	"Equivalence" Point* pH	"Equivalence" Point Designation
pH > 8.3	0.02	8.3 4.5	A B
8.3 ≥ pH ≥ 6	0.02	4.5	B
pH < 6	0.02	4.5 4.2	B C
* volume to reach equivalent point pH must be recorded			

If the volume of 0.02N titrant necessary to reach equivalence point B exceeds 50 mL, the sample must be re-analyzed using a smaller sample volume.

9.4 Data Reduction - The Region 9 Laboratory uses a calculation worksheet that automatically calculates the hydroxide, bicarbonate and carbonate alkalinity. The client sample ID, lab ID, aliquot in mL, initial pH, normality of the acid used, initial buret volume in mL, the buret volume reading after titrating to pH 8.30 (if required) in mL, the

buret reading after titrating to pH 4.50 in mL and the buret reading after titrating to pH 4.2 (if required) in mL are manually enetered into the worksheet. The calculation worksheet automatically determines the alkalinity. The calculation worksheet is an electronic version of the alkalinity benchsheet. Total alkalinity and phenolphthalein alkalinity can be calculated from the titration data. Also, an estimate of the carbonate system species can be determined (i.e, hydroxide, carbonate, and bicarbonate alkalinity). The details of the calculations are provided in the following subsections.

9.4.1 Total Alkalinity Calculation, Alkalinity > 20 mg/L

$$T_{Alk} = \frac{V_B \times N_{H_2SO_4}}{V_S} \times \frac{50{,}000\ mg\ CaCO_3}{eq}$$

where

T_{Alk}	=	total alkalinity in units of mg/L $CaCO_3$.
V_B	=	volume of titrant to reach equivalence point B, mL.
$N_{H_2SO_4}$	=	normality of sulfuric acid titrant, eq/L.
V_S	=	sample volume titrated, mL.

9.4.2 Total Alkalinity Calculation, Alkalinity ≤ 20 mg/L

$$T_{Alk} = \frac{(2 \times V_B - V_C) \times N_{H_2SO_4}}{V_S} \times \frac{50{,}000\ mg\ CaCO_3}{eq}$$

where:

T_{Alk}	=	total alkalinity in units of mg/L $CaCO_3$.
V_B	=	volume of titrant to reach equivalence point B, mL.
V_C	=	volume of titrant to reach equivalence point C, mL.
$N_{H_2SO_4}$	=	normality of sulfuric acid titrant, eq/L.
V_S	=	sample volume titrated, mL.

9.4.3 Phenolphthalein Alkalinity Calculation

$$P_{Alk} = \frac{V_A \times N_{H_2SO_4}}{V_S} \times \frac{50{,}000\ mg\ CaCO_3}{eq}$$

where:

P Alk	=	phenolphthalein alkalinity in units of mg/L $CaCO_3$
V A	=	volume of titrant to reach equivalence point A, mL.
NH_2SO_4	=	normality of sulfuric acid titrant, eq/L.
V S	=	sample volume titrated, mL.

9.4.4 Carbonate System Species Calculations - Alkalinity in a carbonate system is comprised of three species; hydroxide, carbonate, and bicarbonate ions. The concentration of each species can be estimated from the *T Alk* and *P Alk* values as summarized in the table below.

Alkalinity Results	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Alkalinity
P Alk = 0	0	0	*T Alk*
P Alk < ½ *T Alk*	0	2×*P Alk*	*T Alk* - 2×*P Alk*
P Alk = ½ *T Alk*	0	2×*P Alk*	0
P Alk > ½ *T Alk*	2×*P Alk* - *T Alk*	2(*T Alk* - *P Alk*)	0
P Alk = *T Alk*	*T Alk*	0	0

9.5 Sample data should be reported in units of mg/L for aqueous samples. 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 Raw Data - Data from the preparation and standardization of titrants and sample titration data must be recorded on the Alkalinity Analysis Bench Sheet. An example is provided in Attachment C. The bench sheets are maintained in Room 207.

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 results on a QC summary report with calculated relative percent difference (RPD). (Attachment E)
QCS and QL 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 and C)

11 REFERENCES

11.1 Method 2320, *Alkalinity*, Standard Methods for the Examination of Water and Wastewater, 20th Edition, (1998).

11.2 Orion Combination pH Electrode Instruction Manual, 1991 Orion Research, Incorporated.

11.3 EA 940 Expandable IonAnalyzer Instruction Manual, 1985 Orion Research, Incorporated.

11.4 Method 310.1, *Alkalinity*, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, 1983.

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

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

11.7 Region 9 Laboratory SOP 880, *Demonstration of Laboratory Capability and Analyst Proficiency.*

Attachment A
Deviations From Reference Method

A.1 This SOP includes routine quality control procedures based on EPA Region 9 Laboratory policy which are in addition to those listed in Standard Method 2320. These include the analysis of a QL standard and laboratory duplicate.

A.2 The Region 9 Laboratory will only titrate samples with the 0.02 N H_2SO_4 titrant; samples that require more than 50 mL titrant will be re-analyzed with a smaller aliquot.

A.3 Sodium carbonate (Na_2CO_3) is dried at 180°C where the method recommends 250°C.

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
Alkalinity Worksheet Log Book

Page: ____ of ____

Alkalinity Worksheet

Case Information		Sample Integrity		Instrumentation				Laboratory Control Samples		
Case Identification				Instrument ID		ORION EA 940				
Sample Delivery Group		VTSR Date		Electrode ID		ORION		Concentration	High Level	Low Level
Site Name		VTSR Time		Electrode Calibration				True Value (mg/L)	100.00	11.00
Site ID Code		Analysis Start Date		pH	pH	pH	Slope	Analysis Value (mg/L)		
Data File Location		Analysis Start Time		4.00	7.00	10.00		Percent Recovery		
		Sample Source Information								
Analyst:		High Level LCS						Reviewer:		
Date:		Low Level LCS						Date:		

Sample				Acid	Buret Volume Reading				Total Volume			Alkalinity			
Identification Number		Aliquot	Initial	Normality	Initial	pH = 8.30	pH = 4.50	pH = 0.30	pH = 8.30	pH = 4.50	pH = 0.30	Hydroxide	Carbonate	Bicarbonate	Total
EPA	Laboratory	(mL)	pH	(N)	(mL)	(mL)	(mL)	(mL)	(mL)	(mL)	(mL)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
LCSW	LCS High														
LCSW	LCS low														
PBW															

Attachment D
Analytical Spreadsheet

EPA REGION 9 LABORATORY-RICHMOND, CA
SUMMARY OF ANALYTICAL RESULTS

Case Number:	R01SXX	Analysis:	Fluoride, Chloride, Sulfate, Nitrate-N + Nitrite-N, TKN TDS, TSS, Hardness, and Alkalinity
Site:	DUMMY		
SDG:	011CCA	Matrix:	Water
Date:	06/13/01		

Sample No.	N/A			N/A			N/A			N/A			05/18/01			Quantitative
Sample I.D.	DUMMY			DUMMY			DUMMY			DUMMY			Forgent Blank			Limit
Lab Sample I.D.	ABDDDDD			ABEEEEE			ABFFFFF			ABGGGGG			N/A			N/A
Date of Collection	05/18/01			05/18/01			05/11/01			05/11/01			N/A			N/A
Units	mg/L			mg/L			mg/L			mg/L			mg/L			mg/L
Analyte	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result	Q	Com	Result
[illegible]	[illegible]			[illegible]			0.6			[illegible]			0.1	U		[illegible]
Chloride	2			4			6			6			1	U		1
[illegible]	[illegible]			[illegible]			[illegible]			[illegible]			[illegible]			[illegible]
Nitrate-N + Nitrite N	0.3	U		0.3	U		0.3	U		0.3	U		0.3	U		0.3
[illegible]	[illegible]			[illegible]			[illegible]			[illegible]			[illegible]			[illegible]
Total Dissolved Solids	740			290			1600			1700			20	U		20
[illegible]	[illegible]			[illegible]			[illegible]			[illegible]			[illegible]			[illegible]
Hardness	510			210			150			440			5	U		5
[illegible]	[illegible]			[illegible]			[illegible]			[illegible]			[illegible]			[illegible]
Bicarbonate Alkalinity	170			190			10	U		10	U		10	U		10
[illegible]	[illegible]			[illegible]			[illegible]			[illegible]			[illegible]			[illegible]
TOC	10			10			2	U		11			2	U		2

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 E
QC Summary Report

US E.P.A.
REGION 9 LABORATORY
June 14, 2001
Case Number: R01SXX
SDG: 011ZZA

Laboratory Duplicate (DUMMY)

Analyzed Date	Analyte	Sample Result (mg/L CaCO3)	Duplicate Result (mg/LCaCO3)	RPD	Q
05/16/01	Carbonate Alkalinity	0	0	N/A	
05/16/01	Bicarbonate Alkalinity	182.33	181.35	0	
05/16/01	Total Alkalinity	182.33	181.35	0	

Note: Duplicate RPD which is N/A is due to sample and/or duplicate results which are less than the QL.

Laboratory Duplicate (DUMMY)

Analyzed Date	Analyte	Sample Result (mg/L CaCO3)	Duplicate Result (mg/LCaCO3)	RPD	Q
05/17/01	Carbonate Alkalinity	0	0	N/A	
05/17/01	Bicarbonate Alkalinity	31.2	31.2	0	
05/17/01	Total Alkalinity	31.2	31.2	0	

Note: Duplicate RPD which is N/A is due to sample and/or duplicate results which are less than the QL.

Laboratory Duplicate (HR-SEN-SWU-AW)

Analyzed Date	Analyte	Sample Result (mg/L CaCO3)	Duplicate Result (mg/LCaCO3)	RPD	Q
05/21/01	Carbonate Alkalinity	0	0	N/A	
05/21/01	Bicarbonate Alkalinity	169.65	170.63	0	
05/21/01	Total Alkalinity	169.65	170.63	0	

Note: Duplicate RPD which is N/A is due to sample and/or duplicate results which are less than the QL.

