SAP Worksheet #1 -- Title and Approval Page
(UFP-QAPP Manual Section 2.1)

Final

SAMPLING AND ANALYSIS PLAN
(Field Sampling Plan and Quality Assurance Project Plan)
28 November 2011

LONG TERM MONITORING, SITE 40
NAVAL WEAPONS STATION SEAL BEACH
CALIFORNIA

Prepared for:
NAVFAC Southwest
U.S. Department of the Navy
Southwest Division
Naval Facilities Engineering Command
San Diego, California

Prepared by:
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Prepared under:
Contract No. N62473-09-D-2626 CTO 0004
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Review Signatures: Carol Moldoveanu — November 28, 2011
Carol Moldoveanu — Date
Quality Program Manager, CKY Joint Venture

Approval Signatures: Narciso Ancog — 11/28/2011
Narciso Ancog — Date
Quality Assurance Officer, NAVFAC Southwest

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EXECUTIVE SUMMARY

This Sampling and Analysis Plan (SAP) has been prepared for the Department of the Navy (Navy) by CKY Incorporated (CKY) under Southwest Division, Naval Facilities Engineering Command (NAVFAC SW) Environmental Multiple Award Contract (EMAC) No. N62473-09-D-2626, Contract Task Order (CTO) No. 4. The SAP describes the field sampling procedures and quality assurance project procedures to be implemented by the CKY and its subcontractors for the subject project. The project objective is to perform long-term monitoring at Installation Restoration Program (IRP) Site 40 at the Naval Weapons Station (NAVWPNSTA) Seal Beach, Seal Beach, California. The Navy is the lead agency responsible for overseeing the progress of work for the project in accordance with requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). State regulatory oversight is provided by the California Department of Toxic Substances Control (DTSC) and the Regional Water Quality Control Board (RWQCB), Santa Ana Region.

NAVWPNSTA Seal Beach is located about 30 miles south of the Los Angeles urban center. The facility consists of approximately 5,000 acres of land along the Pacific Coast within the city of Seal Beach in Orange County, California (Figure 1). Originally commissioned in 1944, NAVWPNSTA Seal Beach provides fleet combatants with ready-for-use ordnance and serves as a supply point for the operating forces of the Navy and United States Marine Corps forces in the Southern California region. Figure 2 shows a map of NAVWPNSTA Seal Beach, including the location of IRP Site 40.

IRP Site 40 (Figure 3) includes a concrete pit located in the Locomotive Shop (Building 240) and a gravel area located north of, and adjacent to, the building. Four railroad spurs terminated in Building 240 and provided locomotive access to the repair shop. The rail hub is no longer active and the rails are being removed. The concrete pit formerly provided a collection point for oil and solvents spilled during locomotive maintenance activities. Until 1978, oil that collected in the pit discharged into the gravel area through a drainpipe. The pipe was plugged in 1978. Currently, the area north of Building 240 is paved and the area northwest of Building 240 is unpaved.

A number of studies and investigations have been conducted at NAVWPNSTA Seal Beach. Upon review of IRP Site 40's operational history and site-specific groundwater investigative data, the Navy determined that this site contained elevated concentrations of tetrachloroethene (PCE) and trichloroethene (TCE) in groundwater, thus requiring a response action. This decision is documented in the Record of Decision (ROD) (Navy 2004). The Navy initiated the remedial action for the impacted groundwater at IRP Site 40 to reduce any potential threats to human health and the surrounding environment. The remedial action was determined to be enhanced in situ bioremediation (EISB) and performance monitoring, monitored natural attenuation (MNA), and land-use controls (LUCs). The chemicals of concern (COCs) at the site were determined to be chlorinated ethenes (CEs), including PCE, TCE, dichloroethene (DCE), and vinyl chloride (VC) in groundwater (BEI 2000).

The EISB response action was implemented in 2005 with the direct injection of sodium lactate solution with water combined with bioaugmentation using a commercially available CE-respiring bacterial culture (containing *Dehalococcoides* spp. [Dhc]) (TtEC 2006b). Hydrogen Release Compound (HRC®) was injected in 2007 to improve the delivery and distribution of lactate and in 2008 to address residual contamination at the site. Groundwater and vapor monitoring has been performed periodically (annually or more frequently) from October 2005

through May 2010. Overall, significant reductions in total CE concentrations have been observed in all monitoring wells (TtEC 2011). While microbiological and geochemical data suggest an environment favorable for continuing reductive dechlorination, the potential for enhanced bioremediation has likely reached its limit. Accordingly, slower, localized biodegradation, along with other natural attenuation processes, will likely dominate the further reduction of CE levels. As anticipated, MNA will likely be sufficient to reach target cleanup goals (TCGs). In terms of the contaminant evaluation, PCE and TCE have been degraded to levels below TCGs in all wells. Residual low levels of cis-1,2-DCE and VC remain in excess of their TCGs, forming dilute plumes in the central and southwest portions of the site (TtEC 2011).

The primary objective of the sampling and analysis activities for the project is to collect groundwater and vapor samples to monitor progress of the MNA. CKY will continue the current annual monitoring by performing the following activities:

- Collecting groundwater samples from 10 wells which currently do not meet the ROD-specified criterion of not exceeding a TCG for over one year and from 7 additional wells deemed necessary to assess plume dynamics.
- Analyzing the groundwater samples for volatile organic compounds (VOCs), field parameters, geochemical parameters, dissolved gases, and Dhc.
- Collecting soil gas samples at 8 wells that had high concentrations of methane.
- Analyzing the soil gas samples for VOCs and methane.
- Collecting field measurements for methane, carbon dioxide, carbon monoxide, oxygen, and hydrogen sulfide at 17 wells.
- Collecting field measurements for methane from surface emissions at areas within IRP Site 40, inside Buildings 240 and 249, and inside the manholes located within the Site.

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Attachment 2 Example Chain-of-Custody Form, Sample Label, and Custody Seal

Acronyms and Abbreviations

µg/L	micrograms per liter
AR	Administrative Record
ARAR	Applicable or Relevant and Appropriate Requirements
ASTM	American Society for Testing and Materials
bgs	below ground surface
CA	corrective action; California
CalEPA	California Environmental Protection Agency
Calscience	Calscience Environmental Laboratories, Inc.
CAS	Chemical Abstract Service
CD	compact disc
CE	chlorinated ethene
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CKY	CKY Incorporated
COC	chemical of concern
COD	chemical oxygen demand
COPC	chemical of potential concern
CQC	Contractor Quality Control
CSM	conceptual site model
CTO	contract task order
DCE	dichloroethene
Dhc	*Dehalococcoides ethenogenes* spp.
DL	detection limit
DoD	U.S. Department of Defense
DOT	U.S. Department of Transportation
DQI	data quality indicator
DQO	data quality objective
DTSC	California Department of Toxic Substances Control
EISB	enhanced in situ bioremediation
ELAP	Environmental Laboratory Accreditation Program
EPA	United States Environmental Protection Agency
ERSE	Extended Removal Site Evaluation
ESQD	explosives safety quantity distance
EWI	Environmental Work Instruction
FD	field duplicate
FS	feasibility study
FSI	focused site inspection

Acronyms and Abbreviations (continued)

GC	gas chromatograph; gas chromatography
GC/MS	gas chromatograph/mass spectrometer; gas chromatography/mass spectrometry
HRC®	Hydrogen Release Compound
IDW	investigation derived waste
IRP	Installation Restoration Program
LCS	laboratory control sample
LDC	Laboratory Data Consultants, Inc.
LOD	limit of detection
LOQ	limit of quantitation
LUC	land use control
MCL	maximum contaminant level
MDL	method detection limit
MNA	monitored natural attenuation
MS/MSD	matrix spike/matrix spike duplicate
NAVFAC	Naval Facilities Engineering Command
NAVWPNSTA	Naval Weapons Station
Navy	U.S. Department of Navy
NEDD	Naval Electronic Data Deliverable
NIRIS	Naval Installation Restoration Information Solution
NLT	Not later than
OSHA	Occupational Safety and Health Administration
PAL	project action limit
PCE	tetrachloroethene
PID	photoionization detector
PM	project manager
ppb/v	parts per billion by volume
PPE	personal protective equipment
PQL	project quantitation limit
PQOs	project quality objectives
PT	proficiency testing (previously known as performance evaluation (PE) sample)
QA	quality assurance
QAO	Quality Assurance Officer
QAPP	Quality Assurance Project Plan
QC	quality control
QCM	Quality Control Manager
QL	quantitation limit
qPCR	quantitative polymerase chain reaction
QSM	Quality Systems Manual

Acronyms and Abbreviations (continued)

RAO	remedial action objective
ROD	Record of Decision
RPD	relative percent difference
RPM	Remedial Project Manager
RSD	relative standard deviation
RWQCB	Regional Water Quality Control Board
SAP	Sampling and Analysis Plan
SBNWR	Seal Beach National Wildlife Refuge
SI	site inspection
SOP	standard operating procedure
SSHO	Site Safety and Health Officer
TCE	trichloroethene
TDS	total dissolved solids
TGC	Target Cleanup Goal
TOC	total organic carbon
UFP	Uniform Federal Policy
VC	vinyl chloride
VOA	volatile organic analysis
VOC	volatile organic compound

SAP Worksheet #2 -- SAP Identifying Information
(UFP-QAPP Manual Section 2.2.4)

Site Name/Number: Long Term Monitoring, Installation Restoration Program (IRP) Site 40, Naval Weapons Station (NAVWPNSTA) Seal Beach, California
Operable Unit: 4
Contractor Name: CKY Incorporated (CKY)
Contract Number: N62473-09-D-2626
Contract Title: Environmental Multiple Award Contract II
Work Assignment Number (optional): CTO 0004

1. This sampling and analysis plan (SAP) was prepared in accordance with the requirements of the *Uniform Federal Policy for Quality Assurance Plans (UFP-QAPP)* (EPA 2005) and United States (U.S.) Environmental Protection Agency (EPA) *Guidance for Quality Assurance Project Plans, EPA QA/G-5* (EPA 2002).

2. Identify regulatory program: Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

3. This SAP is a project specific SAP.

4. List dates of scoping sessions that were held:

   Project Kickoff Meeting September 26, 2011

5. List dates and titles of any SAP documents written for previous site work that are relevant to the current investigation:

   Tetra Tech EC, Inc., "Addendum 2 to the Final Sampling and Analysis Plan, Enhanced In Situ Bioremediation, Installation Restoration Program Site 40 (Concrete Pit/Gravel Area), Naval Weapons Station Seal Beach, Seal Beach, California." September 12, 2008.

   Tetra Tech EC, Inc., "Addendum 1 to the Final Sampling and Analysis Plan, Enhanced In Situ Bioremediation, Installation Restoration Program Site 40 (Concrete Pit/Gravel Area), Naval Weapons Station Seal Beach, Seal Beach, California." March 15, 2006.

   Bechtel Environmental, Inc., "Sampling and Analysis Plan Supplement to the Final Sampling and Analysis Plan, Enhanced In Situ Bioremediation, Installation Restoration Program Site 40 (Concrete Pit/Gravel Area), Naval Weapons Station Seal Beach, Seal Beach, California." April 2006.

   Tetra Tech EC, Inc., "Final Sampling and Analysis Plan, Enhanced In Situ Bioremediation Installation Restoration Program Site 40 (Concrete Pit/Gravel Area), Naval Weapons Station Seal Beach, Seal Beach, California." February 24, 2005.

6. List organizational partners (stakeholders) and identify the connection with lead organization:

Organization Partners/Stakeholders	Connection
California Department of Toxic Substances Control (DTSC)	document review and state regulatory oversight
California Regional Water Quality Control Board (RWQCB)	document review and state regulatory oversight

7. Lead organization: Naval Facilities Engineering Command (NAVFAC) Southwest.

8. If any required SAP elements and required information are not applicable to the project or are provided elsewhere, then note the omitted SAP elements and provide an explanation for their exclusion below:

   Worksheet #8 Specialized Personnel Training Requirements Training Table: This worksheet is not applicable to the project because no specialized training is required. The table for Worksheet #8 is not included in this SAP.

   Worksheet #21 Project Sampling SOP References Table: This worksheet is not applicable to the project because project sampling procedures are described in Worksheet #14.

UFP-QAPP Worksheet #	Required Information	Crosswalk to Related Information
A. Project Management and Objectives		
Documentation		
1	Title and Approval Page	
2	SAP Identifying Information	
3	Distribution List	
4	Project Personnel Sign-Off Sheet	
Project Organization		
5	Project Organizational Chart	
6	Communication Pathways	
7	Personnel Responsibilities and Qualifications Table	
8	Special Personnel Training Requirements Table	Not applicable (see explanation on worksheet #2)
Project Planning/ Problem Definition		
9	Project Planning Session Documentation Project Scoping Session Participants Sheet	
10	Problem Definition, Site History, and Background Site Maps (historical and present)	Figures 1-5
11	Site-specific Project Quality Objectives	
12	Measurement Performance Criteria Table	
13	Secondary Data Criteria and Limitations Table	
14	Summary of Project Tasks	
15	Reference Limits and Evaluation Table	
16	Project Schedule/Timeline Table	
B. Measurement Data Acquisition		
Sampling Tasks		
17	Sampling Design and Rationale	
18	Sampling Locations and Methods/ SOP Requirements Table Sample Location Map(s)	Figures 6-8
19	Field Sampling Requirements Table	
20	Field Quality Control Sample Summary Table	
21	Project Sampling SOP References Table	Sampling procedures described on Worksheet 14
22	Field Equipment Calibration, Maintenance, Testing, and Inspection Table	
Analytical Tasks		
23	Analytical SOPs Analytical SOP References Table	SOPs included in Attachment 1
24	Analytical Instrument Calibration Table	
25	Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table	
Sample Collection		
26	Sample Handling System Documentation	
27	Sample Custody Requirements, Procedures/SOPs Example Chain-of-Custody Form and Seal	Example forms included in Attachment 2
Quality Control Samples		
28	QC Samples Table	
Data Management Tasks		
29	Project Documents and Records Table	
30	Analytical Services Table	
C. Assessment Oversight		
31	Planned Project Assessments Table	
32	Assessment Findings and Corrective Action Responses Table	
33	QA Management Reports Table	
D. Data Review		
34	Verification (Step I) Process Table	
35	Validation (Steps IIa and IIb) Process Table	
36	Validation (Steps IIa and IIb) Summary Table	
37	Usability Assessment	

Notes:
QA quality assurance
QC quality control
SOP standard operating procedure

SAP Worksheet #3 -- Distribution List
(UFP-QAPP Manual Section 2.3.1)

SAP Recipients	Title	Organization	Telephone Number (Optional)	E-mail Address or Mailing Address
Brenda Reese	Remedial Project Manager	NAVFAC Southwest	(619) 532-4209	brenda.reese@navy.mil 1220 Pacific Hwy, San Diego, CA 92132
Pei-Fen Tamashiro	Activity POC	NAVWPNSTA Seal Beach	(562) 626-7897	pei-fen.tamashiro@navy.mil 800 Seal Beach Blvd., Seal Beach, CA 90740-5000
Narciso Ancog	QA Officer	NAVFAC Southwest	(619) 532-3046	narciso.ancog@navy.mil 1220 Pacific Hwy, San Diego, CA 92132
John Broderick	Project Manager	RWQCB Santa Ana Region	(951) 782-4494	jbroderick@waterboards.ca.gov 3737 Main Street, Ste. 500, Riverside, CA 92501
Stephen Niou	Project Manager	DTSC	(714) 484-5458	SNiou@dtsc.ca.gov 5796 Corporate Avenue, Cypress, CA 90630
Carol Moldoveanu	Quality Program Manager	CKY	(336) 765-8904	cmoldov@ckyinc.com
Howard Wittenberg	Project Manager	CKY	(510) 519-4000	howard@ckyinc.com
Noah Rivera	Project QC Manager	CKY	(503) 320-8700	nrivera@ckyinc.com
Larry Pennock	Site Supervisor/SSHO	CKY	(208) 818-0951	lpennock@ckyinc.com
Tim Theisen	Project Chemist	CKY	(920) 360-1561	ttheisen@ckyinc.com
Cade Klock	Data Manager	CKY	(510) 519-4000	cklock@ckyinc.com
Linda Scharpenberg	Lab Project Manager	Calscience	(714) 895-5494 x306	lscharpenberg@calscience.com
Linda Rauto	Senior Chemist	Laboratory Data Consultants	(760) 634-0437	lrauto@lab-data.com

Calscience = Calscience Environmental Laboratories, Inc.
CKY = CKY Incorporated
DTSC = California Department of Toxic Substances Control
NAVWPNSTA = Naval Weapons Station
QA = quality assurance
QC = quality control
SSHO = Site Safety and Health Officer
RWQCB = Regional Water Quality Control Board

SAP Worksheet #4 -- Project Personnel Sign-Off Sheet

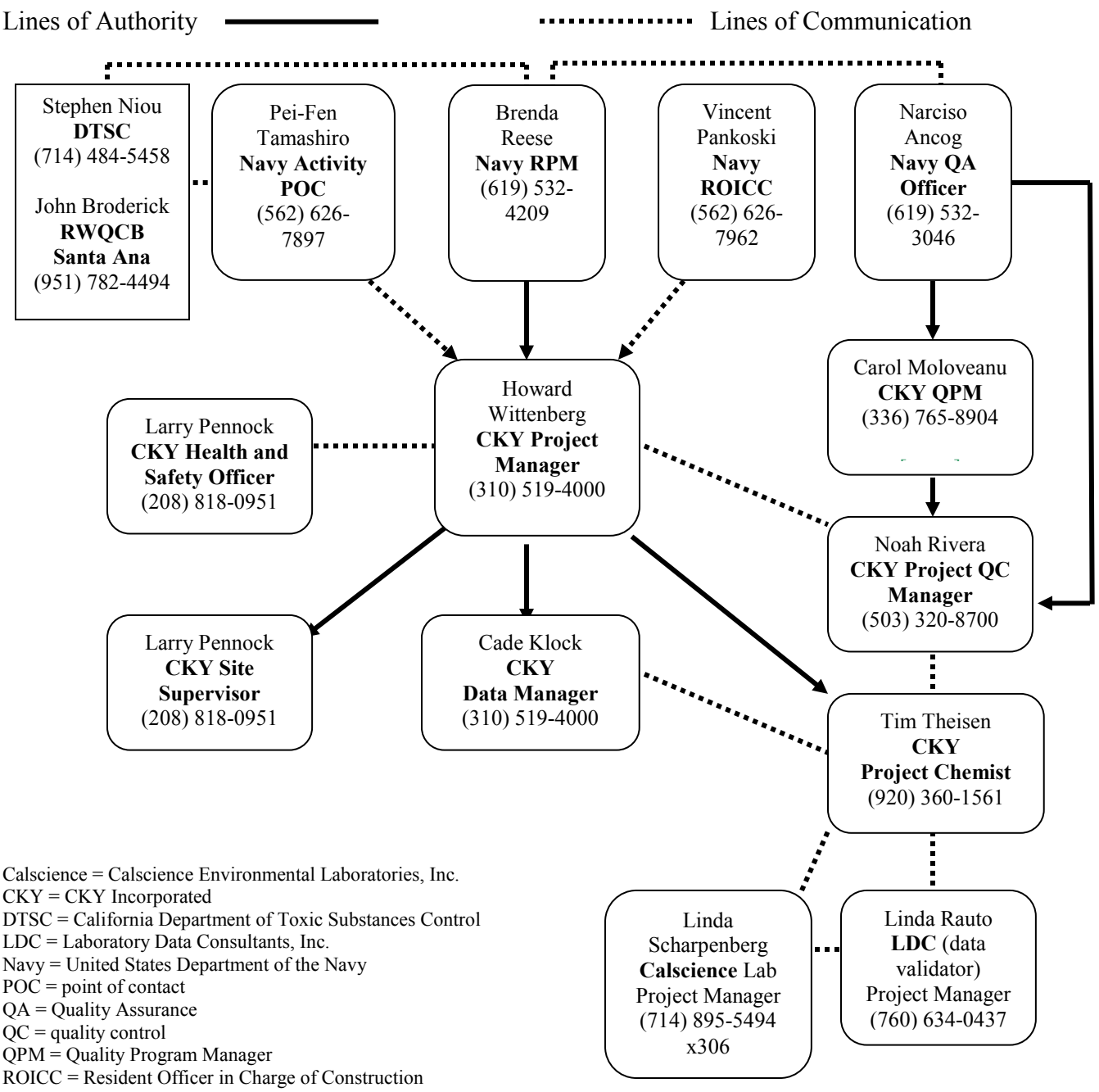
(UFP-QAPP Manual Section 2.3.2)

The Project Personnel Sign-Off Sheet documents that all key project personnel performing work have read this site-specific SAP and will carry out the tasks as described. The project manager, site safety coordinator, and other oversight personnel are responsible for communicating the requirements of the applicable portions of the SAP to all field personnel. To ensure that on-site field personnel have read and understood the SAP, the supervisory personnel will meet with each and review the SAP before any work is conducted on site. The sign-off sheet, which will be included in the central project file, will be signed by all on-site personnel after they read the SAP. However, if only a portion of the SAP was reviewed, then personnel will note which sections were reviewed on the sign-off sheet.

Name	Organization/Title/Role	Telephone Number	Signature/email receipt	SAP Section Reviewed	Date SAP Read
Howard Wittenberg	CKY Project Manager	(310) 519-4000		all	
Noah Rivera	CKY Project QC	(503) 320-8700		all	
Larry Pennock	CKY SSHO CKY Site Supervisor	(208) 818-0951		all	
Tim Theisen	CKY Project Chemist	(920) 360-1561		all	
Cade Klock	Data Manager	(510) 519-4000		all	
Linda Scharpenberg	Calscience Lab Project Manager	(714) 895-5494 x306		Worksheets #7, 12, 19, 20, 23, 24, 25, 28, 31, 35, and 36	
Linda Rauto	LDC Senior Chemist	(760) 634-0437			

Calscience = Calscience Environmental Laboratories, Inc.
CKY = CKY Incorporated
LDC = Laboratory Data Consultants, Inc.
QC = quality control
SAP = Sampling and Analysis Plan
SSHO = Site Safety and Health Officer

SAP Worksheet #5 – Project Organizational Chart
(UFP-QAPP Manual Section 2.4.1)



Calscience = Calscience Environmental Laboratories, Inc.
CKY = CKY Incorporated
DTSC = California Department of Toxic Substances Control
LDC = Laboratory Data Consultants, Inc.
Navy = United States Department of the Navy
POC = point of contact
QA = Quality Assurance
QC = quality control
QPM = Quality Program Manager
ROICC = Resident Officer in Charge of Construction
RPM = Remedial Project Manager
RWQCB = Regional Water Quality Control Board

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SAP Worksheet #6 -- Communication Pathways
(UFP-QAPP Manual Section 2.4.2)

Communication Drivers	Responsible Entity	Name	Phone Number and/or email	Procedure (timing, pathway to from, etc.)
Approval of amendments to the SAP	NAVFAC Southwest QAO	Narciso Ancog	(619) 532-3046	Any major changes to the SAP must be approved by Navy QAO before the changes can be implemented. Approval normally occurs within two weeks of receipt of amendment.
SAP review and concurrence	DTSC RWQCB	Stephen Niou John Broderick	(714) 484-5458 (951) 782-4494	DTSC and RWQCB will review and concur on the SAP.
Initiation and/or notification of real time modifications	CKY PM	Howard Wittenberg	(310) 519-4000	CKY PM will submit request to NAVFAC SW RPM by phone, email, or fax by COB the next business day.
Approval of real time modifications	NAVFAC Southwest RPM	Brenda Reese	(619) 532-4209	Approval of change to be obtained from RPM prior to sampling
Recommendation to stop work and initiation of corrective action	CKY Project QCM	Noah Rivera	(503) 320-8700	CKY QCM will notify CKY PM and Navy RPM of recommendation to stop work and initiation of corrective action of a quality control deficiency by phone, email, or fax within 1 business day. If the work stoppage will occur for longer than one day, the CKY PM will meet with the Navy RPM to resolve the issue.
Reporting of issues related to analytical data quality, e.g. inability to meet reporting limits	Laboratory PM	Linda Scharpenberg	(714) 895-5494 x306	All QA/QC issues with project field samples will be reported by lab project manager to H. Wittenberg within 2 business days.
Reporting of issues related to analytical data quality, e.g. rejected results.	Data Validator	Linda Rauto	(760) 634-0437	All QA/QC issues with analytical data will be reported by data validator to CKY PM within 3 weeks.
Notification of Non-Usable Analytical Data	CKY Project Chemist	Tim Theisen	(920) 360-1561	If significant problems are identified by the laboratory or the project team that impact the usability of the data (i.e. the data is rejected or the data quality objectives are not met), the program Chemist will notify the NAVFACSW RPM and the NACFACSW QAO within 24 hours or the next business day

CKY = CKY Incorporated
DTSC = California Department of Toxic Substances Control
NAVFAC SW = Naval Facilities Engineering Command, Southwest
QAO = Quality Assurance Officer
QCM = Project Quality Control Manager

QPM = Quality Program Manager
RPM = Remedial Project Manager
RWQCB = Regional Water Quality Control Board

The CKY Project Manager (PM) will submit weekly updates and monthly progress reports via fax or electronic mail to the NAVFAC Southwest Remedial Project Manager (RPM). Any activities related to sampling and analysis, including preliminary sample results, will be reported on the progress reports. The Project Quality Control (QC) Manager reports directly to the Project Manager and has authority to initiate a stop work order to correct quality concerns. If the work stoppage will occur for longer than one day, the CKY PM will meet with the NAVFAC Southwest RPM to resolve the issue.

The CKY project team will be in daily contact with the NAVFAC Southwest team regarding project progress and analytical results. This ensures timely discussion/review of data quality and interpretation, as well as identifying/deciding any areas that need further actions.

SAP Worksheet #7 -- Personnel Responsibilities Table
(UFP-QAPP Manual Section 2.4.3)

Name	Title/Role	Organizational Affiliation	Responsibilities
Brenda Reese	Lead Organization Project Manager	NAVFAC Southwest	Performs contractor oversight. Ensures project scope of work requirements are fulfilled. Oversees project cost and schedule. Acts as lead interface with regulators.
Narciso Ancog	QA Officer	NAVFAC Southwest	Reviews and approves SAP and all amendments to the SAP. May audit or review any activity that may affect project quality. Has authority to stop work if non-conformance is identified.
Howard Wittenberg	Project Manager	CKY Incorporated	Manages all project activities. Acts as primary contact between client RPM and contractor. Ensures adherence to quality requirements of contract and plans. Reviews and signs progress reports.
Carol Moldoveanu	Quality Program Manager	CKY Incorporated	Responsible for overall QA. Develops and maintains a comprehensive QA program. Is responsible for audits, reviews of work performed, and recommendations to project personnel regarding quality. Prepares SAP. Provides oversight and assurance as to compliance with the SAP.
Noah Rivera	Project QC Manager	CKY Incorporated	Directs field sampling and field QC procedures in accordance with this SAP. Has authority to initiate a work stoppage to correct quality concerns.
Tim Theisen	Project Chemist	CKY Incorporated	Implements SAP. Coordinates with laboratory. Validates all field and laboratory analytic data. Implements CA when necessary.
Larry Pennock	Project Site Safety and Health Officer (SSHO)	CKY Incorporated	Has authority to initiate a work stoppage to correct safety concerns.
	Project Site Supervisor		Supervises all field work. Prepares weekly updates and monthly progress reports.
Cade Klock	Environmental sampler (and Data Manager)	CKY Incorporated	Collects onsite samples. Prepares chain-of-custody records. Performs field-screening tests.
Linda Scharpenberg	Laboratory Project Manager	Calscience.	Provides oversight and assurance as to compliance with the SAP for off-site chemical analyses.
Linda Rauto	Operations Manager/Sr. Chemist	Laboratory Data Consultants (LDC)	Provides independent data review and validation.

Calscience = Calscience Environmental Laboratories, Inc.
CKY = CKY Incorporated
DTSC = California Department of Toxic Substances Control
EPA = United States Environmental Protection Agency
NAVFAC = Naval Facilities Engineering Command
QA = Quality Assurance
QC = quality control
QPM = Quality Program Manager
RPM = Remedial Project Manager
RWQCB = Regional Water Quality Control Board
SSHO = Site Safety and Health Officer

SAP Worksheet #8 -- Special Personnel Training Requirements Table

(UFP-QAPP Manual Section 2.4.4)

Only routine OSHA 40-hour HAZWOPER training is required for personnel working on this project. No specialized training is required.

SAP Worksheet #9 -- Project Scoping Session Participants Sheet
(UFP-QAPP Manual Section 2.5.1)

KICKOFF MEETING MINUTES
CKY Incorporated
CONTRACT N62473-09-D-2626 CTO 0004

Long Term Monitoring, Site 40 and Five Year Review, Sites 40 and 70 at Naval Weapons Station Seal Beach, California

DEPARTMENT OF THE NAVY
NAVFAC SW, DESERT IPT
SAN DIEGO, CALIFORNIA 92132
MEETING PLACE: Naval Weapons Station Seal Beach
DATE and TIME: September 26, 2011, 10:00

I. Project Team Introductions

Name	Role/Position
Brenda Reese	Navy Remedial Project Manager (RPM)
Crystal Irvin**	Contract Specialist
Pei-Fen Tamashiro	Activity POC
Scott Kehe**	ROICC
Jerry Huang*	CKY Program Manager
Howard Wittenberg	CKY Project Manager
Carol Moldoveanu*	CKY Quality Control Manager

* attendance by teleconference
** Not present

a. Communication with Navy/Among Team Members – The CKY PM will be main point of contact for the Navy. The CKY PM will have daily contact with the CKY field team during site work and will communicate regularly with Navy RPM with field status updates.

The Navy will assist in overseeing the CKY safety program for fieldwork; however, CKY is responsible for all safety aspects while in the field. The CKY PM or designee will submit daily production and quality control reports to project team via email. The CKY PM will coordinate with Navy for access to the site before conducting fieldwork.

NWSSB is access controlled, CKY will need to get RAPIDGate passes for all project personnel required to be onsite.

A pre-construction meeting will be held prior to the start of field activities.

II. Contractual

a. Project is subject to all terms and conditions of the master EMAC contract and the awarded contract task order dated 08 September 2011.
b. Only written changes are allowed to authorize changes to the contract, verbal change order are not allowed

c. Invoice packages to be submitted through WAWF (only invoice to be submitted in WAWF)

III. Background and Scope of Work by Work Element (WE)

Background – IRP Site 40 includes a concrete pit located in Building 240, the Locomotive Shop and a gravel area located north of and adjacent to the building. The concrete pit formerly provided a collection point for oil and solvents spilled during locomotive maintenance activities. Until 1978, oil that collected in the pit discharged into the gravel area through a drainpipe. The pipe was plugged in 1978. Currently, the area north of Building 240 is paved and the area northwest of Building 240 is unpaved. Four railroad spurs terminate in Building 240 and provide locomotive access to the repair shop.

Site 70 was the former NASA Research Testing and Evaluation Area, a rocket engine test facility located just south of Westminster Blvd and east of Seal Beach Blvd. Groundwater at the site is impacted by the past use of chlorinated solvents, primarily TCE, with dissolved phase chlorinated solvents and possible DNAPL reported. Groundwater impacts extend vertically from the water table near the source area to approximately 165 feet below ground surface near the down gradient end of the dissolved-phase plume. Horizontally, impacts extend approximately 4000 feet southeast of the source area.

a. Overall Scope and Objective – This task order is to complete long term monitoring at Site 40 and prepare a Five-Year Review for Sites 40 and 70. There will be two monitoring events under this contract task order; one at the end of this year and one a year later or as directed by the RPM.

b. WE 1 – Project Management / Meetings

   CKY will provide all project management, infrastructure, and contract administrative support as required to successfully complete the project. This CTO involves attendance of this kickoff meeting as well as RPM/RAB meetings held quarterly. CKY will attend all RPM meetings as required by the RPM and up to 3 RAB meetings. The CKY PM will provide advance copies of meeting agendas, figures, and presentations as requested by the RPM, and will submit meeting minutes in an electronic format within 10 days of the meeting.

   CKY will provide monthly project reports with schedule updates, activities performed, billing status, technical issues, and planned work. The CKY PM will communicate with the Navy RPM regularly to ensure that the Navy is apprised of the project status, schedule, challenges, and recommended solutions. During fieldwork, weekly coordination meetings will be held via teleconference to discuss project field activities and issues.

c. WE 2 – Plans

   CKY will prepare a Work Plan that will include a QC Plan and a Sampling and Analysis Plan. CKY will also develop a site specific Accident Prevention Plan including Site Safety and Health Plan and Activity Hazard Analysis. The APP shall reference NWS Seal Beach's enrollment in OSHA's Voluntary Protection Program.

Each submittal will be prepared and submitted to the Navy for review and approval. The Sampling and Analysis Plan will be submitted directly to the Navy QAO (Nars) for review and approval. The Accident Prevention Plan will be submitted to the NAVFAC SW Safety Reviewer (Almario) and the Navy and Marine Corps Public Health Center (Don Coons) for review and comment. The RPM and ROICC will approve RTCs to the safety plans.

d. WE 3 – Field Work

LTM at Site 40

The annual groundwater monitoring program will be continued and wells selected for monitoring by natural attenuation will be assessed for optimization. These include wells that do not exceed the Target Cleanup Goal for two events. This project includes monitoring up to 19 wells, 14 of which have been pre-determined. The remaining wells will be selected during the development of the Work Plans and SAP.

Wells for which all contaminants of concern fall below TCGs for two consecutive monitoring events will be requested to be removed from the program. Conversely if wells are increasing in concentration down gradient wells may be added to the program. CKY will analyze sample results and may request reducing the analytical suite to eliminate analyses that are not providing useful data.

Soil Gas and Surface Emissions Monitoring

Annual soil gas and surface emission monitoring will be performed at the points identified in the RFP as well as up to 5 additional sample points. Sampling consists of field measurements as well as the collection of soil gas samples.

e. WE 4 –Reports

CKY will prepare and submit an LTM Summary Report similar to the one provided as reference in the RFP for each of the two monitoring events. The reports will be prepared in internal draft, draft, and final versions. CKY will also prepare a Five-Year Review document for Sites 40 and 70.

IV. Project Schedule

The project was awarded on 08 September 2011 and the period of performance is 600 days. The contract completion date is 30 April 2013. A project schedule is being developed and will be submitted separately.

V. Other Notes

1. Base related questions including access go directly to the Activity POC, not base security
2. Copy Navy RPM and Activity POC on all project related correspondence
3. Work trucks are to use the Westminster gate for base access
4. RPM meetings are held the 2nd Tuesday of the quarter
5. The 5-Year Review Report will encompass activities from 2005-2010
6. A site walk was performed by the Navy RPM, Activity POC, and CKY PM

SAP Worksheet #10 – Problem Definition
(UFP-QAPP Manual Section 2.5.2)

The groundwater at Installation Restoration Program (IRP) Site 40 remains with residual contamination following several remedial response actions, including enhanced in site bioremediation (EISB). The initial primary chemicals of concern (COCs) for IRP Site 40 groundwater were two chlorinated ethenes (CEs), tetrachloroethene (PCE) and trichloroethene (TCE). Because the biological degradation of PCE and TCE results in the formation of dichloroethene (DCE) and vinyl chloride (VC), these chemicals are also considered COCs. The Target Cleanup Goals (TCGs) for IRP Site 40 groundwater were developed based on an analysis of Applicable or Relevant and Appropriate Requirements (ARARs) (Navy 2004) and are listed in Worksheet #10, Table 10-1. These TCGs support the Remedial Action Objective (RAO) of restoring the shallow aquifer underlying NAVWPNSTA Seal Beach as a potential drinking water supply to the extent practical. The values listed in Table 10-1 are federal Maximum Contaminant Levels (MCLs) for drinking water promulgated by EPA and California MCLs established by the Department of Health Services, as documented in the Record of Decision (ROD) (Navy 2004). The attainment area for this remedial action is defined as the footprint of the PCE plume at IRP Site 40 at the beginning of the project as shown on Figure 3.

This Worksheet presents the conceptual site model (CSM) for IRP Site 40.

Site Location and Background

NAVWPNSTA Seal Beach is located about 30 miles south of the Los Angeles urban center and consists of approximately 5,000 acres of land along the Pacific Coast within the city of Seal Beach in Orange County, California (Figure 1). NAVWPNSTA Seal Beach is bordered on the southwest by Anaheim Bay, on the north by Interstate 405 (San Diego Freeway), on the east by Bolsa Chica Road, on the west by Seal Beach Boulevard, and on the southeast by a flood control channel. Originally commissioned in 1944, NAVWPNSTA Seal Beach provides fleet combatants with ready-for-use ordnance. Figure 2 shows a map of NAVWPNSTA Seal Beach, including the location of IRP Site 40.

Site Historical Operations

Originally commissioned in 1944, NAVWPNSTA Seal Beach provides fleet combatants with ready-for-use ordnance. IRP Site 40 (Figure 3) includes a concrete pit located in the Locomotive Shop (Building 240) and a gravel area located north of, and adjacent to, the building. The concrete pit formerly provided a collection point for oil and solvents spilled during locomotive maintenance activities. Until 1978, oil that collected in the pit discharged into the gravel area through a drainpipe. The pipe was plugged in 1978.

Site Environmental Setting

Physical Setting and Climate

NAVWPNSTA Seal Beach is located within the Los Angeles-Orange County coastal plain. This northwest-trending structural basin is approximately 50 miles long and 20 miles wide with deposits as much as 20,000 feet thick. Basin morphology was developed through the mechanisms of folding, faulting, erosion, and fluctuating sea levels (JEG 1994).

Most of NAVWPNSTA Seal Beach lies on predominantly flat alluvial deposits in the southeastern portion of the Los Angeles Basin. The Los Angeles Basin is bounded on the north by the Santa Monica Mountains; on the northeast by the Repetto and Puente Hills; on the east and southeast by the Santa Ana Mountains and the San Joaquin Hills; and on the south, southwest, and west by the Palos Verdes Hills and the Pacific Ocean. The land at NAVWPNSTA Seal Beach slopes evenly from approximately 20 feet above sea level in the northwestern part of NAVWPNSTA Seal Beach to sea level in the tidal flats of the Seal Beach National Wildlife Refuge (SBNWR) in the southeast (Figure 2).

The area climate is classified as a marine-influenced Southern California coastal region with mild winters that average 52 degrees Fahrenheit (°F) and summers that average 68 °F. Temperature ranges from winter lows in the 30s °F to summer highs in the 90s °F. Annual precipitation averages 12.5 inches, with approximately 90 percent occurring between the months of November and April. Although precipitation is low, a high humidity level is sustained because of the proximity of the Pacific Ocean (JEG 1994). Prevailing winds average 3.8 miles per hour from the west. Occasional strong, dry winds from the northeast, known as the "Santa Anas," occur in the fall, winter, and early spring (JEG 1994).

Site Geology

The geologic units observed at IRP Site 40 are as follows (BNI 1999):

- Surficial soils – Silty sands and clayey sands, as well as sandy clay and clays, with considerable lithological variation laterally
- First sand unit – Sands to silty sands within a few feet of the water table extending to 7.5 to 10 feet below ground surface (bgs)
- Second sand unit – Saturated sands to silty sands at 9 to 21 feet bgs, extending to 28 to 41 feet
- Third sand unit – Saturated sands to silty sands at 38 to 52 feet bgs, depending on the location
- Lower permeability intervals containing clay, silty clay, and silt separate the coarser-grained units noted above.

Site Hydrogeology and Water Quality

The groundwater underlying the NAVWPNSTA is within the Lower Santa Ana River Groundwater Basin (Santa Ana Pressure Sub-basin) (RWQCB 1995). Beneficial uses of groundwater within the Santa Ana Pressure Sub-basin include municipal and domestic supply, agricultural, industrial service supply, and industrial process supply. Currently, shallow groundwater underlying IRP Site 40 does not serve as a water source for any of the beneficial uses designated in the Water Quality Control Plan, Santa Ana River Basin (Basin Plan) (RWQCB 1995).

Groundwater levels in the principal freshwater zone fluctuate from year to year because of variations in pumping, infiltration, and recharge. Recharge to this aquifer is primarily from unconfined upgradient areas and from unlined rivers that are hydraulically connected to the aquifer. Seasonal variations occur with highs in the wet winter months and with lows in the dry summer months when large quantities of water are used for irrigation (JEG 1994).

Based on a tidal influence study from the Extended Removal Site Evaluation (ERSE), water levels are locally tidally influenced (BNI 1999). The data indicated that the water table occurred at an approximate depth of 8 to 9 feet bgs. There are no continuous shallow confining layers evident at IRP Site 40.

The principal freshwater body tapped to supply NAVWPNSTA Seal Beach is a large confined aquifer occupying two zones. The first zone is about 75 to 200 feet deep and saline; and it is no longer used for water supply. The second zone is approximately 250 to 1,000 feet deep. This aquifer is the primary water supply source both to the NAVWPNSTA and neighboring cities (JEG 1994).

Previous Response Actions

Previous response actions completed at the Site include the following:

The selected remedy for groundwater at IRP Site 40 is EISB, monitored natural attenuation (MNA), and land use controls (LUCs). EISB involves stimulation of biological reductive dechlorination by addition of a suitable substrate – initially an aqueous solution of sodium lactate. Detailed explanations of the process and mechanisms are provided in the Remedial Action Work Plan (TtEC 2005) and the prior EISB performance monitoring report (TtEC 2006a). Based on pilot test results, the remedy also included bioaugmentation using KB-1, a commercially available CE-respiring bacterial culture containing *Dehalococcoides* spp. [Dhc]). In addition, the remedy was optimized using a slow release lactate based substrate to help in treating areas where delivery of the sodium lactate solution proved problematic. Activities conducted as part of the EISB process are described in more detail in the Final Comprehensive Performance Monitoring Report (TtEC 2011).

The following is a list of the major field activities performed through September 2005 as part of the EISB remedial action:

- Installation of groundwater monitoring and injection wells, and soil gas/vapor monitoring wells and probes
- Baseline sampling and analysis of groundwater samples
- Biostimulation (sodium lactate injection) Round 1
- Biweekly and monthly field testing and monthly sampling and laboratory analysis of groundwater samples
- Bioaugmentation Round 1 (recirculation of Dhc-laden water from a well which had been bioaugmented previously)
- Biostimulation Round 2 (sodium lactate injection)
- Bioaugmentation Round 2 (injection of KB-1)

The following are the major field activities performed between October 2005 and May 2010 as part of the EISB remedial action:

- Periodic monitoring of groundwater (water level measurement, groundwater sampling and analysis, soil gas sampling and analysis, and surface emissions monitoring)
- Optimization evaluation

- Hydrogen Release Compound (HRC®) injection (Round 1)
- Investigation beneath Building 240
- HRC® injection, Round 2

Current and Potential Future Land Use

NAVWPNSTA Seal Beach encompasses about 5,000 acres. Explosives safety quantity distance (ESQD) arcs that restrict development to specific permitted uses cover approximately 75 percent of the 5,000 acres. Two agricultural outleases totaling approximately 2,000 acres are used for farming (irrigated and dry land farming) and maintenance. Approximately 100 acres of land is currently being leased for oil production (including Oil Island). In addition to the outleased land, the SBNWR, a major biological resource, encompasses approximately 911 acres. The areas covered by the ESQD arcs overlap the agricultural outlease areas and portions of the SBNWR.

Other land uses on NAVWPNSTA Seal Beach include residential, ordnance transfer operations, weapons production/evaluation, quality assurance, storage (inert and explosive), and administration/community support.

Land to the south, southwest, northwest, north, and northeast of NAVWPNSTA Seal Beach is used for residential purposes. Boeing Space and Communications Group is the only major commercial/industrial use bordering the station on the west. The city of Seal Beach Police Department also borders the station on the west. The Bolsa Chica Channel borders NAVWPNSTA Seal Beach to the south and east. This channel is fenced in and discharges directly to Anaheim Bay. The Sunset Aquatic Park borders the station to the south and is situated on a 63-acre parcel within the corporate boundaries of the city of Seal Beach. The park is a commercial development consisting of 260 boat slips, park facilities, a marine repair yard, a boat launch, the harbor patrol office, and public picnic areas. Future land uses for the adjacent cities include commercial/industrial, limited residential, and open land uses.

NAVWPNSTA is an active base. Land use is expected to remain the same in the foreseeable future. NAVWPNSTA Seal Beach is fenced, and access is restricted/controlled; therefore, off-station populations would not likely be directly exposed to on-station chemicals of potential concern (COPCs).

Nature and Extent of Contamination

IRP Site 40 is contaminated primarily with CEs. The site has a region of soil contamination and a groundwater contaminant plume extending to approximately 66 feet bgs. The lateral and vertical extent of the plume has been delineated. The groundwater gradient is relatively flat, and movement of the plume in groundwater is relatively slow. The sediments span a wide range of lithologies and grain sizes (BEI 2000).

Previous investigations identified the potential sources of contamination at IRP Site 40. In 1995, Jacobs Engineering Group Inc. (JEG) conducted a Site Inspection (SI) of 16 sites within Operable Unit 4, including IRP Site 40 (JEG 1995). The SI identified a release to groundwater of the COPCs carbon tetrachloride and PCE (JEG 1995). The SI recommended conducting a Focused Site Inspection (FSI). The FSI report concluded that a chlorinated hydrocarbon plume containing PCE, TCE, and cis-1,2-DCE at levels exceeding federal MCLs for drinking water exists beneath the site (JEG 1996). The FSI delineated the lateral extent of the plume in the

shallow groundwater as approximately 270 feet by 200 feet, but did not determine a vadose zone source.

Bechtel National, Inc. further investigated soil contamination at IRP Site 40 during the ERSE (BNI 1999). The ERSE concluded that the potential for continued leaching of soil COPCs to groundwater is low to negligible. Releases of chlorinated compounds migrated through the soil, resulting in a groundwater plume containing primarily PCE with lesser concentrations of TCE, cis-l,2-DCE, trans-1,2-DCE, and chloroform. However, concentrations of these compounds in the vadose-zone soil indicated most of the original releases had already leached to groundwater or volatilized to the atmosphere (BNI 1999). The ERSE concluded that the potential for transport of soil COPCs through runoff was low to negligible. The ERSE further concluded that human health risk for soils was below the National Contingency Plan (NCP)-defined departure point, and site development should not adversely impact ecological receptors (BNI 1999).

The lateral and vertical extent of the groundwater contaminant plume was delineated (BNI 1999). The main contaminant, PCE, was present at depth intervals of less than 20 feet, 20 to 45 feet, and greater than 45 feet bgs. See the Feasibility Study (FS) (BEI 2000) for more details.

Contaminant Fate and Transport

The ERSE (BNI 1999) concluded the following:

- The potential for continued leaching of CEs from soil to groundwater is low to negligible.
- There is a negligible potential for CEs to have migrated deeper than that determined by the ERSE sampling. Downward migration of CEs apparently has been limited to approximately 66 feet bgs (BNI 1999).
- A slight downward gradient was indicated by the typical head difference of 0.1 to 0.2 foot at well pairs in October 1997; thus the potential for downward migration exists. Based on the absence of significant concentrations of CEs below the second interbedded unit, the slight downward gradient has not caused an impact at lower intervals.
- Significant biodegradation of PCE has occurred, and conditions are conducive to continued degradation; therefore, natural attenuation will continue to reduce existing CE concentrations.
- The potential for the CE plume to reach the SBNWR boundary at concentrations exceeding acceptable levels is low because of lithologic controls on groundwater flow and the apparent degradation taking place.

The ERSE concluded that no complete exposure pathway exists between chemicals in groundwater and ecological receptors at IRP Sites 40. Thus, chemicals reported in groundwater were not evaluated further for ecological risk. For the human-health screening risk assessment, COPCs were screened by comparing their maximum reported concentrations in soil and groundwater with concentrations representing a level of acceptable risk. The basic tenet of this approach is that the risk presented by a given concentration of a chemical is acceptable when it does not exceed the concentration established by regulatory agencies. Detailed results for the human-health screening risk assessment are presented in the FS (BEI 2000) and summarized as follows for IRP Site 40.

The human-health risk screening for IRP Site 40 groundwater estimated a total cancer risk of 4.1 x 10^{-3} and a hazard index of 85, resulting primarily from PCE and TCE. Approximately 88 percent of the total cancer risk is from PCE, and 85 percent of the total hazard index is from PCE and TCE.

Conceptual Site Model

The site physical conceptual model (Figure 5) generally represents the location and assumed lateral continuity of the hydrostratigraphic units beneath the IRP Site 40 vicinity. The model incorporates the uppermost soil layer, approximately 80 feet bgs, which includes Late Pleistocene sediments of the Lakewood Formation. The model was developed during the ERSE (BNI 1999).

Step 1: State the Problem

Previous site investigations indicated that PCE, TCE, and DCE were present in groundwater at IRP Site 40 at levels exceeding state and federal MCLs, thus requiring remedial action. Remedial action was implemented and has reduced the levels of PCE and TCE to below TCGs in all wells. However, residual low levels of cis-1,2-DCE and VC remain in excess of TCGs, forming dilute plumes in the central and southeast portions of the site. Soil gas data suggest high concentrations of methane gas (a natural microbial by-product of substrate-enhanced anaerobic bioremediation) persist within the vadose zone at the site. High methane gas concentrations exceeding lower explosive levels in the vadose zone remain a health and safety concern for any subsurface and intrusive activities within the site.

Question 1: What is the environmental question that is being answered?

Are concentrations of COCs in groundwater below TCGs?

TABLE 10-1
TARGET CLEANUP GOALS FOR IRP SITE 40 GROUNDWATER
(micrograms per liter)

Analyte	Federal Maximum Contaminant Level [a]	California Maximum Contaminant Level [b]	Controlling ARAR
cis-1,2-dichloroethene	70	6	6
trans-1,2-dichloroethene	100	10	10
trichloroethene	5	5	5
tetrachloroethene	5	5	5
vinyl chloride	2	0.5	0.5

Notes:
[a] U.S. Environmental Protection Agency Safe Drinking Water Act, Title 40 *Code of Federal Regulations*, Part 141.
[b] *California Code of Regulations*, Title 22, Section 64439, Requirements, and Section 64444, Maximum Contaminant Levels.

Abbreviations and Acronyms:
ARAR – applicable or relevant and appropriate requirement
IRP – Installation Restoration Program

SAP Worksheet #11 -- Project Quality Objectives/Systematic Planning Process Statements (UFP-QAPP Manual Section 2.6.1)

This worksheet documents the development of project quality objectives (PQOs) by providing responses to the following critical questions.

Step 2: Identify the Goal of the Study

Question 2: What are the Project Action Limits (PALs)?

PALs for this site are the TCGs as documented in the ROD and shown in Table 10-1.

Question 3: What will the data be used for?

Analytical data collected as part of this investigation will be used to evaluate CE contamination at the Site.

Decisions:

- Are the concentrations of CEs in an individual well less than the TCGs for two consecutive monitoring events?
- Are the concentrations of CEs in all wells that have been monitored for MNA less than the TCGs for at least 1 year?

Step 3: Identify Information Inputs

Question 4: What types of data are needed?

The information inputs that will be used to accomplish the goals of the study are as follows:

- Validated chemical data from previous investigations; and
- Validated chemical data obtained during this investigation. Groundwater analysis will include volatile organic compounds (VOCs), geochemical parameters (anions, cations, total dissolved solids, chemical oxygen demand, and total organic carbon), dissolved gases, and Dhc. Soil gas analysis will include methane and VOCs.

Question 5: Are there any special data quality needs in order to support environmental decisions?

Laboratory reporting limits should meet the PALs identified in Worksheet #15.

Step 4: Define the Boundaries of the Study

Question 6: Where, when, and how should the data be collected/generated?

The specific samples to be collected define the physical boundaries for this study and are set forth in Worksheet #18 and on Figures 6, 7 and 8 of this SAP. Vertical study boundaries include: (1) collecting groundwater samples from existing monitoring wells that are screened up to 60 feet bgs; and (2) collecting soil gas samples from existing vapor and groundwater monitoring wells that are screened up to 60 feet bgs.

The temporal boundary is defined by the time to complete the investigation and assumes adherence by all involved parties to the schedule presented in this SAP in Worksheet #16. The

first round of monitoring is scheduled for December 2011, and the second round is scheduled to occur in December 2012. As stated in Worksheet #14, soil gas sampling will not be performed during or within 5 days of a significant rain event (1/2 inch or greater) or during passage of weather frontal systems. No wildlife breeding seasons affect the project schedule.

Sampling methodology is described in Worksheet #14.

Step 5: Develop the Analytic Approach

List the PQOs in the form of if/then qualitative and quantitative statements:

If concentrations of CEs in an individual well are less than the TCGs for two consecutive monitoring events, then long-term monitoring for that well may be discontinued (with regulatory concurrence); else, the well will continue to be included in the long-term monitoring program.

If concentrations of CEs in all wells that have been monitored for MNA are less than the TCGs for at least 1 year, then the Site may be recommended for "no further action"; else, the long-term monitoring program will be continued.

TGCs for this project are listed in Worksheets #10 (Table 10-1) and #15.

Step 6: Specify Performance or Acceptance Criteria

Statistically derived limits on sampling design error are not quantifiable because a judgmental sampling design is being followed. The number and types of samples to be collected are based on specific site details and previous sampling locations and results (see Worksheet #17).

To maximize data comparability and to minimize the sampling error, groundwater and soil gas sampling will be conducted using field sampling and processing methods as described in Worksheet #14. To limit decision errors, published analytical method and laboratory-specific performance requirements will be the primary determiners of data quality objectives (DQOs) for precision and accuracy.

Step 7: Develop the Plan for Obtaining Data

The progress of the MNA will continue to be monitored by performance of the following activities:

- Collecting groundwater samples from 10 wells which currently do not meet the ROD-specified criterion of not exceeding a TCG for over one year and from 7 additional wells deemed necessary to assess plume dynamics.
- Analyzing the groundwater samples for VOCs, field parameters, geochemical parameters, dissolved gases, and Dhc.
- Collecting soil gas samples at 8 wells that had high concentrations of methane.
- Analyzing the soil gas samples for VOCs and methane.
- Collecting field measurements for methane, carbon dioxide, carbon monoxide, oxygen, and hydrogen sulfide at 17 wells.
- Collecting field measurements for methane from surface emissions at areas within IRP Site 40, inside Buildings 240 and 249, and inside the manholes located within the Site.

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SAP Worksheet #12 – Measurement Performance Criteria Table
(UFP-QAPP Manual Section 2.6.2)

12.1 Field Quality Control Samples, Soil Gas

QC Sample	Analytical Group	Frequency	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
Co-located Field Duplicate	Methane VOCs	10%	Precision – Overall	NA	S + A
Ambient air blank		1 per day	Accuracy	No quantitative criteria	S
Matrix spike/matrix spike duplicate	VOCs	5%	Accuracy/Bias	RPD < 30% when results ≥ LOQ for both replicates	A

RPD = relative percent difference; LOQ = limit of quantitation; PQL = project quantitation limit; QC = quality control; VOC = volatile organic compound

12.2 Field Quality Control Samples, Water

QC Sample	Analytical Group	Frequency	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
Co-located Field Duplicate	all	10%	Precision – Overall	NA	S + A
Matrix spike/matrix spike duplicate		5%	Accuracy/Bias	RPD < 30% when results ≥ LOQ for both replicates	A
Equipment rinsate blank		1 per day	Accuracy	No target analytes > PQL Goal	S
Trip blank	VOCs	1 per cooler	Accuracy	No target analytes > PQL Goal	S

RPD = relative percent difference; LOQ = limit of quantitation; PQL = project quantitation limit; QC = quality control; VOC = volatile organic compound

SAP Worksheet #13 -- Secondary Data Criteria and Limitations Table
(UFP-QAPP Manual Section 2.7)

Secondary Data	Data Source (originating organization, report title and date)	Data Generator(s)	How Data Will Be Used	Limitations on Data Use
Results from previous investigations, historical information regarding locations and use, site maps showing locations of previous abatement activities and sampling.	Final Record of Decision/Remedial Action Plan, Operable Unit 4, IRP Site 40, Naval Weapons Station Seal Beach, Seal Beach, California. May 2004.	Department of the Navy	For determination of chemicals of concern, areas of concern, and extent of contamination.	none
	Final Remedial Design/Work Plan, Enhanced In Situ Bioremediation Installation Restoration Program Site 40 (Concrete Pit/Gravel Area), Naval Weapons Station Seal Beach, Seal Beach, California. February 24, 2005.	Tetra Tech EC, Inc.	For description of investigative procedures.	none
	Final Comprehensive Performance Monitoring Report (October 2005 Through May 2010), Full-Scale Enhanced In Situ Bioremediation Remedial of Chlorinated Volatile Organic Compounds, Installation Restoration Program Site 40, Naval Weapons Station Seal Beach, Seal Beach, California. March 8, 2011.		For description of investigative procedures and to guide sample locations.	none

SAP Worksheet #14 -- Summary of Project Tasks
(UFP-QAPP Manual Section 2.8.1)

The following sections list the sampling procedures and sample handling protocols to be used for sampling activities for the long-term monitoring program at NAVWPNSTA Seal Beach. The soil gas sampling procedures are in accordance with DTSC's "Draft Advisory – Active Soil Gas Investigations," (CalEPA 2010). Worksheet #17 describes the sampling design for this project. Worksheet #19 lists the sample containers, preservatives, and holding time requirements for each analytical method. Worksheet #22 lists the calibration, maintenance, testing, and inspection requirements for field equipment.

Pre-sampling Tasks:

Prior to sampling, field personnel will read all necessary work plans and health and safety plans (HASPs) and obtain any specialized training required. Field supplies will be ordered and laboratories will be notified of upcoming sampling events. Site access and or disturbance permits will be obtained, if necessary.

Rainfall or barometric pressure fluctuations may negatively affect soil gas sampling (CalEPA 2010). Therefore, soil gas sampling should not be conducted during or within 5 days of a significant rain event (1/2 inch or greater) or during passage of weather frontal systems.

Investigation Field Activities

Field Documentation

Documentation procedures are used to facilitate the tracking of field activities as part of the data management process. The level of detail recorded in the field will allow for the reconstruction of a given work activity by a qualified peer, without the aid of the originator. Written field documentation is required for this project, and will consist of field logbooks and field forms. Controlled, pre-paginated, and permanently bound logbooks will be used to record field observations and measurements (i.e., sample ID numbers, chain-of-custody record numbers, and significant observations and/or events) to provide a permanent record of daily field activities. The project name, project number, site location, sampling event, project leader, and the telephone number and address of the business office will be listed in each field logbook in permanent, indelible ink. Corrections will consist of single line-out deletions that will be initialed and dated by the person making the correction. All entries will be signed and dated, and the remaining space on each page will be crossed out. Written descriptions of field activities will be objective, factual, and free of personal opinions.

Field documentation, including field logbooks, field sampling forms, and chain-of-custody records, will be archived for a period of not less than 10 years. Field team members responsible for recording daily activities will be familiar with the requirements of this section.

More details on the sample handling system and sample custody requirements are provided in Worksheets #26 and #27, respectively.

Soil Gas Sampling

For each probe, the well head and entire sampling train (valves, tubing, fittings, laboratory-provided soil vapor manifold, gauges and SUMMA™ canister) will be placed in an enclosure (i.e., shroud); and leak testing will be conducted in accordance with the California Environmental Protection Agency (CalEPA) Advisory – Active Soil Gas Investigation (CalEPA 2010). Helium, used as a tracer compound for leak testing, will be introduced into the shroud and monitored for concentration stability using a hand-held helium detector. The helium concentration maintained in the shroud (approximately 20 to 30 percent) will be at least 10 percent or two orders of magnitude higher than the reporting limit of the laboratory helium analysis and/or field meter to provide sufficient resolution.

Helium screening will be performed both in the laboratory and in the field. On site helium screening will be conducted by drawing soil gas into a Tedlar bag via a lung-box, and screening the contents of the bag using a helium meter. If leaks are detected in real time, corrections to the fittings and/or seals will be made prior to collection of a sample for laboratory analysis.

Purge volume testing will be conducted to ensure that stagnant and/or ambient air is removed from the sampling system. Purging will consist of removing approximately three volumes of stagnant soil gas using an air pump with an adjusted flow rate of 100 cubic centimeters per minute; and the purge volume will be calculated based on the dimensions of the above-ground gauges, tubing, sampling equipment, and below-ground tubing. Following purging, soil gas samples will be collected in 1-liter SUMMA™ canisters with a laboratory-provided flow regulator (combined with a laboratory-provided soil vapor sampling manifold) set to approximately 200 milliliters per minute for a sampling period of approximately 4 minutes. Laboratory-supplied SUMMA™ canisters will be batch certified by the laboratory prior to field receipt.

<u>Soil Gas Field Testing</u>

Monitoring of the soil gas/vapor wells and probes will include field measurement for methane, hydrogen sulfide, oxygen, carbon dioxide, and carbon monoxide concentrations. An explosive gas meter (Landtec Model GEM 2000 Plus) will be used for measuring these field parameters in parts per million by volume (ppmv). A photoionization detector instrument will be used to detect VOC concentrations in parts per million (ppm) for worker safety. The instruments will be equipped with pumps to allow samples to be drawn through a tube connected to the well sampling port. The following procedures will be used for soil gas field testing.

Check probe condition and structural integrity and suitability for monitoring. After the probe is inspected, connect a magnahelix vacuum pressure gauge to it to check for pressure in inches of water. If the probe is influenced by negative pressure, then it should not be sampled with the GEM 2000 because the machine could be damaged by overworking to overcome the negative pressure, and it may not detect gas at the correct concentration, even if there is some being generated and migrating. All probes will be purged for 30 seconds before connecting the GEM 2000 for monitoring.

(Note: Prior to taking any reading, allow the GEM 2000 to warm-up at least 5 minutes. This will stabilize the instrument and any internal gas-measurement detectors.)

Once purging is complete, the following procedures should be followed at each gas monitoring point:

1. Record the vapor well or probe number identification and time of reading
2. Open the sample port to the probe
3. Connect the GEM 2000 flexible intake tube assembly to the probe
4. Allow the instrument to take the sample until there is a steady reading for the gas concentration on the display for 30 seconds
5. Record the percent methane, percent carbon dioxide, percent oxygen, percent carbon monoxide, percent hydrogen sulfide, and barometric pressure on the data sheet
6. Remove the GEM 2000 intake tube

Surface Emissions Testing

A GEM 2000 will be used for methane testing for surface emissions following the same basic procedures described above for soil gas testing. The instrument probe will be placed at the crack or about an inch above the crack or the surfaces being monitored. The probe will be held for at least 2 minutes or until the instrument shows steady readings. A site map will be used to record the field measurements.

Collection of Soil Gas Samples for Laboratory Analysis

Gas samples will be collected using evacuated SUMMA™ canisters, Teflon tubing, a "T" fitting, and the sampling train in accordance with DTSC procedures (CalEPA 2010) and described below. Samples will be analyzed by a Navy-approved and state-certified laboratory. The SUMMA™ canisters are "self-filling" vacuum samplers that draw in an air sample when they are opened); no sampling pumps will be required to fill the canisters. Pumps will be used to evacuate the Teflon tubing. Teflon tubing avoids the possibility of cross-contamination from sampling equipment, and the "T" fitting is used to collect two samples simultaneously (to facilitate duplicate sampling).

- After the system is purged of ambient air but before the pump is turned off, approximately 2 inches of the sampling line closest to the entrance port of the pump should be folded over itself and the tubing should be clamped to keep ambient air from reentering the system.
- To prevent ambient air from entering the canister during sample collection, ensure all connections are airtight.
- Ensure the connecting lines between the sample inlet and the canisters are as short as possible to minimize their volume. The flow rate into the canister should remain relatively constant over the entire sampling period.
- Measure the canister pressure reading, ambient air temperature, and ambient air pressure, and record the readings in the field logbook prior to sample collection.
- Open the canister pressure valve, which will allow the evacuated stainless-steel canister to draw in soil gas until the canister reaches ambient pressure.
- When the sampling valve on the canister shows that ambient pressure has been reached, close the sampling valve and remove the canister from the sampling line.
- Measure and record the post-sampling pressure reading on the canister pressure valve.
- Label the canister and its corresponding field datasheet with the sample number.

Groundwater Sampling

Groundwater samples will be collected from 17 existing groundwater monitoring wells (locations shown on Fig. 5 and wells listed on Worksheet #18). Before each well is sampled, organic vapor concentrations will be measured at the top of the well using a photoionization detector (PID) and recorded on the groundwater sampling sheets. Field staff will also measure and record the groundwater level at each well.

Groundwater samples will be collected in preserved volatile organic analysis (VOA) vials (for VOC and dissolved gas analyses), 250-milliliter amber bottles (for total organic carbon [TOC] analysis), and polyethylene bottles (for other geochemical parameters). The samples will be collected with a bladder pump, using low flow-rate micro-purge methodology as follows.

- Air line tubing will be attached to the air port on the top of the bladder pump; sample discharge tubing will be attached to the water port; and a safety cable will be secured to the bladder pump, if applicable based on the model;
- The pump will be lowered into the well to a depth corresponding to the approximate center of the saturated screen section;
- An air compressor will be connected to the pump controller and turned on to begin purging;
- The pump rate will be maintained at 200 to 500 milliliters per minute and adjusted such that drawdown in the well does not exceed 0.3 feet;
- Field indicator parameters (i.e., temperature, specific conductivity, dissolved oxygen, oxidation reduction potential, and pH) will be monitored during purging using a flow-through analytical cell or clean container;
- When the field parameters have stabilized (i.e., temperature and specific conductivity values remain within 3 percent, and pH remains within 0.1 units for three consecutive readings collected at 3- to 5-minute intervals), a groundwater sample will be collected by diverting flow from the discharge tubing directly into the sample container (i.e., VOA). Samples will not be collected from the discharge of a flow-through cell.

The samples will be shipped under chain-of-custody protocol to a California Environmental Laboratory Accreditation Program (ELAP) certified and/or Department of Defense (DoD) ELAP accredited analytical laboratory for analyses: VOCs, anions (sulfate, chloride, nitrate, nitrite), cations (calcium, iron, magnesium, potassium, sodium), total dissolved solids (TDS), chemical oxygen demand (COD), TOC, dissolved gases (methane, ethene, and ethane), and Dhc.

QA/QC Sampling

Field duplicates for the groundwater and soil gas samples will be collected at a minimum rate of 10 percent. In addition, an ambient air blank (for soil gas sampling) and an equipment rinsate blank (following equipment decontamination for groundwater sampling) will be collected once per day. A trip blank will accompany the container holding the water samples.

Equipment Decontamination

During sampling activities, field personnel will decontaminate non-disposable/non-dedicated sampling equipment and monitoring equipment after use. Field personnel will take appropriate

measures to decontaminate sample equipment at the beginning of each day and prior to use at each sample location to prevent cross-contamination. Decontamination will, in general, consist of rinsing with an Alconox® or equivalent solution and rinsing with deionized/distilled water. Water and soil generated during decontamination activities will be collected and managed as investigation derived waste (IDW).

Chain-of-Custody Documentation

A Chain-of-Custody Record Form creates an accurate written record that can be used to trace the possession and handling of the sample from the moment of its collection through analysis. A copy of the chain-of-custody form will be retained in the project files, while the original chain-of-custody form will accompany the sample or group of samples as they are transferred from one custodian to another.

A chain-of-custody form must be completed for each cooler and should include only the samples contained within that cooler. Complete separate forms for different levels of data packages required, i.e, use one form for samples that require Level III data packages and another form for samples that require Level IV data packages. For this project, select 10% of the samples of each media sampled and for each analytical method for Level IV data packages and specify Level III data packages for the remainder of the samples. When transferring possession of the samples, the individuals relinquishing and receiving will sign, date, and note the time on the chain-of-custody form. The chain-of-custody form is filled out as listed below:

- Enter header information (sample collection location, site, date, project number).
- Enter sample specific information (sample identification date and time of collection, matrix description, sample technique or type, container type, preservative in sample container, parameters or methods of analyses requested, level of data packages requested).
- Sign, date, and enter the time under the “Relinquished by” entry.
- Have the person receiving the sample sign the “Received by” entry. If shipping samples by a common carrier, print the carrier to be used in this space (i.e., Federal Express).
- If a carrier is used, enter the airbill number under “Remarks,” in the bottom right corner;
- Place the original (top, signed copy) of the Chain-of-Custody Record Form in a plastic zipper-type bag or other appropriate sample-shipping package. Retain the copy with field records.

The chain-of-custody form is completed using waterproof ink. Any corrections are made by drawing a line through and initialing and dating the change, then entering the correct information. Erasures are not permitted.

More detail regarding sample custody requirements is provided in Worksheet #27.

Management of IDW

The IDW generated during sampling activities will include the following:

Water: Liquid IDW will consist of wastewater generated during well sampling and decontamination of field sampling and monitoring equipment. Liquid IDW will be stored in labeled, steel, Department of Transportation (DOT)-approved 55-gallon drums. Waste

characterization samples will be collected for the purpose of profiling the wastewater for treatment, transportation, and disposal offsite. No permitting will be required.

Other Solid Waste: Other solid waste generated during sampling activities will include personal protective equipment (PPE), and miscellaneous trash. This waste will be disposed of as non-regulated solid waste.

Analysis Tasks

The performance of the analyses will adhere to the method specifications as well as the laboratory-specific standard operating procedures (SOPs) listed in Worksheet #23 and included in Attachment 1.

Gas samples will be analyzed for VOCs by full-scan gas chromatography/mass spectrometry (GC/MS) method EPA TO-I5. A sample aliquot will be withdrawn from the whole air sample in the SUMMA™ canister and passed through a mass flow controller and then either cryofocused by liquid argon or concentrated using a multisorbent bed. The focused air will then be flashheated through a hydrophobic drying system that removes water from the sample stream before analysis by GC/MS. EPA Method TO-15 will provide quantitation and speciation of the standard VOCs. The samples will also be analyzed for methane by American Society for Testing and Materials (ASTM) Method D-1946. ASTM D-1946 provides a QC check for field measurements collected using the methane meter.

Groundwater samples will be analyzed for VOCs by EPA Method 8260B; anions (sulfate, chloride, nitrate, nitrite) by EPA Method 300.0, cations (calcium, iron, magnesium, potassium, sodium) by EPA Method 6010B, TDS by Standard Method (SM) 2540C, COD by EPA Method 410.4, TOC by SM 5310B, dissolved gases (methane, ethene, and ethane) by Method RSK-175M, and Dhc by CENSUS quantitative polymerase chain reaction (qPCR).

Worksheet #15 documents the project-required reporting limits for this project. Worksheet #19 specifies sample volume, preservation, and holding time requirements for these methods. Worksheet #28 includes project-specific precision and accuracy goals for the methods.

Data Management and Review

Fixed laboratory data will be transferred from the laboratory to the Project Chemist in hard copy and electronic formats. Hard copies of the laboratory deliverables will be used to verify the accuracy of electronic data. The original hard copies of laboratory deliverables will then be stored in the office project file.

The laboratory will maintain and follow its own detailed procedures for laboratory record keeping for support of the validity of all analytical work. Each data package submitted to the Project Chemist will contain the laboratory's written certification that the requested analytical method was run and that all QA/QC checks were within established control limits on all samples, with exceptions noted. The Project Chemist will be responsible for ensuring fixed-lab data quality and effective data management and also assist in interpreting data.

Analytical results generated in electronic format by the laboratory will be delivered directly to an independent third-party contractor for data validation (90% at EPA Level III and 10% at EPA Level IV) in accordance with the validator's SOPs and EPA National Functional Guidelines (EPA 2008 and 2010) as appropriate for the analytical methods. The data validation strategy will

be consistent with Navy guidelines. The data reviewer is required to request any missing information needed from the laboratory. Elimination of the data from the review process is not allowed. All data will be qualified as necessary in accordance with established criteria. Data summary packages for Level III validation will consist of sample results and QC summaries, including calibration and internal standard data. Data summary packages for Level IV validation will consist of sample results, QC summaries, and all raw data associated with the sample results and QC summaries. Data validation will include review of the following: holding times, blanks, matrix spike/matrix spike duplicate samples, laboratory control samples and sample duplicates, field duplicate samples, calibration summary information, and laboratory reporting limits. Validated data will then be transmitted in electronic format and inputted directly to the CKY computer systems. Laboratory data will be reviewed and measured against the requirements of the approved SAP; and data validation reports will be reviewed to ensure that data are accurately reported in contract deliverables. After the field and laboratory sample data have been reviewed and validated, the data will be prepared in Navy Electronic Data Deliverable (NEDD) format and uploaded to the Naval Installation Restoration Information Solution (NIRIS) database in accordance with Environmental Work Instruction (EWI) #6 (NFECSW 2005).

Data Storage, Archiving, Retrieval, and Security will be managed as follows:

The project work plans, including this SAP, quarterly and annual reports, and all other documents that have legal bearing and were used to make decisions regarding the response actions for the project site, will be submitted to NAVFAC SW's CERCLA Administrative Record (AR) in accordance with EWI #4 (NAVFAC SW 2007). The AR is available for public review and is located at 1220 Pacific Highway, San Diego, CA. Three paper copies of each document, each with accompanying compact disc (CD), will be submitted: one unbound and 3-hole punched original for the official AR and two bound copies for the Information Repository. Each CD will have all the original source files for the entire document in native format (.doc, .xls, .dwg, etc.) plus one complete .pdf version (mirror image) of the entire document in the same page order and layout as the official original paper document except for raw laboratory data submitted in electronic format.

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SAP Worksheet #15 -- Reference Limits and Evaluation Table
(UFP-QAPP Manual Section 2.8.1)

Matrix: Soil Gas
Analytical Group: VOCs

Analyte	CAS number	Project Action Limit[a] (ppb/v)	Project Action Limit Reference [a]	Project QL Goal (ppb/v)	Laboratory-specific [b] (ppb/v)		
					LOQ	LOD	DL
1,1,1-trichloroethane	71-55-6	1,000,000	residential RBC	500,000	0.5	0.2	0.0996
1,1,2,2-tetrachloroethane	79-34-5	18	residential RBC	9.0	0.5	0.2	0.1060
1,1,2-trichloro-1,2,2-trifluoroethane	76-13-1	13,800,000	residential RBC	6,900,000	0.5	0.2	0.1001
1,1,2-trichloroethane	79-00-5	67	residential RBC	34	0.5	0.2	0.1214
1,1-dichloroethane	75-34-3	670	residential RBC	335	0.5	0.2	0.1028
1,1-dichloroethene	75-35-4	92,000	residential RBC	46,000	0.5	0.2	0.1096
1,2,4-trichlorobenzene	120-82-1	1,610	residential RBC	805	2.5	1.25	0.7221
1,2,4-trimethylbenzene	95-63-6	2,800	residential RBC	1,400	1.25	0.5	0.3265
1,2-dibromoethane	106-93-4	15.1	residential RBC	8.0	0.5	0.2	0.1113
1,2-dichlorobenzene	95-50-1	92,000	residential RBC	46,000	0.5	0.2	0.1101
1,2-dichloroethane	107-06-2	51	residential RBC	26	0.5	0.2	0.0948
1,2-dichloropropane	78-87-5	107	residential RBC	54	0.5	0.2	0.1141
1,3,5-trimethylbenzene	108-67-8	2,800	residential RBC	1,400	0.5	0.2	0.1680
1,3-dichlorobenzene	541-73-1	51,000	residential RBC	25,500	0.5	0.2	0.1301
1,4-dichlorobenzene	106-46-7	97	residential RBC	48	0.5	0.2	0.1345
2-butanone	78-93-3	2,300,000	residential RBC	1,150,000	0.5	0.2	0.0990
2-hexanone	591-78-6	2,300,000 [c]	residential RBC	1,150,000	2.5	1.25	0.5175
4-ethyltoluene	622-96-8	2,300,000 [d]	residential RBC	1,150,000	0.5	0.2	0.1824
4-methyl-2-pentanone	108-10-1	1,380,000	residential RBC	690,000	0.5	0.2	0.1513
benzyl chloride	100-44-7	21.9	residential RBC	11	1.25	0.5	0.3944
benzene	71-43-2	37	residential RBC	19	0.5	0.2	0.0941
bromodichloromethane	75-27-4	29	residential RBC	15	0.5	0.2	0.1017
bromoform	75-25-2	970	residential RBC	485	0.5	0.2	0.1524
bromomethane	74-83-9	2,300	residential RBC	1,150	0.5	0.2	0.0929
carbon disulfide	75-15-0	320,000	residential RBC	160,000	0.5	0.2	0.0991
carbon tetrachloride	56-23-5	26	residential RBC	13	0.5	0.2	0.0985
chlorobenzene	108-90-7	28,000	residential RBC	14,000	0.5	0.2	0.1085
chloroethane	75-00-3	4,600,000	residential RBC	2,300,000	1.25	0.5	0.1545
chloroform	67-66-3	200	residential RBC	100	0.5	0.2	0.0900
chloromethane	74-87-3	600	residential RBC	300	0.5	0.2	0.0977
cis-1,2-dichloroethene	156-59-2	16,000	residential RBC	8,000	0.5	0.2	0.1325

Analyte	CAS number	Project Action Limit[a] (ppb/v)	Project Action Limit Reference [a]	Project QL Goal (ppb/v)	Laboratory-specific [b] (ppb/v)		
					LOQ	LOD	DL
cis-1,3-dichloropropene	10061-01-5	67 [e]	residential RBC	34	0.5	0.2	0.1394
dibromochloromethane	124-48-1	40	residential RBC	20	0.5	0.2	0.1123
dichlorodifluoromethane (Freon 12)	75-71-8	92,000	residential RBC	46,000	0.5	0.2	0.1442
ethanol	100-41-4	804,000 [f]	residential RBC	402,000	0.5	0.2	0.1138
ethylbenzene	87-68-3	430	residential RBC	215	1.25	0.2	0.1809
hexachlorobutadiene	179601-23-1	48.7	residential RBC	25	2.5	1	0.7604
m,p-xylenes	75-09-2	47,000	residential RBC	23,500	2.5	1.25	1.0000
methylene chloride	1634-04-4	1,100	residential RBC	550	0.5	0.2	0.1189
methyl tert-butyl ether	95-47-6	4,100	residential RBC	2,050	0.5	0.2	0.1207
o-xylene	100-42-5	47,000	residential RBC	23,500	0.5	0.2	0.1789
styrene	127-18-4	466,000	residential RBC	233,000	0.5	0.2	0.1108
tetrachloroethene	108-88-3	180	residential RBC	90	0.5	0.2	0.1176
toluene	156-60-5	2,300,000	residential RBC	1,150,000	0.5	0.2	0.1867
trans-1,2-dichloroethene	10061-02-6	32,000	residential RBC	16,000	0.5	0.2	0.1021
trans-1,3-dichloropropene	79-01-6	67	residential RBC	34	0.5	0.2	0.1069
trichloroethene	75-69-4	540	residential RBC	270	0.5	0.2	0.0774
trichlorofluoromethane (Freon 11)	108-05-4	320,000	residential RBC	160,000	1.25	0.5	0.4549
vinyl acetate	75-01-4	91,900	residential RBC	49,950	0.5	0.2	0.1009
vinyl chloride	71-55-6	14	residential RBC	7.0	0.5	0.2	0.0996

[a] Project Action Limits are not applicable for this project. Results will be analyzed only for consistency with historical data for the site and will not be compared to their associated screening level. Listed are risk-based concentrations (RBC) for residential exposure from vapor intrusion, which were calculated using the methodology provided in "Interim Final Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air," California Department of Toxic Substances Control Revised February 5, 2005. The average soil gas-to-indoor air attenuation factor of 0.0027 provided in DTSC (2005) for buildings without engineered fill was used to calculate the RBC.

[b] Laboratory-specific DLs, LODs, and LOQs are limits that an individual laboratory can achieve when performing a specific analytical method.

[c] 2-butanone used as a surrogate

[d] Toluene used as a surrogate

[e] 1,3-dichloropropene used as a surrogate

[f] Methanol used as a surrogate

CAS = Chemical Abstract Service
DL = detection limit
LOD = limit of detection
LOQ = limit of quantitation
Ppb/v = parts per billion by volume
RBC = risk-based concentration
VOC = volatile organic compound

SAP Worksheet #15 -- Reference Limits and Evaluation Table (continued)
(UFP-QAPP Manual Section 2.8.1)

Matrix: Soil gas
Analytical Group: dissolved gases

Analyte	CAS number	Project Action Limit (%V)	Project Action Limit Reference	Project QL Goal (%V)	Laboratory-specific (%V)		
					LOQ	LOD	DL
methane	74-82-8	na	na	na	0.50	0.25	0.1553

%V = percent volume
CAS = Chemical Abstract Service
DL = detection limit
LOD = limit of detection
LOQ = limit of quantitation
na = not applicable
QL = quantitation limit

SAP Worksheet #15 -- Reference Limits and Evaluation Table (continued)
(UFP-QAPP Manual Section 2.8.1)

Matrix: Water
Analytical Group: VOCs

Analyte	CAS number	Project Action Limit (µg/L)	Project Action Limit Reference	Project QL Goal (µg/L)	Laboratory-specific[1] (µg/L)		
					LOQ	LOD	DL
1,1,1-trichloroethane	71-55-6	NA	NA	NA	5.0	0.5	0.30
1,1,2-trichloroethane	79-00-5	NA	NA	NA	1.0	0.5	0.38
1,1-dichloroethane	75-34-3	NA	NA	NA	5.0	0.5	0.28
1,1-dichloroethene	75-35-4	NA	NA	NA	1.0	0.5	0.43
1,2,4-trimethylbenzene	95-63-6	NA	NA	NA	5.0	0.5	0.36
1,2-dichloroethane	107-06-2	NA	NA	NA	1.0	0.5	0.24
1,3,5-trimethylbenzene	108-67-8	NA	NA	NA	5.0	0.5	0.28
2-butanone (MEK)	78-93-3	NA	NA	NA	10	5.0	2.2
2-hexanone	591-78-6	NA	NA	NA	10.0	5.0	2.1
4-methyl-2-pentanone (MIBK)	108-10-1	NA	NA	NA	10.0	5.0	4.4
benzene	71-43-2	NA	NA	NA	1.0	0.5	0.14
bromodichloromethane	75-27-4	NA	NA	NA	5.0	0.5	0.21
bromoform	75-25-2	NA	NA	NA	10.0	1.0	0.50
carbon disulfide	75-15-0	NA	NA	NA	5.0	0.5	0.41
carbon tetrachloride	56-23-5	NA	NA	NA	1.0	0.5	0.23
chlorobenzene	108-90-7	NA	NA	NA	5.0	0.5	0.17
chloroethane	75-00-3	NA	NA	NA	10.0	5.0	2.3
chloroform	67-66-3	NA	NA	NA	5.0	0.5	0.46
chloromethane	74-87-3	NA	NA	NA	10.0	5.0	1.8
cis-1,2-dichloroethene	156-59-2	6	Target Cleanup Goal [2]	3	1.0	0.5	0.48
dibromochloromethane	124-48-1	NA	NA	NA	1.0	0.5	0.25
dichlorodifluoromethane	75-71-8	NA	NA	NA	1.0	0.5	0.46
ethylbenzene	100-41-4	NA	NA	NA	1.0	0.5	0.14
isopropylbenzene	98-82-8	NA	NA	NA	5.0	1.0	0.58
m,p-xylenes	108-38-3 106-42-3	NA	NA	NA	10.0	1.0	0.24
methylene chloride	75-09-2	NA	NA	NA	10.0	1.0	0.64
methyl-tert-butyl-ether	1634-04-4	NA	NA	NA	1.0	0.5	0.31
o-xylene	95-47-6	NA	NA	NA	1.0	0.5	0.23
tertiary-butyl alcohol	75-65-0	NA	NA	NA	25	5.0	4.6
tetrachloroethene	127-18-4	5	Target Cleanup Goal [2]	2.5	5.0	0.5	0.39

Analyte	CAS number	Project Action Limit (µg/L)	Project Action Limit Reference	Project QL Goal (µg/L)	Laboratory-specific[1] (µg/L)		
					LOQ	LOD	DL
toluene	108-88-3	NA	NA	NA	1.0	0.5	0.24
trans-1,2-dichloroethene	156-60-5	10	Target Cleanup Goal [2]	5	1.0	0.5	0.37
trichloroethene	79-01-6	5	Target Cleanup Goal [2]	2.5	1.0	0.5	0.37
trichlorofluoromethane	75-69-4	NA	NA	NA	10.0	5.0	1.7
1,1,2-trichloro-1,2,2-trifluoroethane	76-13-1	NA	NA	NA	1.0	0.5	0.45
vinyl chloride	75-01-4	0.5	Target Cleanup Goal [2]	0.25	1.0 [3]	0.5	0.30

[1] Laboratory-specific DLs, LODs, and LOQs are limits that an individual laboratory can achieve when performing a specific analytical method.

[2] Project Action Limits are the Target Cleanup Goals as documented in the "Final Record of Decision/Remedial Action Plan, Operable Unit 4, IRP Site 40, Naval Weapons Station Seal Beach, Seal Beach, California," Department of the Navy, May 2004.

[3] The LOQ exceeds the PAL. The laboratory will make every effort to ensure that the Project QL Goal is met.