Appendix B-14
Biological Oxygen Demand (BOD)

Approved by TCA
Date Approved 3/2/99

STANDARD OPERATING PROCEDURE FOR:
3.3 *Biochemical Oxygen Demand (5 days, 20°C)*

1. REFERENCED METHODS
   1a. Standard Methods for the Examination of Water and Wastewater, 5210, 18th Edition (1992); EPA 405.1, EPA-600/4-79-020, 1983.

2. SCOPE AND APPLICATION
   A BOD test is an empirical bioassay-type procedure which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present. Standard test conditions include dark incubation at 20°C for a specified time period (5 days). Actual environmental conditions of temperature, biological populations, water movement, sunlight, and oxygen concentration cannot be accurately reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.

3. SUMMARY OF METHOD
   A sample of waste, or an appropriate dilution, is incubated for 5 days at 20°C in the dark. A reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand.

4. SAMPLE COLLECTION, STORAGE AND PRESERVATION
   Samples for BOD analysis may degrade significantly during storage between collection and analysis, resulting in low BOD values. Minimize reduction of BOD by analyzing the sample promptly or by cooling it to near-freezing temperature during storage. However, even at low temperature, keep holding time to a minimum. Warm chilled or frozen samples to 20°C before analysis.

5. APPARATUS
   5a. Incubation bottles: 250 to 300ml capacity, with ground-glass stoppers. Clean bottles with a detergent, rinse thoroughly, and drain before use.

   5b. Air incubator: Temperature controlled at 20 ±1°C.

   5c. Orion Research oxygen electrode (with funnel and built in stirrer, membrane/electrode modules, batteries).

   5d. Dissolved oxygen meter, Model 862, Orion w / built-in stirrer.

6. REAGENTS

6a. Phosphate buffer solution: Dissolve 8.5g KH_2PO_4, 21.75g K_2HPO_4, 33.4g $Na_2HPO_4.7H_2O$, and 1.7g NH_4Cl in about 500ml distilled water and dilute to 1 liter. The pH should be 7.2 without further adjustment. Discard reagent if there is any sign of biological growth in the stock bottle.

6b. Magnesium sulfate solution: Dissolve 22.5g $MgSO_4.7H_2O$ in distilled water an dilute to 1 liter.

6c. Calcium chloride solution: Dissolve 27.5g CaCl2 in distilled water and dilute to 1 liter.

6d. Ferric chloride solution: Dissolve 0.25g $FeCl_3.6H_2O$ in distilled water and dilute to 1 liter.

6e. Acid and alkali solutions, 1 N: For neutralization of caustic or acid waste samples.

6f. Sodium sulfite solution, 0.025 N: Dissolve 1.575g Na_2SO_3 in 1,000ml distilled water. *This solution is not stable; prepare daily.*

6g. Nitrification inhibitor: Reagent-grade 2-chloro-6-(trichloromethyl) pyridine.

6h. Glucose-glutamic acid solution: Dry reagent-grade glucose and reagent-grade glutamic acid at 103°C for 1 hour. Add 150mg glucose and 150mg glutamic acid to distilled water and dilute to 1 liter. Prepare fresh immediately before use.

6i. Ammonium chloride solution: Dissolve 1.15g NH_4Cl in about 500ml distilled water, adjust pH to 7.2 with NaOH solution and dilute to 1 L. Solution contains 0.3mgN/ml.

6j. Alpha-trol check standard.

7. PROCEDURE

7a. Preparation of dilution water: Add 20ml each of phosphate buffer, $MgSO_4$, $CaCl_2$ and $FeCl_3$ solution in 5 gallons of deionized water or distilled water. Bring dilution water temperature to 20°C. Saturate with dissolved oxygen (DO) by aerating with filtered air for at least 2 hours. Store in cotton-plugged bottles long enough for water to become saturated with DO. Protect water quality by using clean glassware, tubing and bottles. Premade pillows made by Hach consisting of phosphate, MgSO4, CaCl2, and FeCl3 buffers could also be used in place of the above buffer solutions.

7b. Dilution water check: Use this procedure as a rough check on quality of dilution water. If dilution water has not been stored for quality improvement, add

sufficient seeding material to produce a DO uptake of 0.05 to 0.1mg/L in 5 days at 20°C.

Do not add seeds to dilution water that has been stored for quality improvement. Incubate a BOD bottle full of dilution water for 5 days at 20°C. Determine initial and final DO. The DO uptake in 5 days at 20°C should not be more than 0.2mg/l and preferably not more than 0.1mg/L. If the oxygen depletion of a candidate water exceeds 0.2mg/L obtain a satisfactory water by improving purification or from another source. Alternatively, if nitrification inhibition is used, store the dilution water, seeded as prescribed in the preceding paragraph, in a darkened room at room temperature until the oxygen uptake is sufficiently reduced to meet the dilution water check criteria.

Check quality of stored dilution water used, except that adding more seed in dilution water blanks test is unnecessary.

Storage is not recommended when BODs are to be determined without nitrification inhibition because nitrifying organisms may develop during storage.

Check stored dilution water to determine whether sufficient ammonia remains after storage. If not, add ammonium chloride solution to provide a total of 0.45mg ammonia/L as nitrogen.

7c. Glucose-glutamic acid check: Because the BOD test is a bioassay, results can be influenced greatly by the presence of toxicants or by use of poor seeding material. Distilled water is frequently contaminated with copper; some sewage seeds are relatively inactive. Low results always are obtained with such seeds and waters. Periodically check dilution water quality, seed effectiveness, and analytical technique by making BOD measurements on pure organic compounds.

In general, for BOD determinations not requiring an adapted seed, use a mixture of 50mg glucose/L and 150mg glutamic acid/L as a "standard" check solution. Glucose has an exceptionally high and variable oxidation rate but when it is used with glutamic acid, the oxidation rate is stabilized and is similar to that obtained with many municipal wastes. Alternatively, if a particular wastewater contains an identifiable major constituent that contributes to the BOD, use this compound in place of the glucose-glutamic acid.

Add 6ml of glucose-glutamic acid standard check solution and 3ml of the polyseed solution to each BOD bottle. BOD for glucose-glutamic acid check standard should be 198 ±30.5mg/l.

7d. Alpha-trol check - Like the glucose-glutamic acid, alpha-trol is also used to verify the quality of the addition water and the effectiveness of the seed. Add 3, 4, and 5 mL of alpha-trol standard check solution and 3 mL of the polyseed

solution to each BOD bottle. BOD for alpha-trol check standard should be 228-252 mg/L.

7e. Seeding:

7(e)1 Seed source

It is necessary to have present a population of micro-organisms capable of oxidizing the biodegradable organic matter in the sample. Domestic wastewater, unchlorinated or otherwise-undisinfected effluents from biological waste treatment plants, and surface waters receiving wastewater discharges contain satisfactory microbial populations.

Some samples do not contain a sufficient microbial population (for example, some untreated industrial wastes, disinfected wastes, high-temperature wastes, or wastes with extreme pH values). For such wastes seed the dilution water by adding a population of microorganisms. The preferred seed is effluent from a biological treatment system processing the waste. Where this is not available, use supernatant from domestic wastewater after settling at room temperature for at least one hour but no longer than 36 hours. When effluent from a biological treatment process is used, inhibition of nitrification is recommended.

Some samples may contain materials not degraded at normal rates by the microorganisms in settled domestic wastewater. Seed such samples with an adapted microbial population obtained from the undisinfected effluent of a biological process treating the waste.

In the absence of such a facility, obtain seed from the receiving water below (preferably 3 to 8km) the point of discharge. When such seed sources also are not available, develop an adapted seed in the laboratory by continuously aerating a sample of settled domestic wastewater and adding small daily increments of waste. Optionally use a soil suspension or activated sludge to obtain the initial microbial population.

Determine the existence of a satisfactory population by testing the performance of the seed in BOD tests on the sample. BOD values that with time of adaptation to a steady high value indicate successful seed adaptation.

7(e)2 Polyseed capsule:

Place the content of one Polyseed capsule (discard the gelatin capsule) in one-half liter of dilution water. Aerate and stir the Polyseed solution for sixty minutes. For best results, seed prepared in this way should be used within six hours of rehydration.

7(e)3 Seed control:

Determine BOD of the seeding material as for any other sample. This is the seed control. Prepare the seed control using 10, 15 and 20ml of polyseed solution. A plot of DO depletion, in milligrams per liter, versus milliliters should present a straight line for which the slope indicates DO depletion per milliliter of seed. Determine what the DO depletion reading is at 3 mL.

Add 3ml of polyseed solution to dilution water. The DO uptake of seeded dilution water should be between 0.6 and 1.0mg/l.

7f. Sample Pretreatment:

7(f)1 Samples containing caustic alkalinity or acidity - Neutralize samples to pH 6.5 to 7.5 with a solution of sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH) of such strength that the quantity of reagent does not dilute the sample by more than 0.5%. The pH of seeded dilution water should not be affected by the lowest samples dilution.

7(f)2 Samples containing residual chlorine compounds - If possible, avoid samples containing residual chlorine by sampling ahead of chlorination processes. If the sample has been chlorinated but no detectable chlorine residual is present, seed the dilution water. If residual chlorine is present, dechlorinate and seed the dilution water.

Do not test chlorinated/dechlorinated samples without seeding the dilution water. In some samples chlorine will dissipate within 1 to 2 hours of standing in the light. This often occurs during sample transport and handling.