µg/L = micrograms per liter
CAS = Chemical Abstract Service
DL = detection limit
LOD = limit of detection
LOQ = limit of quantitation
NA = not applicable
PAL = project action limit
QL = quantitation limit
VOC = volatile organic compound

SAP Worksheet #15 -- Reference Limits and Evaluation Table (continued)
(UFP-QAPP Manual Section 2.8.1)

Matrix: Water
Analytical Group: dissolved gases

Analyte	CAS number	Project Action Limit (µg/L)	Project Action Limit Reference	Project QL Goal (µg/L)	Laboratory-specific (µg/L)		
					LOQ	LOD	DL
methane	74-82-8	na	na	na	0.167	0.0668	0.0334
ethane	74-84-0	na	na	na	0.366	0.1345	0.06725
ethene	74-85-1	na	na	na	0.431	0.1725	0.0566

µg/L = micrograms per liter
CAS = Chemical Abstract Service
DL = detection limit
LOD = limit of detection
LOQ = limit of quantitation
na = not applicable
QL = quantitation limit

SAP Worksheet #15 -- Reference Limits and Evaluation Table (continued)
(UFP-QAPP Manual Section 2.8.1)

Matrix: Water
Analytical Group: anions

Analyte	CAS number	Project Action Limit (mg/L)	Project Action Limit Reference	Project QL Goal (mg/L)	Laboratory-specific (mg/L)		
					LOQ	LOD	DL
sulfate	14808-79-8	na	na	na	2.0	0.5	0.132
chloride	16887-00-6	na	na	na	2.0	0.5	0.132
nitrate	14797-55-8	na	na	na	0.1	0.05	0.021
nitrite	14797-65-0	na	na	na	0.2	0.05	0.021

CAS = Chemical Abstract Service
DL = detection limit
LOD = limit of detection
LOQ = limit of quantitation
mg/L = milligrams per liter
na = not applicable
QL = quantitation limit

SAP Worksheet #15 -- Reference Limits and Evaluation Table (continued)
(UFP-QAPP Manual Section 2.8.1)

Matrix: Water
Analytical Group: cations

Analyte	CAS number	Project Action Limit (mg/L)	Project Action Limit Reference	Project QL Goal (mg/L)	Laboratory-specific (mg/L)		
					LOQ	LOD	DL
calcium	14127-61-8	na	na	na	0.1	0.01	0.0086
iron	15438-31-0	na	na	na	0.1	0.01	0.0067
magnesium	22537-22-0	na	na	na	0.1	0.01	0.0085
potassium	24203-36-9	na	na	na	1.0	0.5	0.1672
sodium	7646-69-7	na	na	na	1.0	0.15	0.1117

CAS = Chemical Abstract Service
DL = detection limit
LOD = limit of detection
LOQ = limit of quantitation
mg/L = milligrams per liter
na = not applicable
QL = quantitation limit

SAP Worksheet #15 -- Reference Limits and Evaluation Table (continued)
(UFP-QAPP Manual Section 2.8.1)

Matrix: Water
Analytical Group: geochemical parameters

Analyte	CAS number	Project Action Limit (mg/L)	Project Action Limit Reference	Project QL Goal (mg/L)	Laboratory-specific (mg/L)		
					LOQ	LOD	DL
total dissolved solids	na	na	na	na	2.0	1.6	0.8202
chemical oxygen demand	na	na	na	na	7.0	6.0	2.990
total organic carbon	7440-44-0	na	na	na	5	2	0.237

CAS = Chemical Abstract Service
DL = detection limit
LOD = limit of detection
LOQ = limit of quantitation
mg/L = milligrams per liter
na = not applicable
QL = quantitation limit

SAP Worksheet #15 -- Reference Limits and Evaluation Table (continued)
(UFP-QAPP Manual Section 2.8.1)

Matrix: Water
Analytical Group: *Dehalococcoides*

Analyte	CAS number	Project Action Limit (cells/sample)	Project Action Limit Reference	Project QL Goal (cells/sample)	Laboratory-specific (cells/sample)		
					LOQ	LOD	DL
Dehalococcoides spp.	na	na	na	na	500	100	100

CAS – Chemical Abstract Service
DL – detection limit
LOD – limit of detection
LOQ – level of quantitation
na – not applicable

SAP Worksheet #16 -- Project Schedule / Timeline Table (optional format)
(UFP-QAPP Manual Section 2.8.2)

Activity	Organization	Dates (MM/DD/YY)		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
Collection and shipment of samples, first round	CKY	12/20/2011	12/23/2011	Daily CQC reports	NLT 24 hours after workday
Collection and shipment of samples, second round		12/18/2012	12/21/2012		
Lab analysis of samples, first round	Calscience	12/21/2011	01/24/2012	EDD and comprehensive chemical data packages	EDD 10 days, packages 20 business days after receipt of samples
Lab analysis of samples, second round		12/19/2012	01/24/2013		
Data review, first round	CKY	02/03/2012	02/23/2012	Monthly Progress Report	30 days after completion of all analyses
Data review, second round		02/04/2013	02/22/2013		
Data validation, first round	LDC	01/25/2012	02/13/2012	Data validation report	3 weeks after receipt of data packages
Data validation, second round		01/25/2013	02/14/2013		
Usability assessment, first round	CKY	02/17/2012	03/14/2012	Monthly Progress Report	30 days after receipt of validation report
Usability assessment, second round		02/15/2013	03/15/2012		
NEDD population/NIRIS upload, first round	LDC	02/17/2012	03/14/2012	Validated data in NEDD format	Before 4/30/2013
NEDD population/NIRIS upload, second round		02/15/2013	03/15/2012		
Data summaries	CKY	07/02/2012	01/25/2012	Long Term Monitoring Summary Report	End of contract performance 4/30/2013

Calscience = Calscience Environmental & Marine Chemistry Laboratories
CKY = CKY Incorporated
CQC = Contractor Quality Control
EDD = electronic data deliverable
NEDD = Navy Electronic Data Deliverable
NIRIS = Naval Installation Restoration Information Solution
NLT = no later than

The project schedule is included in the project work plan (to which this SAP is an appendix).

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SAP Worksheet #17 -- Sampling Design and Rationale
(UFP-QAPP Manual Section 3.1.1)

The sampling and analytical program was specifically developed to address the goals of this monitoring project, and is based primarily on a review of available data and previous sample locations.

The sampling and analytical program consists of the following:

- Collecting groundwater samples from 10 wells (MW-40-7, MW-40-8, MWW-40-14, MW-40-22, MW40-30, MW-40-31, MW-40-32, MW-40-36, MW-40-37, and IW-4) that currently do not meet the ROD-specified criterion of not exceeding a TCG for over one year and from 7 additional wells (MW-40-6, MW-40-13, MW-40-34, MW-40-35, IW-2, IW-10, and IW-18) deemed necessary to assess plume dynamics (locations shown on Figure 6).
- Analyzing the groundwater samples for VOCs, field parameters, geochemical parameters, dissolved gases, and Dhc.
- Collecting soil gas samples at 8 wells (VW-40-02, VW-40-03, VW-40-04, VW-40-06, IW-1, IW-3, MW-40-32, and MW-40-37) that had high concentrations of methane (locations shown on Figure 7).
- Analyzing the soil gas samples for VOCs and methane.
- Collecting field measurements for methane, carbon dioxide, carbon monoxide, oxygen, and hydrogen sulfide at 17 soil gas monitoring wells and probes within wells (locations shown on Figure 7).
- Collecting field measurements for methane from surface emissions at areas within IRP Site 40, inside Buildings 240 and 249, and inside the manholes located within the Site (locations shown on Figure 8).

In general, the sample locations were selected judgmentally to provide current delineation of COCs; and the number of samples was chosen to provide adequate coverage of the investigation area, while adhering to the budget and schedule constraints for this project. The sampling and analytical program focuses on soil gas and groundwater because COCs have previously been detected in these media at the Site. The project monitoring program follows the recommendations in the Comprehensive Performance Monitoring Report (TTEMI 2011).

In addition to those monitoring wells that were selected because their concentrations of COCs exceeded the TCGs in the most recent sampling event, wells that are strategically located in relation to the most recently delineated COC plume also were selected for monitoring: MW-40-6 is a shallow upgradient well, MW-40-13 will serve as a deep downgradient check, MW-40-34 will be used as a shallow cross gradient check, MW-40-35 is a deep centrally located check well, IW-2 will be used as a cross-gradient check, and IW-10 and IW-18 are near the downgradient edge of the May 2010 plume.

Groundwater samples will be analyzed by off-site laboratory for VOCs, geochemical parameters (anions, cations, TDS, COD, and TOC), dissolved gases, and Dhc. VOC analysis will be performed by EPA Method 8260B, anions (sulfate, chloride, nitrate, nitrite) by EPA Method

300.0, cations (calcium, iron, magnesium, potassium, sodium) by EPA 6010B, total dissolved solids by SM 2540C, chemical oxygen demand by EPA Method 410.4, total organic carbon by SM 5310B, dissolved gases (methane, ethane, ethene) by RSK-175M, and Dhc by CENSUS qPCR. VOC results for COCs will be analyzed for trends, to determine if monitoring of additional downgradient wells may be appropriate, and to determine if wells for which all COCs fall below TCGs for two consecutive monitoring events may be removed from the monitoring program (with regulatory concurrence). MNA data will be used to assess biodegradation activity (e.g. whether sufficient TOC is present for continued dechlorination of COCs at the Site) and to determine whether the analytical suite may be reduced (with regulatory concurrence) to eliminate analyses which are not providing useful data.

The eight locations selected for soil gas sampling had high (76.8% to 91.9%) methane concentrations in the May 2010 event. Soil gas samples will be analyzed by off-site laboratory for VOCs by EPA Method TO-15 and methane by ASTM D-1946. Helium screening for leak testing will be performed in the field with a helium meter and in the laboratory by ASTM D-1946. Soil gas VOC results indicate the presence of CEs, mainly PCE, TCE, and VC, and will be evaluated to determine whether conducting active venting of the vadose zone to remove these residual contaminants is necessary.

Field testing for methane and other field parameters will be measured with a handheld field instrument, e.g. a Landtec GEM 2000. Concentrations of methane, which persist in vadose zone soils, could potentially become problematic from a health and safety perspective in the event of subsurface activity (e.g., within utility manholes) and risks associated with vapor intrusion into nearby buildings that may be occupied.

SAP Worksheet #18 – Location-Specific Sampling Locations and Methods/SOP Requirements Table
(UFP-QAPP Manual Section 3.1.1)

Sampling Location / ID Number	Matrix	Approximate Depth (feet bgs)	Analytical Group	Number of Samples	Sampling SOP Reference
Well Sampling					
MW-40-06	water	20.3 – 30.3	VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	Worksheet #14
MW-40-07	water	20.0 – 30.0	VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
MW-40-08	water	20.0 – 30.0	VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
MW-40-13	water	45.0 – 55.0	VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
MW-40-14	water	30.0 – 40.0	VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
MW-40-22	water	15.3 – 35.5	VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
MW-40-30	soil gas	15.0 – 35.0	field parameters [1]		
	water		VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
MW-40-31	soil gas	42.0 – 52.0	field parameters [1]		
	water		VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
MW-40-32	soil gas	15.0 – 35.0	VOCs, methane/helium[2], and field parameters [3]		
	water		VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
MW-40-34	soil gas	15.0 – 35.0	field parameters [1]		
	water		VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
MW-40-35	soil gas	45.0 – 55.0	field parameters [1]		
	water		VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
MW-40-36	soil gas	15.0 – 35.0	field parameters [1]		
	water		VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
MW-40-37	water	15.0 – 35.0	VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
	soil gas		VOCs, methane/helium[2], and field parameters [3]		

Sampling Location / ID Number	Matrix	Approximate Depth (feet bgs)	Analytical Group	Number of Samples	Sampling SOP Reference
IW-1	soil gas	15.0 – 35.0	VOCs, methane/helium[2], and field parameters [3]		Worksheet #14
IW-2	water	15.0 – 35.0	VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
IW-3	soil gas	15.0 – 35.0	VOCs, methane/helium[2], and field parameters [3]		
IW-4	water	15.0 – 35.0	VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
IW-7	soil gas	15.0 – 35.0	field parameters [1]		
IW-10	soil gas	15.0 – 35.0	field parameters [1]		
	water		VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
IW-18	soil gas	14.0 – 34.0	field parameters [1]		
	water		VOCs, anions, cations, TDS, COD, TOC, dissolved gases, Dhc, and field parameters [1]	1	
VW-40-01	soil gas	2.5 – 7.5	field parameters [1]		
VW-40-02	soil gas	2.5 – 7.5	VOCs, methane/helium[2], and field parameters [3]	1	
VW-40-03	soil gas	3.0 – 10.0	VOCs, methane/helium[2], and field parameters [3]	1	
VW-40-04	soil gas	3.0 – 10.0	VOCs, methane/helium[2], and field parameters [3]	1	
VW-40-06	soil gas	3.0 – 10.0	VOCs, methane/helium[2], and field parameters [3]	1	

[1] Field parameters for water sampling include dissolved oxygen, oxidation/reduction potential, pH, temperature, and electrical conductivity.
[2] Helium will be analyzed for leak testing purposes. In accordance with the CalEPA Advisory – Active Soil Gas Investigation, a leak that comprises less than 5 percent of the sample will be considered acceptable. Helium concentrations indicating greater than 5 percent leakage will be noted and discussed as part of the data validation process; and additional sampling may be required.
[3] Field parameters for soil gas sampling include methane, carbon dioxide, carbon monoxide, oxygen, and hydrogen sulfide.

bgs = below ground surface
COD = chemical oxygen demand
Dhc = *Dehalococcoides* spp.
SOP = standard operating procedure
TDS = total dissolved solids
TOC = total organic carbon
VOC = volatile organic compound

SAP Worksheet #18 – Location-Specific Sampling Locations and Methods/SOP Requirements Table (continued)

Sampling Location [1] / ID Number	Matrix	Approximate Depth (feet bgs)	Analytical Group	Number of Samples	Sampling SOP Reference
Surface Emissions Sampling					
Various, inside Building 239	soil gas	0	methane	approximately 14	Worksheet #14
Various, exterior perimeter Building 239	soil gas	0	methane	approximately 5	
Various, inside Building 240	soil gas	0	methane	approximately 24	
Various, exterior perimeter Building 240	soil gas	0	methane	approximately 17	
Various, east of Building 240	soil gas	0	methane	approximately 6	
Various, south of railroad tracks	soil gas	0	methane	approximately 21	
Inside Site 40 manholes	soil gas	0.5	methane	approximately 2	

[1] Locations as shown on Figure 8, including areas where methane gas could migrate into the buildings through cracks, utility penetrations, or other pathways in the floor slab; outside the buildings, in the work zones, at the EISB system area boundary, at cracks in the asphalt pavement, and at the sewer or other utility manhole covers near the injection areas.

bgs = below ground surface
SOP = standard operating procedure

SAP Worksheet #19 – Field Sampling Requirements Table
(UFP-QAPP Manual Section 3.1.1)

Matrix	Analytical Group	Analytical and Preparation Method/SOP Reference[1]	Containers (number, size, and type)	Minimum Sample Volume	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time [2] (preparation/ analysis)
Soil gas	VOCs	EPA TO-15: M380, R6.4	1 or 6 liter Summa™ canister	400 mL	Light/Heat protected	30 days
	methane	ASTM 1946M: M390, R1.1	1-L Tedlar bag, or 1 or 6 liter Summa™ canister	1 mL	Light/Heat protected	3 days 14 days
Water	VOCs	SW5030/SW8260B: M212/M311, R3.2/0.0	3 x 40-ml VOA vials w/ Teflon-lined septa	40 mL	No Headspace HCl to pH < 2, >0ºC - 6ºC	14 days/14 days
	cations	SW3005A or SW3010A / SW6010B: M220 or M223/M601, R3.4 or 3.1/5.2	125 mL poly	50 mL	HNO3 to pH <2	180 days
	anions	E300.0: M703, R3.4	250 mL poly	10 mL	>0ºC - 6ºC	48 hours: NO2, NO3 28 days CL, SO4
	T-DS	SM 2540C: M713, R2.5	1 liter ppoly	1 liter	>0ºC - 6ºC	7 days
	COD	E410.4: M724, R2.1	250 mL glass or poly	2.5 mL	No Headspace H_2SO_4 to pH <2, >0ºC - 6ºC	28 days
	TOC	SM 5310B: M726, R1.1	250 mL glass w/ Teflon-lined septa	40 mL	No Headspace H_2SO_4 to pH <2, >0ºC - 6ºC	28 days
	methane/ ethane/ ethene	RSK-175: M386, R2.3	2 x 40-ml VOA vials w/ Teflon-lined septa	40 mL	No Headspace HCl to pH < 2, >0ºC - 6ºC	14 days
	Dhc	MICRO/ MI SOP qPCR	1 liter poly or Bio-flo filter	1 L	(4±2) °C	48 hours

[1] Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23).
[2] Maximum holding time is calculated from the time the sample is collected to the time the sample is prepared/extracted.

°C = degrees Celsius
ASTM = American Society for Testing and Materials
COD = chemical oxygen demand
Dhc = *Dehalococcoides* spp.
EPA = U.S. Environmental Protection Agency
mL = milliliter
SOP = Standard Operating Procedure
TDS = total dissolved solids
TOC = total organic carbon
VOA = volatile organic analysis
VOC = volatile organic compound

SAP Worksheet #20 -- Field Quality Control Sample Summary Table
(UFP-QAPP Manual Section 3.1.1)

Matrix	Analytical Group	No. of Sampling Locations	No. of Field Duplicates	No. of MS/MSDs[1]	No. of Field Blanks	No. of Equipment Blanks	No. of VOA Trip Blanks	No. of PT [2] Samples	Total No. of Samples to Lab
Soil gas	VOCs	8	1	0	1[3]	na	0	0	10
	methane	8	1	0	0	na	0	0	9
Water	methane, ethane, ethene	17	2	1 (5%/day)	0	2 (1/day/source)	0	0	22
	TOC	17	2	1 (5%/day)	0	2 (1/day/source)	0	0	22
	COD	17	2	1 (5%/day)	0	2 (1/day/source)	0	0	22
	TDS	17	2	0	0	2 (1/day/source)	0	0	21
	anions	17	2	1 (5%/day)	0	2 (1/day/source)	0	0	22
	cations	17	2	1 (5%/day)	0	2 (1/day/source)	0	0	22
	VOCs	17	2	1 (5%/day)	0	2 (1/day/source)	1	0	23

[1] Although the MS/MSD is not typically considered a field QC it is included here because location determination is often established in the field.

[2] The number of Batch or Project-specific proficiency testing (PT) samples is optional but highly recommended.

[3] One ambient air blank will be collected for TO-15 analysis

COD	chemical oxygen demand
FD	field duplicate
MS/MSD	matrix spike/matrix spike duplicate
na	not applicable
TDS	total dissolved solids
TOC	total organic carbon
VOA	volatile organic analysis
VOC	volatile organic compound

SAP Worksheet #21 -- Project Sampling SOP References Table

(UFP-QAPP Manual Section 3.1.2)

Reference Number	Title, Revision Date and/or Number	Originating Organization of Sampling SOP	Equipment Type	Modified for Project Work (Y/N)	Comments

not applicable

Note: SOP references are not required because all sampling procedures are described in Worksheets #14 and #17.

SOP = Standard operating procedure

SAP Worksheet #22 -- Field Equipment Calibration, Maintenance, Testing, and Inspection Table
(UFP-QAPP Manual Section 3.1.2.4)

Field Equipment	Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference	Comments
Mini Rae Plus Classic PGM-76	Calibration	daily	Within manufacturer's recommended value	Re-calibrate according to manufacturer's instructions	CKY SSHO	Manufacturer's instructions	
	Maintenance	As required	Follow manufacturer's guidelines	Repair as necessary– see comments			Changing filters, batteries and sensor module, probe assembly and lamp cleaning is the maintenance performed on hand-held instruments. Pump replacement can also be completed
	Testing	Response check	Follow manufacturer's guidelines	Repeat check or repair			
	Inspection	Prior to each use	No physical defects; calibration current; battery charge >60%; no light leaks; no loose cables	Replace batteries; repair unit as needed based on user inspection; tighten or change cables			Annual manufacturer's inspection
YSI 556 MPS with flow cell	Calibration	weekly	Within manufacturer's recommended value	Re-calibrate according to manufacturer's instructions	CKY QCM	Manufacturer's operations manual	
	Maintenance	As required	Follow manufacturer's guidelines	Return for service as necessary– see comments			Instrument is not user repairable; after cleaning and decontaminating, return to YSI authorized service center for evaluation and/or repair.
	Testing	Prior to each use	Batteries fresh or battery pack charged >60%	Replace batteries or recharge battery pack			
	Inspection	Prior to each use	No physical defects; calibration current; battery charge >60%; clean sensors; no loose cables	Replace batteries; clean sensors; tighten or change cables			

Field Equipment	Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference	Comments
Ces-Landtec GEM 2000	Calibration	As indicated by instrument startup test or temperature change > 20º	Self-test indicator okay; no erratic gas readings	Perform field calibration with zero gas mixture; then with relevant known certified gas concentration	CKY QCM	Manufacturer's user's guide	Use cold start function only as last resort—will erase memory, reset all settings and internal time/date to default settings
	Maintenance	Once every 4 weeks	Battery charge indicator not flashing	Fully discharge and recharge batteries.	CKY QCM		Store instrument in clean, dry, warm environment.
	Testing	Startup self-test when instrument is switched on	All indicators normal (no errors or warnings)	Perform relevant calibration or recharge batteries per displayed warning.	CKY QCM		If other warnings or errors are displayed, contact manufacturer for further information.
	Inspection	Prior to each use	Inlet-port filter clean and dry; water trap fitted with clean dry filter; calibration current; battery charge >25%;date and time display correct	Perform calibration checks; fully recharge battery pack; clear and reset date/time	CKY QCM		

CKY = CKY Incorporated
QCM = Project Quality Control Manager
SOP = standard operating procedure
SSHO = Site Safety and Health Officer

SAP Worksheet #23 -- Analytical SOP References Table
(UFP-QAPP Manual Section 3.2.1)

Lab SOP Number [1]	Title, Revision Date, and / or Number	Definitive or Screening Data	Matrix and Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
M380	EPA TO-15- VOC's in Air by GC/MS – Rev 6.2	definitive	Air - VOCs	GC/MS	Calscience	N
M386	RSK 175 – Dissolved Gases	definitive	Water – RSK 175	GC	Calscience	N
M212 / M311	SW5030 / SW8260 – Purge and Trap for Aqueous Samples / VOCs by GC/MS – Rev 3.1 / 0.0	definitive	Water – VOCs	GC/MS	Calscience	N
M703	E300.0 Determination of Inorganic Anions by IC – Rev 3.3	definitive	Water – Nitrate and Nitrite, Chloride and Sulfate	Ion Chromatography (IC)	Calscience	N
M220 or M223 / M601	E3005 or E3010 / SW6010B – Acid Digestion of Aqueous Samples – Metals by ICP/AES – Rev 3.3 or 3.1 / 5.2	definitive	Water - Metals	Inductively Coupled Plasma (ICP)	Calscience	N
M713	SM2540C – Total Dissolved Solids – Rev 2.5	definitive	Water - Total Dissolved Solids	Balance	Calscience	N
M726	SM5310B – Total Organic Carbon R 1.1	definitive	Water - TOC	TOC analyzer	Calscience	N
M724	E410.4 – Chemical Oxygen Demand by Closed Reflux Colorimetric Technique R 2.1	definitive	Water - COD	Spectrophotometer	Calscience	N
DNA-qPCR	Quantitative Polymerase Chain Reaction (qPCR), Rev. 2.0, 1/10/2011	definitive	Water - Dhc	ABI 7300 PCR system	Microbial Insights [2]	N

[1] Copies of the analytical SOPs are included in Attachment 1.
[2] Subcontracted to Calscience.

ABI	Applied Biosystems instrument
Calscience	Calscience Environmental Laboratories, Inc.
COD	chemical oxygen demand
Dhc	*Dehalococcoides* spp.
GC	gas chromatograph
GC/MS	gas chromatograph/mass spectrometer
PCR	polymerase chain reaction
SOP	standard operating procedure
TOC	total organic carbon
VOC	volatile organic compound

SAP Worksheet #24 -- Analytical Instrument Calibration Table
(UFP-QAPP Manual Section 3.2.2)

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
Gas Chromatograph /Mass Spectrometer (GC/MS)	BFB Tuning	Prior to calibration and every 12 hours during sample analysis	m/z Relative Abundance Criteria 50 15 - 40% of m/z 95 75 30 - 60% of m/z 95 95 base peak, 100% relative abundance 96 5 – 9% of m/z 95 173 < 2% of m/z 174 174 > 50% of m/z 95 175 5 – 9% of m/z 174 176 > 95% but < 101% of m/z 174 177 5 – 9% of m/z 176	Retune instrument and verify.	Analyst	M311/M380
GC/MS	Minimum 5-point Initial calibration for all analytes (ICAL)	Initially, after the BFB Tune Check, and as needed thereafter	Average RF for SPCCs: VOCs - ≥ 0.30 for chlorobenzene and 1,1,2,2-tetrachloroethane, ≥0.1 for chloromethane, bromoform, and 1,1-dichloroethane RSD for 123-TCP – 20% RSD for RFs for CCCs: VOCs - ≤30% and one option below: 1): RSD for each analyte ≤ 15% 2): linear least squares regression r ≥ 0.995 when RSD >15% 3): non-linear – COD r2 ≥ 0.99 (minimum of 6 points)	Locate the source of the problem. If expected RFs or regressions are not met, check for standard degradation or perform instrument maintenance to correct the problem, and then repeat initial calibration.		
GC/MS	Initial Calibration Verification (ICV) Second Source Standard	Immediately after ICAL	Value of second source for all analytes within ±20% of expected value	Prepare fresh standard and re-analyze ICV to rule out standard degradation or inaccurate injection. If problem persists, perform instrument maintenance to correct the problem and repeat ICAL.		

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
GC/MS	Continuing Calibration Verification (CCV)	Daily, following the BFB tune check, before sample analysis, and every 12 hours of analysis time	Average RF for SPCCs: RF≥0.30 for chlorobenzene and 1,1,2,2-tetrachloroethane, ≥0.1 for chloromethane, bromoform, and 1,1-dichloroethane %Difference ≤20%	Identify possible cause for the nonconformance, then rerun CCV to rule out standard degradation or inaccurate injection. If that fails, repeat initial calibration.	Analyst	M311/M380
GC/MS	Retention time Window position Establishment for each analyte and surrogate	Once per ICAL	Position shall be set using the midpoint standard of the initial calibration curve. Updated with CCV as needed.	NA		
GC/MS	Evaluation of relative retention times (RRT)	With each sample	RRT of ea. Target analyte in ea. Calibration standard within ± 0.06 RRT units.	Identify possible cause for the nonconformance, then rerun ICAL.		
GC/MS	Retention time window position established for each analyte and surrogate	Once per ICAL	Position shall be set using the midpoint standard of the initial calibration curve. Updated with CCV as needed.	NA		
GC/MS	Evaluation of relative retention times (RRT)	With each sample	RRT of each target analyte in each calibration standard within ± 0.06 RRT units.	Identify possible cause for the nonconformance, then rerun ICAL.		
GC	3 to 5-point Initial calibration for all analytes (ICAL)	Initially, as needed thereafter	1) RSD ≤ 20% for all analytes	Locate the source of the problem. If expected RSD is not met, check for standard degradation or perform instrument maintenance to correct the problem then repeat initial calibration.	Analyst	M386
GC	Initial Calibration Verification (ICV)	Following ICAL	All analytes within ±15% of expected value	Prepare fresh standard and re-analyze CCV to rule out standard degradation or inaccurate injection. If problem persists perform instrument maintenance to correct the problem and repeat ICAL.		

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
GC	Continuing Calibration Verification (CCV)	Every 24 hours	All analytes within ±15% of expected value	Prepare fresh standard and re-analyze CCV to rule out standard degradation or inaccurate injection. If problem persists perform instrument maintenance to correct the problem and repeat ICAL.	Analyst	M386
Ion Chromatograph (IC)	minimum of 3 points plus a calibration blank	Initially, as needed thereafter	1) RSD ≤ 15% for all analytes Or, 2) Linear – least squares regression r > 0.995	Locate the source of the problem. If expected RSD/Coefficient is not met, check for standard degradation or perform instrument maintenance to correct the problem then repeat initial calibration.	Analyst	M703
IC	Initial / Continuing Calibration Verification (ICV / CCV)	ICV – Immediately following ICAL; CCV – Prior to sample analysis, after every 10 samples and closing	All analytes within ±15% of expected value.	Prepare fresh standard and re-analyze CCV to rule out standard degradation or inaccurate injection. If problem persists perform instrument adjustment and/or maintenance to correct the problem and repeat ICAL.	Analyst	M703
Inductively Coupled Plasma (ICP)	Initial calibration for all analytes. Minimum one high standard and calibration blank.	Daily initial calibration prior to sample analysis	N/A, unless more than one standard is used, in which case r ≥ 0.995	Prepare fresh standard and re-analyze ICV to rule out standard degradation or inaccurate injection. If problem persists perform instrument maintenance to correct the problem and repeat ICAL.	Analyst	M601
ICP	Initial Calibration Verification (ICV)	Immediately after ICAL, prior to sample analysis	± 10% of expected value	Prepare fresh standard and re-analyze ICV to rule out standard degradation or inaccurate injection. Perform instrument maintenance to correct the problem and repeat ICAL.	Analyst	M601
ICP	Continuing Calibration Verification (CCV)	After every 10 samples and at the end of the analysis sequence	± 10% of expected value RSD of replicate integrations <5%	Prepare fresh standard and re-analyze CCV to rule out standard degradation or inaccurate injection. Perform instrument maintenance to correct the problem and repeat ICAL.	Analyst	M601
ICP	Initial Calibration Blank (ICB) Continuing Calibration Blank (CCB)	After each ICAL/ICV 1/10 samples, after CCV	No detects ≥ ½ RL	Reanalyze with all associated samples	Analyst	M601
ICP	ICSA/ICSAB	Beginning Daily	80%-120% recovery; Evaluate non-interferent ICSA results with absolute values ≥2x MDL	Terminate analysis, correct problem, recalibrate instrument, check calibration, and re-run all samples analyzed since last compliant ICS.	Analyst	M601

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
TOC Analyzer	Initial Calibration (ICAL)	Daily prior to sample or QC analysis	Correlation coefficient (r^2) ≥0.995	Locate the source of the problem. If outliers exist, prepare fresh standards and repeat ICAL. If problem persists, perform photometric linearity check. If maximum absorbance is non-compliant, replace the spectrometer lamp and repeat ICAL.	Analyst	M726
TOC Analyzer	Initial Calibration Verification (ICV)	Immediately after ICAL, prior to sample analysis	within ± 15% of expected value	Prepare fresh standard and re-analyze ICV to rule out standard degradation or inaccurate injection. If problem persists perform instrument maintenance to correct the problem and repeat ICAL.	Analyst	M726
TOC Analyzer	Continuing Calibration Verification (CCV)	Daily before sample analysis, at the end of the analysis sequence	within ±15% of expected value	Repeat calibration and reanalyze all samples since last successful ICAL	Analyst	M726
TOC Analyzer	ICB CCB	After each ICAL/ICV 1/10 samples, after CCV	No detects ≥ ½ QL	Reanalyze with all associated samples	Analyst	M726
Spectrophotometer	Initial Calibration (ICAL)	Daily prior to sample or QC analysis	Correlation coefficient (r^2) ≥0.995	Locate the source of the problem. If outliers exist, prepare fresh standards and repeat ICAL. If problem persists, perform maintenance and recalibrate	Analyst	M724
Spectrophotometer	Continuing Calibration Verification (CCV)	Daily before sample analysis, at the end of the analysis sequence	within ±5% of expected value	Repeat calibration and reanalyze all samples since last successful ICAL	Analyst	M724
Spectrophotometer	ICB CCB	After each ICAL/ICV 1/10 samples, after CCV	No detects ≥ ½ QL	Reanalyze with all associated samples	Analyst	M724
Gravimetric	Analytical Balance Calibration Check	Daily before sample analysis	±0.1% of certified weight value.	Clean the balance, center the level indicator and repeat calibration check.	Analyst	M713
ABI 7300	Initial	Primary-annual	Standard Curve R2>0.95	Rerun assay/check reagents	Lab Manager	DNA-qPCR
	Continuing Calibration	Secondary-every assay	CT value within 2 units of same point on standard curve	Rerun assay/check reagents		

[1] Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23).

ABI = Applied Biosystems instrument
BFB = 4-boromofluorobenzene
CCB = continuing calibration blank
CCC = calibration check compound
CCV = continuing calibration verification
CT = cycle threshold
GC/MS = gas chromatograph/mass spectrometer
ICAL = initial calibration
ICB = initial calibration blank
ICS = internal control standard
ICV = initial calibration verification
MDL = method detection limit
m/z = mass-to-charge ratio
QL = quantitation limit
R2 = coefficient of determination
RF = response factor
RRT = relative retention time
RSD = relative standard deviation
SOP = standard operating procedure
SPCC = system performance check compound
TOC = total organic carbon

SAP Worksheet #25 -- Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table
(UFP-QAPP Manual Section 3.2.3)

Instrument/ Equipment	Maintenance Activity[1]	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person[2]	SOP Reference[3]
GC/MS, GC, ICP, IC, TOC Analyzer, Gravimetric	Parameter Setup	Physical check	Physical check	Initially; prior to ICAL or CCV, as required	Predetermined optimum parameter settings	Reset if incorrect	Analyst	All listed in Table #23
GC/MS	Tune MS	Analyze tune Standard	Tune standard passes criteria	Initially and every 12 hours following	Refer to Table #24 for GC/MS tune criteria	Retune MS	Analyst	M311/M380
ICP	ICS/ICSA	Instrument Performance	Conformance to interference check	Prior to sample analysis	Within ± 20% of expected value	Reanalyze ICS. If problem persists, perform maintenance, repeat calibrations and reanalyze all associated samples.	Analyst	M601
ICP	ICB/CCB	Instrument Performance	Instrument contamination check	After every ICV/CCV	No analytes detected ≥ 3X IDL	Determine possible source of contamination, correct the problem, reanalyze calibration blank and all associated samples.	Analyst	M601
TOC Analyzer	ICB/CCB	Instrument performance	Instrument contamination check	After every calibration verification	No analytes detected > 3xIDL	Determine possible source of contamination and apply appropriate measure to correct the problem. Reanalyze calibration blank and all associated samples.	Analyst	M726
ABI 7300	Dye calibration	Dye plate	Run dye plate	6 months	Spectra follows normal pattern	Contact manufacturer	Anita Biernacki	DNA-qPCR
ABI 7300	Background	Water plate	Run water plate	Monthly	No spectra detected	Clean instrument and rerun		DNA-qPCR

[1] Specify the appropriate reference letter or number from the Analytical Standard Operating Procedures (SOP) References table (Worksheet #23).

ABI = Applied Biosystems instrument
CCV = continuing calibration verification
GC = gas chromatograph
GC/MS = gas chromatograph/mass spectrometer
IC = ion chromatograph
ICAL = internal calibration
ICB = initial calibration blank
ICP = inductively coupled plasma
ICSA = interference check solution A
IDL = instrument detection limit
MS = mass spectrometer
SOP = standard operating procedure
TOC = total organic carbon

SAP Worksheet #26 -- Sample Handling System
(UFP-QAPP Manual Appendix A)

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
Sample Collection (Personnel/Organization): Tim Theisen/Larry Pennock, CKY
Sample Packaging (Personnel/Organization): Tim Theisen/Larry Pennock, CKY
Coordination of Shipment (Personnel/Organization): Tim Theisen/Larry Pennock, CKY
Type of Shipment/Carrier: Federal Express (alternatively, samples may be carried by personal vehicle and hand delivered to the lab or they may be picked up at the site by laboratory personnel)
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (Personnel/Organization): Laboratory project managers, CTL and Air Toxics
Sample Custody and Storage (Personnel/Organization): Laboratory project managers, CTL and Air Toxics
Sample Preparation (Personnel/Organization): Laboratory project managers, CTL and Air Toxics
Sample Determinative Analysis (Personnel/Organization): Laboratory project managers, CTL and Air Toxics
SAMPLE ARCHIVING
Field Sample Storage (No. of days from sample collection): none
Sample Extract/Digestate Storage (No. of days from extraction/digestion): 40
Biological Sample Storage (No. of days from sample collection): not applicable to this project
SAMPLE DISPOSAL
Personnel/Organization: Laboratory project managers, CTL and Air Toxics
Number of Days from Analysis: 60

SAP Worksheet #27 – Sample Custody Requirements
(UFP-QAPP Manual Section 3.3.3)

Field Sample Custody Procedures (sample collection, packaging, shipment, and delivery to laboratory):

Custody records completed by the sampler will accompany all shipments of samples. Each cooler will have a custody form listing the samples in the cooler. It is possible that more than one custody form will be needed per cooler to list all the samples contained in the cooler. The purpose of these forms is to document the transfer of a group of samples traveling together; when the group of samples changes, a new custody record is initiated. The original custody record always travels with the samples; the initiator of the record keeps a copy.

A copy of the chain-of-custody form completed by the Field Sampling Team will be submitted to the QCM. The laboratory will receive the original chain-of-custody form plus a carbon copy. The chain-of-custody forms will be retained in the master job file.

Sample packaging and shipping procedures are based on EPA specifications, DOT regulations, and Corps ER 1110-1-263. All samples will be shipped as “Environmental Samples” and not as hazardous material. Ice will be placed in each cooler to maintain a temperature of 4° C to meet sample preservation requirements. All samples will be delivered to the laboratory within 24 hours of collection. The following are general packaging procedures:

1. Sample labels with adhesive backing will be securely attached to each sample container.
2. Labeled sample containers will then be sealed into plastic bubble-wrap bags or Ziploc-type bags prior to being loaded into the sample coolers.
3. Insulated plastic or metal-clad plastic coolers will be used as shipping containers. The drain plugs will be taped shut (using strapping tape) on the inside and outside. Several plastic bubble-wrap sheets will be placed on the interior bottom and sides of the coolers for shock absorption. One to three inches of Styrofoam pellet packing material may also be placed in the bottom of the coolers for additional shock absorption at the discretion of the QCM.
4. Styrofoam pellets may also be placed between sample containers to protect the containers from breakage during shipment and handling.
5. The paperwork intended for the laboratory will be placed inside a plastic bag. The bag will be sealed and taped to the inside of the cooler lid. The original custody form will be included in the paperwork sent to the laboratory.
6. Two signed custody seals will be placed over the lid of the cooler, one on the right front and one on the upper left, and covered with clear plastic tape.
7. The cooler will be securely taped shut with strapping tape wrapped completely around the cooler at least once in a minimum of two locations.
8. "Up Arrow" symbols will be placed on all four sides of cooler.
9. The completed shipping label will be attached to the top of the cooler. The cooler will then be delivered to the overnight courier.

The project laboratories will be notified, two weeks prior to sample collection and again two days prior to arrival of samples, of the approximate number of samples, matrix, and requested analyses.

Laboratory Sample Custody Procedures (receipt of samples, archiving, disposal):

When the samples arrive at the laboratory, the personnel receiving the sample cooler will sign the chain-of-custody form and enter a laboratory identification number on the form. Revisions to the analysis request forms transmitted by facsimile or via email. Copies of these requests will be provided by the

laboratory with the hard copy data. The identification number will be used by the laboratory for internal tracking of the samples. In some cases, a separate analysis request form may be submitted to the laboratory. Both laboratory and sample numbers will be cited when analyses are requested (if the laboratory number is available) and the analytical results are reported.

Damaged sample containers, sample labeling discrepancies between sample container labels and chain-of-custody forms, and analytical request discrepancies will be noted on a sample receipt form, and the QCM and Project Manager will be notified for problem identification and resolution.

Sample Identification Procedures:

Example Sample Label and Custody seal is presented in Attachment 2.

A sample numbering system will be used to identify each sample collected and submitted for chemical analysis. The purpose of this numbering system is to assist in tracking samples and facilitate retrieval of sample data.

All sample containers will be labeled at the time of sampling. The sample identification numbers for each sampling effort will be used on sample labels, data tracking forms, field data forms, chain-of-custody forms, and all other applicable documentation. The QCM will maintain a listing of all sample identification numbers in the project field logbook.

Chain-of-custody Procedures:

Attachment 2 to this SAP includes an example chain-of-custody form.

Chain-of-custody procedures are employed to maintain and document sample possession. A sample is considered under a person's custody if it is in that person's physical possession, within visual sight of that person after taking physical possession, secured by that person so that the sample cannot be tampered with, or secured by that person in an area that is restricted to unauthorized personnel.

The following procedures will be followed when using custody record sheets.

1. The originator will fill in all requested information from the sample labels.
2. The person receiving custody will check the sample label and tag information against the custody form. The person receiving custody will also check sample condition and note anything unusual under "Remarks" on the custody form.
3. The originator will sign the "Relinquished by" box and keep a copy of the custody form.
4. After delivery by the commercial carrier, the person receiving custody will sign in the "Received by" box adjacent to the "Relinquished by" box (may also be filled in by recipient as "Federal Express" of other carrier name). All signatures and entries will be dated.
5. When custody is transferred to the analytical laboratory, blank signature spaces may be left and the last "Received by" signature box used. Another approach is to run a line through the unused signature boxes.
6. In all cases, it must be readily seen that the same person receiving custody has relinquished it to the next custodian.
7. If samples are left unattended or a person refuses to sign, this will be documented and explained on the custody form.

SAP Worksheet #28 -- Laboratory QC Samples Table
(UFP-QAPP Manual Section 3.4)

Matrix Water
Analytical Group VOCs
Analytical Method 8260B
SOP Reference M311

QC Sample	Frequency / Number	Method/ SOP QC Acceptance Limits	Corrective Action (CA)	Person(s) Responsible for CA	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	One per batch	No detects ≥1/2 QL	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.	Lead Chemist	Accuracy, Contamination	No detects ≥1/2 QL
LCS/LCSD	One per batch	See Table 1 below	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed. Discuss in narrative		Accuracy, Precision	See table 1 below
MS/MSD	One per batch	See Table 1 below	None – Flag data		Accuracy, Precision	See table 1 below
Surrogate	All environmental and laboratory samples	See Table 1 below	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.		Accuracy/Bias	See table 1 below

LCS/LCSD = laboratory control sample/laboratory control sample duplicate
MS/MSD = matrix spike/matrix spike duplicate
QL = quantitation limit
RPD = relative percent difference
SOP = standard operating procedure
VOC = volatile organic compound

TABLE 1 - EPA 8260B QC Limits Table for Water

Compound Name	LCS/LCSD	MS/MSD	RPD	Compound Name	LCS/LCSD	MS/MSD	RPD
1,1,1,2-Tetrachloroethane	80-130	80-130	0-20	Chlorobenzene	80-120	80-120	0-20
1,1,1-Trichloroethane	65-130	65-130	0-20	Chloroethane	60-135	60-135	0-20
1,1,2,2-Tetrachloroethane	65-130	65-130	0-20	Chloroform	65-135	65-135	0-20
1,1,2-Trichloroethane	75-125	75-125	0-20	Chloromethane	40-125	40-125	0-20
1,1-Dichloroethane	70-135	70-135	0-20	Dibromochloromethane	60-135	60-135	0-20
1,1-Dichloroethene	70-130	70-130	0-20	Dibromomethane	75-125	75-125	0-20
1,1-Dichloropropene	75-130	75-130	0-20	Dichlorodifluoromethane	30-155	30-155	0-20
1,2,3-Trichlorobenzene	55-140	55-140	0-20	Ethylbenzene	75-125	75-125	0-20
1,2,3-Trichloropropane	75-125	75-125	0-20	Hexachloro-1,3-Butadiene	50-140	50-140	0-20
1,2,4-Trichlorobenzene	65-135	65-135	0-20	Isopropylbenzene	75-125	75-125	0-20
1,2,4-Trimethylbenzene	75-130	75-130	0-20	Methylene Chloride	55-140	55-140	0-20
1,2-Dibromo-3-Chloropropane	50-130	50-130	0-20	Naphthalene	55-140	55-140	0-20
1,2-Dibromoethane	80-120	80-120	0-20	Styrene	65-135	65-135	0-20
1,2-Dichlorobenzene	70-120	70-120	0-20	Tetrachloroethene	45-150	45-150	0-20
1,2-Dichloroethane	70-130	70-130	0-20	Toluene	75-120	75-120	0-20
1,2-Dichloropropane	75-125	75-125	0-20	t-1,2-Dichloroethene	60-140	60-140	0-20
1,3,5-Trimethylbenzene	75-130	75-130	0-20	Trichloroethene	70-125	70-125	0-20
1,3-Dichlorobenzene	75-125	75-125	0-20	Trichlorofluoromethane	60-145	60-145	0-20
1,3-Dichloropropane	75-125	75-125	0-20	Vinyl Chloride	50-145	50-145	0-20
1,4-Dichlorobenzene	75-125	75-125	0-20	c-1,3-Dichloropropene	70-130	70-130	0-20
2,2-Dichloropropane	70-135	70-135	0-20	c-1,2-Dichloroethene	70-125	70-125	0-20
2-Butanone	30-150	30-150	0-20	n-Butylbenzene	70-135	70-135	0-20
2-Chlorotoluene	75-125	75-125	0-20	n-Propylbenzene	70-130	70-130	0-20
2-Hexanone	55-130	55-130	0-20	o-Xylene	80-120	80-120	0-20
4-Chlorotoluene	75-130	75-130	0-20	p-Isopropyltoluene	75-130	75-130	0-20
4-Methyl-2-Pentanone	60-135	60-135	0-20	sec-Butylbenzene	70-125	70-125	0-20
Acetone	40-140	40-140	0-20	t-1,3-Dichloropropene	55-140	55-140	0-20
Benzene	80-120	80-120	0-20	tert-Butylbenzene	70-130	70-130	0-20
Bromobenzene	75-125	75-125	0-20	p/m-Xylene	75-130	75-130	0-20
Bromochloromethane	65-130	65-135	0-20	Methyl-t-Butyl Ether (MTBE)	65-125	65-125	0-20
Bromodichloromethane	75-120	75-120	0-20	1,2-Dichloroethane-d4	70-120	---	---
Bromoform	70-130	70-130	0-20	1,4-Bromofluorobenzene	75-120	---	---
Bromomethane	30-145	30-145	0-20	Dibromofluoromethane	85-115	---	---
Carbon Disulfide	35-160	35-160	0-20	Toluene-d8	85-120	---	---
Carbon Tetrachloride	65-140	65-140	0-20				

LCS/LCSD = laboratory control sample/laboratory control sample duplicate
MS/MSD = matrix spike/matrix spike duplicate
QC = quality control
RPD = relative percent difference

SAP Worksheet #28 -- Laboratory QC Samples Table (continued)

Matrix Water
Analytical Group anions (sulfate, chloride, nitrate, nitrite)
Analytical Method EPA 300.0
SOP Reference M703

QC Sample	Frequency/ Number	Method/SOP QC Acceptance Limit	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1/batch	No detects ≥ ½ RL	Reanalyze with all associated samples	Lead Chemist	Accuracy, Contamination	No detects ≥ ½ RL
LCS/LCSD	1/batch	% recovery: 90 – 110% % RPD: 0 – 15%	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed. Discuss in narrative	Lead Chemist	Accuracy / Precision	% recovery: 90 – 110% % RPD: 0 – 15%
MS/MSD	1/batch	% recovery: 80 – 120% % RPD: 0 – 20%	None – Flag Data	Lead Chemist	Accuracy / Precision	% recovery: 80 – 120% % RPD: 0 – 20%

LCS/LCSD = laboratory control sample/laboratory control sample duplicate
MS/MSD = matrix spike/matrix spike duplicate
QC = quality control
RL = reporting limit
RPD = relative percent difference
SOP = standard operating procedure

SAP Worksheet #28 -- Laboratory QC Samples Table (continued)

Matrix Water
Analytical Group cations (calcium, iron, magnesium, potassium, sodium)
Method/ EPA 6010B
SOP Reference M601

QC Sample	Frequency/ Number	Method/SOP QC Acceptance Limit	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1/batch	No detects ≥ ½ QL	If sufficient sample volume is available, re-extract and reanalyze affected samples. If volume is not sufficient, reanalyze extracts. Qualify data as needed.	Lead Chemist	Accuracy, Contamination	No detects ≥ ½ QL
LCS/LCSD	1/batch	% recovery: 80%-120% % RPD: 0 - 20%	If sufficient sample volume is available, re-extract and reanalyze affected samples. If volume is not sufficient, reanalyze extracts. Qualify data as needed. Discuss in narrative	Lead Chemist	Accuracy, Precision	% recovery: 80%-120% % RPD: 0 - 20%
MS/MSD	1/batch	% recovery: 80%-120% % RPD: 0 - 20%	None – Flag data	Lead Chemist	Accuracy, Precision	% recovery: 80%-120% % RPD: 0 - 20%
Post-digestion Spike	1/batch	% recovery: 75%-125%	None	Lead Chemist	Accuracy	% recovery: 75%-125%
Serial Dilution	1/batch	≤10% for analytes with concentration >50x QL	None	Lead Chemist	Accuracy	≤10% for analytes with concentration >50x QL
Lab Duplicate (if analyzed)	1/batch	≤20% RPD	None	Lead Chemist	Precision	≤20% RPD
ICSA/AB	Beginning Daily	80%-120% recovery; Evaluate non-interferent ICSA results with absolute values ≥2x MDL	Terminate analysis, correct problem, recalibrate instrument, check calibration, and re-run all samples analyzed since last compliant ICS.	Lead Chemist	Accuracy	80%-120% recovery; Evaluate non-interferent ICSA results with absolute values ≥2x MDL

ICS = internal control standard
ICSA = interference check solution
ICSA/AB = interference check solution AB
LCS/LCSD = laboratory control sample/laboratory control sample duplicate
MDL = method detection limit
MS/MSD = matrix spike/matrix spike duplicate
QC = quality control
QL = quantitation limit
RPD = relative percent difference
SOP = standard operating procedure

SAP Worksheet #28 -- Laboratory QC Samples Table (continued)

Matrix Water
Analytical Group TDS
Method/ SM 2540C
SOP Reference M713

QC Sample	Frequency/ Number[1]	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1/batch	No detects ≥ RL	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy, contamination	No detects ≥ RL
Sample Duplicate	1/20 samples	0-10% RPD	None	Analyst	Precision	0-10% RPD

RL = reporting limit
RPD = relative percent difference
SOP = standard operating procedure
TDS = total dissolved solids

SAP Worksheet #28 -- Laboratory QC Samples Table (continued)

Matrix Water
Analytical Group TOC
Analytical Method SM 5310B
SOP Reference M726

QC Sample:	Frequency / Number	Method/ SOP QC Acceptance Limits	Corrective Action (CA)	Person(s) Responsible for CA	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	One per batch	No detects ≥ ½ QL	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy	No detects ≥ ½ QL
LCS/LCSD	One pair per batch	80-120% RPD≤20%	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.		Accuracy/Precision	80-120% RPD≤20%
MS/MSD	One pair per batch	75-125% RPD≤25%	None – Flag Data		Accuracy/Precision	75-125% RPD≤25%

LCS/LCSD = laboratory control sample/laboratory control sample duplicate
MS/MSD = matrix spike/matrix spike duplicate
QL = quantitation limit
RPD = relative percent difference
SOP = standard operating procedure
TOC = total organic carbon

SAP Worksheet #28 -- Laboratory QC Samples Table (continued)

Matrix Water
Analytical Group COD
Analytical Method EPA 410.4
SOP Reference M724

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per batch	No detects ≥ ½ QL	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy	No detects ≥ ½ QL
LCS/LCSD	1 pair per batch	80-120% RPD≤20%	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.		Accuracy/ Precision	80-120% RPD≤20%
MS/MSD	1 pair per batch	75-130% RPD≤25%	None – Flag Data		Accuracy/ Precision	75-125% RPD≤25%
Sample Duplicate	1 per batch if sufficient volume	RPD≤25%	None		Precision	RPD≤25%

COD = chemical oxygen demand
LCS/LCSD = laboratory control sample/laboratory control sample duplicate
MS/MSD = matrix spike/matrix spike duplicate
QL = quantitation limit
RPD = relative percent difference
SOP = standard operating procedure

SAP Worksheet #28 -- Laboratory QC Samples Table (continued)

Matrix Water
Analytical Group dissolved gases
Analytical Method RSK 175
SOP Reference M386

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per batch	No detects ≥ ½ QL	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy	No detects ≥ ½ QL
LCS/LCSD	1 pair per batch	80-120% RPD≤20%	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.		Accuracy/Precision	80-120% RPD≤20%
Duplicate	1 pair per batch	RPD≤25%	None – Flag Data		Accuracy/Precision	RPD≤25%

LCS/LCSD = laboratory control sample/laboratory control sample duplicate
QL = quantitation limit
RPD = relative percent difference
SOP = standard operating procedure

SAP Worksheet #28 -- Laboratory QC Samples Table (continued)

Matrix Water
Analytical Group Dhc
Analytical Method CENSUS qPCR
SOP Reference DNA-qPCR

QC Sample	Frequency / Number	Method / SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per analytical batch	CT < or = Assay Negative Control	Rerun assay or reextract samples if problem persists	Lab analyst	Representativeness	Not detected
Surrogate	NA	NA	NA		Accuracy	
LCS or LCS/LCSD pair if insufficient sample for MS/MSD	1 per analytical assay plate	CT value within 2 units of same point on standard curve	Rerun assay / check reagents		Precision/ Accuracy	+/-2CT units
MS/MSD	At client's request & with sample submission	CT value within 4 units of other sample (duplicate)	Rerun assay; if still not within 4 Ct units, flag J (estimate)		Precision/ Accuracy	+/- 20%

CT = cycle threshold
LCS/LCSD = laboratory control sample/laboratory control sample duplicate
MS/MSD = matrix spike/matrix spike duplicate
QL = quantitation limit
SOP = standard operating procedure

SAP Worksheet #28 -- Laboratory QC Samples Table (continued)

Matrix Soil gas
Analytical Group VOCs
Analytical Method TO-15
SOP Reference M380

QC Sample	Frequency / Number	Method/ SOP QC Acceptance Limits	Corrective Action (CA)	Person(s) Responsible for CA	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1/batch	No detects ≥ ½ RL	If sufficient sample volume is available, reanalyze blank, QC and affected samples. If volume is not sufficient, qualify data as needed.	Analyst	Accuracy, Bias, Contamination	No detects ≥ ½ RL
LCS/LCSD	1 pair per batch	Historical limits for reported analytes – refer to Table 2 (below)	If sufficient sample volume is available, reanalyze QC and affected samples. If volume is not sufficient, qualify data as needed. Discuss in narrative		Accuracy, Precision	% Recovery / % Relative Percent Difference (RPD)
Surrogate	All environmental and laboratory samples	Historical limits for reported analytes – refer to Table 2 (below)	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.		Accuracy/Bias	% Recovery
Internal Standard	All environmental and laboratory samples	-50% - +100%	If sufficient sample volume is available, reanalyze affected samples. If volume is not sufficient, qualify data as needed.		Accuracy, Representativeness	Areas within -50% to +100% of ICAL midpoint standard

ICAL = internal calibration
LCS/LCSD = laboratory control sample/laboratory control sample duplicate
MS/MSD = matrix spike/matrix spike duplicate
QC = quality control
RL = reporting limit
RPD = relative percent difference
SOP = standard operating procedure

TABLE 2 – EPA Method TO-15 QC Limits Table

Analyte	LCS / LCSD %REC	%RPD	Analyte	LCS / LCSD %REC	%RPD
1,1,1-Trichloroethane	50-150	0-35	Chloroethane	50-150	0-35
1,1,2,2-Tetrachloroethane	50-150	0-35	Chloroform	50-150	0-35
1,1,2-Trichloro-1,2,2-Trifluoroethane	50-150	0-35	Chloromethane	50-150	0-35
1,1,2-Trichloroethane	65-149	0-37	Dibromochloromethane	50-150	0-35
1,1-Dichloroethane	50-150	0-35	Dichlorodifluoromethane	50-150	0-35
1,1-Dichloroethene	50-150	0-35	Ethanol	50-150	0-35
1,2,4-Trichlorobenzene	50-150	0-35	Ethylbenzene	52-154	0-38
1,2,4-Trimethylbenzene	50-150	0-35	Hexachloro-1,3-Butadiene	50-150	0-35
1,2-Dibromoethane	54-144	0-36	Methylene Chloride	50-150	0-35
1,2-Dichlorobenzene	34-160	0-47	Styrene	50-150	0-35
1,2-Dichloroethane	69-153	0-35	Tetrachloroethene	56-152	0-40
1,2-Dichloropropane	67-157	0-35	Toluene	56-146	0-43
1,3,5-Trimethylbenzene	50-150	0-35	t-1,2-Dichloroethene	50-150	0-35
1,3-Dichlorobenzene	50-150	0-35	Trichloroethene	63-159	0-34
1,4-Dichlorobenzene	36-156	0-47	Trichlorofluoromethane	50-150	0-35
2-Butanone	50-150	0-35	Vinyl Acetate	50-150	0-35
2-Hexanone	50-150	0-35	Vinyl Chloride	45-177	0-36
4-Ethyltoluene	50-150	0-35	c-1,3-Dichloropropene	61-157	0-35
4-Methyl-2-Pentanone	50-150	0-35	c-1,2-Dichloroethene	50-150	0-35
Benzene	60-156	0-40	o-Xylene	52-148	0-38
Benzyl Chloride	50-150	0-35	t-1,3-Dichloropropene	50-150	0-35
Bromodichloromethane	50-150	0-35	p/m-Xylene	42-156	0-41
Bromoform	62-134	0-38	Methyl-t-Butyl Ether (MTBE)	50-150	0-35
Bromomethane	50-150	0-35	*1,2-Dichloroethane-d4*	*76-136*	---
Carbon Disulfide	50-150	0-35	*1,4-Bromofluorobenzene*	*71-131*	---
Carbon Tetrachloride	64-154	0-32	*Toluene-d8*	*72-126*	---
Chlorobenzene	50-150	0-35			

%REC = percent recovery
%RPD = relative percent difference
LCS/LCSD = laboratory control sample/laboratory control sample duplicate
QC = quality control

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SAP Worksheet #29 -- Project Documents and Records Table
(UFP-QAPP Manual Section 3.5.1)

Document	Where Maintained[1]
Project Planning Documents (Work Plan, Health and Safety Plan, etc.)	A. CKY project file B. CKY project file, NAVFAC SW Administrative Record (AR)
Field Data Collection Logs (with identification of QC samples)	A. CKY project file B. CKY project file
Field Logbook	A. CKY project file B. CKY project file
Chain-of-Custody Forms	A. CKY project file B. CKY project file
Weekly Updates and Monthly Progress Reports	A. CKY project file B. CKY project file
Corrective Action Reports and documentation of results	A. CKY project file B. CKY project file
Laboratory Data Packages including: Chain-of-Custody Forms Cooler Receipt Forms Sample Receipt and Sample Tracking Forms Sample Cross Reference and Laboratory Sample Identification Numbers Tabulated data summary forms and raw data for field samples, standards, QC checks, and QC Forms Case Narrative Sample chronology (time of receipt, extraction, and analysis) Definitions of Laboratory Qualifiers Instrument calibration reports Corrective Action Reports and documentation of results Reporting forms with final results and laboratory signatures	A. CKY project file, project laboratory files B. project laboratory files, NAVFAC SW office project file, and NAVFAC SW AR
Electronic data deliverable from laboratory in NEDD format	A. CKY project file, project laboratory files, and NAVFAC SW AR
Electronic data deliverable of validated data in NEDD format	A. CKY project file, LDC files B. NIRIS and NAVFAC SW AR
Laboratory certification	A. CKY project file, project laboratory files B. project laboratory files, CKY project file
Data Validation Report	A. CKY project file, LDC files B. CKY project file, and NAVFAC SW AR

[1] A = during project; B = after project completion

AR = Administrative Record
CKY = CKY Incorporated
LDC = Laboratory Data Consultants, Inc.
NAVFAC SW = Naval Facilities Engineering Command, Southwest Division
NEDD = Navy Electronic Data Deliverable
NIRIS = Naval Installation Restoration Information Solution
QC = quality control

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SAP Worksheet #30 -- Analytical Services Table
(UFP-QAPP Manual Section 3.5.2.3)

Matrix	Analytical Group	Sample Locations/ID Number	Analytical Method / SOP	Data Package Turnaround Time	Laboratory / Organization[1] (name and address, contact person and telephone number)	Backup Laboratory / Organization[1] (name and address, contact person and telephone number)
Soil gas	VOCs	All soil gas samples	EPA Method TO-15 / M380	21 business days	Calscience Environmental Laboratories, Inc. 7440 Lincoln Way Garden Grove, CA 92841 Linda Scharpenberg (714) 895-5494 x306	EMAX Laboratories, Inc. 1835 W. 205th Street Torrance, CA 90501 Jim Carter (310) 618-8889 x105
	methane		ASTM 1946 – Fixed Gases			
Water	VOCs	All water samples	EPA Method 8260B / M311	21 business days		
	anions		EPA Method 300.0 / M703			
	cations		EPA Method 6010B / M601			
	TDS		SM 2540C / M713			
	COD		EPA Method 410.4 / M724			
	TOC		SM 5310B / M726			
	Dissolved gases		RSK 175 / M386			
	Dhc		CENSUS qPCR / DNA-qPCR			Microbial Insights, Inc. 2340 Stock Creek Blvd. Rockford, TN 37853 (865) 573-8188

[1] Laboratories are State of California and NELAC Certified and DOD ELAP accredited.

ASTM = American Society for Testing and Materials
COD = chemical oxygen demand
Dhc = *Dehalococcoides* spp.
EPA = United States Environmental Protection Agency
qPCR = quantitative polymerase chain reaction
SOP = standard operating procedure
TDS = total dissolved solids
TOC = total organic carbon
VOC = volatile organic compound

SAP Worksheet #31 -- Planned Project Assessments Table
(UFP-QAPP Manual Section 4.1.1)

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person(s) Responsible for Performing Assessment (title and organizational affiliation)	Person(s) Responsible for Responding to Assessment Findings (title and organizational affiliation)	Person(s) Responsible for Identifying and Implementing Corrective Actions (CAs) (title and organizational affiliation)	Person(s) Responsible for Monitoring Effectiveness of CA (title and organizational affiliation)
Field readiness review	once	internal	CKY	CKY Project QCM	CKY Project Manager	CKY Project QCM	CKY Project QCM
Field activity audit	Minimum 1/month	internal	CKY	CKY Project Chemist, CKY Project QCM	CKY Project Manager	CKY Project Chemist, CKY QPM	CKY Project QCM
Data review	once	internal	CKY	CKY Project Chemist	Laboratory Manager, Calscience	CKY Project Chemist, Lab Manager, Calscience	Lab Manager, Calscience

CKY = CKY Incorporated
Calscience = Calscience Environmental Laboratories, Inc.
QCM = Quality Control Manager
QPM = Quality Program Manager

SAP Worksheet #32 -- Assessment Findings and Corrective Action Responses
(UFP-QAPP Manual Section 4.1.2)

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings (name, title, organization)	Timeframe of Notification	Nature of Corrective Action (CA) Response Documentation	Individual(s) Receiving CA Response (name, title, organization)	Timeframe for Response
Field activity audit	memo	Howard Wittenberg, CKY PM	1 day after audit	Corrective Action Report (CAR)	Brenda Reese, NAVFAC SOUTHWEST RPM	30 days
Data review	memo	Brenda Reese, NAVFAC SOUTHWEST RPM	30 days after receipt of data packages	CAR	Brenda Reese, NAVFAC SOUTHWEST RPM	60 days

CKY = CKY Incorporated
NAVFAC = Naval Facilities Engineering Command
PM = project manager
RPM = remedial project manager

SAP Worksheet #33 – Quality Assurance Management Reports Table
(UFP QAPP Manual Section 4.2)

Type of Report	Frequency (daily, weekly monthly, quarterly, annually, etc.)	Projected Delivery Date(s)	Person(s) Responsible for Report Preparation (title and organizational affiliation)	Report Recipient(s) (title and organizational affiliation)
Weekly Updates	weekly	weekly during field activities	CKY PM	NAVFAC Southwest RPM
Monthly Progress Reports	monthly	monthly throughout project duration	CKY PM	NAVFAC Southwest RPM
Results of field audits	monthly	With daily CQC report	CKY QCM	CKY Program Manager (ultimately NAVFAC Southwest)

CKY = CKY Incorporated
CQC = contractor quality control
NAVFAC = Naval Facilities Engineering Command
PM = project manager
QCM = project quality control manager
RPM = remedial project manager

SAP Worksheet #34 –Verification (Step I) Process Table
(UFP-QAPP Manual Section 5.2.1)

Verification Input	Description	Internal/ External	Responsible for Verification (name, organization)
Chain of Custody	Chain-of-custody forms will be checked against cooler contents and signed. Copies will be kept in the field documentation and the originals will be shipped inside the cooler.	internal	Noah Rivera, CKY
Field Data Logbook	Data from logbooks will be reviewed for completeness and accuracy.	internal	Noah Rivera, CKY
Laboratory Data Packages	Content of lab data packages will be reviewed for completeness, organization, and signatures.	internal	Linda Scharpenberg, Calscience
Laboratory Data Packages	Content of lab data packages will be reviewed for completeness, organization, and signatures.	external	Tim Theisen, CKY
Electronic Data Deliverable (EDD)	Values in EDD will be checked against hardcopy of lab reports.	internal	Linda Scharpenberg, Calscience
EDD	Values in EDD will be checked against hardcopy of lab reports.	external	Linda Rauto, LDC

[1] IIa=compliance with methods, procedures, and contracts [see Table 10, page 117, UFP-QAPP manual, V.1, March 2005.]
IIb=comparison with measurement performance criteria in the SAP [see Table 11, page 118, UFP-QAPP manual, V.1, March 2005]

Calscience = Calscience Environmental Laboratories, Inc.
CKY = CKY Incorporated
EDD = electronic data deliverable
LDC = Laboratory Data Consultants, Inc.

SAP Worksheet #35 –Validation (Steps IIa and IIb) Process Table

(UFP-QAPP Manual Section 5.2.2) (Figure 37 UFP-QAPP Manual) (Table 9 UFP-QAPP Manual)

Step IIa / IIb[1]	Validation Input	Description	Responsible for Validation (name, organization)
IIa	Sampling Methods and Procedures	Establish that required sampling procedures were used and that any deviations were documented.	Tim Theisen, CKY
IIa	Sampling Handling	Ensure that required sample handling, receipt, and storage procedures were followed, and that any deviations were documented.	Tim Theisen, CKY
IIa	Holding times	Ensure that samples were analyzed within holding times specified in method. If not, confirm that deviations were documented and appropriate notifications made.	Linda Scharpenberg, Calscience
IIa	Analytical Methods and Procedures	Establish that required analytical methods were used and that any deviations were noted. Ensure that the QC samples met performance criteria and that any deviations were documented.	Linda Scharpenberg, Calscience
IIa	Data Qualifiers	Determine that the laboratory data qualifiers were defined in the laboratory data package and applied as specified.	Linda Scharpenberg, Calscience
IIb	Sampling Plan	Determine whether the SAP was executed as specified.	Tim Theisen, CKY
IIb	Project Quantitation Limits	Determine that quantitation limits (QLs) were achieved, as stated in the SAP, and that the laboratory successfully analyzed a standard at the QL.	Linda Rauto, LDC
IIb	Performance Criteria	Evaluate QC data against project-specific performance criteria in the SAP.	Linda Rauto, LDC

[1] IIa=compliance with methods, procedures, and contracts [see Table 10, page 117, UFP-QAPP manual, V.1, March 2005.]
IIb=comparison with measurement performance criteria in the SAP [see Table 11, page 118, UFP-QAPP manual, V.1, March 2005]

Calscience = Calscience Environmental Laboratories, Inc.
CKY = CKY Incorporated
LDC = Laboratory Data Consultants, Inc.
QC = quality control
QL = quantitation limit
SAP = Sampling and Analysis Plan

SAP Worksheet #36 – Analytical Data Validation (Steps IIa and IIb) Summary Table
(UFP-QAPP Manual Section 5.2.2.1)

Step IIa / IIb [1]	Matrix	Analytical Group	Validation Criteria	Data Validator (title and organizational affiliation)
IIa	water	dissolved gases	Calscience SOPs, RSK-175M, and DoD QSM [2]	Project Manager, Calscience; Chemist, LDC
IIa	water	anions	Calscience SOPs, EPA Method 300.0, and DoD QSM [2]	
IIa	water	cations	Calscience SOPs, EPA Method 6010B, and DoD QSM [2]	
IIa	water	TDS	Calscience SOPs, SM 2540C, and DoD QSM [2]	
IIa	water	COD	Calscience SOPs, EPA Method 410.4, and DoD QSM [2]	
IIa	water	TOC	Calscience SOPs, SM 5310B, and DoD QSM [2]	
IIa	water	VOCs	Calscience SOPs, EPA Method 8260B, and DoD QSM [2]	
IIa	soil gas	VOCs	Calscience SOPs, EPA Method TO-15, and DoD QSM [2]	
		methane	Calscience SOPs, ASTM D-1946, and DoD QSM [2]	
IIb	water	TOC, COD	LDC SOPs, NAVFAC SW EWI #1[3], and US EPA Level II Guidelines [4]	Chemist, LDC
IIb	water	dissolved gases, TDS	LDC SOPs, NAVFAC SW EWI #1[3], and US EPA Level II Guidelines [5]	
IIb	water	anions, cations	LDC SOPs, NAVFAC SW EWI #1[3], and US EPA Level III and IV Guidelines[5]	
IIb	water	VOCs	LDC SOPs, NAVFAC SW EWI #1[3], and US EPA Level III and IV Guidelines[4]	
IIb	soil gas	VOCs	LDC SOPs, NAVFAC SW EWI #1[3], and US EPA Level III and IV Guidelines[4]	

[1] IIa=compliance with methods, procedures, and contracts [see Table 10, page 117, UFP-QAPP manual, V.1, March 2005.]
IIb=comparison with measurement performance criteria in the SAP [see Table 11, page 118, UFP-QAPP manual, V.1, March 2005]

[2] DoD, 2009. *Quality Systems Manual for Environmental Laboratories*, Final, Version 4.2, October 2010.

[3] Naval Facilities Engineering Command, Southwest Division, 2001a, *Environmental Work Instruction 3EN2.1-Chemical Data Validation*.

[4] U.S. Environmental Protection Agency, 2008, *Contract Laboratory Program National Functional Guidelines for Superfund Organic Data Review*, EPA-540/R-08-01. June 2008. (This document to be followed only as appropriate for project methods.)

[5] U.S. Environmental Protection Agency, 2010, *Contract Laboratory Program National Functional Guidelines for Superfund Inorganic Data Review*, EPA-540/R-10-011. January 2010. (This document to be followed only as appropriate for project methods.)

ASTM = American Society for Testing and Materials
Calscience = Calscience Environmental Laboratories, Inc. (subcontracted laboratory
CKY = CKY Incorporated (prime contractor)
COD = chemical oxygen demand
DoD = Department of Defense
EPA = United States Environmental Protection Agency
LDC = Laboratory Data Consultants (data validation subcontractor)
QC = quality control
SOP = standard operating procedure
TDS = total dissolved solids
TOC = total organic carbon
VOC = volatile organic compound

Data Package Deliverables (EPA Level II) will include:
Inventory Sheet, Case Narrative, Shipping/Receiving Documents (airbills, chain-of-custody forms, sample receipt forms, etc.),
Sample Data (Tabulated Summary Form for Field Sample Results
QC Data (Surrogate Percent Recovery Tabulated Summary Form, LCS Tabulated Summary Form, MS/MSD Recovery Tabulated Summary Form, Method Blank Tabulated Summary Form, and
Miscellaneous Data (telephone communication log).

Data Package Deliverables (90% EPA Level III and 10% EPA Level IV) will include:
Inventory Sheet, Case Narrative, Shipping/Receiving Documents (airbills, chain-of-custody forms, sample receipt forms, etc.),
Sample Data (Tabulated Summary Form for Field Sample Results, Chromatograms from both columns for each sample, GC integration report or data system printouts and calibration plots for each sample, Gel permeation chromatography sample chromatograms, Sample preparation/extraction/digestion log and logbook pages, and Sample analysis run log and logbook pages),
Standards Data (MDL Study Tabulated Summary Form, Initial Calibration Tabulated Summary Form, Continuing Calibration Tabulated Summary Form, GC chromatrograms and data system printout for al GC standards, GPC Calibration Tabulated Summary Form, Florisil Cartridge Check Tabulated Summary Form, and Standards preparation logbook pages),
QC Data (Surrogate Percent Recovery Tabulated Summary Form, MS/MSD Recovery Tabulated Summary Form, Method Blank Tabulated Summary Form, QC raw data, chromatograms, quantitation reports, etc., and QC sample preparation logbook pages), and
Miscellaneous Data (Original preparation and analysis forms or copies of preparation and analysis logbook pages, Screening records, All instrument output, including strip charts, from screening activities, Preparation logs raw data, Percent solids determination log, and Other records e.g., telephone communication log).

SAP Worksheet #37 -- Usability Assessment
(UFP-QAPP Manual Section 5.2.3)

Summarize the usability assessment process and all procedures, including interim steps and any statistics, equations, and computer algorithms that will be used:
The data validation report will provide most of the critical input for the usability assessment. Assessment requirements and procedures are outlined elsewhere in this SAP and in the guidance documents. The content of the usability report, listed below, indicates the steps in the assessment process.

Describe the evaluative procedures used to assess overall measurement error associated with the project:
The project team will evaluate field observations and the data and present these in the Investigation Report. Analytical results will be evaluated through the verification and validation steps discussed in this SAP. The QPM will provide input on the suitability of the results for the purposes intended. The investigation results will be evaluated against the project DQOs (see Worksheet #11) and requirements of the data users or decision makers. Limitations on the use of the data will be addressed as a factor in the uncertainty associated with the decision-making process. Where the validation qualifiers impact the overall data interpretation and project recommendations, the reports will discuss the issue and the effect on the conclusions and recommendations.

Identify the personnel responsible for performing the usability assessment:
Tim Theisen, CKY Project Chemist, will perform the usability assessment and prepare the summary tables and usability report portions of the Long Term Monitoring Report.

Describe the documentation that will be generated during usability assessment and how usability assessment results will be presented so that they identify trends, relationships (correlations), and anomalies:
The usability report will present the results of the usability assessment in the following sections:

- Project Scope – will address sampling and field activities covered by this SAP.
- Project Description – will describe the site background and sampling strategy.
- Sampling Procedures – will discuss any deviations from the SAP and any field work variances
- Quality Control Activities – will provide numbers and types of QC samples collected, discussion of any QC problems encountered and field and laboratory QC activities, including any deviations from the plans.
- Analytical Procedures – will describe briefly the preparatory and analytical procedures used.
- Chemical Data Quality Assessment – will include a Summary Data Quality Assessment (based on project quality objectives), with tables for Detected Analytes (hits only), Results (all validated), Rejected Results, and discussions of overall assessment of data quality, procedures used for data assessment, and any results reflecting significant deviations.
- Conclusions and Recommendations
- References used to review the data.
- Appendices, including Laboratory Data Qualifier Definitions and Field Work Variance.

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FIGURES

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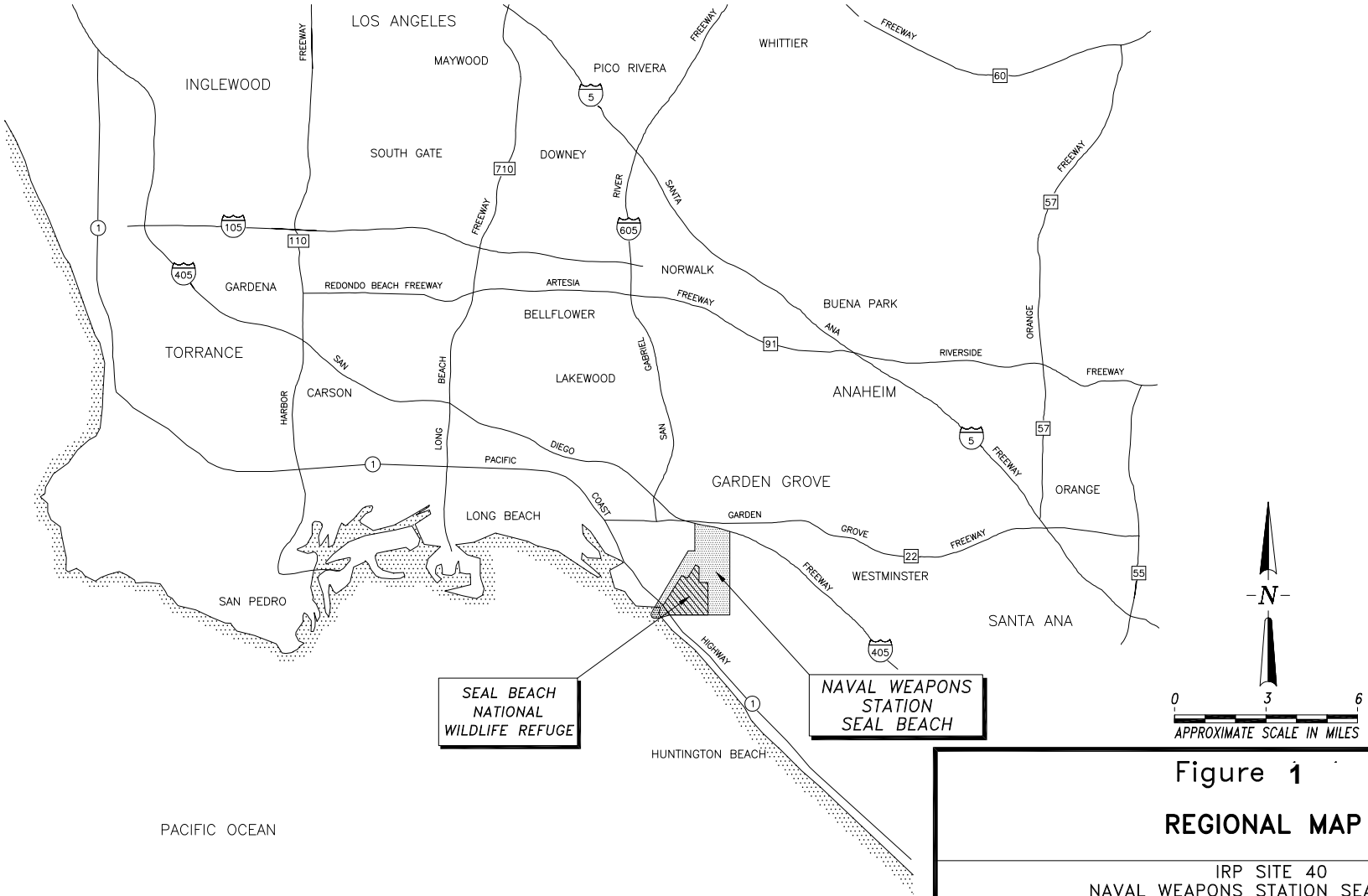


SOURCE: CH2M HILL 2002.

Figure 1

REGIONAL MAP

IRP SITE 40
NAVAL WEAPONS STATION SEAL BEACH
SEAL BEACH, CALIFORNIA

CKY Incorporated

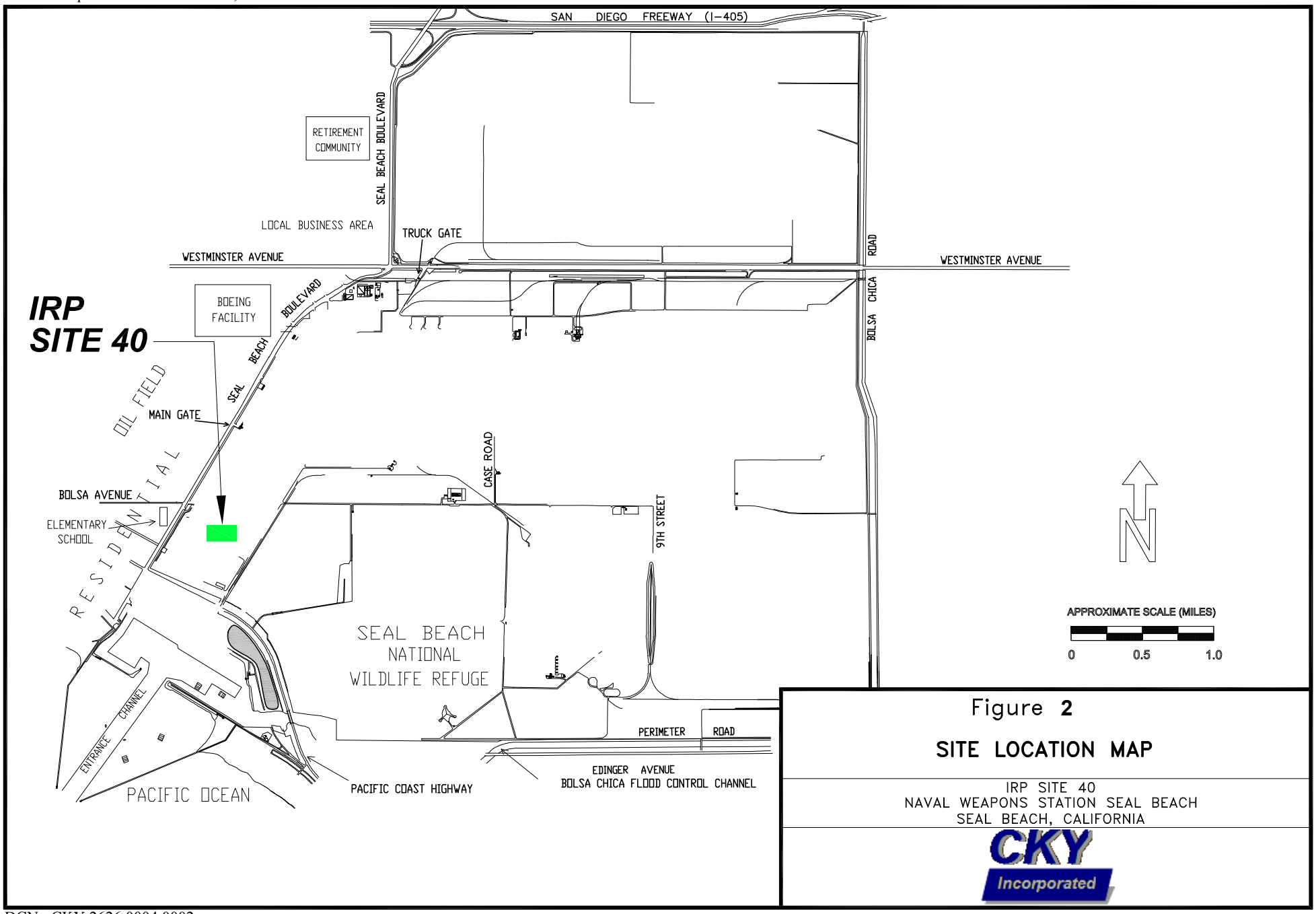
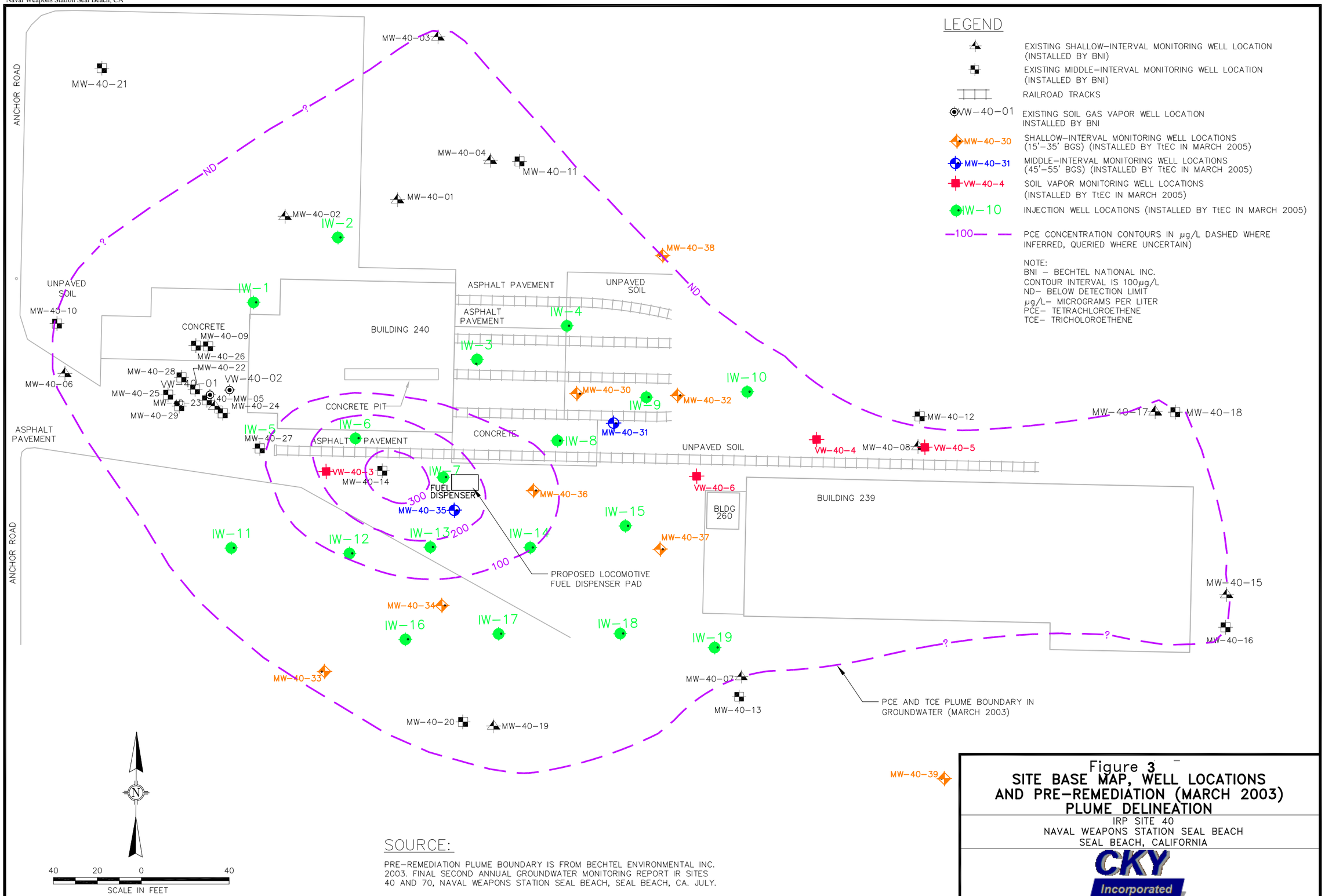