Pretreat samples only when Cl_2 exceeds 1 on the chlorine kit. For samples in which chlorine residual does not dissipate in a reasonably short time, destroy chlorine residual by adding Na_2SO_3 solution. Determine required volume of Na_2SO_3 solution on a 100-to 1000-ml portion of neutralized sample by adding 10ml of 1+1 acetic acid or 1+50H_2SO_4, 10ml potassium iodide (KI) solution (10g/100ml), and titrating with Na_2SO_3 solution to the starch-iodine end point. Add to neutralized sample the volume of Na_2SO_3 solution determined by the above test, mix, and after 10 to 20 minutes check sample for residual chlorine.

7(f)3 Samples containing other toxic substances - Certain industrial wastes, for example, plating wastes, contain toxic metals. Such samples often require special study and treatment.

7(f)4 Samples supersaturated with DO - Samples containing more than 9mg DO/L at 20°C may be encountered in cold waters or in water where photosynthesis occurs. To prevent loss of oxygen during incubation of such samples, reduce DO to saturation at 20°C by bringing sample to about 20°C in partially filled bottle while agitating by vigorous shaking or by aerating with clean, filtered compressed air.

7(f)5 Sample temperature adjustment - Bring samples to 20 ±1°C before making dilutions.

7(f)6 Nitrification inhibition - If nitrification inhibition is desired add 3.33mg 2-chloro-6-(trichloromethyl) pyridine (TCMP) to each bottle before capping or add sufficient amounts to the dilution water to make a final concentration of 10mg/l.

(Note: Some commercial formulations are not 1005 TCMP; adjust dosage accordingly). Samples that may require nitrification inhibition include, but are not limited to, biologically treated effluents, samples seeded with biologically treated effluents, and river waters. Note the use of nitrogen inhibition in reporting results.

7g. Dilution technique: Dilutions that result in a residual DO of at least 1 mg/L and a DO uptake of at least 2mg/L after 5 days incubation produce the most reliable results. Make several dilutions of prepared sample to obtain a DO uptake in this range. Experience with a particular sample will permit use of a smaller number of dilutions. A more rapid analysis, such as COD, may be correlated approximately with BOD and serve as a guide in selecting dilutions. In the absence of prior knowledge, use the following dilutions: 0.0 to 1.0% for strong industrial wastes, 1 to 5% for raw and settled wastewater, 5 to 25% for biologically treated effluent, and 25 to 100% of polluted river waters.

Prepare dilutions either in graduated cylinders and then transfer to BOD bottles or prepare directly in BOD bottles. Either dilution method can be combined with any DO measurement technique. The number of bottles to be prepared for each dilution depends on the DO technique and the number of replicates desired. In this case run three replicates.

When using graduated cylinders to prepare dilutions, and when seeding is necessary, either add seed directly to dilution or to individual cylinders before dilution. Seeding of individual cylinders avoids a declining ratio of seed to sample as increasing dilutions are made. When dilutions are prepared directly in BOD bottles and when seeding is necessary, add seed directly to dilution water or directly to the BOD bottles.

7(g)1 Dilutions prepared in graduated cylinders - If the azide modification of the titrimetric iodometric method (Section 421B) is used, carefully

siphon dilution water, seeded if necessary, into the 1- to 2-L capacity graduated cylinder. Fill cylinder half full without entraining air. Add desired quantity of carefully mixed sample and dilute to appropriate level with dilution water. Mix well with a plunger-type mixing rod; avoiding entraining air. Siphon mixed dilution into two BOD bottles. Determine initial DO on one of these bottles. Stopper the second bottle tightly, water-seal, and incubate for 5 days at 20°C. If the membrane electrode method is used for DO measurement, siphon dilution mixture into one BOD bottle. Determine initial DO on this bottle and replace any displaced contents with sample dilution to fill the bottle. Stopper tightly, water-seal, and incubate for 5 days at 20°C.

7(g)2Dilutions prepared directly in BOD bottles - Using a wide-tip volumetric pipet, add the desired sample volume to individual BOD bottles of known capacity. Add 3 mL polyseed solution to the individual BOD bottles. Fill bottles with enough dilution water, so that insertion of stopper will displace all air, leaving no bubbles. For dilutions greater than 1:100 make a primary dilution in a graduated cylinder before making final dilution in the bottle. When using titrimetric iodometric methods for DO measurement, prepare two bottles at each dilution. Determine initial DO on one bottle. Stopper second bottle tightly, waterseal, and incubate for 5 days at 20°C. If the membrane electrode method is used for DO measurement, prepare only one BOD bottle for each dilution. Determine initial DO on this bottle and replace any displaced contents with dilution water to fill the bottle. Stopper tightly, waterseal, and incubate for 5 days at 20°C.

7h. Determination of initial DO: If the sample contains materials that react rapidly with DO, determine initial DO immediately after filling BOD bottle with diluted sample. If rapid initial DO uptake is insignificant, the time period between preparing dilution and measuring initial DO is not critical. Use the azide modification of the iodometric method (Section 421B) or the membrane electrode method (Section 421F) to determine initial DO on all sample dilutions, dilution water blanks, and where appropriate, seed controls.

7i. Dilution water blank: Use a dilution water blank as a rough check on quality of unseeded dilution water and cleanliness of incubation bottles. Together with each batch of samples incubate a bottle of unseeded dilution water. Determine initial and final DO. The DO uptake should not be more than 0.2mg/L and preferably not more than 0.1mg/L.

7j. Run QC EPA check sample in triplicate.

7k. Incubation: Incubate at 20°C ±1°C BOD bottles containing desired dilutions, seed controls, dilution water blanks, and glucose-glutamic acid checks.

7l. Record pH and Cl_2 of the samples. Refer to 7(f)1 and 7(f)2 for treatments.

7m. Determination of final DO: After 5 days incubation, determine DO in sample dilutions, blanks, and checks. If either the blanks, the glucose-glutamic acid check standards, or the alpha-trol fall out of range, the whole test must be repeated.

8. CALCULATION

When dilution water is not seeded:

$$\text{BOD mg/L} = \frac{D_1 - D_2}{P}$$

When dilution water is seeded:

$$\text{BOD mg/L} = \frac{(D_1 - D_2) - (B_1 - B_2)\,f}{P}$$

Simplified version:

$$\frac{(\text{DO uptake sample}) - (\text{DO update blank sample})}{\text{ml of sample}} \times 300$$

where:

D_1 = DO of diluted sample immediately after preparation, mg/L
D_2 = DO of diluted sample after 5 days incubation at 20°C, mg/L
P = Decimal volumetric fraction of sample used
B_1 = DO of seed control before incubation, mg/L (d)
B_2 = DO of seed control after incubation, mg/L (d)
f = ratio of seed in sample to seed in control = (% seed in D1)/(% seed in B1).

Appendix B-15
Chemical Oxygen Demand (COD)

STANDARD OPERATING PROCEDURE

CHEMICAL OXYGEN DEMAND (COLORIMETRIC, MANUAL)

SOP No.:	EMAX-410.4	Revision No.	1	Date:	29-Oct-02
Prepared By:	Nenita Barbero			Date:	10-29-02
Approved By:	Kenette Pimentel QA Manager			Date:	10.29.02
Approved By:	Kam Pang Laboratory Director			Date:	10/29/02

Control Number: 410.4-01- Uncontrolled Copy

1.0 SCOPE AND APPLICATION

1.1. This method determines the quantity of oxygen to oxidize organic matter in an aqueous sample. This SOP is an adaptation of EPA Method 410.4.

1.2. The applicable manual range is 10-900 mg/L.

2.0 SUMMARY OF METHOD

2.1. Sample, blanks and standards in sealed tubes are heated in an oven or block digestor in the presence of dichromate at 150°C. After two hours, the tubes are removed from the oven or digestor, cooled and measured spectrophotometrically at 600 nm.

2.2. **Interference**

2.2.1. Chlorides are quantitatively oxidized by dichromate and represent a positive interference. *Mercuric sulfate is added to the digestion tubes to complex the chlorides.*

3.0 REPORTING LIMITS

3.1. **Method Detection Limit (MDL)**

3.1.1. Analyze a minimum of seven (7) spiked samples and their QC samples as described in Section 10.

3.1.2. Perform the MDL validation on each instrument for this analysis. Refer to EMAX-QA04 for details.

3.2. **Method Reporting Limit (RL)**

3.2.1. Detection level is equal to the concentration of the lowest calibration point, unless otherwise specified by the project.

4.0 DYNAMIC RANGE

4.1. The highest quantifiable range requiring no dilution is equal to the concentration of the highest calibration point (see Section 9.1.2). All samples analyzed above this range shall be considered over-range and shall require dilution to properly quantitate.

4.2. The lowest quantifiable range of diluted samples is equal to the lowest calibration point. All diluted samples analyzed below this range shall be considered or over diluted and shall require lower dilution factor to properly quantitate

5.0 PRESERVATION AND HOLDING TIME

5.1. Samples received in the laboratory should be collected in glass bottles. Use of plastic containers is permissible if it is known that no organic contaminants are present in containers.

5.2. Samples are preserved with H_2SO_4 to a pH < 2 and maintained cool to 4 °C until analysis. Samples with no chemical preservative and maintained at 4 °C, must be analyzed within 24 hours from the time of collection.

6.0 ASSOCIATED SOPs

6.1. EMAX-DM01 Data Flow & Review

6.2. EMAX-QA04 MDL/IDL/RL

6.3. EMAX-QA08 Corrective Action

6.4. EMAX-QC02 Analytical Standard Preparation

6.5. EMAX-SM04 Analytical and QC Sample Labeling

7.0 SAFETY

7.1. Read all MSDS of chemicals listed in this SOP.

7.2. All reagents, standards, and samples shall be treated as potential hazards. Observe the standard laboratory safety procedures. Protective gear, i.e., lab coat, safety glasses, gloves, shall be worn at all times when performing this procedure.