Figure 2

SITE LOCATION MAP

IRP SITE 40
NAVAL WEAPONS STATION SEAL BEACH
SEAL BEACH, CALIFORNIA

CKY Incorporated


LEGEND
EXISTING SHALLOW-INTERVAL MONITORING WELL LOCATION (INSTALLED BY BNI)
EXISTING MIDDLE-INTERVAL MONITORING WELL LOCATION (INSTALLED BY BNI)
RAILROAD TRACKS
VW-40-01 EXISTING SOIL GAS VAPOR WELL LOCATION INSTALLED BY BNI
MW-40-30 SHALLOW-INTERVAL MONITORING WELL LOCATIONS (15'-35' BGS) (INSTALLED BY TtEC IN MARCH 2005)
MW-40-31 MIDDLE-INTERVAL MONITORING WELL LOCATIONS (45'-55' BGS) (INSTALLED BY TtEC IN MARCH 2005)
VW-40-4 SOIL VAPOR MONITORING WELL LOCATIONS (INSTALLED BY TtEC IN MARCH 2005)
IW-10 INJECTION WELL LOCATIONS (INSTALLED BY TtEC IN MARCH 2005)
100 PCE CONCENTRATION CONTOURS IN µg/L DASHED WHERE INFERRED, QUERIED WHERE UNCERTAIN)
NOTE:
BNI - BECHTEL NATIONAL INC.
CONTOUR INTERVAL IS 100µg/L
ND- BELOW DETECTION LIMIT
µg/L- MICROGRAMS PER LITER
PCE- TETRACHLOROETHENE
TCE- TRICHOLOROETHENE
ANCHOR ROAD
MW-40-21
MW-40-03
MW-40-04
MW-40-11
MW-40-01
MW-40-02
IW-2
MW-40-38
ND
UNPAVED SOIL
MW-40-10
IW-1
CONCRETE
MW-40-09
MW-40-26
MW-40-22
BUILDING 240
ASPHALT PAVEMENT
UNPAVED SOIL
IW-4
IW-3
MW-40-06
MW-40-28
VW-40-01
VW-40-02
MW-40-25
MW-40-23
40-MW-05
MW-40-24
MW-40-29
CONCRETE PIT
MW-40-30
IW-9
MW-40-32
IW-10
MW-40-12
MW-40-17
MW-40-18
ASPHALT PAVEMENT
IW-5
MW-40-27
IW-6
ASPHALT PAVEMENT
CONCRETE
IW-8
MW-40-31
UNPAVED SOIL
VW-40-4
MW-40-08
VW-40-5
VW-40-3
MW-40-14
IW-7
FUEL DISPENSER
300
MW-40-35
MW-40-36
VW-40-6
BLDG 260
BUILDING 239
IW-15
IW-11
IW-12
IW-13
200
IW-14
MW-40-37
100
PROPOSED LOCOMOTIVE FUEL DISPENSER PAD
MW-40-15
MW-40-34
IW-16
IW-17
IW-18
IW-19
MW-40-16
MW-40-33
MW-40-07
MW-40-13
PCE AND TCE PLUME BOUNDARY IN GROUNDWATER (MARCH 2003)
MW-40-20
MW-40-19
MW-40-39
N
40 20 0 40
SCALE IN FEET
SOURCE:
PRE-REMEDIATION PLUME BOUNDARY IS FROM BECHTEL ENVIRONMENTAL INC. 2003. FINAL SECOND ANNUAL GROUNDWATER MONITORING REPORT IR SITES 40 AND 70, NAVAL WEAPONS STATION SEAL BEACH, SEAL BEACH, CA. JULY.
Figure 3
SITE BASE MAP, WELL LOCATIONS AND PRE-REMEDIATION (MARCH 2003) PLUME DELINEATION
IRP SITE 40
NAVAL WEAPONS STATION SEAL BEACH
SEAL BEACH, CALIFORNIA
CKY Incorporated

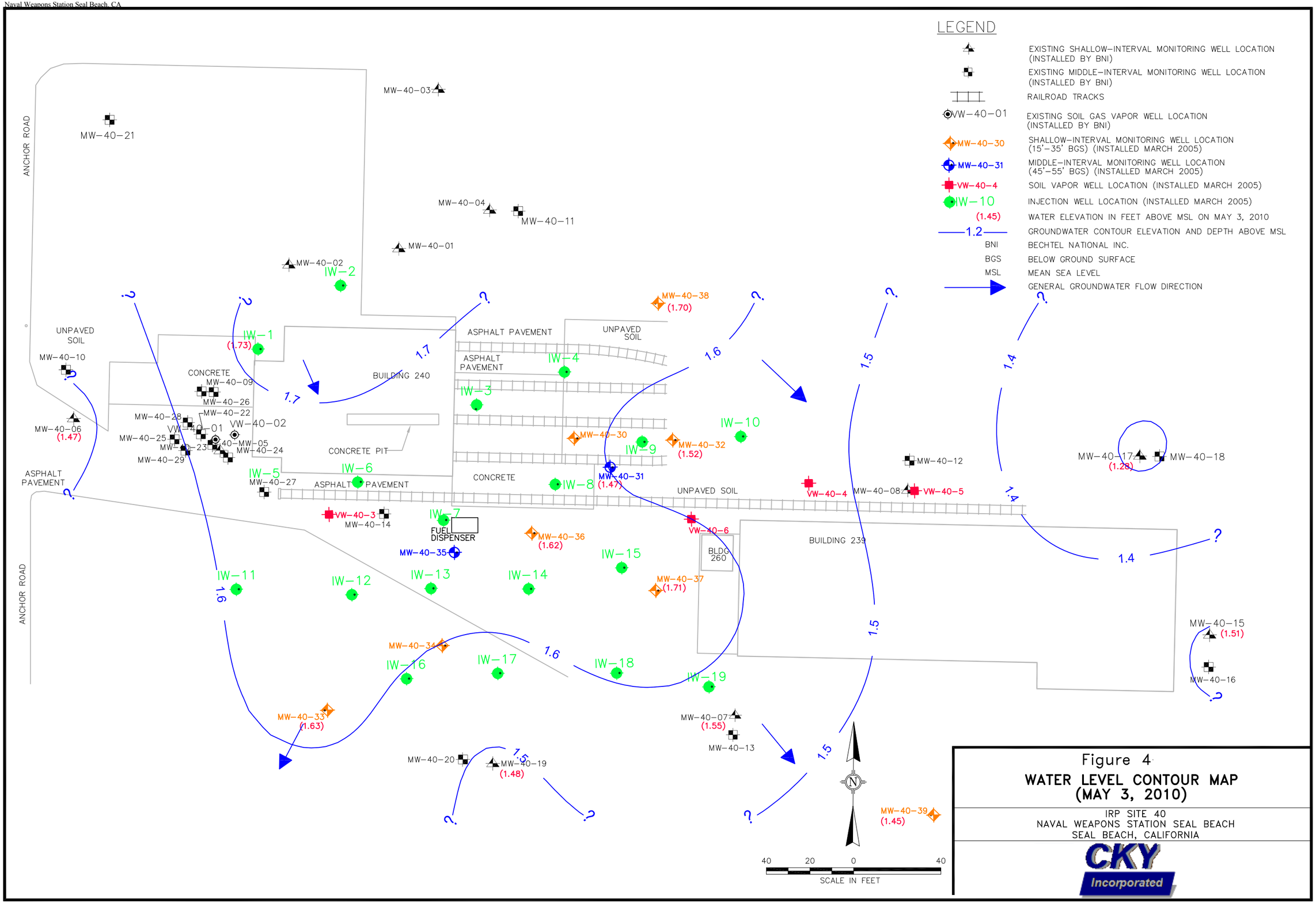
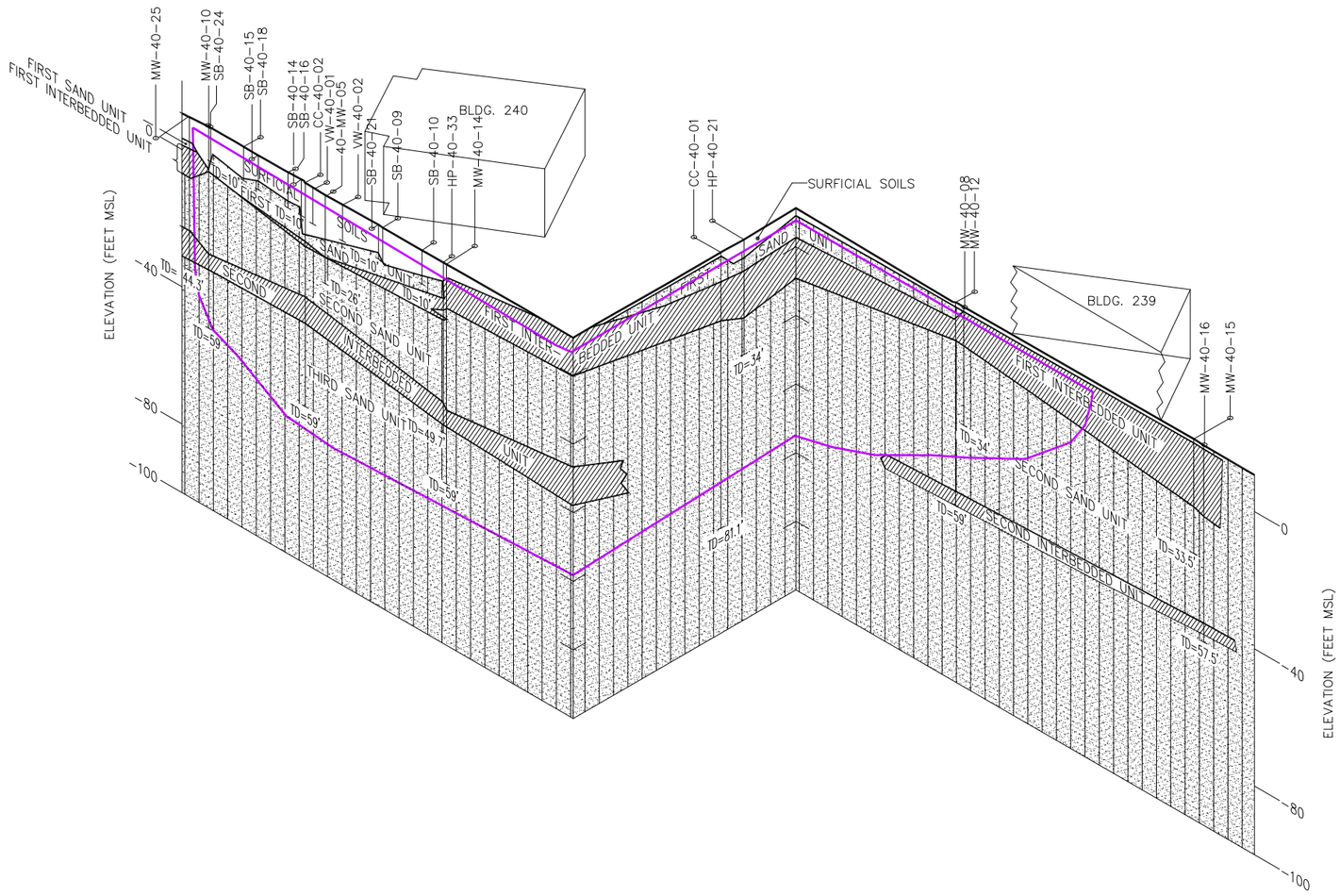


Figure 4
WATER LEVEL CONTOUR MAP (MAY 3, 2010)

IRP SITE 40
NAVAL WEAPONS STATION SEAL BEACH
SEAL BEACH, CALIFORNIA

CKY Incorporated



LEGEND

SUBSURFACE STRATIGRAPHIC SYMBOLS

PREDOMINANTLY FINE-GRAINED UNIT (CLAY, SILT, SILTY CLAY, CLAYEY SILT, SANDY CLAY AND SANDY SILT)

PREDOMINANTLY COARSE-GRAINED UNIT (SAND, SILTY SAND AND CLAYEY SAND)

UNIT BOUNDARY

APPROXIMATE EXTENT OF VOC PLUME IN GROUNDWATER

IR – INSTALLATION RESTORATION

SOURCE:

BECHTEL ENVIRONMENTAL, INC. 2003. FINAL SECOND ANNUAL GROUNDWATER MONITORING REPORT IR SITES 40 AND 70, NAVAL WEAPONS STATION SEAL BEACH, SEAL BEACH, CALIFORNIA. JULY.

0 80 160

FEET

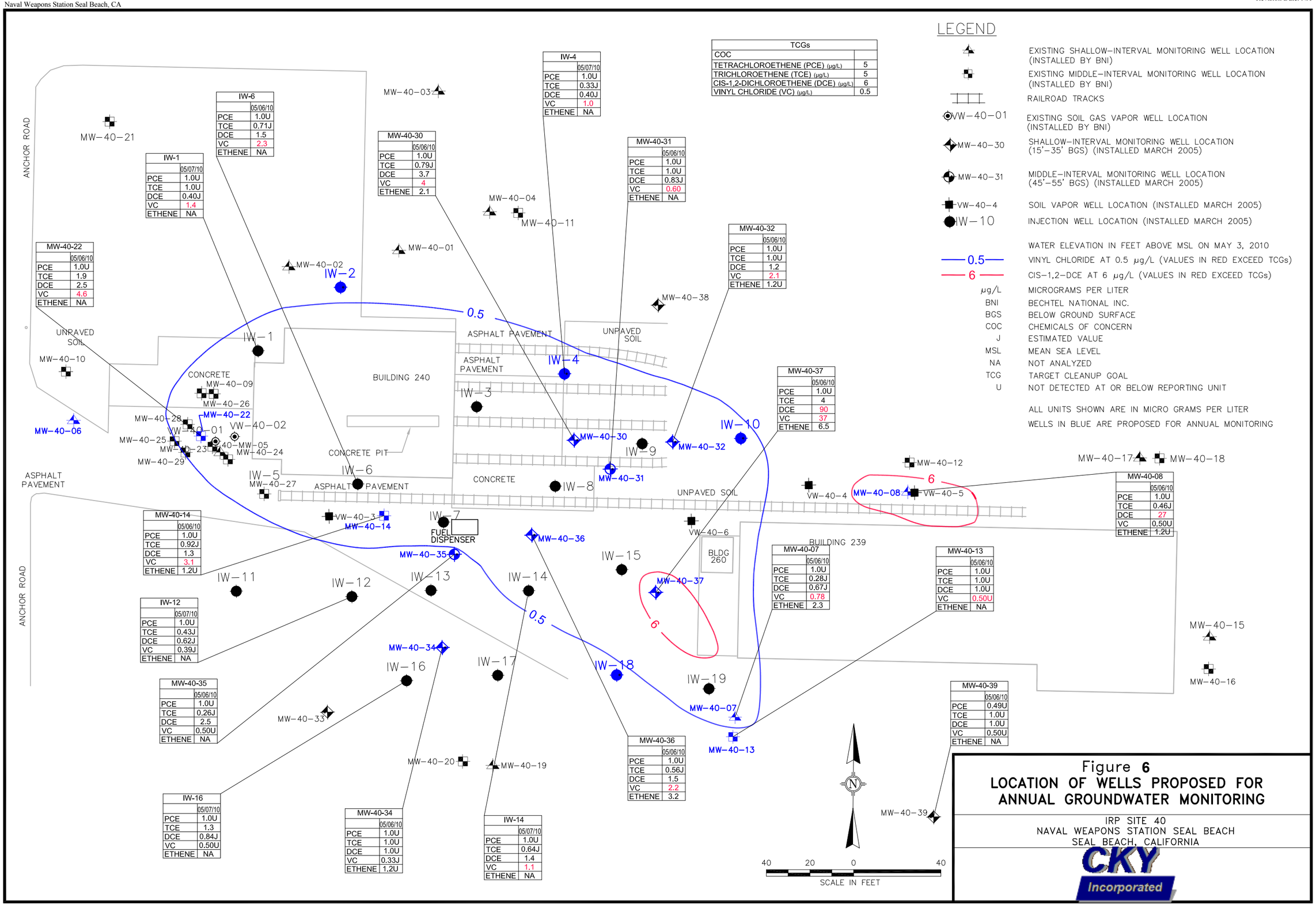
VERTICAL SCALE: 1 INCH = 40 FEET

Figure **5**

SITE PHYSICAL – CONCEPTUAL MODEL

IRP SITE 40
NAVAL WEAPONS STATION SEAL BEACH
SEAL BEACH, CALIFORNIA

CKY Incorporated



TCGs	
COC	
TETRACHLOROETHENE (PCE) (µg/L)	5
TRICHLOROETHENE (TCE) (µg/L)	5
CIS-1,2-DICHLOROETHENE (DCE) (µg/L)	6
VINYL CHLORIDE (VC) (µg/L)	0.5

IW-4	05/07/10
PCE	1.0U
TCE	0.33J
DCE	0.40J
VC	1.0
ETHENE	NA

IW-6	05/06/10
PCE	1.0U
TCE	0.71J
DCE	1.5
VC	2.3
ETHENE	NA

IW-1	05/07/10
PCE	1.0U
TCE	1.0U
DCE	0.40J
VC	1.4
ETHENE	NA

MW-40-30	05/06/10
PCE	1.0U
TCE	0.79J
DCE	3.7
VC	4
ETHENE	2.1

MW-40-31	05/06/10
PCE	1.0U
TCE	1.0U
DCE	0.83J
VC	0.60
ETHENE	NA

MW-40-22	05/06/10
PCE	1.0U
TCE	1.9
DCE	2.5
VC	4.6
ETHENE	NA

MW-40-32	05/06/10
PCE	1.0U
TCE	1.0U
DCE	1.2
VC	2.1
ETHENE	1.2U

MW-40-37	05/06/10
PCE	1.0U
TCE	4
DCE	90
VC	37
ETHENE	6.5

MW-40-08	05/06/10
PCE	1.0U
TCE	0.46J
DCE	27
VC	0.50U
ETHENE	1.2U

MW-40-14	05/06/10
PCE	1.0U
TCE	0.92J
DCE	1.3
VC	3.1
ETHENE	1.2U

MW-40-07	05/06/10
PCE	1.0U
TCE	0.28J
DCE	0.67J
VC	0.78
ETHENE	2.3

MW-40-13	05/06/10
PCE	1.0U
TCE	1.0U
DCE	1.0U
VC	0.50U
ETHENE	NA

IW-12	05/07/10
PCE	1.0U
TCE	0.43J
DCE	0.62J
VC	0.39J
ETHENE	NA

MW-40-35	05/06/10
PCE	1.0U
TCE	0.26J
DCE	2.5
VC	0.50U
ETHENE	NA

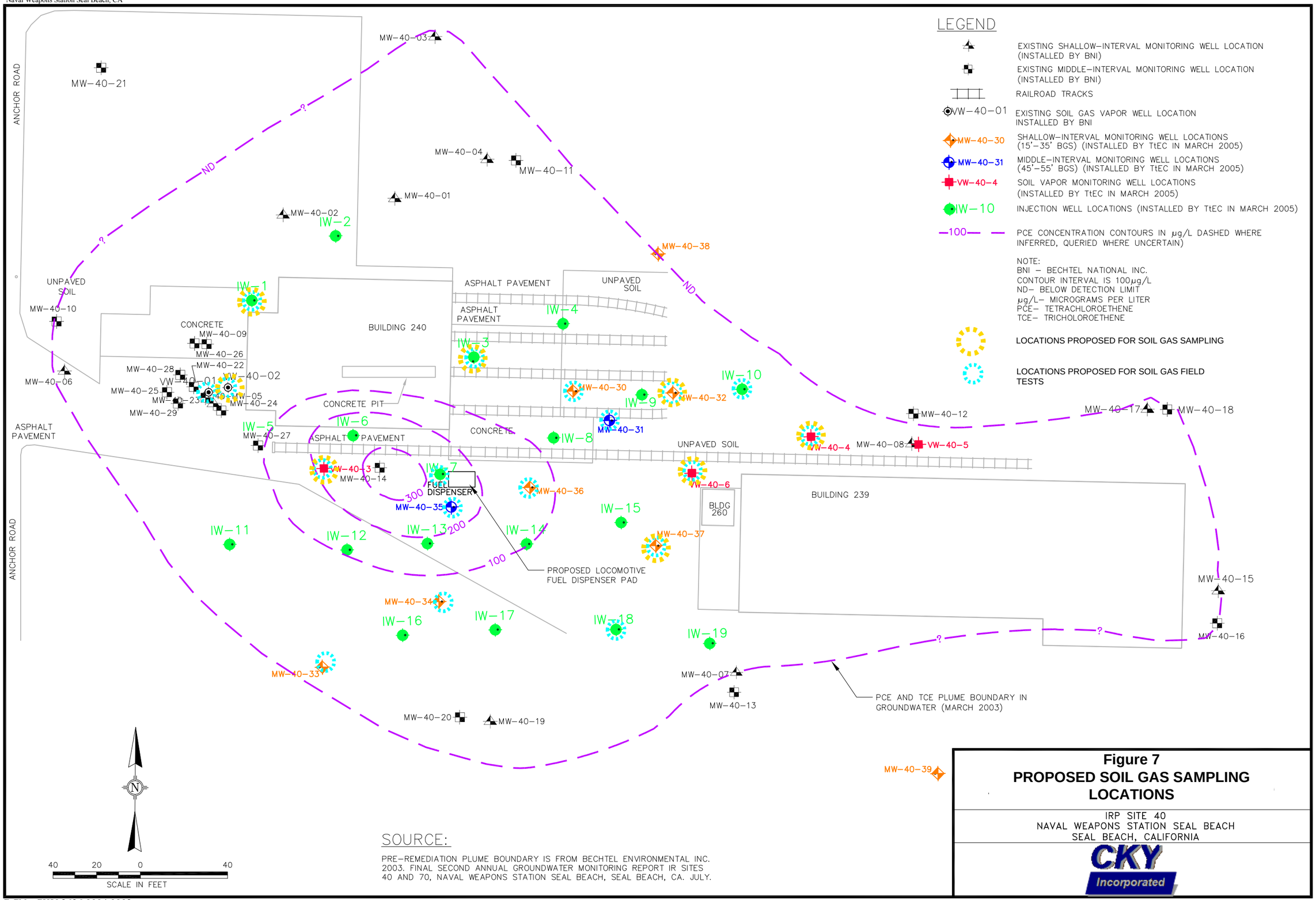
MW-40-39	05/06/10
PCE	0.49U
TCE	1.0U
DCE	1.0U
VC	0.50U
ETHENE	NA

MW-40-36	05/06/10
PCE	1.0U
TCE	0.56J
DCE	1.5
VC	2.2
ETHENE	3.2

IW-16	05/07/10
PCE	1.0U
TCE	1.3
DCE	0.84J
VC	0.50U
ETHENE	NA

MW-40-34	05/06/10
PCE	1.0U
TCE	1.0U
DCE	1.0U
VC	0.33J
ETHENE	1.2U

IW-14	05/07/10
PCE	1.0U
TCE	0.64J
DCE	1.4
VC	1.1
ETHENE	NA


LEGEND
EXISTING SHALLOW-INTERVAL MONITORING WELL LOCATION (INSTALLED BY BNI)
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100 PCE CONCENTRATION CONTOURS IN µg/L DASHED WHERE INFERRED, QUERIED WHERE UNCERTAIN)
NOTE:
BNI - BECHTEL NATIONAL INC.
CONTOUR INTERVAL IS 100µg/L
ND- BELOW DETECTION LIMIT
µg/L- MICROGRAMS PER LITER
PCE- TETRACHLOROETHENE
TCE- TRICHOLOROETHENE
LOCATIONS PROPOSED FOR SOIL GAS SAMPLING
LOCATIONS PROPOSED FOR SOIL GAS FIELD TESTS
ANCHOR ROAD
MW-40-21
MW-40-03
MW-40-04
MW-40-11
MW-40-01
MW-40-02
IW-2
MW-40-38
ND
UNPAVED SOIL
MW-40-10
IW-1
CONCRETE
MW-40-09
MW-40-26
MW-40-22
BUILDING 240
ASPHALT PAVEMENT
IW-4
IW-3
MW-40-06
MW-40-28
VW-40-01
VW-40-02
MW-40-25
MW-40-23
MW-40-05
MW-40-24
MW-40-29
CONCRETE PIT
IW-6
IW-5
MW-40-27
MW-40-30
IW-9
VW-40-32
IW-10
MW-40-31
IW-8
MW-40-12
MW-40-17
MW-40-18
VW-40-4
MW-40-08
VW-40-5
VW-40-3
MW-40-14
IW-7
FUEL DISPENSER
MW-40-35
MW-40-36
VW-40-6
BLDG 260
BUILDING 239
IW-15
MW-40-37
IW-11
IW-12
IW-13
IW-14
300
200
100
PROPOSED LOCOMOTIVE FUEL DISPENSER PAD
MW-40-34
IW-16
IW-17
IW-18
IW-19
MW-40-15
MW-40-16
MW-40-33
MW-40-07
MW-40-13
MW-40-20
MW-40-19
PCE AND TCE PLUME BOUNDARY IN GROUNDWATER (MARCH 2003)
MW-40-39
N
40 20 0 40
SCALE IN FEET
SOURCE:
PRE-REMEDIATION PLUME BOUNDARY IS FROM BECHTEL ENVIRONMENTAL INC. 2003. FINAL SECOND ANNUAL GROUNDWATER MONITORING REPORT IR SITES 40 AND 70, NAVAL WEAPONS STATION SEAL BEACH, SEAL BEACH, CA. JULY.
Figure 7
PROPOSED SOIL GAS SAMPLING LOCATIONS
IRP SITE 40
NAVAL WEAPONS STATION SEAL BEACH
SEAL BEACH, CALIFORNIA
CKY Incorporated

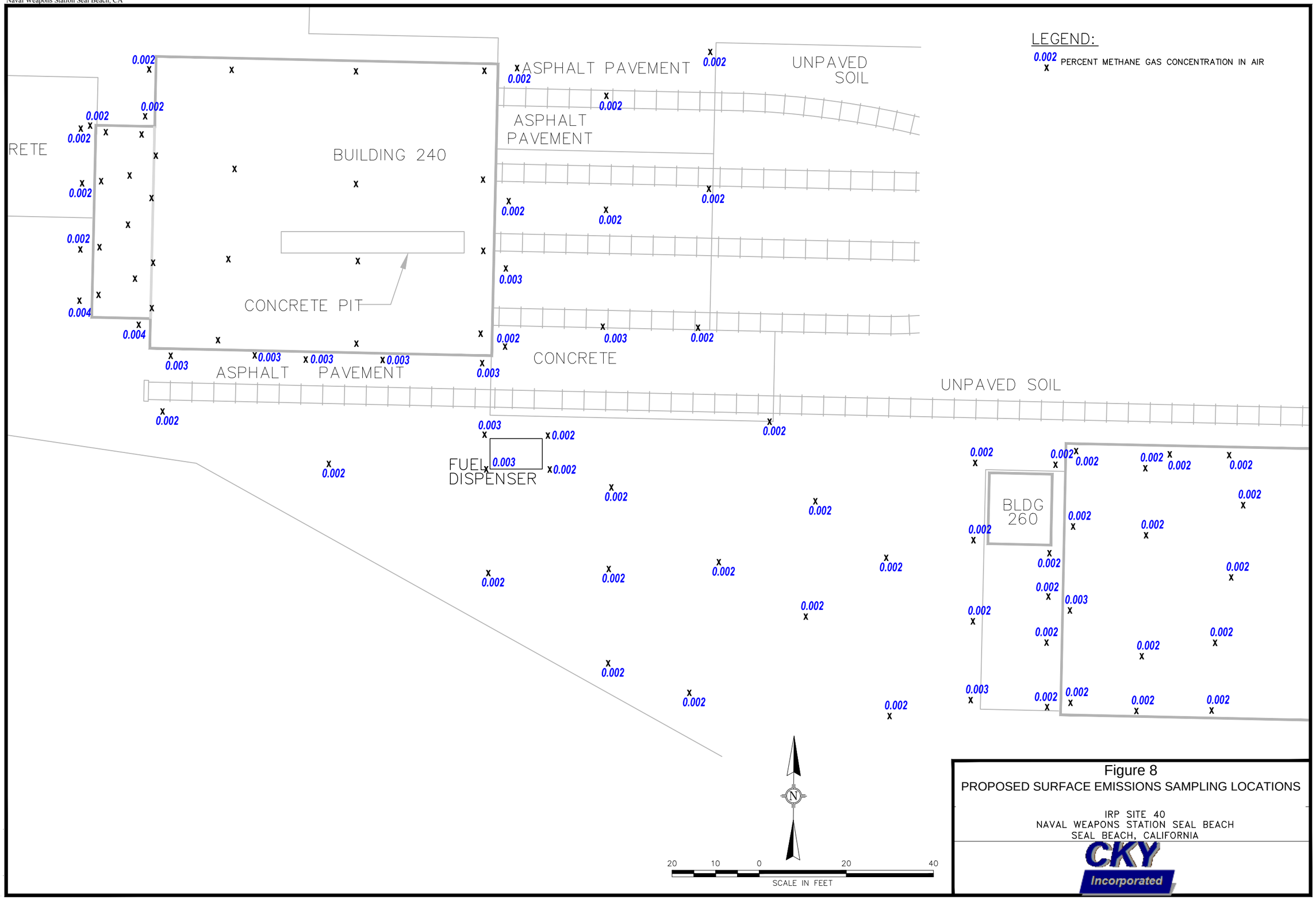

Figure 8
PROPOSED SURFACE EMISSIONS SAMPLING LOCATIONS

IRP SITE 40
NAVAL WEAPONS STATION SEAL BEACH
SEAL BEACH, CALIFORNIA

CKY Incorporated

Attachment 1

ANALYTICAL STANDARD OPERATING PROCEDURES

M220 Calscience Environmental Laboratories, Inc. 2011. "EPA Method 3005A, Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA, ICP-AES, or ICP-MS Spectrometry, Revision 3.4," November.

M601 Calscience Environmental Laboratories, Inc. 2011. "EPA Method 6010B, Inductively Couples Plasma – Atomic Emission Spectrometry (ICP-AES), Revision 5.2," May.

M703 Calscience Environmental Laboratories, Inc. 2011. "EPA 300.0/9056, Determination of Inorganic Anions by Ion Chromatography, Revision 3.4," August.

M713 Calscience Environmental Laboratories, Inc. 2010. "SM 2540 C / EPA Method 160.1, Total Dissolved Solids (Filterable Residue, Gravimetric), Revision 2.5," February.

M724 Calscience Environmental Laboratories, Inc. 2006. "Standard Method 5220D / EPA Method 410.4 / 410.4M, Chemical Oxygen Demand (COD) by Closed Reflux, Colorimetric Technique, Revision 2.1," July.

M726 Calscience Environmental Laboratories, Inc. 2010. "SM 5310 B/D / EPA Method 415.1, Total Organic Carbon (TOC), Revision 1.1," July.

M386 Calscience Environmental Laboratories, Inc. 2011. "RSK-175(M), Dissolved Gases in Ground Water by GC Headspace Equilibration Technique, Revision 2.3," November.

M212 Calscience Environmental Laboratories, Inc. 2011. "EPA Method 5030C, Purge-and-Trap for Aqueous Samples, Revision 3.2," November.

M311 Calscience Environmental Laboratories, Inc. 2010. "EPA Method 8260B, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS), Revision 0.0," November.

M380 Calscience Environmental Laboratories, Inc. 2011. "EPA Methods TO-14A/15, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) in Air using Summa® Canisters or Tedlar™ Bags Revision 6.4," May.

DNA-qPCR Microbial Insights, Inc. 2011. "Quantitative Polymerase Chain Reaction (qPCR), Revision 2.0," January.

Title : **EPA METHOD 3005A, ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA, ICP-AES, OR ICP-MS SPECTROMETRY**

Document No. : SOP-M220
Revision No. : 3.4
Supersedes : 3.3

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Revision 3.4 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ **MANAGEMENT** 11/11/11 **DATE**

_____ **QA DEPARTMENT** 11-10-11 **DATE**

ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

1. METHOD IDENTIFICATION

1.1. EPA Method 3005A, Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA, ICP-AES, or ICP-MS Spectrometry.

2. APPLICABLE MATRICES

2.1. This method is applicable to ground and surface waters.

3. DETECTION LIMITS

3.1. Refer to the determinative (analytical) method for detection limit data.

4. SCOPE AND APPLICATION

4.1. EPA Method 3005A is an acid digestion procedure used to prepare surface and ground water samples for analysis by flame atomic absorption spectrometry (FLAA), by inductively coupled plasma-atomic emission spectrometry (ICP-AES), or by inductively coupled plasma-mass spectrometry (ICP-MS). Samples for the analysis of the following metals can be prepared by this method:

FLAA, ICP-AES, or ICP-MS Analysis

aluminum (Al)	cobalt (Co)	nickel (Ni)
antimony (Sb)	copper (Cu)	potassium (K)
barium (Ba)	iron (Fe)	silver (Ag)
beryllium (Be)	lead (Pb)	sodium (Na)
cadmium (Cd)	magnesium (Mg)	thallium (Tl)
calcium (Ca)	manganese (Mn)	vanadium (V)
chromium (Cr)	molybdenum (Mo)	zinc (Zn)

ICP-AES or ICP-MS Analysis Only

arsenic (As)	selenium (Se)

4.2. Upon client request, additional target analytes may be added to this procedure. However, it needs to be demonstrated that any added elements lend themselves to determinative method, either by regulatory reference or validation studies.

4.3. This method is restricted to use by or under the supervision of analysts/technicians experienced in the use of the equipments and apparatus required to execute the procedure.

5. METHOD SUMMARY

5.1. Total Recoverable Metals

5.1.1. The entire sample is acidified with nitric acid at the time of sample collection. After receipt at the laboratory, the sample is then heated with acid and substantially reduced in volume. The digestate is diluted to volume prior to analysis.

5.1.2. All water samples, with the exception of true drinking waters, must be digested prior to analysis.

5.1.2.1. Drinking water samples must be identified as such and must be colorless, transparent samples having a pH of < 2, a turbidity of < 1 NTU, no odor, and be of a single phase. Drinking water samples meeting the above description may be analyzed directly by inductively coupled plasma-atomic emission spectrometry or inductively coupled plasma-mass spectrometry without digestion.

5.2. Dissolved Metals

5.2.1. The entire sample is filtered through a 0.45-µm membrane filter, and the filtrate is acidified with nitric acid at the time of sample collection. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Holding Times: The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.8. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.9. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.10. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.11. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.12. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.13. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.14. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.15. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.16. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.17. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.18. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.19. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.20. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.21. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.22. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.23. Terms Specific to Metals Analysis

6.23.1. Dissolved Metals: The concentration of metals determined in an unacidified sample that pass through a 0.45-µm membrane filter.

6.23.2. Suspended metals: The concentration of metals determined in an unacidified sample that are retained by a 0.45-µm membrane filter.

6.23.3. Total Recoverable Metals (Total Acid Soluble Metals): The concentration of metals determined in an unfiltered sample following digestion using hot mineral acid.

7. INTERFERENCES

7.1. This digestion procedure may not be sufficiently rigorous to destroy some metal complexes.

7.2. Precipitation may lower silver concentration and cause inaccurate analysis.

7.3. Avoid contact with rubber, metal-based paints, cigarette smoke, paper tissues, and all metals products including those made of stainless steel, galvanized metals, and brass to prevent introducing metals into samples.

7.4. During digestion, do not let samples boil. Antimony is easily lost by volatilization from hydrochloric media.

7.5. Avoid using glass if analyzing for aluminum or silica.

7.6. Conventional fume hoods can contribute significantly to sample contamination, particularly during acid digestion in open containers. Keep vessels covered with watch glasses and turn spouts away from incoming air to reduce air-borne contamination.

7.7. Different filters display different sorption and filtration characteristics. For trace metal analysis, test filter and filtration system to verify complete recovery of metals.

7.8. Do not allow the digestates to become dry. Low recoveries of metals may result.

7.9. Sample container materials can introduce either positive or negative errors in measurement, particularly at low or ultra-trace levels, by contributing contaminants through leaching or surface desorption, or by depleting concentrations through adsorption. Additionally, the sample containers should be compatible with the reagents used for sample preservation. Thus, the collection and containment of a sample prior to analysis require particular attention.

7.9.1. Sample contamination introduced through field collection activities including sample containment and shipment can be assessed from the analysis of equipment rinsates and trip blanks.

7.9.2. Procedure for cleaning metals analytical labware can be found in SOP-T014.

7.10. Refer to the determinative method for other potential interferences.

8. SAFETY

8.1. Acids are corrosive. Hence, precautions must be taken to avoid inhalation, ingestion, or skin contact.

8.2. Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

8.3. All sample preparation activities should be performed in an operational fume hood appropriate for use with acids.

8.3.1. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides.

8.3.2. All operational fume hoods are to remain energized continuously in order to minimize acidic atmospheric or toxic gas buildup.

8.4. For the safety of the analyst, cracked or broken glassware should be immediately discarded into a broken glassware receptacle. Broken glassware shall not be used in any step of the digestion.

8.5. To ensure the safety of the analyst during any possible emergency situation, it is recommended that chemists do not perform digestions alone. Another chemist shall be present during any digestion process.

8.6. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.7. Material Safety Data Sheets (MSDS) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Digestion tubes (vials), 3-oz (90-mL), 93-mm × 33-mm ID, graduated, snap closure, with hinge lids, polypropylene, disposable, Capitol Vial P/N 03EDM31/33 or equivalent.

9.2. Autosampler vessels, 15-mL or 16-mL, translucent polypropylene, disposal.

9.3. Watch glass, ribbed, polypropylene, appropriate diameter to cover vial.

9.4. pH indicator paper, narrow range. pH range should include the desired pH.

9.5. Graduated cylinder, 100-mL, glass, Class A.

9.6. Volumetric flasks, 100-mL and 1000-mL, glass, Class A.

9.7. Pipetters, 10–100-µL, 100–1000-µL, 0.5–5.0-mL, and 1–10-mL, calibrated, adjustable, with disposable tip.

9.8. Dispensers, 1–10-mL, 2.5–25-mL, and 5–50-mL, adjustable.

9.9. Thermometer, calibrated, capable of accurately measuring at 95°C.

9.10. Block digester, equipped with water bath, capable of maintaining 90–95°C.

9.11. Centrifuge, Fisher Scientific Centrific Benchtop Centrifuge Model 225 or equivalent.

9.12. Centrifuge tubes, 50-mL, with lids, plastic, disposable.

9.13. Turbidimeter, HF Scientific Micro 100 Laboratory Turbidimeter or equivalent.

9.14. Turbidimeter cuvettes, 28-mm × 70-mm, clear, colorless glass, with threaded light shield caps.

9.14.1. Keep cuvettes scrupulously clean, both inside and out.

9.14.2. Discard scratched or etched cuvettes.

9.15. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.

9.16. Syringe filtration apparatus:

9.16.1. Syringe, 10-mL, polypropylene, eccentric tip, disposable, BD Lab Syringe P/N 305462 or equivalent.

9.16.2. Filter, 0.45-µm effective pore size, 30-mm diameter, hydrophilic polyvinylidene difluoride (PVDF) membrane, polypropylene housing,

disposable, National Scientific Company F2500-5 Target Syringe Filter or equivalent.

9.16.2.1. The 0.45-µm filter is used for dissolved metals determination.

9.16.3. Filter, 20-µm effective pore size, 90-mm diameter, cellulose, Whatman Ashless Grade 41 Quantitative Filter Paper or equivalent.

9.16.3.1. The 20-µm filter is used for total recoverable metals determination.

9.17. Vacuum filtration apparatus:

9.17.1. Vacuum apparatus.

9.17.2. Buchner funnel, ceramic, capable of supporting a 90-mm diameter filter.

9.17.3. Filtration flask, 500-mL, glass, with tubulation.

9.17.4. Filter, 0.45-µm effective pore size, 90-mm diameter, hydrophilic polyethersulfone membrane, Pall Corporation Supor-450 60206 Membrane Filter or equivalent.

9.17.4.1. The 0.45-µm filter is used for dissolved metals determination.

9.17.5. Filter, 20-µm effective pore size, 90-mm diameter, cellulose, Whatman Ashless Grade 41 Quantitative Filter Paper or equivalent.

9.17.5.1. The 20-µm filter is used for total recoverable metals determination.

9.18. Refer to the specific SOPs of the determinative methods for additional equipment and supplies.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, distilled or deionized.

10.1.2. Nitric acid, HNO_3, 68.0–70.0% (v/v), concentrated, clear to yellow liquid, trace metals grade or equivalent.

10.1.3. Nitric acid, HNO_3, 1:1 or 1+1 (v/v).

10.1.3.1. Prepare the 1:1 HNO_3 solution by slowly adding 1.25 L of concentrated HNO_3 to 1.25 L of reagent water.

10.1.4. Hydrochloric acid, HCl, 36.5–38.0% (v/v), concentrated, colorless to pale yellow liquid, trace metals grade or equivalent.

10.1.5. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Refer to the specific SOPs of the determinative methods for standards.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Water samples should be collected in 250-mL pre-cleaned high density polyethylene (HDPE) containers with Teflon-lined closures.

11.1.1. Water samples for dissolved metals determination shall be filtered within 15 minutes of sample collection by client field personnel. The filtrates shall be preserved with 1:1 HNO_3 solution to pH < 2.

11.1.1.1. If the samples are field filtered but not preserved, upon receipt at the laboratory, the samples must be preserved with 1:1 HNO_3 solution to pH < 2 and allowed to rest <u>for at least 24 hours</u> prior to digestion and analysis.

11.1.2. Water samples for total recoverable metals determination shall be preserved with 1:1 HNO_3 solution to pH < 2.

11.1.2.1. If the samples are not preserved, upon receipt at the laboratory, the samples must be preserved with 1:1 HNO_3 solution to pH < 2 and allowed to rest <u>for at least 24 hours</u> prior to digestion and analysis.

11.2. Although not required for all metals analyses, it is highly recommended the samples are maintained in a chill state (0°C ≤ 6°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.3. Upon receipt, the samples are stored in a 0°C –6°C cooler.

11.3.1. Unfiltered water samples for dissolved metals determination must be filtered as soon as possible and preserved with 1:1 HNO_3 solution to pH < 2 immediately after filtration.

11.3.1.1. The samples may then be analyzed, or digested and analyzed within 6 months of sample collection.

11.3.2. Filtered water samples with acid preservation (pH < 2) for dissolved metals determination must be analyzed, or digested and analyzed within 6 months of sample collection.

11.3.3. Filtered water samples without acid preservation (pH ≥ 2) for dissolved metals determination must be preserved with 1:1 HNO_3 solution to pH < 2 and allowed to sit <u>for at least 24 hours</u> prior to digestion, and digested and analyzed within 6 months of sample collection.

11.3.4. Water samples with acid preservation (pH < 2) for total recoverable metals determination must be digested and analyzed within 6 months of sample collection.

11.3.5. Water samples without acid preservation (pH ≥ 2) for total recoverable metals determination must be preserved with 1:1 HNO_3 solution to pH < 2 and allowed to sit <u>for at least 24 hours</u> prior to digestion, and digested and analyzed within 6 months of sample collection.

11.4. Refer to the specific SOPs of the determinative methods for additional information on sample preservation and holding times.

12. QUALITY CONTROL

12.1. Event Based Quality Control (LCS/LCSDs and MBs)

12.1.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.1.2. One MB consisting of clean reagent water is required every day digestions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

12.1.3. ***One LCS/LCSD pair*** consisting of the specified analytes spiked into clean reagent water is required every day digestions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

12.1.4. The MB/LCS/LCSD is processed concurrently with the associated samples. In the processing of the MB/LCS/LCSD, reagents and procedures identical to those for actual samples are used.

12.2. Matrix Based Quality Control (MS/MSDs)

12.2.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD).

12.2.2. One MS/MSD pair consisting of the actual sample matrix spiked with known concentrations of specific target analytes is required for every batch of 20 samples per matrix or portion thereof digested concurrently.

12.2.3. The sample which is spiked for the MS/MSD is processed concurrently with the associated samples. In the processing of the MS/MSD, reagents and procedures identical to those for actual samples are used.

12.3. Refer to the specific SOPs of the determinative methods for additional information on quality control.

13. CALIBRATION AND STANDARDIZATION

13.1. Top Loading Balance

13.1.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights.

13.1.2. Calibration shall be within ± 2% at 1 g (± 0.02 g) and at 100 g (± 2 g). If the values are not within these limits, recalibrate the balance.

13.2. Pipetter

13.2.1. Calibrate the pipetter according to the procedure outlined in the Pipetter Calibration Check Logbook.

13.3. Dispenser

13.3.1. Calibrate the dispenser according to the procedure outlined in the Dispenser Calibration Check Logbook.

13.4. Thermometer

13.4.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T042, "Thermometer Calibration."

13.5. Turbidimeter

13.5.1. Calibrate the turbidimeter according to the procedure outlined in the current revision of SOP-M770, "Turbidity (Nephelometric Method)."

14. ►PROCEDURE

14.1. Unfiltered Water Sample Preparation for Dissolved Metals Determination

14.1.1. If a water sample was not filtered within 15 minutes of sample collection, filter the sample as soon as possible upon receipt at the laboratory.

14.1.2. Assemble a vacuum filtration apparatus with a clean 0.45-µm membrane filter. Record the membrane filter lot (or identification) number in the Acid Preservation and Filtration Logbook.