7.3. All wastes generated during analytical process shall be placed in the waste containers. These wastes shall be endorsed to waste disposal section for proper disposal.

7.4. Water samples shall be neutralized to pH 7 (± 2) prior to disposal.

7.5. If for any reason, solvent and/or other reagents get in contact with your skin or any other part of your body, rinse the affected body part thoroughly with tap water. If irritations persist inform your supervisor immediately so that proper action can be taken.

8.0 INSTRUMENTS, CHEMICALS, AND SUPPLIES

8.1. **Instruments and Supplies**

Block digestor	Lachat Instrument or equivalent
Spectrophotometer	SPEC20D, Milton Roy at 600 nm or equivalent
Culture tubes	25 x 150 mm culture tube with TFE-fluorocarbon lines screw caps
Micropipets	Variable

8.2. **Chemicals and Reagents**

Reagent Water	NanoPure or equivalent
Digestion Solution & Catalyst Solution	Accu-Test Micro COD, Bioscience Inc.Catalog # 174-334 or equivalent

8.2.1. In the absence of manufactured premixed digestion solution, the following reagents are prepared:

8.2.1.1. Silver sulfate catalyst solution: Dissolve 22 gm of Ag_2SO_4 in 4.09 kg (9 lb.) bottle of concentrated sulfuric acid (H_2SO_4).

8.2.1.2. Potassium Dichromate Digestion Solution: Add 10.216 gm of potassium dichromate ($K_2Cr_2O_7$), 167 ml concentrated H_2SO_4 (Sp. Gr. 1.84) and 33.3 gm of mercuric sulfate ($HgSO_4$) to 750 ml reagent water, mix, cool and dilute to 1 liter, mix thoroughly.

8.2.1.3. H_2SO_4 sampler wash solution. Add 500 ml concentrated H_2SO_4 to 500 ml reagent water, slowly let it cool.

9.0 STANDARDS

9.1. Standard Preparation

9.1.1. Refer to EMAX-QC02 for proper preparation of analytical standard.

9.2. **Stock Standard**

9.2.1. Dissolve 0.851 g of potassium hydrogen phthalate (KHP) in distilled water, dilute to 1 liter volume. Concentration is 1000 mg/L COD. Solution is stable for 3 months when refrigerated in the absence of visible biological growth.

9.3. **Calibration Standards**

9.3.1. The initial calibration of consists of five standards and a reagent pure water blank

Standard	Aliquot from Stock (ml)	Final Concentration (mg/L)
S0	-	0
S1	0.10	10
S2	0.30	30
S3	0.50	50
S4	1.00	100
S5	1.50	150

9.3.2. Initial Calibration Verification Standard (ICV). Similarly. using a KPH purchased from a different vendor, prepare ICV at 70 mg/L.

9.3.3. Continuing Calibration Standard (CCV). Similarly, using the primary standard stock solution, prepare CCV at 70 mg/L.

9.3.4. Lab Control Sample (LCS)

9.3.4.1. *LCS is a certified COD standard purchased from ERA Catalog # 503 or equivalent.*

10.0 PROCEDURES

10.1. **Sample Preparations**

10.1.1. **Manufactured Premixed Digestion Solution**

10.1.1.1. Preheat laboratory block digestor to 150°C.

10.1.1.2. Open the sealed COD digestion/catalyst solution.

10.1.1.3. Carefully add 2.5-ml of sample down the side of the tube such that a layer is formed on top of the digestion solution.

10.1.1.4. Similarly, prepare the calibration standards as described in 10.1.3.

10.1.1.5. Carefully replace the twist tube cap.

10.1.1.6. Thoroughly mix the sealed tubes by shaking.

10.1.1.7. Check the temperature of the block digestor. Temperature should be 150 °C (± 2°)

10.1.1.8. Place the tubes in the block digestor maintaining 150 °C temperature for 2 hours.

10.1.1.9. Remove tubes from block digestor and allow to cool.

10.1.1.10. Allow suspended precipitate to settle and wipe the outside of the tube clean. Samples are now ready for analysis.

10.1.2. **Laboratory Prepared Digestion Solution**

10.1.2.1. Place 1.5 ml potassium dichromate digestion solution in twist tube or glass ampule.

10.1.2.2. Add 3.5 ml of silver sulfate catalyst solution, mix and allow to cool. If mixed reagents are to be stored, place the capped or sealed solution in the dark.

10.1.2.3. Homogenize solution if necessary.

10.1.2.4. Carefully add 2.5 ml of samples, standards, and blanks down the side of the tube forming a top layer.

10.1.2.5. Replace cap or seal the ampules and mix thoroughly. Care is used in this mixing process, as solution will become hot.

10.1.2.6. Place ampules or tubes in the oven or block digestor heated at 150 °C for 2 hours.

10.1.2.7. Allow to cool then let condensate inside tube settle. The samples are now ready for analysis.

10.1.3. Chemical Reactions

10.1.3.1. For dichromate oxidation with potassium acid phthalate:

10.1.3.2. $41\ H_2SO_4 + 10\ K_2Cr_2O_7 + 2\ KC_8H_5O_4 \rightarrow 10\ Cr_2(SO_4)_3 + 11\ K_2SO_4 + 16\ CO_2 + 46\ H_2O$

10.2. **Instrument Parameters**

10.2.1. Turn the instrument on and let it stabilize for at least one hour.

10.2.2. Set the wavelength of spectrophotometer at 600 nm.

10.2.3. Set the absorbance reading to zero using S0.

10.3. **Calibration**

10.3.1. **Initial and Continuing Calibration Verification**

10.3.1.1. Read the absorbance of each calibration standard.

10.3.1.2. Using the Linear Program, plot the absorbance against the concentration to acquire correlation coefficient and calibration factor.

10.3.1.3. Check Appendix 1 for acceptance criteria.

10.3.2. **Initial Calibration Check**

10.3.2.1. Read the absorbance of ICV standard. Read absorbance of S0 and record as ICB.

10.3.2.2. Calculate result using Eq-14.1 and Percent Recovery using Eq-14.2

10.3.2.3. Check Appendix 1 for acceptance criteria.

10.4. **Analysis**

10.4.1. Refer to Appendix 1 for all related Quality Control parameters, frequency, acceptance criteria and corrective action.

10.4.2. **Analytical Sequence**

10.4.2.1. ICAL

10.4.2.2. ICV

10.4.2.3. Method Blank

10.4.2.4. LCS

10.4.2.5. 20 samples

10.4.2.6. CCV

10.4.3. Data interpretation of samples should be done by the same procedure as the calibration and check standards.

10.4.4. Dilute and reanalyze all samples detected above the calibration range.

10.5. **Data Reduction**

10.5.1. Check that the analytical data generated indicating positive results are qualitatively and quantitatively correct.

10.5.2. Check that analytical results are generated by the prescribed calibration schedule of the method.

10.5.3. Collect all data and information for the report generator program.

10.5.4. Run the report generator program for lab chronicle, sample results, QC samples and calibrations.

10.5.5. Write the Case Narrative.

10.6. **Calculations**

10.6.1. Calculate for Sample Result

$$COD = A * CF * DF \qquad \text{Eq-10.6.1}$$

where:

COD	-	Chemical Oxygen Demand, in mg/L
A	-	Absorbance
CF	-	Calibration Factor from the ICAL curve
DF	-	Dilution Factor

10.6.2. Calculate for Percent Recovery

$$R = \frac{C_f}{C_v} * 100 \qquad \text{Eq-10.6.2}$$

where:

C_f	-	Concentration found
C_v	-	Known concentration

10.6.3. Calculate for Accuracy

$$\%D = \frac{@abs(S - D)}{S} * 100 \qquad \text{Eq-10.6.3}$$

where:

S	-	Sample result for the first determination
D	-	Sample result of the second determination

10.6.4. Calculate for Standard Deviation

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}{n-1}} \qquad \text{Eq-10.6.4}$$

where:

SD	-	Standard Deviation
x_i	-	result at the ith measurement
$\bar{x}$	-	mean of all measurements
n	-	number of measurements

10.6.5. Calculate for MDL

$$MDL = SD * 3.14 \qquad \text{Eq-10.6.5}$$

10.7. **Report Generation**

10.7.1. Assemble the analytical report in the order listed below.

10.7.1.1. Lab Chronicle

10.7.1.2. Sample Results [Form 1, raw data]

10.7.1.3. QC Results [Method Blanks, LCS/LCSD, MS/MSD, Sample Duplicates, each with raw data]

10.7.1.4. Calibration [Initial Calibration, Second Source Verification, Continuing Calibration, each with raw data]

10.7.1.5. Analytical Log

10.7.1.6. Sample Preparation Log

10.7.1.7. Non-Conformance Report (if any)

10.8. **Data Review**

10.8.1. Check the data entry against the analytical log.

10.8.2. Check Method Blank against reporting limit.

10.8.3. Check LCS against QC limits.

10.8.4. Check the Case Narrative to contain the following issues:

- Holding Time
- Method Blank

- LCS
- Sample Duplicates
- Anomalies (if any)

11.0 QUALITY CONTROL

11.1. Refer to Appendix 1 for all related Quality Control parameters, frequency, acceptance criteria and corrective action.

11.2. A minimum of 5-point initial calibration must be performed prior to analysis.

11.3. A second source standard shall be analyzed to verify the initial calibration concentrations.

11.4. A method blank, LCS and duplicate sample shall be analyzed in every 20 sample or a fraction thereof.

11.5. A calibration check standard shall be analyzed at the end of the analytical run.

11.6. A valid MDL must exist prior to sample analysis.

11.7. Photometric Linearity Check of the spectrophotometer shall be performed at least once a year.

12.0 NON-CONFORMANCE REPORT (NCR)

12.1. Corrective action for each Quality Control procedure is summarized in Appendix 1.

12.2. Other anomalies encountered during the analytical process not listed in Appendix 1 shall require a non-conformance report (NCR). Refer to EMAX-QA08.