14.1.2.1. A syringe filtration apparatus may be utilized instead.

14.1.3. Decant a sufficient volume of the water sample into the Buchner funnel and apply vacuum to filter the sample.

14.1.3.1. For MB/LCS/LCSD, decant a sufficient volume of clean reagent water.

14.1.3.2. For MS/MSD, decant a sufficient volume of water sample in each analytical batch selected for spiking.

14.1.3.3. For hard-to-filter sample, transfer the sample to a centrifuge tube, and centrifuge for 10 minutes at high speed to separate most of the suspended matters from the liquid phase prior to filtration.

14.1.3.3.1. Process the MB/LCS/LCSD/MS/MSD in the same manner.

14.1.4. Collect at least 50 mL of the water sample filtrate in a clean digestion tube and label appropriately. Record the digestion tube lot (or identification) number in the Acid Preservation and Filtration Logbook.

14.1.5. Preserve the water sample filtrate with 1:1 HNO_3 solution to pH < 2 immediately after filtration. Record the date and time when the 1:1 HNO_3 solution was added and the 1:1 HNO_3 solution identification number in the Acid Preservation and Filtration Logbook.

14.1.5.1. If the sample will be filtered and then immediately digested, record the filtration information and check the "Filter and Digest" column in the logbook.

14.1.5.2. If the sample will be held after filtration and preservation, and then digested prior to analysis, check the "Filter and Preserve" column in the logbook.

14.1.6. Mix a water sample filtrate thoroughly.

14.1.7. For project specific requirement, measure the turbidity of a drinking water sample filtrate as outlined in the current revision of SOP-M770.

14.1.8. Measure exactly 50 mL of the well-mixed water sample filtrate or exactly 50 mL of the diluted filtrate into a clean digestion tube. Record the volume of filtrate used to the nearest 1 mL.

14.1.8.1. For MB/LCS/LCSD, measure exactly 50 mL of reagent water filtrate designated as MB/LCS/LCSD.

14.1.8.2. For MS/MSD, measure exactly 50 mL of water sample filtrate designated as MS/MSD.

14.1.9. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spikes and laboratory control samples.

14.1.10. Proceed to Section 14.4.

14.2. Filtered Water Sample Preparation for Dissolved Metals Determination

14.2.1. Mix a water sample filtrate thoroughly.

14.2.2. Check the pH by transferring a few drops of the water sample filtrate onto a narrow-range pH paper.

14.2.2.1. If the pH is ≥ 2, preserve the water sample filtrate with 1:1 HNO_3 solution to pH < 2 ***and allow to sit*** for at least 24 hours prior to digestion. Record the date and time when the 1:1 HNO_3 solution was added and the 1:1 HNO_3 solution identification number in the Acid Preservation and Filtration Logbook.

14.2.2.1.1. Check the "Preserve Only" column in the logbook.

14.2.3. For project specific requirement, measure the turbidity of a drinking water sample filtrate as outlined in the current revision of SOP-M770.

14.2.4. Measure exactly 50 mL of the well-mixed water sample filtrate or exactly 50 mL of the diluted filtrate into a clean digestion tube. Record the volume of filtrate used to the nearest 1 mL.

14.2.4.1. For MB/LCS/LCSD, measure exactly 50 mL of clean reagent water.

14.2.4.2. For MS/MSD, measure exactly 50 mL of water sample filtrate in each analytical batch selected for spiking.

14.2.5. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spikes and laboratory control samples.

14.2.6. Proceed to Section 14.4.

14.3. Water Sample Preparation for Total Recoverable Metals Determination

14.3.1. Mix a water sample thoroughly.

14.3.2. Check the pH by transferring a few drops of the water sample onto a narrow-range pH paper.

14.3.2.1. If the pH is ≥ 2, preserve the water sample with 1:1 HNO_3 solution to pH < 2 ***and allow to sit*** for at least 24 hours prior to digestion. Record the date and time when the 1:1 HNO_3 solution was added and the 1:1 HNO_3 solution identification number in the Acid Preservation and Filtration Logbook.

14.3.2.1.1. Check the "Preserve Only" column in the logbook.

14.3.3. For project specific requirement, measure the turbidity of a drinking water sample as outlined in the current revision of SOP-M770.

14.3.4. Measure exactly 50 mL of the well-mixed water sample or exactly 50 mL of the diluted sample into a clean digestion tube. Record the volume of sample used to the nearest 1 mL.

14.3.4.1. For MB/LCS/LCSD, measure exactly 50 mL of clean reagent water.

14.3.4.2. For MS/MSD, measure exactly 50 mL of water sample in each analytical batch selected for spiking.

14.3.5. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spikes and laboratory control samples.

14.3.6. Proceed to Section 14.4.

14.4. Digestion

14.4.1. Add 1.0 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl into the digestion tube.

14.4.2. Place the digestion tube in the pre-heated block digester and cover the digestion tube with a clean watch glass.

14.4.3. Heat the sample (filtrate) at 90–95°C for approximately 2 hours or until the apparent volume reaches 15–20 mL.

14.4.3.1. Do not allow the digestate to boil or become dry.

14.4.3.2. If the digestate becomes dry, discard the digestate, and re-prepare the sample (filtrate).

14.4.4. Remove the digestion tube from the block digester and allow the digestate to cool.

14.4.4.1. Wash down the digestion tube wall and the watch glass with reagent water.

14.4.5. Adjust the final volume of the digestate to 50 mL with reagent water.

14.4.6. If the digestate appears to be turbid, perform the following procedure.

14.4.6.1. For hard-to-filter digestate, transfer the digestate to a centrifuge tube, and centrifuge for 10 minutes at high speed to separate most of the suspended matters from the liquid phase.

14.4.6.2. Assemble a vacuum filtration apparatus with a clean 20-µm quantitative filter and apply vacuum to filter the digestate. A syringe filtration apparatus may be utilized instead to filter the digestate. Record the quantitative filter lot (or identification) number in the Acid Preservation and Filtration Logbook.

14.4.6.3. Collect the filtered digestate in a clean autosampler vessel. Record the digestion tube lot (or identification) number in the Acid Preservation and Filtration Logbook.

14.5. Batching

14.5.1. Up to 20 field samples received at different times throughout the day may be batched together as long as the same equipment and reagents are used for the preparation/digestion event associated with the batch. This approach is considered "open batch."

14.5.1.1. As this approach allows for many samples (up to 20) over the course of a day to be batched together, the start and end times for the digestion process must be recorded in the preparation log for each sample.

14.5.2. Refer to the project's Quality Assurance Project Plan (QAPP) for additional batching requirement.

14.6. Thoroughly document all aspects of the digestion in the Metals Sample Preparation Logbook. This logbook includes, but is not limited to:

14.6.1. Digestion date, start time, and finish time.

14.6.1.1. The start and stop time of each sample digestion must be accurately recorded in the logbook. If all samples were started and finished at the same time, then an 'arrow down' approach may be used in the logbook. If a batch is open, and a sample is added on after the digestion process of the other batch samples has begun, then the actual start and stop time for each additional sample must be recorded in the logbook.

14.6.1.2. All samples must undergo the entire digestion process regardless when the digestion process was started.

14.6.2. Sample pH and turbidity.

14.6.3. Sample matrix, initial volume, and final volume.

14.6.4. Digestion temperature.

14.6.5. Reagent and material lot (or identification) numbers.

14.6.6. Standard lot (or identification) number, concentration, and volume added.

14.6.7. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

15. CALCULATIONS

15.1. The dilution factor is calculated as follows:

$$D = \frac{V_f}{V_i}$$

where: D = dilution factor.
V_f = volume of sample or digestate after dilution in mL.
V_i = volume of sample or digestate before dilution in mL.

15.2. Refer to the determinative method for additional calculations.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In

general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Refer to the determinative method for data assessment and acceptance criteria.

18.2. Additional information regarding internal quality control checks is provided in SOP-T020.

18.3. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Refer to the determinative method for contingencies for out-of-control or unacceptable data.

20.2. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 3005A, USEPA, Revision 1, July 1992.

22.2. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.3. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.4. *Inorganic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Three, USEPA, Revision 4, February 2007.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: EPA Method 3005A Procedure Outline.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 3005A are noted.

24.1.1. Equipment and Supplies

24.1.1.1. The specification of digestion vessel is modified.

24.1.2. Sample Preservation

24.1.2.1. The concentration of the preservation chemical is modified.

24.1.3. Procedure

24.1.3.1. The volume of the sample used for digestion is modified.

24.1.3.2. The volume of concentrated HNO_3 used for digestion is modified.

24.1.3.3. The volume of concentrated HCl used for digestion is modified.

24.1.3.4. The final volume of the digestate is modified.

24.1.3.5. The order of the final filtration and dilution is modified.

24.1.3.6. The definition of a batch is modified

Appendix A

EPA Method 3005A Procedure Outline

EPA METHOD 3005A PROCEDURE OUTLINE

Total Recoverable (TR) Metals for FLAA/ICP Aqueous

PROCEDURE

1) Measure exactly 50 mL of well-mixed water sample into a clean 3-oz digestion tube.
2) Add 1.0-mL concentrated HNO_3 and 2.5-mL concentrated HCl.
3) Cover with ribbed polypropylene watch glass.
4) Heat the sample at 90–95°C for approximately 2 hours or until the apparent volume reaches 15–20 mL.
5) Cool and adjust the final volume to 50 mL with reagent water.

REAGENTS

1) Reagent water, interferant free
2) Concentrated HNO_3, trace metals grade for equivalent
3) Concentrated HCl, trace metals grade for equivalent

MB/LCS/LCSD - per batch of 20 samples
MS/MSD - per batch of 20 samples

APPROVED BY: _____

DATE: _____

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Title : **EPA METHOD 6010B, INDUCTIVELY COUPLED PLASMA – ATOMIC EMISSION SPECTROMETRY (ICP-AES)**

Document No. : SOP-M601
Revision No. : 5.2
Supersedes : 5.1

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Revision 5.2 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 05/12/11
MANAGEMENT **DATE**

_____ 05-12-11
QA DEPARTMENT **DATE**

ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

1. METHOD IDENTIFICATION

1.1. EPA Method 6010B, Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES).

2. APPLICABLE MATRICES

2.1. This method is applicable to groundwater samples, aqueous samples, TCLP/SPLP/WET extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes.

3. DETECTION LIMITS

3.1. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions.

3.2. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices.

4. SCOPE AND APPLICATION

4.1. EPA Method 6010B is used to determine trace elements, including metals, in solution. Except groundwater samples, all aqueous and solid matrices require acid digestion prior to analysis. Groundwater samples that have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. If either option is used, instrument software should be programmed to correct for intensity differences of the internal standard between samples and standards.

4.2. The method is applicable to the elements listed in Appendix A. Appendix A also lists the recommended analytical wavelengths and estimated instrument detection limits for the elements in clean aqueous matrices with insignificant background interferences. Elements and matrices other than those listed in Appendix A may be analyzed by this method if performance at the concentrations of interest (see Section 12.) is demonstrated.

4.3. This method is restricted to use by or under the supervision of analysts experienced in the use of inductively coupled plasma emission spectrometer, skilled in the interpretation of atomic emission spectra, and knowledgeable in the correction of spectral, chemical, and physical interferences described in this method.

5. METHOD SUMMARY

5.1. EPA Method 6010B describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic 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 radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices.

5.2. Background correction is required for trace element determination. Background emission must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used should be as free as possible from spectral interference and should reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences identified in Section 7. should also be recognized and appropriate corrections made. Alternatively, multivariate calibration methods may be utilized. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

5.3. Prior to analysis, samples must be solubilized or digested using the appropriate sample preparation methods. Acceptable preparatory methods include, but are not limited to, the following:

Sample Digestion/Preparation	Method No.	SOP No.
Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA/ICP	EPA 3005A	M220
Acid Digestion of Aqueous Samples/Extracts for Total Metals for Analysis by FLAA/ICP	EPA 3010A	M223
Acid Digestion of Sediments, Sludges, and Soils	EPA 3050B	M222
Toxicity Characteristic Leaching Procedure (TCLP)	EPA 1311	M226
Synthetic Precipitation Leaching Procedure (SPLP)	EPA 1312	M227
Waste Extraction Test Procedure (STLC/TTLC)	CCR T22.11.5.A-II	M228

5.4. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the

start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.13. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.14. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.15. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.16. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.17. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.18. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.19. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.20. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.21. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.22. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.23. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.24. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.25. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.26. ►Terms Specific to ICP-AES Analysis

6.26.1. Linear Dynamic Range: The concentration range over which the analytical curve remains linear.

6.26.2. Method of Standard Addition (MSA): The standard-addition technique involves the use of the unknown and the unknown plus one or more known amounts of standard.

6.26.3. Optimum Concentration Range: A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions employed.

6.26.4. Post Digestion (Matrix) Spike: A sample which has been extracted in the same manner as the other samples, but to which a known amount of target analytes has been added to the sample extractant. Post digestion spikes are used to evaluate the accuracy of the method without the losses incurred through the extraction process.

6.26.5. Sensitivity: The slope of the analytical curve, i.e., the functional relationship between emission intensity and concentration.

7. INTERFERENCES

7.1. 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 unresolved overlap of molecular band spectra.

7.1.1. Compensation for background emission and stray light can usually be conducted by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be

included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

7.1.2. To determine the appropriate location for off-line background correction, the analyst 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 automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine 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 in the sample at high concentration, a more appropriate test would be to use a concentration near the upper limit of the analytical range.

7.1.3. Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction **require** that the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive or positively biased determinations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Analysts may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Appendix B. For multivariate calibration methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

7.1.4. When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e., false positive analyte concentrations) arising from 100 mg/L of the interference element. For example, if As is to be determined at 193.696 nm in a sample containing approximately 10 mg/L of Al. According to Appendix B, 100 mg/L of Al will yield a false positive signal for an As level equivalent to approximately 0.01085 mg/L. Therefore, the presence of 10 mg/L of Al will result in a false positive signal for As equivalent to approximately 0.001085 mg/L. The analyst is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Appendix B. The

interference effects must be evaluated for each individual instrument, since the intensities will vary.

7.1.5. Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, 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 background correction 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. Analysts should continuously note that some samples may contain uncommon elements that could contribute spectral interferences.

7.1.6. The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences (see Appendix B) as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst shall utilize a computer routine for automatic correction on all analyses.

7.1.7. Analysts using sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest for several samples. The range for lead, for example, would be from 220.6 to 220.1 nm. This procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

7.1.8. If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If after the subtraction of the calibration blank, the apparent analyte concentration falls outside of this range, in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

7.1.9. When interelement corrections are applied, their accuracy should be verified daily, by analyzing spectral interference check solutions. The correction factors or multivariate correction matrices tested on a daily basis must be within the 20% criteria for 5 consecutive days. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change occurs, such as one in the torch, nebulizer, injector, or plasma conditions. Standard solutions should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

7.1.10. When interelement corrections are <u>not</u> used, verification of absence of interferences is required.

7.1.10.1. One method is to use a computer software routine for comparing the determinative data to established limits for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration (i.e., greater than the analyte instrument detection limit), or a false negative analyte concentration, (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

7.1.10.2. Another method is to analyze an interference check solution which contains similar concentrations of the major components of the samples (> 10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is ≥ 20% of the analyte concentration, the analyte must be determined (1) using analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

7.2. 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 containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, by using an internal standard, or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization by using a tip washer, by using a high solids nebulizer, or by diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance. This may be accomplished with the use of mass flow controllers. The dilution test (see Section 12.12.) will help determine if a physical interference is present.

7.3. Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating

conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

7.3.1. The MSA should be used if an interference is suspected or a new matrix is encountered. When the MSA is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences, such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences.

7.3.2. An alternative to using the MSA is to use the internal standard technique. Add one or more elements that are both not found in the samples and verified to not cause an interelement spectral interference to the samples, standards, and blanks. Yttrium or scandium is often used. The concentration should be sufficient for optimum precision, but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences, especially in high solids matrices.

7.4. Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to equal to or less than the method detection limit should be noted. Until the required rinse time is established, it is suggested that the rinse period be at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon the project specific data quality objectives (DQOs).

7.5. Analysts are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of

the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

7.6. The dashes in Appendix B indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

7.7. The calibration blanks (Section 10.2.3.1.) may restrict the sensitivity of the detection limit or degrade the precision and accuracy of the analysis. Clean chemistry methods and procedures are necessary in reducing the magnitude and variability of the calibration blank.

8. SAFETY

8.1. All sample preparation activities should be performed in an operational fume hood appropriate for use with acids.

8.2. All operational fume hoods are to remain energized continuously in order to minimize acidic atmospheric buildup.

8.3. Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

8.4. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.5. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Inductively Coupled Argon Plasma Emission Spectrometer: Perkin-Elmer Optima 4300/5300 DV Optical Emission Spectrometer or equivalent configured with the following components:

9.1.1. Computer-controlled emission spectrometer with background correction.

9.1.2. Radio-frequency (RF) generator compliant with FCC regulations.

9.1.3. Mass-flow controller for argon nebulizer gas supply.

9.1.4. Peristaltic pump.

9.1.5. Autosampler, Perkin-Elmer AS 90 or equivalent.

9.1.6. Argon gas supply, high purity.

9.1.7. Nitrogen gas supply, high purity, for purge only.

9.1.8. PC based data system or equivalent.

9.2. Volumetric flasks, 100-mL, 500-mL, and 1000-mL, Class A.

9.3. Pipetters, 10–100-µL, 100–1000-µL, 0.5–5.0-mL, and 1–10-mL, adjustable, with disposable tip.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Hydrochloric acid, HCl, concentrated, trace metals grade for equivalent.

10.1.2. Hydrochloric acid, HCl, 1:1 (v/v).

10.1.2.1. Prepare the solution by slowly adding 500 mL of concentrated HCl to 400 mL of reagent water and diluting to 1 L with additional reagent water.

10.1.3. Nitric acid, HNO_3, concentrated, trace metals grade for equivalent.

10.1.4. Nitric acid, HNO_3, 1:1 (v/v).

10.1.4.1. Prepare the solution by slowly adding 500 mL of concentrated HNO_3 to 400 mL of reagent water and diluting to 1 L with additional reagent water.

10.1.5. Rinse blank, HCl-HNO_3-H_2O, 1:1:8 (v/v/v).

10.1.5.1. Prepare the rinse blank by slowly adding 1 part of concentrated HCl and 1 part of concentrated HNO_3 to 8 parts of reagent water.

10.1.5.2. The rinse blank consists of 10% (v/v) HCl and 10% (v/v) HNO_3 in reagent water.

10.1.5.3. The rinse blank is used to flush the system between standards and samples to minimize memory interferences (see Section 7.4.).

10.1.6. Reagent water, interferant free.

10.1.7. Chips, Teflon.

10.1.8. Beads, glass.

10.1.9. All reagents must be inspected and documented prior to use.

10.2. Standards

10.2.1. Stock Standard Solutions

10.2.1.1. Pre-certified stock standard solutions (ultra-high purity grade or equivalent), each in sealed polyethylene bottles, containing various concentrations of target analytes are used to prepare calibration and check standards.

10.2.1.2. Prior to preparing the calibration or check standards, analyze each stock standard solution separately to determine possible spectral interference or the presence of impurities.

10.2.2. Initial Calibration Standard Solutions

10.2.2.1. Prepare the initial calibration standard solutions by combining appropriate volumes of the stock standards in volumetric flasks (refer to Appendix C for preparation).

10.2.2.2. Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates.

10.2.2.2.1. If the addition of silver to the recommended acid combination initially results in a precipitate, then add 15 mL of reagent water and warm the flask until the solution clears. Cool and dilute to 100 mL with reagent water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver is stable under these conditions in a water matrix for 30 days, if protected from the light. Higher concentrations of silver require additional HCl.

10.2.2.3. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together.

10.2.2.4. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage.

10.2.3. Blanks

10.2.3.1. Calibration Blank (CB)

10.2.3.1.1. Prepare the CBs by acidifying reagent water to the same concentrations of the acids found in the standards and samples.

10.2.3.1.2. The CB consists of 5% (v/v) HCl and 6% (v/v) HNO_3 in reagent water.

10.2.3.1.3. The CB is used to establish the zero point of the calibration curve.

10.2.3.1.4. The CB is also used either as initial calibration blank (ICB) or as continuing calibration blank (CCB) to monitor contamination.

10.2.3.2. Method Blank (MB)

10.2.3.2.1. Prepare the MBs using the appropriate sample preparation methods (see Section 5.3.).

10.2.3.2.2. The MB is used to identify possible contamination resulting from either the acids or the equipment used during sample processing including filtration.

10.2.3.3. Both CB and MB are required for the analyses of samples prepared by any method other than EPA Method 3040A.

10.2.4. Initial Calibration Verification (ICV) Solutions

10.2.4.1. Prepare the ICV solutions in the same acid matrix by combining compatible elements from a source differing from that used for the initial one-point calibration, and at a concentration within the established linear dynamic range (refer to Appendix C for preparation and Section 12.3. for evaluation).

10.2.5. Continuing Calibration Verification (CCV) Solutions

10.2.5.1. Prepare the CCV solutions by diluting initial calibration standards with equal volume of reagent water (refer to Section 12.7. for evaluation).

10.2.5.2. The CCV solutions contain mid-point concentration of each target analyte.

10.2.6. Internal Standard Solution

10.2.6.1. Prepare the internal standard solution in the same acid matrix (refer to Appendix C for preparation).

10.2.6.2. The internal standard contains 5 ppm each of Ho, Tb, and Y. It is used to reduce or overcome interferences (see Section 7.2. and Section 7.3.).

10.2.7. Potential Interference Check Solution

10.2.7.1. Prepare the potential interference check solution in the same acid matrix.

10.2.7.2. The potential interference check solution contains 200 ppm each of Al, Ca, Cr, Cu, Fe, Mg, Mn, Tl, and V. It is used to establish the potential interference table (see Section 12.1.).

10.2.8. Daily Spectral Interference Check Solutions (ICS-AB and ICS-A)

10.2.8.1. Prepare the daily spectral interference check solutions in the same acid matrix (refer to Appendix C for preparation and Section 12.6. for evaluation).

10.2.8.2. The ICS-AB and ICS-A solutions contain known concentrations of interfering elements. They are used to verify the interelement correction factors.

10.2.9. Spike Standard Solutions

10.2.9.1. Prepare the spike standard solutions in the same acid matrix by combining compatible elements from a source differing from

that used for the initial one-point calibration, and at a concentration within the established linear dynamic range (refer to Appendix C for preparation).

10.2.9.2. The spike standard solutions are used to prepare QC check samples such as matrix spikes (MS/MSDs), post digestion spikes (PDSs), and laboratory control samples (LCS/LCSDs).

10.2.9.3. Add 250 µL of the spike standard to each 5-mL aliquot of MS/MSD leachate (TCLP/SPLP/WET extract) prior to dilution and acidification.

10.2.9.4. Add 250 µL of the spike standard to each 50-mL aliquot of aqueous MS/MSD and LCS/LCSD sample prior to digestion.

10.2.9.5. Add 500 µL of the spike standard to each 2-g aliquot of solid MS/MSD and LCS/LCSD sample prior to digestion.

10.2.9.6. Add 50 µL of the spike standard to each 10-mL aliquot of PDS sample after digestion.

10.2.10. Linear Dynamic Range Solutions

10.2.10.1. Prepare a minimum of three different concentrations of the linear dynamic range solutions in the same acid matrix by diluting the spike standard solutions or the stock standard solutions. The analyst determines the applicable concentrations.

10.2.10.2. The linear dynamic range solutions contain various concentrations of compatible elements. They are used to establish linear dynamic range (see Section 12.5.).

10.2.11. All working standards must be replaced after six months or sooner if comparison with check standards indicates a problem.

10.2.11.1. The stability of low level standards (i.e., < 1 ppm), must be demonstrated prior to use.

10.2.11.2. Prepare fresh standards as needed.

10.2.12. All stock standards must be inspected and documented prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 250-mL pre-cleaned high density polyethylene containers with Teflon-lined closures. Soil samples should be collected in 4-oz pre-cleaned clear glass wide-mouth jars with Teflon-lined closures.

11.1.1. Aqueous samples shall be preserved with 1:1 HNO_3 solution to pH < 2.

11.2. Samples should be maintained in a chilled state (≤ 4°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.3. Upon receipt, the samples are stored in a 4°C cooler.

11.4. Refer to Appendix D for additional information on sample holding time, digestion volumes and suggested collection volumes.

11.4.1. The sample amount required depends upon the sample preparation procedures (i.e. leaching and digestion) necessary for the analysis.

12. QUALITY CONTROL

12.1. Potential Interference Table

12.1.1. Following the initial instrument setup, the potential interference table (see Appendix B) must be established prior to initial calibration.

12.1.1.1. The potential interference table is established by analyzing the potential interference check solution (see Section 10.2.7.).

12.1.2. The potential interference table should be updated annually, when the daily spectral interference check is deemed unacceptable, or when an instrumentation change occurs.

12.2. Initial Calibration (IC)

12.2.1. The initial one-point calibration must be established daily prior to the processing of samples.

12.2.1.1. The calibration curve is established with one calibration blank and one high-level calibration standard.

12.2.2. ►The IC is deemed valid if the %RSD for each analyte is ≤ 5%.

12.2.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.3. Initial Calibration Verification (ICV)

12.3.1. ►The initial calibration is deemed valid if the %RSD for each analyte is ≤ 5%, and the %D for each analyte is ≤ 10%.

12.3.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Investigate, effect corrective action, which may include re-preparation of standard solutions, and recalibration, if necessary.

12.4. Initial Calibration Blank (ICB)

12.4.1. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration > RL (or the limit specified in the project specific DQO).

12.4.2. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Reprepare and reanalyze the ICB.

12.5. Linear Dynamic Range

12.5.1. Following the initial instrument setup, the upper limit of the linear dynamic range for each analyte must be established for each wavelength utilized prior to initial calibration.

12.5.1.1. The upper range limit is established for each wavelength by determining the signal responses from a minimum of three, preferably five, different concentration standards across the range.

12.5.1.2. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file.

12.5.2. Following the establishment of a valid initial calibration, the upper range limit must be checked every six months, and a new upper range limit should be determined whenever there is a significant change in instrument response.

12.5.2.1. The analyst should be aware that if an analyte that is present above its upper range limit is used to apply an interelement correction, the correction may not be valid and those analytes where the interelement correction has been applied may be inaccurately reported.

12.5.3. The upper range limit is deemed valid if the %D for each analyte in a high-level check standard analyzed and quantitated against the calibration curve is ≤ 10%.

12.5.4. Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self-absorption effects. Hence, non-linear second order curve may be used if the instrument allows it.

12.5.4.1. The effective range must be checked, and the correlation coefficient of the second order curve fit should be ≥ 0.995.

12.5.4.2. Non-linear response curves should be revalidated and recalculated every six months. These curves are much more sensitive to changes in operating conditions than the linear lines and should be checked whenever there have been moderate equipment changes.

12.6. Daily Spectral Interference Check (ICS-AB and ICS-A)

12.6.1. Following the establishment of a valid initial calibration, the daily spectral interference check solutions must be analyzed daily prior to sample analysis and at the end of sequence.

12.6.1.1. The daily spectral interference check solutions are utilized to verify either the accuracy of the interelement correction factors if interelement corrections are applied, or the absence of interferences if interelement corrections are not applied.

12.6.2. The daily spectral interference check is deemed acceptable if the %D for each analyte is ≤ 20%.

12.6.3. If these criteria are not met, no sample analysis shall begin. Determine the source of problem, effect corrective action, and reanalyze the ICS-AB and/or ICS-A.

12.6.4. All interelement spectral correction factors or multivariate correction matrices should be updated every six months, when the daily spectral interference check is deemed unacceptable, or when an instrumentation change occurs.

12.7. Continuing Calibration Verification (CCV)

12.7.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof, and at the end of sequence.

12.7.2. The initial calibration is deemed valid if the %RSD for each analyte is ≤ 5%, and the %D for each analyte is ≤ 10%.

12.7.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Effect corrective action and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, recalibrate.

12.8. Continuing Calibration Blank (CCB)

12.8.1. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration > RL (or the limit specified in the project specific DQO).

12.8.2. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Reprepare and reanalyze the CCB.

12.9. Event Based Quality Control (LCS/LCSDs and MBs)

12.9.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.9.2. The acceptance criteria for LCS/LCSD elements are as follows:

12.9.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD element are 80% and 120%, respectively. The RPD is ≤ 20%.

12.9.2.2. All LCS/LCSD elements must be within acceptance limits. However, if a large number of analytes are in the LCS, it

becomes statistically likely that a few will be outside of control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary. Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary.

12.9.2.3. ME is defined as being beyond the LCS control limit (3 standard deviations), but within the ME limits. ME limits are between 3 and 4 standard deviations around the mean.

12.9.2.4. The number of allowable marginal exceedances is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary. This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than 11 analytes.

12.9.2.5. The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number of Analytes Allowed in ME of the LCS Control Limit
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

12.9.2.6. Marginal exceedances must be random. If the same analyte exceeds the LCS control limit 2 out of 3 consecutive LCS, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

12.9.2.7. If the problem was not related to the digestion process, then the LCS/LCSD and all associated sample digestates must be re-analyzed. If the failure was associated with the digestion process, then all associated samples must be re-processed and re-analyzed.

12.9.3. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.9.3.1. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.9.3.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the

effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and/or re-analyzed.

12.10. Matrix Based Quality Control (MS/MSDs and PDSs)

12.10.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and a post digestion spike (PDS).

12.10.2. The acceptance criteria for MS/MSD elements are as follows:

12.10.2.1. The lower and upper acceptance limits for %REC of each MS/MSD element are 75% and 125%, respectively. The RPD is ≤ 20%.

12.10.2.1.1. If historical data is available, then the lower and upper acceptance limits for %REC and %RPD of each MS/MSD element are based upon the historical average recovery ± 3S that is updated at least annually.

12.10.2.2. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.10.2.3. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

12.10.3. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.11. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.12. Dilution Test

12.12.1. If the analyte concentration is sufficiently high, an analysis of a 1:5 dilution should agree within ± 10% of the original determination.

12.12.2. If this criterion is not met, a physical or chemical interference effect shall be suspect. Perform recovery test.

12.13. Recovery Test (Post Digestion Spike Addition)

12.13.1. A PDS sample is prepared by adding the spike standard to a portion of a digested sample, or its dilution.

12.13.2. The acceptance criteria for PDS elements are as follows:

12.13.2.1. The lower and upper acceptance limits for %REC of each PDS element are 75% and 125%, respectively.

12.13.2.2. If the %REC of the PDS elements is not within the established acceptance limits, a matrix effect shall be suspect. Perform MSA on all samples within the batch.

12.14. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Initial Demonstration of Performance

13.1.1. Document the selection criteria for background correction points; analytical dynamic ranges, the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences.

13.1.2. Generate the data using the same instrument, operating conditions, and calibration routine to be used for sample analysis.

13.1.3. Keep the data on file and available for review.

13.2. Pipetter

13.2.1. Calibrate the pipetter according to the procedure outlined in the pipetter calibration logbook.

13.3. Spectrometer Initial Calibration

13.3.1. Establish an acceptable one-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.2.

13.3.2. After obtaining an acceptable one-point calibration curve and prior to processing sample or QC digestates, an ICV standard and ICB must be analyzed to verify the initial calibration. The acceptance criteria for the ICV and ICB are listed in Section 12.3. and Section 12.4.

13.3.3. The initial one-point calibration and ICV should include all anticipated target analytes for the duration of the use of the initial calibration.

14. PROCEDURE

14.1. Instrument Setup

14.1.1. Set up the instrument with proper operating parameters. The instrument must be allowed to become thermally stable (usually requiring at least 30

minutes of operation) prior to calibration. Follow the instructions provided by the instrument manufacturer for operating conditions.

14.1.1.1. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality.

14.1.1.2. Deviations from instructions provided by the instrument manufacturer must be documented and approved by the Group Leader.

14.1.1.3. Use the following ICP-AES operating conditions as guidance.

Operating Condition	Aqueous Solution	Axial Plasma
Forward Power	1100–1450 watts	1100–1450 watts
Viewing Height	14–18 mm	
Argon Coolant Flow	15–19 L/min	15–19 L/min
Argon Nebulizer Flow	0.5–1.5 L/min	0.5–1.5 L/min
Sample Pumping Rate	1.0–3.0 mL/min	1.0–3.0 mL/min
Preflush Time	1 min	1 min
Measurement Time (Sequential Instrument)	~2 sec per wavelength peak	~2 sec per wavelength peak
Measurement Time (Simultaneous Instrument)	10 sec per sample	10 sec per sample

14.1.1.4. Repeatable interference correction factors can be achieved by adjusting the argon aerosol flow to reproduce the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively.

14.1.2. Refer to Appendix A for specific wavelengths. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference.

14.1.3. Optimize the plasma operating conditions prior to the use of the instrument. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure. This routine is not required on a daily basis, but only is required when first setting up a new instrument, or following a change in operating conditions. Apply the following procedure, or the instrument manufacturer's recommendations, to optimize the plasma operating conditions.

14.1.3.1. Ignite the radial plasma and select an appropriate incident RF power. Allow the instrument to become thermally stable (about 30 to 60 minutes of operation). While aspirating a 1000 µg/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. Record the nebulizer gas flow rate or pressure setting

for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.

14.1.3.2. After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of a calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate. Set the peristaltic pump to deliver that rate in a steady even flow.

14.1.3.3. Profile the instrument to align it optically as it will be used during analysis. The following procedure can be used for both horizontal and vertical optimization in the radial mode, but is written for vertical.

14.1.3.3.1. Aspirate a solution containing 10 µg/L of several selected elements. As, Se, Tl, and Pb are the least sensitive of the elements and most in need of optimization. However, other elements may be used, based on the judgment of the analyst. V, Cr, Cu, Li and Mn also have been used with success.

14.1.3.3.2. Collect intensity data at the wavelength peak for each analyte at 1-mm intervals from 14 to 18 mm above the load coil. This region of the plasma is referred to as the analytical zone.

14.1.3.3.3. Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the best net intensity ratios for the elements analyzed or the highest intensity ratio for the least sensitive element.

14.1.3.3.4. Follow the instrument manufacturer's instructions for optimization in the axial mode.

14.1.4. The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits (IDLs).

14.1.5. If either the instrument operating conditions (such as incident power or nebulizer gas flow rate) are changed, or a new torch injector tube with a different orifice internal diameter is installed, then the plasma and viewing height should be re-optimized.

14.1.6. After completing the initial optimization of operating conditions, and before analyzing samples, an interelement spectral interference correction routine to be used for sample analysis must be established and initially verified.

14.1.6.1. A general description of spectral interferences and the analytical requirements for background correction are discussed in Section 7.

14.1.6.2. The criterion for determining the presence of an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls beyond ± one reporting limit from zero. The upper control limit is the analyte instrument detection limit.

14.1.6.3. Once established, the entire routine must be verified every six months. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verifications of the routine should be kept on file.

14.1.7. Before daily calibration, and after the instrument warm-up period, the nebulizer gas flow rate must be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines, the nebulizer gas flow rate should be the same (< 2% change) from day to day.

14.1.8. For operation with organic solvents, the use of the auxiliary argon inlet is recommended, as is the use of solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power, to obtain stable operation and precise measurements.

14.1.9. Program the system to average at least duplicate readings on samples including the calibration standards, the calibration verification standards, the calibration blanks, the QC check samples and method blanks. Report the average.

14.1.9.1. If the %RSD for an analyte in a standard is > 5%, re-analyze the standard. If the %RSD criterion remains unacceptable, investigate, effect corrective action, which may include re-preparation of the standard solution, and recalibrate, if necessary.

14.1.9.2. If the %RSD for an analyte in a sample is > 20%, and the analyte concentration exceeds its RL, re-analyze the sample. If the %RSD criterion remains unacceptable, investigate and effect corrective action.

14.2. Establish sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

14.2.1. Establish method detection limits (MDLs) for all wavelengths utilized for each type of matrix analyzed and for each preparation method used and for each instrument. Additional information regarding determination of detection limits is provided in SOP-T006.

14.2.2. Establish the upper limit of the linear dynamic range for each wavelength utilized (see Section 12.5.).

14.2.3. Verify that the instrument configuration and operating conditions satisfy the analytical requirements, and maintain quality control data confirming instrument performance and analytical results.

14.3. Establish a calibration curve to cover the appropriate concentration range (see Section 13.3.).

14.4. Following the establishment of a valid initial calibration, an ICS-AB and ICS-A must be analyzed daily prior to sample analysis, and an ICS-AB must be analyzed at the end of sequence. The acceptance criteria are listed in Section 12.6.

14.4.1. If a failed ICS-AB/ICS-A is the first of the day, corrective action must be effected prior to analyzing any samples.

14.4.2. If not, effect corrective action and reanalyze all samples since the last acceptable ICS-AB.

14.5. Following the establishment of a valid initial calibration, a CCV standard and CCB must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof, and at the end of sequence. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.7. and Section 12.8.

14.5.1. If a failed CCV/CCB is the first of the day, corrective action must be effected prior to analyzing any samples.

14.5.2. If not, effect corrective action and reanalyze all samples since the last acceptable CCV/CCB.

14.6. Following digestion by one of the methods specified in Section 5.3., the digestates for the QC and actual environmental samples are received in autosampler vials. The autosampler vials are then loaded onto the ICP-AES sample tray.

14.6.1. Preliminary treatment of most matrices is necessary due to the complexity and variability of sample matrices.

14.6.2. All associated QC samples (MB/LCS/LCSD/MS/MSD) for the batch must undergo the same filtration and acidification procedures.

14.6.3. Groundwater samples which have been prefiltered and acidified will not need acid digestion.

14.6.4. Samples which are not digested must either use an internal standard or be matrix-matched with the standards.

14.7. Sample vials are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standard(s)
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) Interference Check Solution AB (ICS-AB)

6) Interference Check Solution A (ICS-A)
7) Continuing Calibration Verification (CCV)
8) Continuing Calibration Blank (CCB)
9) Method Blank (MB)
10) Laboratory Control Samples (LCS)
11) Laboratory Control Sample Duplicates (LCSD)
12) Samples (up to 10, including QC check samples and MBs)
13) Matrix Spike (MS)
14) Matrix Spike Duplicate (MSD)
15) Post Digestion Spike (PDS)
16) Ending ICS-AB
17) Ending CCV
18) Ending CCB

14.7.1. Item 1: The CB is a vial of acidified reagent water used to establish the zero point of the initial calibration curve.

14.7.1.1. Additional calibration blanks may also be added elsewhere in the sequence to rinse the analytical system.

14.7.1.2. The rinse time is set to one minute. Rinse time may be reduced through a suitable demonstration.

14.7.2. Item 2: The initial calibration standard(s) are high-level calibration standard(s) used to establish the initial calibration curve.

14.7.3. Item 3: The ICV is a second source standard used to verify the acceptance of the initial one-point calibration. An acceptable ICV is required daily after initial calibration.

14.7.4. Item 4: The ICB is a vial of acidified reagent water used to monitor contamination. An acceptable ICB is required daily after initial calibration verification.

14.7.5. Items 5, 6, and 16: The ICS-AB and ICS-A are used to verify the accuracy of the interelement correction factors. An acceptable ICS-AB is required daily prior to sample analysis and at the end of sequence. An acceptable ICS-A is required daily prior to sample analysis.

14.7.6. Items 7 and 17: A CCV is used to verify the acceptance of the initial one-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 10 samples or portion thereof, and at the end of sequence.

14.7.7. Items 8 and 18: A CCB is a vial of acidified reagent water used to monitor contamination. An acceptable CCB is required daily prior to sample analysis, after every batch of 10 samples or portion thereof, and at the end of sequence.

14.7.8. Item 9: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

14.7.8.1. For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of clean Teflon chips (or glass beads).

14.7.8.2. One MB is required every day leachings/digestions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.7.8.3. When samples that are leached/digested together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of acidified reagent water must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.

14.7.9. Item 10: The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.7.9.1. For aqueous samples, the LCS consists of the specified elements spiked into clean reagent water. For solid samples, the LCS consists of the specified elements spiked into clean Teflon chips (or glass beads).

14.7.9.2. One LCS is required every day leachings/digestions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.7.10. Item 11: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.7.11. Item 12: Up to 10 sample (including QC check sample and method blank) digestates per batch. Digestates should be sufficiently diluted if concentrations exceed the calibration range. Dilution of digestates will result in increased reporting limits.

14.7.12. Item 13: The MS is an actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.7.12.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the

accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.7.12.2. One MS is required for every batch of 20 samples per matrix or portion thereof digested/leached concurrently.

14.7.13. Item 14: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.7.14. Item 15: The PDS is the same sample matrix from which the MS/MSD samples were prepared, and is spiked with known concentrations of specific target analytes post digestion. The sample which will be spiked for the PDS is processed concurrently with the associated samples. In the processing of the PDS, reagents and procedures identical to those for actual samples are used.

14.7.14.1. The purpose of the PDS is to access matrix effects. The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.7.14.2. One PDS is required for the occurrence of new or unusual matrix included within the batch, or for the failure of dilution test or matrix spike recovery.

14.7.15. Rinse blanks may be added elsewhere in the sequence to rinse the analytical system.

14.8. Ensure that a sufficient amount of rinse blank is present in the rinse blank bottle, and that a sufficient unused volume exists in the waste container at the beginning of the sequence.

14.9. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the run logbook.

14.10. Initiate the sequence.

14.11. Dilution and recovery tests (see Section 12.12. and Section 12.13.) are recommended prior to reporting concentration data for the elements.

14.11.1. It is recommended that these tests be performed with each batch of samples prepared/analyzed to ensure that neither positive nor negative interferences are affecting the measurement of any element or distorting the accuracy of the reported values.

14.12. If spectral overlap is suspected, then the use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

14.13. Method of Standard Additions (MSA)

14.13.1. The standard addition technique involves adding known amounts of a standard solution to one or more aliquots of a digested sample. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. However, it will not correct for additive interferences which cause a baseline shift.

14.13.2. The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_s of a standard analyte solution of concentration C_s. To the second aliquot (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for non-analyte signals. The unknown sample concentration C_x is calculated using the formula listed in Section 15.10. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

14.13.3. Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50% of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100% and 150% of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot is shown in Appendix E. A linear regression program may be used to obtain the intercept concentration.

14.13.4. For the results of the MSA technique to be valid, the following limitations must be taken into consideration:

14.13.4.1. The apparent concentrations from the calibration curve must be linear (correlation coefficient of 0.995 or greater) over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve.

14.13.4.2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

14.13.4.3. The determination must be free of spectral interference and corrected for nonspecific background interference.

14.14. Data Interpretation

14.14.1. Quantitation of a target analyte is based on a reproducible response of the spectrometer within the calibration range and a direct proportionality of the magnitude of response between intensities in the sample digestate and the calibration standard(s).

14.14.1.1. Proper quantitation requires the appropriate selection of a wavelength from which the intensity of an element can be determined.

14.14.1.2. Determine the concentration based on the initial calibration curve.

14.14.1.2.1. The data system is programmed to perform the calculation of concentration.

14.14.1.3. If the instrument response exceeds the calibration range, dilute the digestate and reanalyze.

15. CALCULATIONS

15.1. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{I_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the intensity readings for the target analyte.
I_{ave} = mean of the intensity readings for the target analyte.

15.2. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|C_{expected} - C_{measured}|}{C_{expected}} \times 100$$

where: %D = percent difference.
$C_{expected}$ = concentration of target analyte expected.
$C_{measured}$ = concentration of target analyte measured.

Note: Concentrations must be in equivalent units.

15.3. The recovery of each LCS element is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.4. The recovery of each MS element is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD/PDS).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The relative percent difference is calculated as follows:

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

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.6. The slope and intercept of a linear calibration curve are calculated as follows:

$$M = \frac{I_s - I_b}{C_s - C_b} \qquad B = \frac{C_s I_b - C_b I_s}{C_s - C_b}$$

where: M = slope of the calibration curve.
B = intercept of the calibration curve.
I_s = intensity of calibration standard at a specific wavelength.
I_b = intensity of calibration blank at a specific wavelength.
C_s = concentration of calibration standard.
C_b = concentration of calibration blank.

Note: Concentrations must be in equivalent units.

15.7. The target analyte concentration for a sample digestate is calculated as follows:

$$C_x = \frac{I_x - B}{M}$$

where: C_x = concentration of target analyte in digestate in mg/L.
I_x = intensity of target analyte at a specific wavelength.
B = intercept of the calibration curve.
M = slope of the calibration curve.

15.8. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_x \times V_x \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in mg/L.
C_x = concentration of target analyte in digestate in mg/L.
V_x = volume of digestate in mL.
V_A = volume of aqueous sample digested in mL.
D = dilution factor, if the sample or digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.9. The target analyte concentration for a solid sample is calculated as follows:

$$C_S = \frac{C_x \times V_x \times D}{W_S}$$

where: C_S = concentration of target analyte in solid sample in mg/kg.
C_x = concentration of target analyte in digestate in mg/L.
V_x = volume of digestate in mL.
W_S = mass of solid sample digested in g.
D = dilution factor, if the sample or digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.10. The target analyte concentration from single-addition method is calculated as follows:

$$C_x = \frac{S_B \times V_s \times C_s}{(S_A - S_B) \times V_x}$$

where: C_x = concentration of target analyte in sample.
S_A = analytical signal (corrected for the blank) of solution A.
S_B = analytical signal (corrected for the blank) of solution B.
V_s = volume of target analyte in standard solution.
C_s = concentration of target analyte in standard solution.
V_x = volume of target analyte in sample.

Note: Concentrations and volumes must be in equivalent units.

15.11. All concentrations shall be reported in mg/L (ppm) for aqueous samples, and mg/kg (ppm) for soil and solid waste samples.

15.12. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or

other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD elements are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD element are 80% and 120%, respectively. The RPD is ≤ 20%. All LCS/LCSD elements must be within acceptance limits (see Section 12.9.2. for additional information).

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.3. The acceptance criteria for MS/MSD elements are predetermined. The lower and upper acceptance limits for %REC of each MS/MSD element are 75% and 125%, respectively. The RPD is ≤ 20%.

18.3.1. Refer to Section 12.10.2.1.1. for acceptance criteria if historical data is available.

18.3.2. When the %REC and RPD of the MS/MSD elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.3.3. If the %REC and/or RPD of the MS/MSD elements are not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. The acceptance criteria for PDS elements are predetermined. The lower and upper acceptance limits for %REC of each PDS element are 75% and 125%, respectively.

18.4.1. When the %REC of the PDS elements are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The PDS data shall be reported with the corresponding sample data.

18.4.2. If the %REC of the PDS elements are not within the established acceptance limits, the MSA results shall be reported with the corresponding sample data.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in mg/L (ppm) for aqueous samples, and mg/kg (ppm) for soil and solid waste samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits.

The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD/PDS: Acceptability of the MS/MSD/PDS recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD/PDS data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported element, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject element is to be reported in samples within that analytical batch, the samples reported with that failed element must be reanalyzed with a valid LCS recovery for the element.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject element is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Inductively Coupled Plasma-Atomic Emission Spectrometry*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 6010B, USEPA, Revision 2, December 1996.

22.2. *Inductively Coupled Plasma-Atomic Emission Spectrometry*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 6010C, USEPA, Revision 3, November 2000.

22.3. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.4. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, November 2000.

22.5. *Inorganic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Three, USEPA, Revision 4, November 2000.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Recommended Wavelengths and Estimated Instrumental Detection Limits.

23.2. Appendix B: Potential Interferences (Example), Analyte Concentration Equivalents Arising from Interference at the 100-mg/L Level.

23.3. Appendix C: Standard Solution Preparation.

23.4. Appendix D: Sample Holding Times, Required Digestion Volumes and Recommended Collection Volumes for Metal Determinations in Aqueous and Solid Samples.

23.5. Appendix E: Standard Addition Plot (Example).

23.6. Appendix F: Additional Quality Control Criteria for Navy Project.

Appendix A

RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Calscience Environmental Laboratories, Inc.

Appendix A

Recommended Wavelengths and Estimated Instrumental Detection Limits (IDLs)

Element	Detection Wavelength [a] (nm)	Estimated IDL [b] (µg/L)
Aluminum (Al)	308.215	30
Antimony (Sb)	217.582	21
Arsenic (As)	193.696	35
Barium (Ba)	233.527	0.87
Beryllium (Be)	313.042	0.18
Boron (B)	249.677 × 2	3.8
Cadmium (Cd)	226.502	2.3
Calcium (Ca)	317.933	6.7
Chromium (Cr)	267.716	4.7
Cobalt (Co)	228.616	4.7
Copper (Cu)	324.752	3.6
Iron (Fe)	273.955	4.1
Lead (Pb)	220.353	28
Lithium (Li)	610.362	2.8
Magnesium (Mg)	279.077	20
Manganese (Mn)	257.610	0.93
Molybdenum (Mo)	202.031	5.3
Nickel (Ni)	231.604 × 2	10
Phosphorus (P)	213.617	51
Potassium (K)	766.490	See note [c]
Selenium (Se)	196.026	50
Silica (SiO2)	251.611	17
Silver (Ag)	328.068	4.7
Sodium (Na)	589.592	19
Strontium (Sr)	407.771	0.28
Thallium (Tl)	190.801	27
Tin (Sn)	189.927	17
Titanium (Ti)	336.121	5.0
Vanadium (V)	292.402	5.0
Zinc (Zn)	213.857 × 2	1.2

[a] The wavelengths listed (where ×2 indicates second order) are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted (e.g., in the case of an interference) if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 7.1.). In time, other elements may be added as more information becomes available and as required.

[b] The estimated instrumental detection limits shown are provided as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[c] Highly dependent on operating conditions and plasma position.

Appendix B

POTENTIAL INTERFERENCES (EXAMPLE)

Calscience Environmental Laboratories, Inc.

Appendix B

Potential Interferences (Example)

Analyte Concentration Equivalents Arising from Interference at the 100-mg/L Level [c]

Analyte		Wavelength (nm)	Interferant [ab] Al	Ca	Cr	Cu	Fe	Mg	Mn	Tl	V
Aluminum	Al	308.215	--	0.01926	0.01760	0.00290	--	0.00296	--	0.00470	0.63900
Antimony	Sb	206.836	--	--	1.50400	--	--	0.00116	--	--	--
Antimony	Sb	217.582	--	--	0.00910	--	--	0.00116	--	--	0.14900
Arsenic	As	188.979	--	--	--	0.00290	--	--	0.00440	0.00150	0.00040
Arsenic	As	193.696	--	0.00035	0.04780	--	--	--	--	--	--
Barium	Ba	233.527	0.00009	--	--	--	0.00403	0.00025	--	--	--
Beryllium	Be	313.042	--	--	0.00025	--	--	--	--	--	0.00650
Cadmium	Cd	226.502	--	--	--	--	0.00096	--	--	0.00005	0.00020
Calcium	Ca	317.933	0.00262	--	0.03450	0.00790	0.01350	0.02850	0.01330	0.00760	--
Chromium	Cr	267.716	0.00096	0.00009	--	0.02110	0.00186	0.00090	0.03080	0.00085	--
Cobalt	Co	228.616	0.00023	0.00001	--	0.00050	0.00166	0.00006	0.00045	0.00015	0.00050
Copper	Cu	324.752	0.00325	0.00229	--	--	--	0.00225	0.02680	0.04170	--
Iron	Fe	273.955	0.00617	--	0.01020	0.00660	--	0.00378	0.01140	0.00460	0.21900
Lead	Pb	220.353	--	--	--	0.00710	--	--	0.01530	0.00050	--
Magnesium	Mg	279.077	0.00066	0.00067	--	--	0.00049	--	--	0.00075	--
Manganese	Mn	257.610	--	0.00018	--	--	--	0.00041	--	0.00182	--
Molybdenum	Mo	202.031	0.00142	--	0.00625	0.00045	--	--	--	--	--
Nickel	Ni	231.604	0.00023	0.00002	0.00100	0.00010	0.00034	--	--	0.03940	0.00190
Phosphorus	P	213.617	--	--	--	0.87900	--	--	--	0.00430	0.01840
Potassium	K	766.490	--	--	--	--	--	0.00780	--	--	--
Selenium	Se	196.026	0.00667	--	--	0.00440	--	--	0.05840	--	0.00450
Silver	Ag	328.068	--	--	0.00040	0.00650	--	--	0.00045	--	--
Sodium	Na	589.592	0.09157	0.00801	0.10960	0.00580	--	0.13380	--	0.08005	--
Strontium	Sr	407.771	--	0.00258	0.00065	--	--	--	--	--	--
Thallium	Tl	190.801	0.00082	0.00378	0.04500	0.00445	0.00024	--	--	--	0.05500
Tin	Sn	189.927	0.00032	0.00301	--	0.00045	0.00059	--	0.00085	--	0.00165
Titanium	Ti	336.121	--	--	--	0.00015	0.00003	--	0.00010	0.00010	--
Vanadium	V	292.402	0.00011	--	--	--	--	0.00023	--	0.00025	--
Zinc	Zn	213.857	0.00041	0.00027	0.00285	0.05220	0.01660	0.00033	--	0.00100	--

[a] Dashes indicate that no interference was observed even when interferants were introduced at the following levels:

Al	- 200	mg/L	Mg	- 200	mg/L
Ca	- 200	mg/L	Mn	- 200	mg/L
Cr	- 1000	mg/L	Tl	- 1000	mg/L
Cu	- 1000	mg/L	V	- 1000	mg/L
Fe	- 200	mg/L			

[b] The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

[c] Interferences will be affected by background choice and other interferences may be present.

Appendix C

STANDARD SOLUTION PREPARATION

Calscience Environmental Laboratories, Inc.

Appendix C

Standard Solution Preparation – Initial Calibration Standard

Initial Calibration Standard					
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)
Aluminum	Al	200 + 2000	60 + 7.5	27	1000
Antimony	Sb	200 + 1000	15 + 6	9	1000
Arsenic	As	500	15	7.5	1000
Barium	Ba	2000	7.5	15	1000
Beryllium	Be	50 + 50	15 + 7.5	1.125	1000
Boron	B	100 + 1000	15 + 6	7.5	1000
Cadmium	Cd	100	15	1.5	1000
Calcium	Ca	1000	60	60	1000
Chromium	Cr	20	60	1.2	1000
Cobalt	Co	500	7.5	3.75	1000
Copper	Cu	250	7.5	1.875	1000
Iron	Fe	1000	7.5	7.5	1000
Lead	Pb	500	15	7.5	1000
Lithium	Li	100	60	6	1000
Magnesium	Mg	1000	15	15	1000
Manganese	Mn	100	15	1.5	1000
Molybdenum	Mo	200	6	1.2	1000
Nickel	Ni	20	60	1.2	1000
Phosphorus	P	10000	1.2	12	1000
Potassium	K	400 + 10000	60 + 3	54	1000
Selenium	Se	200	15	3	1000
Silicon	Si	2000	6	12	1000
Silver	Ag	50	15	0.75	1000
Sodium	Na	200 + 10000	60 + 6	72	1000
Strontium	Sr	10	60	0.6	1000
Thallium	Tl	200	15	3	1000
Tin	Sn	1000	6	6	1000
Titanium	Ti	200	6	1.2	1000
Vanadium	V	500	7.5	3.75	1000
Zinc	Zn	100 + 10000	15 + 0.35	5	1000
Bismuth [b]	Bi	1000	0.02	2	10
Sulfur [b]	S	1000	0.02	2	10

[a] Solvent for standard preparation is 5% (v/v) HCl + 6% (v/v) HNO_3. HCl and HNO_3 are concentrated trace metals grade acids.

[b] Bi and S standards are prepared separately.

Appendix C

Standard Solution Preparation – Initial Calibration Verification (ICV) Standard

Initial Calibration Verification (ICV) Standard					
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)
Aluminum	Al	200	4	4	200
Antimony	Sb	200	2	2	200
Arsenic	As	500	2	5	200
Barium	Ba	100	2	1	200
Beryllium	Be	50	2	0.5	200
Boron	B	500	1	2.5	200
Cadmium	Cd	150	2	1.5	200
Calcium	Ca	1000	4	20	200
Chromium	Cr	20	4	0.4	200
Cobalt	Co	100	2	1	200
Copper	Cu	100	2	1	200
Iron	Fe	10000	2	100	200
Lead	Pb	500	2	5	200
Lithium	Li	100	4	2	200
Magnesium	Mg	1000	2	10	200
Manganese	Mn	100	2	1	200
Molybdenum	Mo	100 + 300	2 + 1	2.5	200
Nickel	Ni	20	4	0.4	200
Phosphorus	P	1000	1	5	200
Potassium	K	400	4	8	200
Selenium	Se	200	2	2	200
Silicon	Si	230	1	1.15	200
Silver	Ag	50	2	0.5	200
Sodium	Na	200 + 10000	4 + 1	54	200
Strontium	Sr	10	4	0.2	200
Thallium	Tl	200	2	2	200
Tin	Sn	10000	0.05	2.5	200
Titanium	Ti	1000	1	5	200
Vanadium	V	100	2	1	200
Zinc	Zn	150	2	1.5	200
Bismuth [b]	Bi	1000	0.01	1	10
Sulfur [b]	S	1000	0.01	1	10

[a] Solvent for standard preparation is 5% (v/v) HCl + 6% (v/v) HNO_3. HCl and HNO_3 are concentrated trace metals grade acids.

[b] Bi and S standards are prepared separately.

Appendix C

Standard Solution Preparation – Interference Check Standard AB (ICS-AB)

Interference Check Standard AB (ICS AB)					
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)
Aluminum	Al	1200	10	24	500
Antimony	Sb	10000	0.05	1	500
Arsenic	As	1000	0.5	1	500
Barium	Ba	300	0.5	0.3	500
Beryllium	Be	100	0.5	0.1	500
Bismuth	Bi				
Boron	B	500	0.5	0.5	500
Cadmium	Cd	300	0.5	0.3	500
Calcium	Ca	6000	10	120	500
Chromium	Cr	300	0.5	0.3	500
Cobalt	Co	300	0.5	0.3	500
Copper	Cu	300	0.5	0.3	500
Iron	Fe	5000	10	100	500
Lead	Pb	1000	0.5	1	500
Lithium	Li				
Magnesium	Mg	3000	10	60	500
Manganese	Mn	200	0.5	0.2	500
Molybdenum	Mo	300	0.5	0.3	500
Nickel	Ni	300	0.5	0.3	500
Phosphorus	P				
Potassium	K	20000	0.5	20	500
Selenium	Se	500	0.5	0.5	500
Silicon	Si	230	0.5	0.23	500
Silver	Ag	300	0.5	0.3	500
Sodium	Na	1000	10	20	500
Strontium	Sr				
Thallium	Tl	1000	0.5	1	500
Tin	Sn				
Titanium	Ti	1000	0.5	1	500
Vanadium	V	300	0.5	0.3	500
Zinc	Zn	300	0.5	0.3	500

[a] Solvent for standard preparation is 5% (v/v) HCl + 6% (v/v) HNO_3. HCl and HNO_3 are concentrated trace metals grade acids.

Appendix C

Standard Solution Preparation – Interference Check Standard A (ICS-A)

Interference Check Standard A (ICS A)					
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)
Aluminum	Al	1200	10	24	500
Calcium	Ca	6000	10	120	500
Iron	Fe	5000	10	100	500
Magnesium	Mg	3000	10	60	500
Sodium	Na	1000	10	20	500

[a] Solvent for standard preparation is 5% (v/v) HCl + 6% (v/v) HNO_3. HCl and HNO_3 are concentrated trace metals grade acids.

Standard Solution Preparation – Internal Standard

Internal Standard					
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)
Holmium	Ho	1000	0.5	5	100
Terbium	Tb	1000	0.5	5	100
Yttrium	Y	1000	0.5	5	100

[a] Solvent for standard preparation is 5% (v/v) HCl + 6% (v/v) HNO_3. HCl and HNO_3 are concentrated trace metals grade acids.

Appendix C

Standard Solution Preparation – Spike Standards

Spike Standards 1 & 2					
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)
Aluminum	Al	10000	10	100	1000
Antimony	Sb	10000	10	100	1000
Arsenic	As	10000	10	100	1000
Barium	Ba	10000	10	100	1000
Beryllium	Be	10000	10	100	1000
Boron	B	10000	10	100	1000
Cadmium	Cd	10000	10	100	1000
Calcium	Ca	10000	10	100	1000
Chromium	Cr	10000	10	100	1000
Cobalt	Co	10000	10	100	1000
Copper	Cu	10000	10	100	1000
Iron	Fe	10000	10	100	1000
Lead	Pb	5000 [b]	20	100	1000
Magnesium	Mg	10000	10	100	1000
Manganese	Mn	10000	10	100	1000
Molybdenum	Mo	10000	10	100	1000
Nickel	Ni	10000	10	100	1000
Phosphorus	P	10000	10	100	1000
Potassium	K	10000	100	1000	1000
Selenium	Se	10000	10	100	1000
Silicon	Si	10000	10	100	1000
Silver	Ag	10000	5	50	1000
Sodium	Na	10000	100	1000	1000
Strontium	Sr	10000	10	100	1000
Thallium	Tl	10000	10	100	1000
Tin	Sn	10000	10	100	1000
Titanium	Ti	10000	10	100	1000
Vanadium	V	10000	10	100	1000
Zinc	Zn	10000	10	100	1000
Bismuth [c]	Bi	1000	0.05	0.5	100
Sulfur [c]	S	1000	0.05	0.5	100
Lithium [c]	Li	10000	0.005	0.5	100

[a] Solvent for standard preparation is 5% (v/v) HCl + 6% (v/v) HNO_3. HCl and HNO_3 are concentrated trace metals grade acids.

[b] The 5000-ppm Pb spike solution is prepared from the 10000-ppm pre-certified stock standard solution.

[c] Bi ,S, and Li are spiked directly into 50-mL sample.

Appendix D

SAMPLE HOLDING TIMES, REQUIRED DIGESTION VOLUMES AND RECOMMENDED COLLECTION VOLUMES FOR METAL DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES

Calscience Environmental Laboratories, Inc.

Appendix D

Sample Holding Times, Required Digestion Volumes and Recommended Collection Volumes for Metal Determinations in Aqueous and Solid Samples

Measurement		Digestion Volume (mL) [a, c]	Collection Volume (mL) [a, c]	Treatment/Preservative Holding Time [b]
Inorganic Analytes (except hexavalent chromium and mercury):				
Aqueous				
	Total	50	250	HNO_3 to pH < 2 6 months
	Dissolved	50	250	Filter on site HNO_3 to pH < 2 6 months
	Suspended	50	250	Filter on site 6 months
Solid				
	Total	2 g	4 oz	6 months
Hexavalent Chromium:				
Aqueous		50	250	24 hours Store at 4 ± 2°C until analyzed
Solid		2.5 g	4 oz	1 month to extraction 4 days after extraction Store at 4 ± 2°C until analyzed
Mercury:				
Aqueous				
	Total	50	250	HNO_3 to pH < 2 28 days
	Dissolved	50	250	Filter HNO_3 to pH < 2 28 days
Solid				
	Total	0.2 g	4 oz	28 days Store at 4 ± 2°C until analyzed

[a] Unless stated otherwise.

[b] Either glass or plastic containers may be used.

[c] Any sample volume reduction from the reference method's instructions must be made in the exact proportion as described in the method and representative sampling must be maintained.

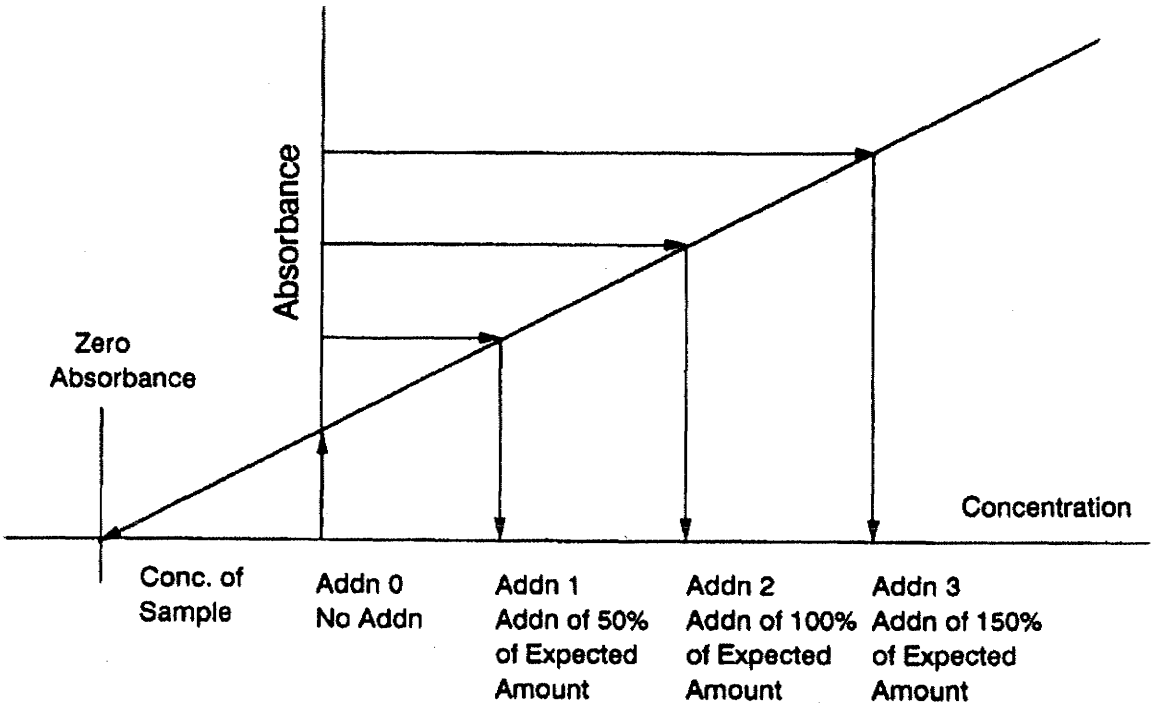
Appendix E

STANDARD ADDITION PLOT (EXAMPLE)

Calscience Environmental Laboratories, Inc.

Appendix E

Standard Addition Plot (Example)



Appendix F

ADDITIONAL QUALITY CONTROL CRITERIA FOR NAVY PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 6010B, Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) – Additional Quality Control Criteria for Navy Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. Stock Standard Solutions

3.1.1. Pre-certified stock standard solutions (ultra-high purity grade or equivalent), each in sealed polyethylene bottles, containing 500 ppb of each target analyte are used to prepare low-level calibration verification standards.

3.2. Low-Level Continuing Calibration Verification (LLCCV) Solutions

3.2.1. Prepare the LLCCV solutions in the same acid matrix by combining compatible elements.

3.2.2. The LLCCV solutions contain 5 ppb and 20 ppb of each target analyte.

3.2.2.1. The 20-ppb LLCCV solution is used to verify the RL of a target analyte with higher MDL.

3.3. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

4. QUALITY CONTROL

4.1. Method Detection Limit (MDL)

4.1.1. MDL study shall be performed annually, or verification checked quarterly for each analyte and matrix.

4.1.1.1. MDL verification must be performed immediately following an MDL study.

4.1.1.2. MDL verification is deemed valid if all analytes in the check sample are reliably detected and identified by method-specific criteria, or if the check sample produces a signal that is at least 3 times the instrument's noise level.

4.1.1.3. If these criteria are not met, run MDL verification check sample at higher level and set MDL higher or reconduct MDL study. No samples shall be analyzed without a valid MDL.

4.2. Instrument Detection Limit (IDL)

4.2.1. IDL study shall be performed at initial instrument setup and when there is significant change on instrument operating conditions.

4.2.2. The IDL for each analyte should be ≤ MDL.

4.2.3. No samples shall be analyzed without a valid IDL.

4.3. Initial Calibration Blank (ICB)

4.3.1. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration > 2 × MDL.

4.3.2. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Reprepare and reanalyze the ICB.

4.4. Daily Spectral Interference Check (ICS-AB and ICS-A)

4.4.1. Following the establishment of a valid initial calibration, the daily spectral interference check solutions must be analyzed daily prior to sample analysis.

4.4.2. The daily spectral interference check is deemed acceptable if the %D for each analyte in the ICS-AB standard is ≤ 20%, and the absolute value of the concentration for each non-spiked analyte in the ICS-A standard is < 2 × MDL (unless it is a verified trace impurity from one of the spiked analytes).

4.4.3. If these criteria are not met, no sample analysis shall begin. Determine the source of problem, effect corrective action, and reanalyze the ICS-AB and/or ICS-A.

4.5. Low-Level Continuing Calibration Verification (LLCCV)

4.5.1. Following the establishment of a valid initial calibration, a LLCCV standard must be analyzed daily prior to sample analysis.

4.5.2. The reporting limit (RL) is deemed valid if the %D for each analyte is ≤ 20%, and the analyte concentration is ≤ RL.

4.5.3. If these criteria are not met, the RL is deemed unacceptable for sample analysis to begin. Effect corrective action and reanalyze the LLCCV.

4.6. Continuing Calibration Blank (CCB)

4.6.1. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration > 2 × MDL.

4.6.2. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Reprepare and reanalyze the CCB. Reanalyze all samples since the last acceptable CCB.

4.6.2.1. The results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed CCB.

4.7. Event Based Quality Control (LCS/LCSDs and MBs)

4.7.1. Laboratory Control Samples (LCS/LCSDs)

4.7.1.1. The lower and upper acceptance limits for %REC of each LCS/LCSD element in aqueous matrix are as follows:

Analyte		Control Limit		ME Limit	
		Lower	Upper	Lower	Upper
Aluminum	Al	80	120	80	120
Antimony	Sn	80	120	80	120
Arsenic	As	80	120	80	120
Barium	Ba	80	120	80	120
Beryllium	Be	80	120	80	120
Cadmium	Cd	80	120	80	120
Calcium	Ca	80	120	80	120
Cobalt	Co	80	120	80	120
Copper	Cu	80	120	80	120
Iron	Fe	80	120	80	120
Lead	Pb	80	120	80	120
Magnesium	Mg	80	120	80	120
Manganese	Mn	80	120	80	120
Molybdenum	Mo	80	120	75	120
Nickel	Ni	80	120	80	120
Potassium	K	80	120	80	120
Selenium	Se	80	120	75	120
Silver	Ag	80	120	75	120
Sodium	Na	80	120	80	120
Thallium	Tl	80	120	80	120
Vanadium	V	80	120	80	120
Zinc	Zn	80	120	80	120

4.7.1.2. The lower and upper acceptance limits for %REC of each LCS/LCSD element in solid matrix are as follows:

Analyte		Control Limit		ME Limit	
		Lower	Upper	Lower	Upper
Aluminum	Al	80	120	75	120
Antimony	Sn	80	120	75	120
Arsenic	As	80	120	80	120
Barium	Ba	80	120	80	120
Beryllium	Be	80	120	80	120
Cadmium	Cd	80	120	80	120
Calcium	Ca	80	120	80	120
Cobalt	Co	80	120	80	120
Copper	Cu	80	120	80	120
Iron	Fe	80	120	80	120
Lead	Pb	80	120	80	120
Magnesium	Mg	80	120	80	120
Manganese	Mn	80	120	80	120
Molybdenum	Mo	80	120	75	120
Nickel	Ni	80	120	80	120

Analyte		Control Limit		ME Limit	
		Lower	Upper	Lower	Upper
Potassium	K	80	120	80	120
Selenium	Se	80	120	75	120
Silver	Ag	75	120	70	125
Sodium	Na	80	120	80	120
Thallium	Tl	80	120	80	120
Vanadium	V	80	120	80	120
Zinc	Zn	80	120	75	120

4.7.2. Method Blanks (MBs)

4.7.2.1. The concentration of a target analyte in an MB should be ≤ ½ RL. The concentrations of common laboratory contaminants should be < RL.

4.7.2.2. If these criteria are not met, investigate and eliminate the source of contamination.

4.7.2.3. Determine whether to reprocess the samples associated with the failed MB based on the following checks:

4.7.2.3.1. The concentration of a target analyte in the MB is ≥ RL as established by the test method or by regulation, and is > 1/10 of the amount measured in any sample.

4.7.2.3.2. The blank contamination affects the sample results as per the test method requirements or the individual project data quality objectives.

4.7.2.4. Any sample that meets either one or both of the checks described in Section 4.7.2.3. shall be reprocessed in a subsequent preparatory batch, except when the sample analysis resulted in a non-detect.

4.7.2.4.1. If no sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

4.8. Matrix Based Quality Control (MS/MSDs and PDSs)

4.8.1. Matrix Spikes (MS/MSDs)

4.8.1.1. The lower and upper acceptance limits for %REC of each MS/MSD element in aqueous matrix are as follows:

Analyte		Control Limit	
		Lower	Upper
Aluminum	Al	80	120
Antimony	Sn	80	120
Arsenic	As	80	120
Barium	Ba	80	120

Analyte		Control Limit	
		Lower	Upper
Beryllium	Be	80	120
Cadmium	Cd	80	120
Calcium	Ca	80	120
Cobalt	Co	80	120
Copper	Cu	80	120
Iron	Fe	80	120
Lead	Pb	80	120
Magnesium	Mg	80	120
Manganese	Mn	80	120
Molybdenum	Mo	80	120
Nickel	Ni	80	120
Potassium	K	80	120
Selenium	Se	80	120
Silver	Ag	80	120
Sodium	Na	80	120
Thallium	Tl	80	120
Vanadium	V	80	120
Zinc	Zn	80	120

4.8.1.2. The lower and upper acceptance limits for %REC of each MS/MSD element in solid matrix are as follows:

Analyte		Control Limit	
		Lower	Upper
Aluminum	Al	80	120
Antimony	Sn	80	120
Arsenic	As	80	120
Barium	Ba	80	120
Beryllium	Be	80	120
Cadmium	Cd	80	120
Calcium	Ca	80	120
Cobalt	Co	80	120
Copper	Cu	80	120
Iron	Fe	80	120
Lead	Pb	80	120
Magnesium	Mg	80	120
Manganese	Mn	80	120
Molybdenum	Mo	80	120
Nickel	Ni	80	120
Potassium	K	80	120
Selenium	Se	80	120
Silver	Ag	75	120
Sodium	Na	80	120
Thallium	Tl	80	120
Vanadium	V	80	120
Zinc	Zn	80	120

5. PROCEDURE

5.1. Following the establishment of a valid initial calibration, an LLCCV standard and CCB must be analyzed daily prior to sample analysis, and a CCV standard and CCB must be analyzed after every batch of 10 samples or portion thereof and at the end of sequence. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. Additional acceptance criteria are listed in Section 4.3., Section 4.5., and Section 4.6.

5.1.1. If LLCCV/CCB fails, corrective action must be effected prior to analyzing any samples.

5.1.2. If CCV/CCB fails, effect corrective action and reanalyze all samples since the last acceptable CCV/CCB.

5.2. Sample vials are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standard(s)
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) Interference Check Solution AB (ICS-AB)
6) Interference Check Solution A (ICS-A)
7) Low-Level Continuing Calibration Verification (LLCCV)
8) Continuing Calibration Blank (CCB)
9) Method Blank (MB)
10) Laboratory Control Samples (LCS)
11) Laboratory Control Sample Duplicates (LCSD)
12) Samples (up to 10, including QC check samples and MBs)
13) Matrix Spike (MS)
14) Matrix Spike Duplicate (MSD)
15) Post Digestion Spike (PDS)
16) ICS-AB
17) ICS-A
18) Continuing Calibration Verification (CCV)
19) Continuing Calibration Blank (CCB)

5.2.1. Items 5, 6, 16, and 17: The ICS-AB/ICS-A is used to verify the accuracy of the interelement correction factors. An acceptable ICS-AB/ICS-A is required daily prior to sample analysis and at the end of sequence.

5.2.2. Item 7: An LLCCV is used to verify the acceptance of the reporting limit on a continuing basis. An acceptable LLCCV is required daily prior to sample analysis.

5.2.3. Item 18: A CCV is used to verify the acceptance of the initial one-point calibration on a continuing basis. An acceptable CCV is required after every batch of 10 samples or portion thereof and at the end of sequence.

5.3. Dilution test is required daily for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

5.4. Recovery test (post digestion spike addition) is required when dilution test fails or when analyte concentration in all samples is < 50 × MDL.

6. REFERENCES

6.1. ►Department of Defense Quality Systems Manuals for Environmental Laboratories, ***Version 4.2, October 2010.***

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Title : **EPA METHOD 300.0/9056, DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY**

Document No. : SOP-M703
Revision No. : 3.4
Supersedes : 3.3 and SOP-M772 Revision 1.0

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APPROVED FOR RELEASE BY: _____ 08/12/11
MANAGEMENT **DATE**

_____ 08-12-11
QA DEPARTMENT **DATE**

ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

1. ►METHOD IDENTIFICATION

1.1. EPA Method 300.0/***9056***, Determination of Inorganic Anions by Ion Chromatography.

2. ►APPLICABLE MATRICES

2.1. ***EPA Method 300.0*** is applicable to drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids ***(after extraction)***, and leachates ***(when no acetic acid is used)***.

2.2. ***EPA Method 9056 is applicable to drinking water, wastewater, and aqueous extracts of solids.***

3. ►DETECTION LIMITS

3.1. The ***estimated quantitation limits (EQLs)*** for these methods are as follows:

	Aqueous	*Aqueous (Refinery)*	*Solid*
Chloride	***1.0 mg/L***	***10 mg/L***	***10 mg/kg (wet-weight)***
Sulfate	***1.0 mg/L***	***10 mg/L***	***10 mg/kg (wet-weight)***
Other	***0.10 mg/L***	***1.0 mg/L***	***1.0 mg/kg (wet-weight)***

3.2. ***The EQLs will be proportionally higher for samples which require dilution or reduced sample size.***

4. ►SCOPE AND APPLICATION

4.1. ***EPA Method 300.0/9056*** is used to determine the concentrations of common inorganic ***anions*** in a variety of matrices.

4.2. The following ***analytes*** are routinely determined by these methods.

Bromide ***(Br^-)***
Chloride ***(Cl^-)***
Fluoride ***(F^-)***
Nitrate ***(NO_3^-) as N***
Nitrite ***(NO_2^-) as N***
ortho-Phosphate ***(PO_4^{3-}) as P***
Sulfate ***(SO_4^{2-})***

4.3. ***Upon client request, additional target analytes may be added to this analysis.*** However, it needs to be demonstrated that any added analytes lend themselves to EPA Method 300.0 ***or EPA Method 9056*** determination, either by regulatory reference or validation studies.

4.4. This method is restricted to use by or under the supervision of analysts experienced in the use of ion chromatograph (IC) and skilled in the interpretation of ion chromatograms.

5. ►METHOD SUMMARY

5.1. EPA Method 300.0 / ***EPA Method 9056*** describe chromatographic procedures that will allow for the separation of common anions and for their quantitative analysis by IC. Detection is achieved using a conductivity detector.

5.1.1. ***The preparation and analytical approaches are similar between both methods. Differences are found in certain quality control criteria as specified in Section 12.***

5.2. ***Prior to analysis, the appropriate sample preparation procedure (Appendix A) must be performed on each sample.***

5.2.1. Aqueous samples are filtered through a 0.45-µm filter and analyzed via direct injection.

5.2.1.1. ***Refinery aqueous samples are pretreated with hydrogen peroxide to remove sulfide prior to filtration.***

5.2.2. Solid samples are extracted using reagent water and filtered through a 0.45-µm filter. The filtered extracts are analyzed via direct injection.

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust ***or correct*** routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to preparation and/or analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. Matrix Spike (spiked sample, fortified sample, or laboratory fortified sample matrix): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.12. Matrix Spike Duplicate (spiked sample duplicate, fortified sample duplicate, or laboratory fortified sample matrix duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.13. Method Blank (laboratory reagent blank): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.14. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.15. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.16. ***Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.***

6.17. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.18. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.19. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.20. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.21. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.22. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.23. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.24. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.25. ***Terms Specific to Anion Analysis***

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

6.25.2. ***Lower limit of quantitation (LLOQ): The lowest point of quantitation, or in most cases, the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels based on the stated project requirements. Analysis of a standard prepared at the LLOQ concentration level or use of the LLOQ as the lowest point calibration standard provides confirmation of the established quantitation sensitivity of the method.***

6.25.3. ***Sensitivity: The ability of an analytical technique or instrument to discriminate between small differences in analyte concentration.***

7. ►INTERFERENCES

7.1. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high level samples should be diluted and then analyzed at the end of the sequence to prevent carryover contamination.

7.2. Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. A large amount of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

7.3. 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 chromatographic baseline.

7.4. Water from the sample injection will cause a negative peak (dip) in the baseline when it elutes because its conductance is less than that of the suppressed eluent. Any ion of interest, especially fluoride, eluting near the negative water peak must be sufficiently resolved from the negative water peak to be accurately quantified. Alternatively, the negative water peak can be eliminated by adding an equivalent of 1 mL of concentrated eluent to 100 mL of each standard and sample.

7.5. Samples that contain particles larger than 0.45 µ m, and reagent solutions that contain particles larger than 0.20 µm require filtration ***to prevent damage to instrument columns and flow systems***.

7.6. Any anion that is not retained or only slightly retained by the column will elute in the range for fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentration of fluoride above 1.5 mg/L, this interference may not be significant; however, it is the responsibility of the analyst to generate precision and accuracy information in each sample matrix.

7.7. The acetate, ***formate, and other monovalent organic acid*** anions elute early during the chromatographic run. The retention times of the anions may differ when large amounts of acetate are present. Therefore, these methods are not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

7.8. ***Bromide and nitrate elute close to one another and thus can be potential interferences for each other. It is advisable to avoid having a bromide to nitrate ratio greater than 1:10 or 10:1 if both anions are to be quantified. If nitrate interferences are noted with bromide, the use of an electrochemical detector is recommended.***

7.9. The quantitation of unretained peaks should be avoided. These include low molecular weight organic acid anions such as formate, acetate, propionate, etc. These anions are conductive and will coelute with or near fluoride and will bias the fluoride quantitation in some drinking water and most wastewaters.

7.10. Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample, the sample should be purged with an inert gas (argon or nitrogen) for approximately 5 minutes or until no chlorine dioxide remains.

7.11. Decreases in retention times and resolution are symptoms of column deterioration which may be caused by the buildup of contaminants on the exchange resin. Refer to the manufacturer's guidelines for instructions on cleaning the column resin and column filter beds or replace the column when signs of declining performance are evident.

8. SAFETY

8.1. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.2. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

8.3. No compounds covered by this method have been tentatively classified as known or suspected human carcinogens.

8.4. ►***The eluent used in the ion chromatograph is basic (pH 10) and can cause eye and skin irritation.***

9. ►EQUIPMENT AND SUPPLIES

9.1. Ion Chromatograph: Dionex ICS-1000 ***High Performance Integrated*** Ion Chromatography System configured with the following components:

9.1.1. ***Serial dual-piston pump, variable speed, 100 µL per revolution.***

9.1.2. Anion self-regenerating suppressor, ***4-mm, 0.5–3.0-mL/min flow rate, ≤ 200-µeq maximum suppression capacity, Dionex ASRS® 300 Anion Self-Regenerating Suppressor or equivalent***.

9.1.2.1. ***For Dionex AS14A anion analytical column, the recommended "8.0-mM Na_2CO_3 / 1.0-mM $NaHCO_3$" eluent flow rate is 1.0 mL/min.***

9.1.3. ***Sample injection loop, 25-µL.***

9.1.4. ***Injection valve.***

9.1.5. Autosampler, ***Dionex AS40 Automated Sampler or equivalent***.

9.1.6. ***Autosampler cassettes, capable of holding 5.0-mL autosampler vials.***

9.1.7. ***Autosampler vials, 5.0-mL capacity, with polyethylene caps and 20-µm sintered polyethylene filters, polypropylene, disposable.***

9.1.7.1. ***Autosampler vials must be verified and documented in the Chemicals and Supplies Verification Logbook prior to use.***

9.1.8. PC based data system, ***Dionex Chromeleon Chromatography Management System Version 6.50, Dionex Chromeleon Chromatography Management System Version 6.80, or equivalent***.

9.2. ***Primary Detection Channel***

9.2.1. Detector: ***Electric*** conductivity ***cell*** detector ***(ECD)***, ***Dionex DS6 Heated Conductivity Cell or equivalent***.

9.2.2. Anion Analytical Column: ***4-mm × 250-mm, 7.0-µm particle diameter, 120-µeq/column capacity, alkyl quaternary ammonium functional group, moderate hydrophobic, Dionex*** IONPAC® AS14A Analytical Column or equivalent.

9.2.3. Guard Column: ***4-mm × 50-mm, 7.0-µm particle diameter, 24-µeq/column capacity, alkyl quaternary ammonium functional group, moderate hydrophobic, Dionex*** IONPAC® AG14A Guard Column or equivalent.

9.3. Reservoir Pressurized Gas: Helium, He, ***99.995%, compressed, Praxair*** 4.5 grade or ***equivalent***.

9.4. Graduated cylinders, 50-mL 100-mL, 500-mL, or other capacity, glass, ***Class A***.

9.5. Volumetric flasks, 10-mL, 100-mL, 250-mL, 500-mL, 1000-mL, or other capacity, Class A.

9.6. Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.

9.7. Pipetters, ***10–100-µL, 100–1000-µL, and 0.5–5.0-mL, adjustable volume***, with disposable tips.

9.8. ***Pipets, transfer, plastic, disposable.***

9.9. ***Tissue wipers, 1-ply, antistatic, VWR® Light-Duty Wipes Tissue Wipers or equivalent.***

9.10. ***Wash bottle, 250-mL or other capacity.***

9.11. ***Drying oven, capable of maintaining 104 ± 1°C.***

9.12. ***Watch glass.***

9.13. ***Desiccator.***

9.14. ***Forceps or tongs, stainless steel.***

9.15. ***Gloves, heat resistant.***

9.16. ***Refer to Appendix A for additional equipment and supplies.***

10. ►REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, ***interferant free, nano-pure***, with resistivity ≥ 17.8 MΩ-cm.

10.1.2. ***Sand, washed, sea or standard Ottawa.***

10.1.3. ***Sodium carbonate, Na_2CO_3, anhydrous, fine white granules, certified reagent grade or equivalent.***

10.1.4. ***Sodium bicarbonate, $NaHCO_3$, fine white crystals, certified reagent grade or equivalent.***

10.1.5. Anion eluent concentrate, $Na_2CO_3/NaHCO_3$, 0.80-M/0.10-M, clear colorless liquid, ***commercially or manually prepared, Dionex AS14A Eluent Concentrate (100X)*** P/N 056937 or equivalent.