13.0 POLLUTION PREVENTION

13.1. Observe all necessary precautions to avoid spillage of acid that may go to the wastewater drains.

13.2. Prepare all standards in the fume hoods.

14.0 WASTE MANAGEMENT

14.1. Collect all waste generated, i.e. extracted samples, filters, wipes, vials, etc. and properly turn them over to the waste disposal unit.

15.0 SUPPLEMENTARY NOTES

15.1. **Definition of Terms**

15.1.1. Batch – is a group of samples that are prepared and/or analyzed at the same time using the same lot of reagents.

15.1.1.1. **Preparation batch** is composed of one to 20 samples of the same matrix, a method blank, a lab control sample and matrix spike/matrix spike duplicate.

15.1.1.2. **Analytical batch** is compose of prepared samples (extracts, digestates, or concentrates), which are analyzed together as a group using an instrument in conformance to the analytical requirement. An analytical batch can include samples originating from various matrices, preparation batches, and can exceed 20 samples.

15.1.2. Calibration – is a determinant measured from a standard to obtain the correct value of an instrument output.

15.1.3. Instrument Method – is a file generated to contain the instrument calibration and instrument parameter settings for a particular analysis.

15.1.4. Instrument Blank – is a target-analyte-free solvent subjected to the entire analytical process to establish zero baseline or background value.

15.1.5. Lab Control Sample (LCS) – is a target-analyte-free sample spiked with a verified known amount of target analyte(s) or a reference material with a certified known value subjected to the entire sample preparation and/or analytical process. LCS is analyze to monitor the accuracy of the analytical system.

15.1.6. Matrix – is a component or form of a sample.

15.1.7. Matrix Spike (MS) – is a sample spiked with a verified known amount of target analyte(s) subjected to the entire sample preparation and/or analytical process. MS is analyze to monitor matrix effect on a method's recovery efficiency.

15.1.8. Matrix Spike Duplicate (MSD) – is a replicate of MS analyzed to monitor precision or recovery.

15.1.9. Method Blank – is a target-analyte-free sample subjected to the entire sample preparation and/or analytical to monitor contamination.

15.1.10. Re-analysis – is a repeated analysis from the same extract/digestate or sample, identified with the Lab Sample ID suffixed with "W".

15.1.11. Reagent Water – is purified water free from any target analyte or any other substance that may interfere with the analytical process.

15.1.12. Re-extract/digest – is a repeated sample preparation process identified with the Lab Sample ID suffixed with "R".

15.1.13. Sample – is a specimen received in the laboratory bearing a sample label traceable to the accompanying COC. Samples collected in different containers having the same field sample ID are considered the same and therefore labeled with the same lab sample ID unless otherwise specified by the project.

15.1.14. Sub-sample – is an aliquot taken from a sample for analysis. Each sub-sample is uniquely identified by the sample preparation ID.

15.1.15. Sample Duplicate – is a replicate of a sub-sample taken from one sample, prepared and analyzed within the same preparation batch.

15.2. **Application of EMAX QC Procedures**

15.2.1. The procedures and QC criteria summarized in this SOP shall be applied to all projects when performing analysis for Chemical Oxygen Demand. In instances where there is project or program specific quality control, the requirements given in the project shall take precedence over this SOP.

15.3. **Air Force Center for Environmental Excellence (AFCEE) Projects**

15.3.1. When samples from AFCEE sponsored projects are analyzed for Chemical Oxygen Demand, the calibration, QC, corrective action, and data flagging requirements shall follow the AFCEE Quality Assurance Project Plan, and project prescribed version.

15.4. U.S Army Corps of Engineers (USACE) Projects

15.3.2. In the absence of QAPP, the default QAPP is the Shell Document, latest version.

15.5. Naval Facilities Engineering Center (NFESC) Projects

15.3.3. In the absence of project QAPP, the default QAPP is the NFESC Interim Guidance Document, latest version.

15.6. Department of Energy Basic Ordering Agreement (DOE-BOA) Projects

15.6.1. For samples from DOE-BOA sponsored projects follow BOA Guidance Document, latest version in the absence of project QAPP.

16.0 REFERENCES

16.1. EPA Test Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised, March 1983

16.2. Standard Methods For the Examination Of Water and Wastewater, 18th Edition, 1992

16.3. Quality Assurance Manual, EMAX Laboratories, as updated.

16.4. Micro - COD Test Methods, BioScience Inc.

17.0 APPENDICES AND FIGURES

17.1. Figures

17.1.1.	Figure 1	-	Typical Calibration Plot

17.2. Appendices

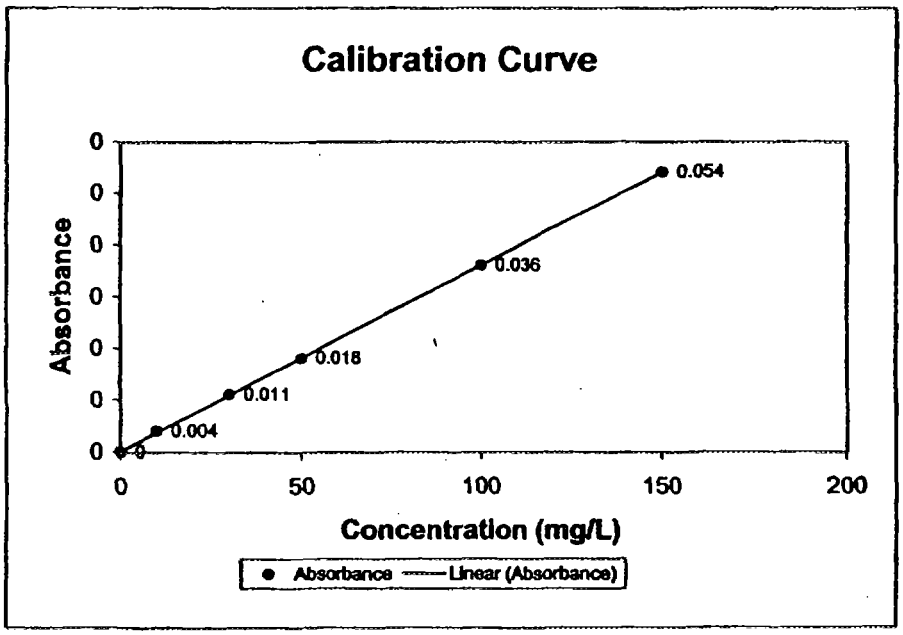
17.2.1.	Appendix 1	-	Summary of In-House Quality Control Procedures
17.2.2.	Appendix 2	-	Method Proficiency
17.2.3.	Appendix 3	-	Analysis Run Log for COD.
17.2.4.	Appendix 4	-	Instrument Maintenance Log for COD

TYPICAL CALIBRATION PLOT

COD
2/28/02

Calibration Level	Concentration	Absorbance
1	0	0
2	10	0.004
3	30	0.011
4	50	0.018
5	100	0.036
6	150	0.054

Calculation	
R^2 (>0.995)	0.999951
Y	0.000359
CF	2788.888889
Comment	Passed



Analyzed by: LA
CDB003W
B129

2-28-02

2/28/02

SUMMARY OF IN-HOUSE QUALITY CONTROL PROCEDURES

QC PROCEDURE	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION	FLAGGING CRITERIA	1st Rvw	2nd Rvw
Multipoint calibration curve	Initial daily calibration prior to sample analysis	Correlation coefficient ≥ 0.995 for linear regression	Correct the problem then repeat initial calibration			
Distilled standards. Sample preparation requiring digestion.	Once per multipoint calibration. All samples (field and QC) and standards.	± 10% of true value	Correct the problem then repeat distilled standards			
Second-source calibration verification	After initial calibration	All analytes within ±15% of expected value.	Correct the problem then repeat initial calibration			
Method blank	One per preparation batch	No analytes detected ≥ RL	Reprep and reanalyze method blank and all samples processed with the contaminated blank	Apply "B" to specific analyte(s) on all associated samples.		
LCS	One LCS per preparation batch	Within EMAX QC Limits	Reprep and reanalyze the LCS and all associated samples.			
MS	One MS per every 20 project samples per matrix	Within EMAX QC Limits	None			
Duplicate Sample	One sample duplicate per every 20 project samples per matrix	RPD ≤20%	None			
				Reviewed by:		
				Date:		

DEMONSTRATION OF CAPABILITY

Analysis: Chemical Oxygen Demand Adaptation: 410.4 Date Analyzed: 06/26/01 Analyzed By: NB

PARAMETER	CDF005W_40	CDF005W_41	CDF005W_44	CDF005W_45	TV (mg/L)	Ave. Conc.	Ave. % Rec.	SD	RPD	QC Criteria	Comments
COD	84.7	84.7	87.3	89.9	85.5	86.7	101	2.5	3	80-120	Passed

ANALYSIS LOG FOR COD

SOP ☐ EMAX-410.4 ☐ Start Date Time End Date Time Book # A70-CD-003

ANALYTICAL BATCH * _____

Data File Name		Lab Sample ID	Sample Amount (ml)	DF	Time	Absorbance	Notes
	* 1						
	* 2						
	* 3						
	* 4						
	* 5						
	* 6						
	* 7						
	* 8						
	* 9						
	* 0						
	* 1						
	* 2						
	* 3						
	* 4						
	* 5						
	* 6						
	* 7						
	* 8						
	* 9						
	* 0						
	* 7						
	* 8						
	* 9						
	* 0						

Instrument No: 70 **Wavelength: 600 nm**

Standard	ID	Conc. (mg/L)
S1		10
S2		30
S3		50
S4		100
S5		150
ICV		70
CCV		70
LCS		

Reagents	ID/LOT#
Digestion/Catalyst Soln	

ICAL Standard Curve

R	
Y	
CF	

Comments: _____

_____

Analyzed By: _____

This is checked during the data review process.

SPECTROMETER MAINTENANCE LOG

Instrument No: 70 **Month:** **Year:** 200 **Book #** M70-001

Date							
Lamp							
PMT							
Transmittance at: 0%							
100%							
Instrument Warm-up (min.)							
Analyst Initial							
Troubleshooting							
Problem(s) Encountered							
Return To Specs (Analyst Initial)							

Code	Problems Encountered	Code	Corrective Action

Photometric Linearity: Wavelength Accuracy: Reviewed By:

Attachment 1
CLP Analytes and Limits

1.0 VOLATILES TARGET COMPOUND LIST AND CONTRACT REQUIRED QUANTITATION LIMITS

	Volatiles	CAS Number	Quantitation Limits Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column (ng)
1.	*Dichlorodifluoromethane*	*75-71-8*	*10*	*10*	*1200*	*(50)*
2.	Chloromethane	74-87-3	10	10	1200	(50)
3.	Vinyl Chloride	75-01-4	10	10	1200	(50)
4.	Bromomethane	74-83-9	10	10	1200	(50)
5.	Chloroethane	75-00-3	10	10	1200	(50)
6.	*Trichlorofluoromethane*	*75-69-4*	*10*	*10*	*1200*	*(50)*
7.	1,1-Dichloroethene	75-35-4	10	10	1200	(50)
8.	*1,1,2-Trichloro-1,2,2-trifluoroethane*	*76-13-1*	*10*	*10*	*1200*	*(50)*
9.	Acetone	67-64-1	10	10	1200	(50)
10.	Carbon Disulfide	75-15-0	10	10	1200	(50)
11.	*Methyl Acetate*	*79-20-9*	*10*	*10*	*1200*	*(50)*
12.	Methylene Chloride	75-09-2	10	10	1200	(50)
13.	*trans-1,2-Dichloroethene*	*156-60-5*	10	10	1200	(50)
14.	*Methyl tert-Butyl Ether*	*1634-04-4*	*10*	*10*	*1200*	*(50)*
15.	1,1-Dichloroethane	75-34-3	10	10	1200	(50)
16.	*cis-1,2-Dichloroethene*	*156-59-2*	10	10	1200	(50)
17.	2-Butanone	78-93-3	10	10	1200	(50)
18.	Chloroform	67-66-3	10	10	1200	(50)
19.	1,1,1-Trichloroethane	71-55-6	10	10	1200	(50)
20.	*Cyclohexane*	*110-82-7*	*10*	*10*	*1200*	*(50)*
21.	Carbon Tetrachloride	56-23-5	10	10	1200	(50)
22.	Benzene	71-43-2	10	10	1200	(50)
23.	1,2-Dichloroethane	107-06-2	10	10	1200	(50)
24.	Trichloroethene	79-01-6	10	10	1200	(50)
25.	*Methylcyclohexane*	*108-87-2*	*10*	*10*	*1200*	*(50)*
26.	1,2-Dichloropropane	78-87-5	10	10	1200	(50)
27.	Bromodichloromethane	75-27-4	10	10	1200	(50)
28.	cis-1,3-Dichloropropene	10061-01-5	10	10	1200	(50)
29.	4-Methyl-2-pentanone	108-10-1	10	10	1200	(50)
30.	Toluene	108-88-3	10	10	1200	(50)
31.	trans-1,3-Dichloropropene	10061-02-6	10	10	1200	(50)
32.	1,1,2-Trichloroethane	79-00-5	10	10	1200	(50)
33.	Tetrachloroethene	127-18-4	10	10	1200	(50)
34.	2-Hexanone	591-78-6	10	10	1200	(50)
35.	Dibromochloromethane	124-48-1	10	10	1200	(50)

1.0 VOLATILES TARGET COMPOUND LIST AND CONTRACT REQUIRED QUANTITATION LIMITS (Con't)

	Volatiles	CAS Number	Quantitation Limits Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column (ng)
36.	*1,2-Dibromoethane*	*106-93-4*	*10*	*10*	*1200*	*(50)*
37.	Chlorobenzene	108-90-7	10	10	1200	(50)
38.	Ethylbenzene	100-41-4	10	10	1200	(50)
39.	Xylenes (total)	1330-20-7	10	10	1200	(50)
40.	Styrene	100-42-5	10	10	1200	(50)
41.	Bromoform	75-25-2	10	10	1200	(50)
42.	*Isopropylbenzene*	*98-82-8*	*10*	*10*	*1200*	*(50)*
43.	1,1,2,2-Tetrachloroethane	79-34-5	10	10	1200	(50)
44.	*1,3-Dichlorobenzene*	*541-73-1*	*10*	*10*	*1200*	*(50)*
45.	*1,4-Dichlorobenzene*	*106-46-7*	*10*	*10*	*1200*	*(50)*
46.	*1,2-Dichlorobenzene*	*95-50-1*	*10*	*10*	*1200*	*(50)*
47.	*1,2-Dibromo-3-chloropropane*	*96-12-8*	*10*	*10*	*1200*	*(50)*
48.	*1,2,4-Trichlorobenzene*	*120-82-1*	*10*	*10*	*1200*	*(50)*

2.0 SEMIVOLATILES TARGET COMPOUND LIST AND CONTRACT REQUIRED QUANTITATION LIMITS

	Semivolatiles	CAS Number	Quantitation Limits Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column (ng)
49.	*Benzaldehyde*	*100-52-7*	*10*	*330*	*10000*	*(20)*
50.	Phenol	108-95-2	10	330	10000	(20)
51.	bis-(2-Chloroethyl) ether	111-44-4	10	330	10000	(20)
52.	2-Chlorophenol	95-57-8	10	330	10000	(20)
53.	2-Methylphenol	95-48-7	10	330	10000	(20)
54.	2,2'-oxybis(1-Chloropropane)[1]	108-60-1	10	330	10000	(20)
55.	*Acetophenone*	*98-86-2*	*10*	*330*	*10000*	*(20)*
56.	4-Methylphenol	106-44-5	10	330	10000	(20)
57.	N-Nitroso-di-n propylamine	621-64-7	10	330	10000	(20)
58.	Hexachloroethane	67-72-1	10	330	10000	(20)
59.	Nitrobenzene	98-95-3	10	330	10000	(20)
60.	Isophorone	78-59-1	10	330	10000	(20)
61.	2-Nitrophenol	88-75-5	10	330	10000	(20)
62.	2,4-Dimethylphenol	105-67-9	10	330	10000	(20)
63.	bis(2-Chloroethoxy) methane	111-91-1	10	330	10000	(20)
64.	2,4-Dichlorophenol	120-83-2	10	330	10000	(20)
65.	Naphthalene	91-20-3	10	330	10000	(20)
66.	4-Chloroaniline	106-47-8	10	330	10000	(20)
67.	Hexachlorobutadiene	87-68-3	10	330	10000	(20)
68.	*Caprolactam*	*105-60-2*	*10*	*330*	*10000*	*(20)*
69.	4-Chloro-3-methylphenol	59-50-7	10	330	10000	(20)
70.	2-Methylnaphthalene	91-57-6	10	330	10000	(20)
71.	Hexachlorocyclo-pentadiene	77-47-4	10	330	10000	(20)
72.	2,4,6-Trichlorophenol	88-06-2	10	330	10000	(20)
73.	2,4,5-Trichlorophenol	95-95-4	25	830	25000	(50)

[1] Previously known by the name bis(2-Chloroisopropyl)ether.

2.0 SEMIVOLATILES TARGET COMPOUND LIST AND CONTRACT REQUIRED QUANTITATION LIMITS (Con't)

	Semivolatiles	CAS Number	Quantitation Limit Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column (ng)
74.	*1,1'-Biphenyl*	*92-52-4*	*10*	*330*	*10000*	*(20)*
75.	2-Chloronaphthalene	91-58-7	10	330	10000	(20)
76.	2-Nitroaniline	88-74-4	25	830	25000	(50)
77.	Dimethylphthalate	131-11-3	10	330	10000	(20)
78.	2,6-Dinitrotoluene	606-20-2	10	330	10000	(20)
79.	Acenaphthylene	208-96-8	10	330	10000	(20)
80.	3-Nitroaniline	99-09-2	25	830	25000	(50)
81.	Acenaphthene	83-32-9	10	330	10000	(20)
82.	2,4-Dinitrophenol	51-28-5	25	830	25000	(50)
83.	4-Nitrophenol	100-02-7	25	830	25000	(50)
84.	Dibenzofuran	132-64-9	10	330	10000	(20)
85.	2,4-Dinitrotoluene	121-14-2	10	330	10000	(20)
86.	Diethylphthalate	84-66-2	10	330	10000	(20)
87.	Fluorene	86-73-7	10	330	10000	(20)
88.	4-Chlorophenyl-phenyl ether	7005-72-3	10	330	10000	(20)
89.	4-Nitroaniline	100-01-6	25	830	25000	(50)
90.	4,6-Dinitro-2-methylphenol	534-52-1	25	830	25000	(50)
91.	N-Nitroso diphenylamine	86-30-6	10	330	10000	(20)
92.	4-Bromophenyl-phenylether	101-55-3	10	330	10000	(20)
93.	Hexachlorobenzene	118-74-1	10	330	10000	(20)
94.	*Atrazine*	*1912-24-9*	*10*	*330*	*10000*	*(20)*
95.	Pentachlorophenol	87-86-5	25	830	25000	(50)
96.	Phenanthrene	85-01-8	10	330	10000	(20)
97.	Anthracene	120-12-7	10	330	10000	(20)
98.	Carbazole	86-74-8	10	330	10000	(20)
99.	Di-n-butylphthalate	84-74-2	10	330	10000	(20)
100.	Fluoranthene	206-44-0	10	330	10000	(20)
101.	Pyrene	129-00-0	10	330	10000	(20)
102.	Butylbenzylphthalate	85-68-7	10	330	10000	(20)
103.	3,3'-Dichlorobenzidine	91-94-1	10	330	10000	(20)
104.	Benzo(a)anthracene	56-55-3	10	330	10000	(20)
105.	Chrysene	218-01-9	10	330	10000	(20)

2.0 SEMIVOLATILES TARGET COMPOUND LIST AND CONTRACT REQUIRED QUANTITATION LIMITS (Con't)

			Quantitation Limits			
	Semivolatiles	CAS Number	Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column (ng)
106.	bis(2-Ethylhexyl) phthalate	117-81-7	10	330	10000	(20)
107.	Di-n-octylphthalate	117-84-0	10	330	10000	(20)
108.	Benzo(b)fluoranthene	205-99-2	10	330	10000	(20)
109.	Benzo(k)fluoranthene	207-08-9	10	330	10000	(20)
110.	Benzo(a)pyrene	50-32-8	10	330	10000	(20)
111.	Indeno(1,2,3-cd)-pyrene	193-39-5	10	330	10000	(20)
112.	Dibenzo(a,h)-anthracene	53-70-3	10	330	10000	(20)
113.	Benzo(g,h,i)perylene	191-24-2	10	330	10000	(20)

3.0 PESTICIDES/AROCLORS TARGET COMPOUND LIST AND CONTRACT REQUIRED QUANTITATION LIMITS[2]

	Pesticides/Aroclors	CAS Number	Quantitation Limits Water µg/L	Soil µg/Kg	On Column (pg)
114.	alpha-BHC	319-84-6	0.050	1.7	5
115.	beta-BHC	319-85-7	0.050	1.7	5
116.	delta-BHC	319-86-8	0.050	1.7	5
117.	gamma-BHC (Lindane)	58-89-9	0.050	1.7	5
118.	Heptachlor	76-44-8	0.050	1.7	5
119.	Aldrin	309-00-2	0.050	1.7	5
120.	Heptachlor epoxide[3]	*1024-57-3*	0.050	1.7	5
121.	Endosulfan I	959-98-8	0.050	1.7	5
122.	Dieldrin	60-57-1	0.10	3.3	10
123.	4,4'-DDE	72-55-9	0.10	3.3	10
124.	Endrin	72-20-8	0.10	3.3	10
125.	Endosulfan II	33213-65-9	0.10	3.3	10
126.	4,4'-DDD	72-54-8	0.10	3.3	10
127.	Endosulfan sulfate	1031-07-8	0.10	3.3	10
128.	4,4'-DDT	50-29-3	0.10	3.3	10
129.	Methoxychlor	72-43-5	0.50	17	50
130.	Endrin ketone	53494-70-5	0.10	3.3	10
131.	Endrin aldehyde	7421-93-4	0.10	3.3	10
132.	alpha-Chlordane	5103-71-9	0.050	1.7	5
133.	gamma-Chlordane	5103-74-2	0.050	1.7	5
134.	Toxaphene	8001-35-2	5.0	170	500
135.	Aroclor-1016	12674-11-2	1.0	33	100
136.	Aroclor-1221	11104-28-2	2.0	67	200
137.	Aroclor-1232	11141-16-5	1.0	33	100
138.	Aroclor-1242	53469-21-9	1.0	33	100
139.	Aroclor-1248	12672-29-6	1.0	33	100
140.	Aroclor-1254	11097-69-1	1.0	33	100
141.	Aroclor-1260	11096-82-5	1.0	33	100

[2]There is no differentiation between the preparation of low and medium soil samples in this method for the analysis of pesticides/Aroclors.

[3]Only the exo-epoxy isomer (isomer B) of heptachlor epoxide is reported on the data reporting forms (Exhibit B).

1.0 VOLATILES TARGET COMPOUND LIST AND CONTRACT REQUIRED QUANTITATION LIMITS

	Volatiles	CAS Number	Quantitation Limits Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column (ng)
1.	*Dichlorodifluoromethane*	*75-71-8*	*10*	*10*	*1200*	*(50)*
2.	Chloromethane	74-87-3	10	10	1200	(50)
3.	Vinyl Chloride	75-01-4	10	10	1200	(50)
4.	Bromomethane	74-83-9	10	10	1200	(50)
5.	Chloroethane	75-00-3	10	10	1200	(50)
6.	*Trichlorofluoromethane*	*75-69-4*	*10*	*10*	*1200*	*(50)*
7.	1,1-Dichloroethene	75-35-4	10	10	1200	(50)
8.	*1,1,2-Trichloro-1,2,2-trifluoroethane*	*76-13-1*	*10*	*10*	*1200*	*(50)*
9.	Acetone	67-64-1	10	10	1200	(50)
10.	Carbon Disulfide	75-15-0	10	10	1200	(50)
~~11.~~	~~*Methyl Acetate*~~	~~*79-20-9*~~	~~*10*~~	~~*10*~~	~~*1200*~~	~~*(50)*~~
12.	Methylene Chloride	75-09-2	10	10	1200	(50)
13.	*trans-1,2-Dichloroethene*	*156-60-5*	10	10	1200	(50)
14.	*Methyl tert-Butyl Ether*	*1634-04-4*	*10*	*10*	*1200*	*(50)*
15.	1,1-Dichloroethane	75-34-3	10	10	1200	(50)
16.	*cis-1,2-Dichloroethene*	*156-59-2*	10	10	1200	(50)
17.	2-Butanone	78-93-3	10	10	1200	(50)
18.	Chloroform	67-66-3	10	10	1200	(50)
19.	1,1,1-Trichloroethane	71-55-6	10	10	1200	(50)
~~20.~~	~~*Cyclohexane*~~	~~*110-82-7*~~	~~*10*~~	~~*10*~~	~~*1200*~~	~~*(50)*~~
21.	Carbon Tetrachloride	56-23-5	10	10	1200	(50)
22.	Benzene	71-43-2	10	10	1200	(50)
23.	1,2-Dichloroethane	107-06-2	10	10	1200	(50)
24.	Trichloroethene	79-01-6	10	10	1200	(50)
~~25.~~	~~*Methylcyclohexane*~~	~~*108-87-2*~~	~~*10*~~	~~*10*~~	~~*1200*~~	~~*(50)*~~
26.	1,2-Dichloropropane	78-87-5	10	10	1200	(50)
27.	Bromodichloromethane	75-27-4	10	10	1200	(50)
28.	cis-1,3-Dichloropropene	10061-01-5	10	10	1200	(50)
29.	4-Methyl-2-pentanone	108-10-1	10	10	1200	(50)
30.	Toluene	108-88-3	10	10	1200	(50)
31.	trans-1,3-Dichloropropene	10061-02-6	10	10	1200	(50)
32.	1,1,2-Trichloroethane	79-00-5	10	10	1200	(50)
33.	Tetrachloroethene	127-18-4	10	10	1200	(50)
34.	2-Hexanone	591-78-6	10	10	1200	(50)
35.	Dibromochloromethane	124-48-1	10	10	1200	(50)

1.0 VOLATILES TARGET COMPOUND LIST AND CONTRACT REQUIRED QUANTITATION LIMITS (Con't)

	Volatiles	CAS Number	Quantitation Limits Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column (ng)
36.	*1,2-Dibromoethane*	*106-93-4*	*10*	*10*	*1200*	*(50)*
37.	Chlorobenzene	108-90-7	10	10	1200	(50)
38.	Ethylbenzene	100-41-4	10	10	1200	(50)
39.	Xylenes (total)	1330-20-7	10	10	1200	(50)
40.	Styrene	100-42-5	10	10	1200	(50)
41.	Bromoform	75-25-2	10	10	1200	(50)
42.	*Isopropylbenzene*	*98-82-8*	*10*	*10*	*1200*	*(50)*
43.	1,1,2,2-Tetrachloroethane	79-34-5	10	10	1200	(50)
44.	*1,3-Dichlorobenzene*	*541-73-1*	*10*	*10*	*1200*	*(50)*
45.	*1,4-Dichlorobenzene*	*106-46-7*	*10*	*10*	*1200*	*(50)*
46.	*1,2-Dichlorobenzene*	*95-50-1*	*10*	*10*	*1200*	*(50)*
47.	*1,2-Dibromo-3-chloropropane*	*96-12-8*	*10*	*10*	*1200*	*(50)*
48.	*1,2,4-Trichlorobenzene*	*120-82-1*	*10*	*10*	*1200*	*(50)*

2.0 SEMIVOLATILES TARGET COMPOUND LIST AND CONTRACT REQUIRED QUANTITATION LIMITS

			Quantitation Limits			
	Semivolatiles	CAS Number	Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column (ng)
~~49.~~	~~Benzaldehyde~~	~~100-52-7~~	~~10~~	~~330~~	~~10000~~	~~(20)~~
50.	Phenol	108-95-2	10	330	10000	(20)
51.	bis-(2-Chloroethyl) ether	111-44-4	10	330	10000	(20)
52.	2-Chlorophenol	95-57-8	10	330	10000	(20)
53.	2-Methylphenol	95-48-7	10	330	10000	(20)
54.	2,2'-oxybis(1-Chloropropane)[1]	108-60-1	10	330	10000	(20)
~~55.~~	~~Acetophenone~~	~~98-86-2~~	~~10~~	~~330~~	~~10000~~	~~(20)~~
56.	4-Methylphenol	106-44-5	10	330	10000	(20)
57.	N-Nitroso-di-n propylamine	621-64-7	10	330	10000	(20)
58.	Hexachloroethane	67-72-1	10	330	10000	(20)
59.	Nitrobenzene	98-95-3	10	330	10000	(20)
60.	Isophorone	78-59-1	10	330	10000	(20)
61.	2-Nitrophenol	88-75-5	10	330	10000	(20)
62.	2,4-Dimethylphenol	105-67-9	10	330	10000	(20)
63.	bis(2-Chloroethoxy) methane	111-91-1	10	330	10000	(20)
64.	2,4-Dichlorophenol	120-83-2	10	330	10000	(20)
65.	Naphthalene	91-20-3	10	330	10000	(20)
66.	4-Chloroaniline	106-47-8	10	330	10000	(20)
67.	Hexachlorobutadiene	87-68-3	10	330	10000	(20)
~~68.~~	~~Caprolactam~~	~~105-60-2~~	~~10~~	~~330~~	~~10000~~	~~(20)~~
69.	4-Chloro-3-methylphenol	59-50-7	10	330	10000	(20)
70.	2-Methylnaphthalene	91-57-6	10	330	10000	(20)
71.	Hexachlorocyclo-pentadiene	77-47-4	10	330	10000	(20)
72.	2,4,6-Trichlorophenol	88-06-2	10	330	10000	(20)
73.	2,4,5-Trichlorophenol	95-95-4	25	830	25000	(50)

[1] Previously known by the name bis(2-Chloroisopropyl)ether.

2.0 SEMIVOLATILES TARGET COMPOUND LIST AND CONTRACT REQUIRED QUANTITATION LIMITS (Con't)

			Quantitation Limit			
	Semivolatiles	CAS Number	Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column (ng)
~~74.~~	~~1,1'-Biphenyl~~	~~92-52-4~~	~~10~~	~~330~~	~~10000~~	~~(20)~~
75.	2-Chloronaphthalene	91-58-7	10	330	10000	(20)
76.	2-Nitroaniline	88-74-4	25	830	25000	(50)
77.	Dimethylphthalate	131-11-3	10	330	10000	(20)
78.	2,6-Dinitrotoluene	606-20-2	10	330	10000	(20)
79.	Acenaphthylene	208-96-8	10	330	10000	(20)
80.	3-Nitroaniline	99-09-2	25	830	25000	(50)
81.	Acenaphthene	83-32-9	10	330	10000	(20)
82.	2,4-Dinitrophenol	51-28-5	25	830	25000	(50)
83.	4-Nitrophenol	100-02-7	25	830	25000	(50)
84.	Dibenzofuran	132-64-9	10	330	10000	(20)
85.	2,4-Dinitrotoluene	121-14-2	10	330	10000	(20)
86.	Diethylphthalate	84-66-2	10	330	10000	(20)
87.	Fluorene	86-73-7	10	330	10000	(20)
88.	4-Chlorophenyl-phenyl ether	7005-72-3	10	330	10000	(20)
89.	4-Nitroaniline	100-01-6	25	830	25000	(50)
90.	4,6-Dinitro-2-methylphenol	534-52-1	25	830	25000	(50)
91.	N-Nitroso diphenylamine	86-30-6	10	330	10000	(20)
92.	4-Bromophenyl-phenylether	101-55-3	10	330	10000	(20)
93.	Hexachlorobenzene	118-74-1	10	330	10000	(20)
~~94.~~	~~Atrazine~~	~~1912-24-9~~	~~10~~	~~330~~	~~10000~~	~~(20)~~
95.	Pentachlorophenol	87-86-5	25	830	25000	(50)
96.	Phenanthrene	85-01-8	10	330	10000	(20)
97.	Anthracene	120-12-7	10	330	10000	(20)
98.	Carbazole	86-74-8	10	330	10000	(20)
99.	Di-n-butylphthalate	84-74-2	10	330	10000	(20)
100.	Fluoranthene	206-44-0	10	330	10000	(20)
101.	Pyrene	129-00-0	10	330	10000	(20)
102.	Butylbenzylphthalate	85-68-7	10	330	10000	(20)
103.	3,3'-Dichlorobenzidine	91-94-1	10	330	10000	(20)
104.	Benzo(a)anthracene	56-55-3	10	330	10000	(20)
105.	Chrysene	218-01-9	10	330	10000	(20)

2.0 SEMIVOLATILES TARGET COMPOUND LIST AND CONTRACT REQUIRED QUANTITATION LIMITS (Con't)

			Quantitation Limits			
	Semivolatiles	CAS Number	Water µg/L	Low Soil µg/Kg	Med. Soil µg/Kg	On Column (ng)
106.	bis(2-Ethylhexyl) phthalate	117-81-7	10	330	10000	(20)
107.	Di-n-octylphthalate	117-84-0	10	330	10000	(20)
108.	Benzo(b)fluoranthene	205-99-2	10	330	10000	(20)
109.	Benzo(k)fluoranthene	207-08-9	10	330	10000	(20)
110.	Benzo(a)pyrene	50-32-8	10	330	10000	(20)
111.	Indeno(1,2,3-cd)-pyrene	193-39-5	10	330	10000	(20)
112.	Dibenzo(a,h)-anthracene	53-70-3	10	330	10000	(20)
113.	Benzo(g,h,i)perylene	191-24-2	10	330	10000	(20)

3.0 PESTICIDES/AROCLORS TARGET COMPOUND LIST AND CONTRACT REQUIRED QUANTITATION LIMITS[2]

	Pesticides/Aroclors	CAS Number	Quantitation Limits Water µg/L	Soil µg/Kg	On Column (pg)
114.	alpha-BHC	319-84-6	0.050	1.7	5
115.	beta-BHC	319-85-7	0.050	1.7	5
116.	delta-BHC	319-86-8	0.050	1.7	5
117.	gamma-BHC (Lindane)	58-89-9	0.050	1.7	5
118.	Heptachlor	76-44-8	0.050	1.7	5
119.	Aldrin	309-00-2	0.050	1.7	5
120.	Heptachlor epoxide[3]	*1024-57-3*	0.050	1.7	5
121.	Endosulfan I	959-98-8	0.050	1.7	5
122.	Dieldrin	60-57-1	0.10	3.3	10
123.	4,4'-DDE	72-55-9	0.10	3.3	10
124.	Endrin	72-20-8	0.10	3.3	10
125.	Endosulfan II	33213-65-9	0.10	3.3	10
126.	4,4'-DDD	72-54-8	0.10	3.3	10
127.	Endosulfan sulfate	1031-07-8	0.10	3.3	10
128.	4,4'-DDT	50-29-3	0.10	3.3	10
129.	Methoxychlor	72-43-5	0.50	17	50
130.	Endrin ketone	53494-70-5	0.10	3.3	10
131.	Endrin aldehyde	7421-93-4	0.10	3.3	10
132.	alpha-Chlordane	5103-71-9	0.050	1.7	5
133.	gamma-Chlordane	5103-74-2	0.050	1.7	5
134.	Toxaphene	8001-35-2	5.0	170	500
135.	Aroclor-1016	12674-11-2	1.0	33	100
136.	Aroclor-1221	11104-28-2	2.0	67	200
137.	Aroclor-1232	11141-16-5	1.0	33	100
138.	Aroclor-1242	53469-21-9	1.0	33	100
139.	Aroclor-1248	12672-29-6	1.0	33	100
140.	Aroclor-1254	11097-69-1	1.0	33	100
141.	Aroclor-1260	11096-82-5	1.0	33	100

[2]There is no differentiation between the preparation of low and medium soil samples in this method for the analysis of pesticides/Aroclors.

[3]Only the exo-epoxy isomer (isomer B) of heptachlor epoxide is reported on the data reporting forms (Exhibit B).

1.0 INORGANIC TARGET ANALYTE LIST AND CONTRACT REQUIRED QUANTITATION LIMITS (CRQLs)

Analyte	CAS Number	ICP-AES CRQL for Water[1,2,3,4] (µg/L)	ICP-AES CRQL for Soil[1,2,3,4,5] (mg/kg)	ICP-MS CRQL for Water[1,2,4] (µg/L)
Aluminum	7429-90-5	200	40	30
Antimony	7440-36-0	60	12	2
Arsenic	7440-38-2	15	3	1
Barium	7440-39-3	200	40	10
Beryllium	7440-41-7	5	1	1
Cadmium	7440-43-9	5	1	1
Calcium	7440-70-2	5000	1000	--
Chromium	7440-47-3	10	2	2
Cobalt	7440-48-4	50	10	0.5
Copper	7440-50-8	25	5	2
Iron	7439-89-6	100	20	--
Lead	7439-92-1	10	2	1
Magnesium	7439-95-4	5000	1000	--
Manganese	7439-96-5	15	3	0.5
Mercury	7439-97-6	0.2	0.1	--
Nickel	7440-02-0	40	8	1
Potassium	7440-09-7	5000	1000	--
Selenium	7782-49-2	35	7	5
Silver	7440-22-4	10	2	1
Sodium	7440-23-5	5000	1000	--
Thallium	7440-28-0	25	5	1
Vanadium	7440-62-2	50	10	1
Zinc	7440-66-6	60	12	1
Cyanide	57-12-5	10	1	--

[1]The CRQLs are the minimum levels of quantitation acceptable under the contract Statement of Work (SOW).

[2]Subject to the restrictions specified in Exhibit D, any analytical method specified in ILM05.2 Exhibit D may be utilized as long as the documented Method Detection Limits (MDLs) are less than one-half the CRQLs.

[3]Mercury is analyzed by cold vapor atomic absorption. Cyanide is analyzed by colorimetry/spectrophotometry.

[4]Changes to the Inorganic Target Analyte List (TAL) (e.g., adding an additional analyte) or CRQLs may be requested under the flexibility clause in the contract.

[5]The CRQLs for soil are based on 100% solids and on the exact weights and volumes specified in Exhibit D. Samples with less than 100% solids may have CRQLs greater than those listed in the table above.