10.1.5.1. ***Prepare the anion eluent concentrate by dissolving 21.198 g of Na_2CO_3 and 2.1002 g of $NaHCO_3$ in reagent water and dilute to 250 mL with additional reagent water.***

10.1.6. Eluent working solution, $Na_2CO_3/NaHCO_3$, 0.008-M/0.001-M.

10.1.6.1. Prepare the eluent working solution by diluting 10 mL of anion eluent concentrate to 1 L with reagent water.

10.1.7. ***Sodium fluoride, NaF, fine white powder, certified reagent grade or equivalent.***

10.1.8. ***Sodium chloride, NaCl, fine white crystals, certified reagent grade or equivalent.***

10.1.9. ***Sodium bromide, NaBr, fine white granules, certified reagent grade or equivalent.***

10.1.10. ***Sodium nitrate, $NaNO_3$, fine white crystalline powder, certified reagent grade or equivalent.***

10.1.11. ***Sodium nitrite, $NaNO_2$, fine yellow-white crystals, certified reagent grade or equivalent.***

10.1.12. ***Potassium sulfate, K_2SO_4, white crystals, certified reagent grade or equivalent.***

10.1.13. ***Potassium phosphate monobasic, KH_2PO_4, white crystals, certified reagent grade or equivalent.***

10.1.14. ***All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.***

10.2. Standards

10.2.1. ***Manually-prepared stock standard solutions, each in sealed amber glass bottle, containing various concentrations of anions in reagent water, are used to prepare working standards.***

10.2.1.1. Dry sufficient mass of each salt at ***103–105***°C for at least 1 hour and cool ***in a desiccator prior to stock standard preparation***.

10.2.1.2. Prepare each stock standard solution by dissolving the appropriate masses of the salts in reagent water and dilute to 250 mL with additional reagent water.

Stock Standard 1			
	Initial	Final	
Analyte	Mass (g)	Conc (mg/L)	Volume (mL)
NaF	0.5525	1000	250
NaCl	8.2426	20000	
NaBr	0.6439	2000	
$NaNO_3$	3.0339	2000	
K_2SO_4	9.0704	20000	

Stock Standard 2			
	Initial	Final	
Analyte	Mass (g)	Conc (mg/L)	Volume (mL)
$NaNO_2$	1.2313	1000	250
KH_2PO_4	1.0986	1000	

10.2.1.3. The stock standard solutions are prepared as follows:

10.2.1.3.1. ***Place a clean 250-mL volumetric flask on an analytical balance and tare.***

10.2.1.3.2. Measure the appropriate mass of each salt into the flask. Tare the balance between each weighing.

10.2.1.3.3. Add 100–200 mL of reagent water and, while holding the neck of the flask, swirl the contents until the solids have dissolved completely.

10.2.1.3.4. Dilute to 250 mL with additional reagent water.

10.2.1.3.5. Cap the flask and invert a minimum of three times to mix thoroughly.

10.2.1.4. The stock standard solution 1 must be stored ***under dark and*** refrigerated conditions, and replaced after six months or sooner.

10.2.1.5. The stock standard solution 2 must be stored ***under dark and*** refrigerated conditions, and replaced after one month or sooner.

10.2.2. ***Manually-prepared working standard solutions, each in sealed volumetric flask, containing various concentrations of anions in reagent water, are used to prepare calibration and check standards.***

10.2.2.1. Prepare each working standard solution by diluting the appropriate volumes of the stock standards 1 and 2 to 100 mL with reagent water.

Working Standard 1				
	Initial		Final	
Analyte	Conc (mg/L)	Volume (mL)	Conc (mg/L)	Volume (mL)
NaF	1000	0.50	5	100
NaCl	20000		100	
NaBr	2000		10	
$NaNO_3$	2000		10	
K_2SO_4	20000		100	
$NaNO_2$	1000	0.50	5	
KH_2PO_4	1000		5	

Working Standard 2				
	Initial		Final	
Analyte	Conc (mg/L)	Volume (mL)	Conc (mg/L)	Volume (mL)
NaF	1000	0.25	2.5	100
NaCl	20000		50	
NaBr	2000		5	
$NaNO_3$	2000		5	
K_2SO_4	20000		50	
$NaNO_2$	1000	0.25	2.5	
KH_2PO_4	1000		2.5	

10.2.2.2. The working standard solutions are prepared as follows:

10.2.2.2.1. Using a calibrated pipetter, measure the appropriate volume of the stock standard 1 into a clean 100-mL volumetric flask.

10.2.2.2.2. Replace the pipetter tip and measure the appropriate volume of the stock standard 2 into the same flask.

10.2.2.2.3. Dilute to 100 mL with reagent water.

10.2.2.2.4. Cap the flask and invert a minimum of three times to mix thoroughly.

10.2.2.3. Alternatively, the working standard solutions may be prepared as follows:

10.2.2.3.1. Using a calibrated pipetter, measure the appropriate volume of the stock standard 1 into a clean specimen container.

10.2.2.3.2. Replace the pipetter tip and measure the appropriate volume of the stock standard 2 into the same specimen container.

10.2.2.3.3. Place the specimen container on an analytical balance and tare.

10.2.2.3.4. Carefully add reagent water to the specimen container until the balance reads 100 g.

10.2.2.3.5. Cap ***and swirl the contents to mix thoroughly***.

10.2.2.4. The working standard solutions must be prepared fresh daily.

10.2.3. ***Calibration Blank (CB)***

10.2.3.1. ***The CB consists of clean reagent water.***

10.2.3.2. ***The CB is used either as initial calibration blank (ICB) or as continuing calibration blank (CCB) to demonstrate the acceptability of the instrument baseline and to isolate the sources of contamination.***

10.2.4. ***Initial Calibration Standard Solutions***

10.2.4.1. ***Dilute the appropriate volume of the working standard 1 to 10.0 mL with reagent water for initial calibration.***

10.2.4.1.1. ***If the negative water peak is known to be interfering with the integration of fluoride peaks at lower calibration levels, add 0.1 mL of the anion eluent concentrate to each calibration standard after diluting to 10.0 mL with reagent water.***

10.2.4.2. ***Use the following calibration levels as guidance to prepare the calibration standards.***

Calibration Level (ppm)			Initial Conc (ppm)	Initial Volume (mL)
A1	A2	A3	A	A
0.05	1.0	0.1	5~100	0.1
1.0	20	2.0	5~100	2.0
2.0	40	4.0	5~100	4.0
2.5	50	5.0	5~100	5.0
3.0	60	6.0	5~100	6.0
4.0	80	8.0	5~100	8.0
5.0	100	10	5~100	10

Note: A1 = F^-, NO_2^- as N, and PO_4^{3-} as P; A2 = Cl^- and SO_4^{2-};
A3 = Br^- and NO_3^- as N

10.2.4.3. ***The midpoint standard is also used as the continuing calibration verification solution.***

10.2.5. ***Initial Calibration Verification (ICV) Solution***

10.2.5.1. ***Measure 10.0 mL of the working standard 2 as the ICV solution for initial calibration verification.***

10.2.5.1.1. ***If the negative water peak is known to be interfering with the integration of fluoride peaks at lower calibration levels, add 0.1 mL of the anion eluent concentrate to the ICV solution.***

10.2.5.2. ***The anions for the ICV solution must be of a source differing from that used for the initial seven-point calibration. If it is of the same source, then it must be of different lot.***

10.2.6. ***Continuing Calibration Verification (CCV) Solution***

10.2.6.1. ***Dilute 50 mL of the working standard 1 to 100 mL with reagent water for continuing calibration verification.***

10.2.6.1.1. ***If the negative water peak is known to be interfering with the integration of fluoride peaks at lower calibration levels, add 1.0 mL of the anion eluent concentrate to the CCV solution after diluting to 100 mL with reagent water.***

10.2.6.2. ***The anions for the CCV solution are of a source same as that used for the initial seven-point calibration.***

10.2.7. ***Refer to Appendix A for additional standards.***

10.2.8. ***All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.***

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 500-mL pre-cleaned ***amber*** glass or ***high density polyethylene (HDPE)*** containers with Teflon-lined closures.

11.1.1. ***No preservation chemicals are required.***

11.2. Solid samples should be collected in 2-oz ***or 4-oz*** pre-cleaned clear ***glass*** wide-mouth jars ***or 6-in decontaminated stainless steel or brass sleeves*** with Teflon-lined closures.

11.3. Samples shall be maintained in a chilled state ***(≤ 4°C)*** post sample collection until received at the laboratory. ***Samples should not be frozen (e.g., do not use dry ice as the refrigerant).***

11.4. Upon receipt, the samples are stored in a 0~6°C cooler.

11.4.1. Aqueous samples for nitrate, nitrite, and ortho-phosphate determinations must be analyzed within 48 hours of sample collection.

11.4.2. Aqueous samples for other anion determinations must be analyzed within 28 days of sample collection.

11.4.3. Solid samples for nitrate, nitrite, and ortho-phosphate determinations must be extracted ***within 7 days of sample collection and analyzed within 48 hours post extraction***.

11.4.4. Solid samples for other anion determinations must be extracted and analyzed within 28 days of sample collection.

12. ►QUALITY CONTROL

12.1. Initial Calibration ***(IC)***

12.1.1. ***An instrument blank is analyzed to demonstrate a stable baseline prior to the analysis of the initial calibration standards.***

12.1.2. The initial ***seven-point*** calibration must be established prior to the processing of sample ***filtrates***.

12.1.2.1. The calibration curve is established with seven calibration standards that bracket the linear calibration range of the instrument with the lowest standard being at or below the RL for each of the associated anions.

12.1.3. ***The IC is deemed valid if the correlation coefficient, r, for linear least squares regression with no weighting factor is ≥ 0.995.***

12.1.3.1. ***For some calibrations, it may be appropriate to force the regression through zero. Forcing the curve through zero is not the same as including the origin (0, 0) as a fictitious point in the calibration. In essence, if the curve is forced through zero, the intercept is set to 0 before the regression is calculated, thereby setting the bias to favor the low end of the calibration range by "pivoting" the function around the origin to find the best fit and resulting in one less degree of freedom. However, forcing the regression through zero must <u>not</u> be used as a rationale for reporting results below the calibration range demonstrated by the analysis of calibration standards.***

12.1.3.2. ***Rationale for forcing the regression through zero must be documented and approved by the Group Leader.***

12.1.4. ***If the r criterion for an analyte is not met, apply one of the alternative calibration options.***

12.1.4.1. ***The first calibration option is linear least squares regression with inverse of concentration weighting factor. The IC is deemed valid if the coefficient of determination, r^2, is ≥ 0.99.***

12.1.4.1.1. ***This option allows a better fitting of the points at the lower calibration levels.***

12.1.4.2. ***The second calibration option is linear least squares regression with inverse square of concentration weighting factor. The IC is deemed valid if the coefficient of determination, r^2, is ≥ 0.99.***

12.1.4.2.1. ***This option also allows a better fitting of the points at the lower calibration levels.***

12.1.5. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.1.5.1. ***If the problem appears to be associated with a single calibration standard, then that one standard may be reanalyzed once within the same analytical shift prior to sample analysis.***

12.2. Initial Calibration Verification ***(ICV)***

12.2.1. ***Immediately*** following the initial calibration, an ICV standard must be analyzed ***to establish a valid initial calibration***.

12.2.2. ***For EPA Method 300.0 determination***, the initial calibration is deemed valid if the %D for each analyte is ≤ 10%. ***For EPA Method 9056 determination, the initial calibration is deemed valid if the %D for each analyte is ≤ 5%.***

12.2.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). ***Document the unacceptable result and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable***, investigate, effect corrective action, which may include re-preparation of standard solutions ***or instrument maintenance***, and ***recalibrate***.

12.3. ***Initial Calibration Blank (ICB)***

12.3.1. ***Immediately following the ICV analysis, an ICB must be analyzed to demonstrate the acceptability of the instrument baseline and to isolate sources of potential contamination in the analytical system.***

12.3.2. ***The analytical system is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration > MDL (or the limit specified in the project specific DQO).***

12.3.3. ***If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Reprepare and reanalyze the ICB. If the ICB criteria remain unacceptable, or the source of contamination cannot be readily identified, recalibrate.***

12.4. ***Linear Calibration Range (LCR)***

12.4.1. ***Following the initial instrument setup, the linearity of the LCR for each analyte must be established prior to initial calibration.***

12.4.1.1. ***The linearity is established for each analyte by determining the signal responses from a minimum of three different concentration standards across the range.***

12.4.2. ***Following the establishment of a valid initial calibration, the linearity must be checked every six months, and a new LCR should be determined whenever a significant change in instrument response is observed or expected.***

12.4.2.1. ***The linearity is checked for each analyte by determining the signal responses from a minimum of three different concentration standards across the range.***

12.4.3. ***The linearity is deemed valid if the %D for each analyte in each check standard analyzed and quantitated against the calibration curve is ≤ 10%.***

12.5. Continuing Calibration Verification ***(CCV)***

12.5.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed ***daily prior to sample analysis (when initial calibration is <u>not</u> performed)***, after every batch of 10 samples or portion thereof ***within a 24-hour shift***, and at the end of sequence.

12.5.2. ***For EPA Method 300.0 determination***, the initial calibration is deemed valid if the %D for each analyte is ≤ 10%. ***For EPA Method 9056 determination, the initial calibration is deemed valid if the %D for each analyte is ≤ 5%.***

12.5.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. ***Document the unacceptable result and*** reanalyze the CCV ***within 2 hours after the failed CCV.*** If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.6. Continuing Calibration Blank ***(CCB)***

12.6.1. ***Immediately following the CCV analysis***, a CCB must be analyzed ***to demonstrate the acceptability of the instrument baseline and to isolate sources of potential contamination in the analytical system***.

12.6.2. ***The analytical system is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration > MDL (or the limit specified in the project specific DQO).***

12.6.3. ***If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Reprepare and reanalyze the CCB. If the CCB criteria remain unacceptable, or the source of contamination cannot be readily identified, recalibrate.***

12.7. Retention Time Windows

12.7.1. Establishment of retention time window width is accomplished by making three injections of CCV standards throughout the course of a 72-hour period. Serial injections over a shorter period of time may result in narrow retention time window width that does not accurately account for variations over several days.

12.7.1.1. Retention time window width is ± 3S (where S is the standard deviation of the three retention times for that analyte) ***or ± 0.1T_R (where T_R is the retention time of that analyte in the specified standard), whichever is greater***.

12.7.2. ***Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a CCV standard at the beginning of an analytical sequence.***

12.7.2.1. ***When initial calibration is performed, daily retention time window for each analyte is the retention time of the analyte in the midpoint calibration standard ± 3S or ± 0.1T_R (where T_R is the retention time of that analyte in the midpoint calibration standard), whichever is greater.***

12.7.2.2. ***When initial calibration is <u>not</u> performed, daily retention time window for each analyte is the retention time of the analyte in the CCV standard ± 3S or ± 0.1T_R (where T_R is the retention time of that analyte in the CCV standard), whichever is greater.***

12.7.3. ***Retention time for each analyte in the calibration verification standard is verified as follows:***

12.7.3.1. ***When initial calibration is performed, the ICV standard and all CCV standards throughout the course of an analytical sequence within a 24-hour shift must fall within the daily retention time window established by the midpoint calibration standard.***

12.7.3.2. ***When initial calibration is <u>not</u> performed, all succeeding CCV standards throughout the course of an analytical sequence within a 24-hour shift must fall within the daily retention time window established by the first CCV standard.***

12.7.3.3. ***If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window width and/or position, if necessary.***

12.8. ***Lower Limit of Quantitation (LLOQ) Check***

12.8.1. ***An LLOQ check sample is analyzed immediately following the ICV/ICB analyses (when initial calibration is performed) or CCV/CCB analyses (when initial calibration is <u>not</u> performed).***

12.8.1.1. ***The concentration of each analyte in the LLOQ check sample is at the established laboratory reporting limit.***

12.8.1.2. ***The LLOQ check sample shall be carried through the entire preparation and analytical procedure.***

12.8.2. ***The lower limit of quantitation is deemed verified if each analyte is detected at within ± 50% of its expected value.***

12.8.3. ***LLOQ check is performed per client request or project specific DQOs to demonstrate the desired detection capability.***

12.9. Event Based Quality Control (LCS/LCSDs and MBs)

12.9.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.9.2. ***The acceptance criteria for LCS/LCSD anions are as follows:***

12.9.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD ***anion are 90% and 110%, respectively. The RPD is ≤ 15%.***

12.9.2.2. All LCS/LCSD anions must be within acceptance limits. If one or more LCS/LCSD ***anions*** are not acceptable, determine the cause of the problem and effect corrective action.

12.9.2.2.1. ***If the extraction process (for solid matrix only) is not the cause of the unacceptable LCS/LCSD recoveries, the LCS/LCSD and all associated sample extracts must be re-analyzed.***

12.9.2.2.2. ***If the extraction process (for solid matrix only) is determined to be the cause of the unacceptable LCS/LCSD recoveries, then all associated samples must be re-extracted and re-analyzed.***

12.9.3. Ideally, the concentrations of target analytes in an MB should be less than ***or equal to the respective method detection limits (MDLs).*** If the concentration of any target analyte exceeds its ***MDL***, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.9.3.1. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.9.3.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be

exercised to determine if the data should be qualified, or rejected and the samples ***re-processed*** and re-analyzed.

12.10. Matrix Based Quality Control (MS/MSDs ***and Sample Duplicates***)

12.10.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) ***and a sample duplicate***.

12.10.1.1. ***A sample duplicate is a selected field sample re-processed and re-analyzed under the same analytical conditions as the associated samples. It is only required per EPA Method 9056 determination, client request, or project specific DQOs.***

12.10.2. The acceptance criteria for MS/MSD ***anions*** are as follows:

12.10.2.1. ***The lower and upper acceptance limits for %REC of each MS/MSD anion are 80% and 120%, respectively. The RPD is ≤ 20%.***

12.10.2.2. When the %REC and RPD of the MS/MSD ***anions*** are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.10.2.3. If the %REC and/or RPD of the MS/MSD ***anions*** are not within the established acceptance limits, the analytical system performance shall be suspect.

12.10.3. ***The acceptance criteria for duplicate anions are as follows:***

12.10.3.1. ***The RPD is ≤ 20%.***

12.10.3.2. ***When the RPD of the duplicate anions are at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.***

12.10.3.3. ***If the RPD of the duplicate anions are not within the established acceptance limits, the analytical system performance shall be suspect.***

12.10.4. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.11. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples ***re-processed and*** re-analyzed.

12.12. Additional information regarding internal quality control checks is provided in SOP-T020.

13. ►CALIBRATION AND STANDARDIZATION

13.1. Analytical Balance

13.1.1. Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights.

13.1.2. Calibration shall be within ***± 0.1% or ± 0.5 mg, whichever is greater***. If the values are not within these limits, recalibrate the balance.

13.2. Thermometer

13.2.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-***T043***, "***Support Equipment – Calibration, Verification, Monitoring***."

13.3. ***Pipetter***

13.3.1. ***Calibrate the pipetter according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."***

13.4. ***Ion Chromatograph Initial Calibration***

13.4.1. ***Establish an acceptable seven-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.1.***

13.4.1.1. ***Recalibration is required for the following maintenance procedures.***

13.4.1.1.1. ***Change, replace, or reverse the analytical column.***

13.4.2. ***After obtaining an acceptable seven-point calibration curve and prior to processing field or QC sample filtrates, an ICV standard and ICB must be analyzed to verify the initial calibration. The acceptance criteria for the ICV and ICB are listed in Section 12.2. and Section 12.3.***

13.4.3. ***The initial seven-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.***

13.4.4. ***Per client request or project specific DQOs, an LLOQ check sample must be analyzed immediately following the ICV/ICB analyses (when initial calibration is performed) to verify the lower limit of quantitation. The acceptance criteria for the LLOQ are listed in Section 12.8.***

13.5. Retention time window ***width for each analyte is generated by running three CCV standards over a 72-hour period. Retention time window width determination shall be performed at method set-up***, following column changes, after major instrument maintenance ***or when a significant retention time shift is suspected***.

13.5.1. ***Document the serial number of the analytical column associated with the retention time window study.***

13.5.2. ***Record the retention time in minutes for each analyte to three decimal places.***

14. ►PROCEDURE

14.1. ***Precautions for Fluoride Determination***

14.1.1. ***Water from filtrate injection will cause a negative peak or dip in the baseline. If fluoride elutes immediately following the negative water peak, accurate integration of the fluoride peak may be difficult at a low concentration level due to the negative water peak.***

14.1.2. ***Reduce or eliminate the negative water peak by adding 0.1 mL of the anion eluent concentrate per 10.0 mL of each blank, standard, or sample filtrate prior to analysis.***

14.1.3. ***If the integration issue persists for the low level fluoride peak after adding the anion eluent concentrate, apply one of the following options.***

14.1.3.1. ***Do not report fluoride using EPA Method 300.0. Use another determinative (analytical) method such as SM 4500-F^- B/C.***

14.1.3.1.1. ***Notify the project manager to obtain the client's approval prior to switching the method.***

14.1.3.2. ***Elevate the RL to the calibration level of the initial calibration standard that can be accurately resolved. The calibration must contain a minimum of three calibration standards for this option to be acceptable.***

14.1.3.2.1. ***Notify the project manager to obtain the client's approval prior to raising the RL.***

14.1.3.3. ***Perform instrument maintenance or other corrective actions which include, but are not limited to, replacing the analytical column, changing the concentration of the eluent working solution, and/or adjusting the eluent flow rate.***

14.1.3.3.1. ***Major change(s) to the instrument operating conditions will require the establishment of a new calibration curve, at a minimum, and***

possibly the establishment and verification of the method detection limit (MDL).

14.2. ***Instrument Setup***

14.2.1. ***Use the following IC operating conditions as guidance to establish the IC control program and flow rate necessary to separate the analytes of interest.***

Description	IC Operating Condition
Pump pressure	2000 ± 200 psi
Eluent flow rate	1.00 mL/min
Conductivity cell temperature	30.0°C
Suppressor	43 mA
Gradient application	
Carbonate	8.0 mM
Bicarbonate	1.0 mM
Sample loop volume	25 µL
Autosampler	
Injection type	loop
Injection mode	proportional delivery
bleed	off
Injections per vial	1
Vial type	5 mL
Rinse mode	rinse after last load
Data collection rate	5.0 Hz

14.2.2. ***Autosampler is set to deliver field or QC sample filtrate from the vial to the sample loop at 4.0 mL/min.***

14.2.3. ***If the negative water peak causes an undesirable baseline, at the "Detection Tab" of the instrument software, enable the "Detect Negative Peaks" parameter and select the "Don't label" option to correct the baseline. Refer to the Dionex Chromeleon Chromatography Management System Tutorial and User Manual for additional information.***

14.3. ***Following the establishment of a valid initial calibration, a CCV standard and CCB must be analyzed daily prior to sample analysis (when initial calibration is <u>not</u> performed), after every batch of 10 samples or portion thereof, and at the end of sequence. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.5. and Section 12.6.***

14.3.1. ***If a failed CCV/CCB is the first of the day, effect corrective action prior to analyzing any samples.***

14.3.2. ***If a failed CCV/CCB is <u>not</u> the first of the day, effect corrective action and reanalyze all samples since the last acceptable CCV/CCB.***

14.3.3. ***Per client request or project specific DQOs, an LLOQ check sample must be analyzed immediately following the CCV/CCB analyses (when initial calibration is <u>not</u> performed) to verify the lower limit of quantitation. The acceptance criteria for the LLOQ are listed in Section 12.8.***

14.4. ***Following preparatory procedures specified in Appendix A, the filtrates for the QC and actual environmental samples are received in autosampler vials. After placing the autosampler vials in the autosampler cassettes, the autosampler cassettes are then loaded onto the system sample tray.***

14.5. ***Standard and sample vials are loaded in the following or other logical order.***

14.5.1. ***If initial calibration is to be performed, the analytical sequence is as follows:***

1) Instrument Blank (IB)
2) Initial Calibration Standards
3) Initial Calibration Verification (ICV)
4) Initial Calibration Blank (ICB)
5) ***LLOQ Check (per client request or project specific DQOs)***
6) Method Blank (MB)
7) Laboratory Control Samples (LCS)
8) Laboratory Control Sample Duplicates (LCSD)
9) Samples (up to 10 per batch, ***including QC check samples and MBs***)
10) ***Sample Duplicate (per EPA Method 9056 determination, client request, or project specific DQOs)***
11) Continuing Calibration Verification (CCV)
12) Continuing Calibration Blank (CCB)
13) Matrix Spike (MS)
14) Matrix Spike Duplicate (MSD)
15) Samples (up to 10 per batch, ***including QC check samples and MBs***)
16) ***Sample Duplicate (per EPA Method 9056 determination, client request, or project specific DQOs)***
17) Ending CCV
18) Ending CCB

14.5.2. ***If initial calibration is <u>not</u> to be performed, the analytical sequence is as follows:***

1) IB
2) CCV
3) CCB
4) ***LLOQ Check (per client request or project specific DQOs)***
5) MB
6) LCS
7) LCSD

8) Samples (up to 10 per batch, ***including QC check samples and MBs***)
9) ***Sample Duplicate (per EPA Method 9056 determination, client request, or project specific DQOs)***
10) CCV
11) CCB
12) MS
13) MSD
14) Samples (up to 10 per batch, ***including QC check samples and MBs***)
15) ***Sample Duplicate (per EPA Method 9056 determination, client request, or project specific DQOs)***
16) Ending CCV
17) Ending CCB

14.5.3. The IB is ***a vial of reagent water*** used to ***demonstrate the stability of the instrument baseline*** and to determine whether the IC system is free of interferants. Additional instrument blanks may also be added elsewhere in the sequence, as necessary (i.e., after suspected high level samples).

14.5.3.1. ***It is recommended to add 2–3 instrument blanks after each refinery aqueous sample.***

14.5.4. The initial calibration standards are used to establish the initial calibration curve.

14.5.4.1. ***Initial calibration is not performed daily. However, the linearity of the linear calibration range is checked semiannually.***

14.5.5. ***The ICV is a second source standard used to verify the acceptance of the initial seven-point calibration. An acceptable ICV is required daily after initial calibration.***

14.5.6. ***The ICB is an aliquot of reagent water used to demonstrate the acceptability of the instrument baseline and to isolate sources of potential contamination in the analytical system. An acceptable ICB is required immediately following ICV.***

14.5.7. ***The LLOQ check sample is used to verify the lower limit of quantitation. Per client request or project specific DQOs, an acceptable LLOQ check is required immediately following ICV and ICB (when initial calibration is performed) or CCV and CCB (when initial calibration is <u>not</u> performed).***

14.5.8. A CCV is used to verify the acceptance of the initial ***seven-point*** calibration on a continuing basis. An acceptable CCV is required ***daily prior to sample analysis (when initial calibration is <u>not</u> performed), after every batch of 10 samples or portion thereof within a 24-hour shift, and at the end of sequence***.

14.5.9. A CCB is ***an aliquot of reagent water*** used to demonstrate the acceptability of the instrument baseline and to isolate sources of potential contamination in the analytical system. ***An acceptable CCB is required immediately following CCV.***

14.5.10. The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

14.5.10.1. For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of washed sea sand.

14.5.10.2. One MB is required ***every day preparatory methods (i.e., peroxide pretreatments, filtrations, extractions, etc.) are performed*** for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.5.10.3. ***When samples that are processed together are analyzed on separate instruments or on separate analytical shifts, the MB associated with those samples must be analyzed on at least one of the instruments. A solvent blank consisting of reagent water must be analyzed on all other instruments where the associated samples are analyzed to demonstrate that the instruments are not contributing contaminants to the samples.***

14.5.11. The LCS is a known matrix which has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.5.11.1. For aqueous samples, the LCS consists of the specified anions spiked into clean reagent water. For solid samples, the LCS consists of the specified anions spiked into washed sea sand.

14.5.11.2. ***One LCS is required every day preparatory methods (i.e., peroxide pretreatments, filtrations, extractions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.***

14.5.12. The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). ***The formula for calculating RPD is listed in Section 15.4.***

14.5.13. Up to 10 sample ***(including QC check sample and method blank)*** filtrates per batch. Sample filtrates with concentrations exceeding the

calibration range should be sufficiently diluted. Dilution of sample filtrates will result in increased reporting limits.

14.5.13.1. ***All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.***

14.5.14. The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.5.14.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). ***The formula for calculating %REC is listed in Section 15.3.***

14.5.14.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.5.15. The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). ***The formula for calculating RPD is listed in Section 15.4.***

14.5.16. ***The sample duplicate is a selected field sample re-processed and re-analyzed under the same analytical conditions. The sample duplicate is processed concurrently with the associated samples. In the processing of the sample duplicate, reagents and procedures identical to those for actual samples are used.***

14.5.16.1. ***The purpose of the sample duplicate is to access matrix effects. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.4.***

14.5.16.2. ***To comply with EPA Method 9056 determination, client request, or project specific data quality objectives (DQOs), one sample duplicate is required daily for every batch of 10 samples or portion thereof, whichever is more frequent.***

14.5.17. ***Solvent blanks may be added elsewhere in the sequence, as necessary (i.e., after suspected high concentration sample extracts), to check for potential carryover or cross-contamination.***

14.6. ***Ensure that a sufficient amount of eluent is present in the eluent reservoir, a sufficient amount of reagent water is present in the autosampler rinse vials,***

and a sufficient unused volume exists in the waste container at the beginning of the sequence.

14.7. Edit the sequence in the data system. After all correct sample information is entered, save the sequence.

14.7.1. The initial calibration standards, ICV, and ICB are analyzed on the day of calibration. However, they are included in the daily sequence for data processing.

14.8. Initiate the sequence.

14.8.1. At the end of the sequence, print the sequence table ***(sample list)***, and record comments, ***observations, or other pertinent information*** relating to sample analysis on the sequence table printout. Apply the instrument run log stamp, and place the sequence table printout in the instrument run log binder.

14.9. Data Interpretation

14.9.1. Establish the daily retention time window for each analyte ***(see Section 12.7.2.1. and Section 12.7.2.2.)***.

14.9.1.1. Tentative identification of an analyte occurs when a peak from a sample filtrate falls within the daily retention time window.

14.9.1.2. Use the ***succeeding CCV standards*** analyzed throughout the course of an analytical sequence ***within a 24-hour shift*** to evaluate retention time stability ***(see Section 12.7.3.)***. If any analyte(s) in the CCV standard fall outside of their daily retention time window(s), determine the cause of the problem and effect appropriate corrective action.

14.9.1.2.1. ***If any analyte(s) in the CCV standard fall outside of their daily retention time window(s), then all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed.***

14.9.2. Quantitation of a target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the magnitude of response between peaks in the sample ***filtrate*** and the calibration standards.

14.9.2.1. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak can be determined.

14.9.2.2. Determine the concentration based on the initial calibration curve.

14.9.2.2.1. ***The data system is programmed to perform the calculation of concentration.***

14.9.2.3. If the instrument response exceeds the calibration range, dilute the ***filtrate*** and reanalyze.

14.9.2.4. ***Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.***

14.9.2.4.1. ***When the instrument software produces proper integrations, it is highly recommended to use the integrations produced by the instrument software for consistency.***

14.9.2.4.2. ***When the instrument software does not produce proper integrations (e.g., selecting an improper baseline, missing the correct peak, integrating a coelution, partially integrating a peak, etc.), manual integrations performed by the analyst are necessary.***

14.9.2.4.3. ***Manual integration should be minimized by properly maintaining the instrument, updating the retention times, and configuring the peak integration parameters.***

15. ►CALCULATIONS

15.1. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|C_{expected} - C_{measured}|}{C_{expected}} \times 100$$

where: %D = percent difference.
$C_{expected}$ = concentration of target analyte expected.
$C_{measured}$ = concentration of target analyte measured.

Note: Concentrations must be in equivalent units.

15.2. The recovery of each LCS anion is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.3. The recovery of each MS anion is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.4. The relative percent difference is calculated as follows:

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

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.5. ***The dilution factor is calculated as follows:***

$$D = \frac{V_f}{V_i}$$

where: ***D = dilution factor.***
V_f = volume of sample, extract, or filtrate after dilution in mL.
V_i = volume of sample, extract, or filtrate before dilution in mL.

15.6. ***The target analyte concentration for an aqueous sample is calculated as follows:***

$$C_A = C_x \times D$$

where: ***C_A = concentration of target analyte in aqueous sample in mg/L.***
C_x = concentration of target analyte in filtrate in mg/L.
D = dilution factor, if the sample or filtrate was diluted prior to analysis.
If no dilution was made, D = 1.

15.7. ***The target analyte concentration for a refinery aqueous sample is calculated as follows:***

$$C_A = \frac{C_x \times V_p \times D}{V_A}$$

where: ***C_A = concentration of target analyte in refinery aqueous sample in mg/L.***
C_x = concentration of target analyte in filtrate in mg/L.
V_p = volume of refinery aqueous sample after peroxide pretreatment in mL.
Unless specified otherwise, V_p = 100.
V_A = volume of refinery aqueous sample used for peroxide pretreatment in mL.
D = dilution factor, if the sample or filtrate was diluted prior to analysis.
If no dilution was made, D = 1.

15.8. The target analyte concentration for a solid sample is calculated as follows:

$$C_S = \frac{C_x \times V_w \times D}{W_S}$$

where: C_S = concentration of target analyte in solid sample in mg/kg.
C_x = concentration of target analyte in ***filtrate*** in mg/L.
V_w = volume of reagent water used prior to extraction in mL.
Unless specified otherwise, V_w = 100.
W_S = mass of solid sample used for extraction in ***g***.
D = dilution factor, if the extract or filtrate was diluted prior to analysis.
If no dilution was made, D = 1.

15.9. All concentrations shall be reported in mg/L (ppm) for aqueous samples, and mg/kg (ppm) for soil and solid waste samples.

15.10. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD ***anions are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD anion are 90% and 110%, respectively. The RPD is ≤ 15%. All LCS/LCSD anions must be within acceptance limits.***

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentrations of target analytes in an MB should be less than ***or equal to the respective method detection limits (MDLs)***. If the concentration of any target analyte exceeds its ***MDL***, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples ***re-processed*** and re-analyzed.

18.3. The acceptance criteria for MS/MSD ***anions are predetermined. The lower and upper acceptance limits for %REC of each MS/MSD anion are 80% and 120%, respectively. The RPD is ≤ 20%.***

18.3.1. When the %REC and RPD of the MS/MSD ***anions*** are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.3.2. If the %REC and/or RPD of the MS/MSD ***anions*** are not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. ***The acceptance criteria for duplicate anions are predetermined. The RPD is ≤ 20%.***

18.4.1. ***When the RPD of the duplicate anions are at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.***

18.4.2. ***If the RPD of the duplicate anions are not within the established acceptance limits, the analytical system performance shall be suspect.***

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. ***All concentrations shall be reported in mg/L (ppm) for aqueous samples, and mg/kg (ppm) for soil and solid waste samples.***

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the Group Leader of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. ►LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported ***anion***, the Group Leader confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required. ***Report the sample and LCS/LCSD data without qualification.***

20.1.2.2. If the LCS result is verified as out-of-control, and the subject ***anion*** is to be reported in samples within that analytical batch, the samples reported with that failed ***anion*** must be reanalyzed with a valid LCS recovery for the ***anion***.

20.1.2.2.1. If a target analyte has a bias high recovery in the LCS, but it is not detected (ND) in the associated samples, the sample data may be reported if all other quality control criteria are met, and

20.1.2.3. If the LCS results are verified as acceptable, ***report data as is***.

20.1.2.4. If the LCS result is verified as out-of-control, and the subject ***anion*** is to be reported in samples within that analytical batch, the samples reported with that failed ***anion*** must be reanalyzed with a valid LCS recovery for the ***anion***.

20.1.2.4.1. ***If the LCS recovery is above criteria and the sample is non-detect for the analyte of interest, results may be reported with narration if all other instrument QC is within criteria. But,***

approval for this departure must be granted by the group leader and/or QA.

20.1.2.5. If the LCS result is verified as out-of-control, and the subject ***anion*** is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. ►REFERENCES

22.1. *Determination of Inorganic Anions by Ion Chromatography*, ***Approved General-Purpose Clean Water Act Analytical Methods***, Method 300.0, USEPA, Revision 2.1, August 1993.

22.2. ***Determination of Inorganic Anions by Ion Chromatography, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1C, Method 9056, USEPA, Revision 0, September 1994.***

22.3. ***Determination of Inorganic Anions by Ion Chromatography, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1C, Method 9056A, USEPA, Revision 1, February 2007.***

22.4. ***Determinative Chromatographic Separations, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000C, USEPA, Revision 3, March 2003.***

22.5. ***Quality Control, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.***

22.6. ***Choosing the Correct Procedure, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.***

22.7. ***Miscellaneous Test Methods, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Five, USEPA, Revision 5, February 2007.***

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. ***Appendix A: Sample Preparation and Extraction Procedures.***

23.2. ***Appendix B: Additional Quality Control Criteria for Department of Defense Project.***

24. MODIFICATIONS

24.1. None.

Appendix A

SAMPLE PREPARATION AND EXTRACTION PROCEDURES

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 300.0/9056, Determination of Inorganic Anions by Ion Chromatography – Sample Preparation and Extraction Procedures.

2. SCOPE AND APPLICATION

2.1. The procedure described herein is in addition to the standard procedure.

2.2. This method is restricted to use by or under the supervision of analysts/technicians experienced in the use of the equipments and apparatus required to execute the procedure.

3. METHOD SUMMARY

3.1. EPA Method 300.0/9056 provides the sample pretreatment, filtration, and extraction procedures prior to analysis.

3.1.1. Aqueous samples are filtered through a 0.45-µm filter and analyzed via direct injection.

3.1.1.1. Refinery aqueous samples are pretreated with hydrogen peroxide to remove sulfide prior to filtration.

3.1.2. Solid samples are extracted using reagent water and filtered through a 0.45-µm filter. The filtered extracts are analyzed via direct injection.

4. INTERFERENCES

4.1. Samples that contain particles larger than 0.45 µm, and reagent solutions that contain particles larger than 0.20 µm require filtration to prevent damage to instrument columns and flow systems.

4.2. Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample, the sample should be purged with an inert gas (argon or nitrogen) for approximately 5 minutes or until no chlorine dioxide remains.

5. SAFETY

5.1. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

5.2. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

6. EQUIPMENT AND SUPPLIES

6.1. Specimen containers, 4.5-oz (120-mL), high density polyethylene (HDPE) or polypropylene, with polypropylene lids, disposable.

6.2. Test tubes, 17-mm × 100-mm (16.0-mL), polystyrene, disposable.

6.2.1. Test tubes must be verified and documented in the Chemicals and Supplies Verification Logbook prior to use.

6.3. Beakers, 50-mL, 100-mL, 500-mL, or other capacity, glass.

6.4. Erlenmeyer flasks, 125-mL or other capacity, glass.

6.5. Autosampler vials, 5.0-mL capacity, with polyethylene caps and 20-µm sintered polyethylene filters, polypropylene, disposable.

6.5.1. Autosampler vials must be verified and documented in the Chemicals and Supplies Verification Logbook prior to use.

6.6. Spatula, stainless steel.

6.7. Syringe filtration apparatus:

6.7.1. Syringe, 10-mL, polypropylene, eccentric tip, disposable, BD Lab Syringe P/N 305462 or equivalent.

6.7.2. Filter, 0.45-µm effective pore size, 30-mm diameter, hydrophilic polyvinylidene difluoride (PVDF) membrane, polypropylene housing, disposable, National Scientific Company F2500-5 Target Syringe Filter or equivalent.

6.7.3. Filter, 0.20-µm effective pore size, 30-mm diameter, nylon membrane with 1-µm glass microfiber pre-filter, polypropylene housing, disposable, National Scientific Company F2502-2 Target Syringe Filter or equivalent.

6.7.4. Syringes and filters must be verified and documented in the Chemicals and Supplies Verification Logbook prior to use.

6.8. Purging apparatus:

6.8.1. Round bottom flask, 1-L or other capacity, 19/38 joint size, two necks, borosilicate glass.

6.8.2. Support stand, cast-iron, equipped with adjustable angle clamps.

6.8.3. Nitrogen, N_2, 99.998%, compressed, Praxair 4.8 grade or higher.

6.9. Centrifuge, 250–6000-rpm variable speed, 1–30-min digital timer, VWR International Clinical 200 Large Capacity Centrifuge or equivalent.

6.10. Ultrasonic bath, VWR Scientific Aquasonic Model 550T Ultrasonic Cleaner or equivalent.

6.11. Parafilm, thermoplastic, Parafilm M® Laboratory Film or equivalent.

6.12. Pipetters, 10–100-µL, 100–1000-µL, and 0.5–5.0-mL, adjustable volume, with disposable tips.

6.13. Pipets, transfer, plastic, disposable.

6.14. Balance, top loading, calibrated, capable of weighing to the nearest 0.01 g.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Reagent water, interferant free, nano-pure, with resistivity ≥ 17.8 MΩ-cm.

7.1.2. Sand, washed, sea or standard Ottawa.

7.1.3. Lead acetate test strips, white color paper.

7.1.3.1. The lead acetate test paper turns black in the presence of hydrogen sulfide and other soluble sulfides.

7.1.4. Hydrogen peroxide, H_2O_2, 30% (v/v), clear colorless liquid, certified, reagent grade or equivalent.

7.1.5. Sodium carbonate, Na_2CO_3, anhydrous, fine white granules, certified reagent grade or equivalent.

7.1.6. Sodium bicarbonate, $NaHCO_3$, fine white crystals, certified reagent grade or equivalent.

7.1.7. Anion eluent concentrate, $Na_2CO_3/NaHCO_3$, 0.80-M/0.10-M, clear colorless liquid, commercially or manually prepared, Dionex AS14A Eluent Concentrate (100X) P/N 056937 or equivalent.

7.1.7.1. Prepare the anion eluent concentrate by dissolving 21.198 g of Na_2CO_3 and 2.1002 g of $NaHCO_3$ in reagent water and dilute to 250 mL with additional reagent water.

7.1.8. Sodium fluoride, NaF, fine white powder, certified reagent grade or equivalent.

7.1.9. Sodium chloride, NaCl, fine white crystals, certified reagent grade or equivalent.

7.1.10. Sodium bromide, NaBr, fine white granules, certified reagent grade or equivalent.

7.1.11. Sodium nitrate, $NaNO_3$, fine white crystalline powder, certified reagent grade or equivalent.

7.1.12. Sodium nitrite, $NaNO_2$, fine yellow-white crystals, certified reagent grade or equivalent.

7.1.13. Potassium sulfate, K_2SO_4, white crystals, certified reagent grade or equivalent.

7.1.14. Potassium phosphate monobasic, KH_2PO_4, white crystals, certified reagent grade or equivalent.

7.1.15. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

7.2. Standards

7.2.1. Manually-prepared stock standard solutions, each in sealed amber glass bottle, containing various concentrations of anions in reagent water, are used to prepare check standards.

7.2.1.1. Dry sufficient mass of each salt at 103–105°C for at least 1 hour and cool in a desiccator prior to stock standard preparation.

7.2.1.2. Prepare each stock standard solution by dissolving the appropriate masses of the salts in reagent water and dilute to 250 mL with additional reagent water.

Stock Standard 1			
	Initial	Final	
Analyte	Mass (g)	Conc (mg/L)	Volume (mL)
NaF	0.5525	1000	250
NaCl	8.2426	20000	
NaBr	0.6439	2000	
$NaNO_3$	3.0339	2000	
K_2SO_4	9.0704	20000	

Stock Standard 2			
	Initial	Final	
Analyte	Mass (g)	Conc (mg/L)	Volume (mL)
$NaNO_2$	1.2313	1000	250
KH_2PO_4	1.0986	1000	

7.2.1.3. The stock standard solutions are prepared as follows:

7.2.1.3.1. Place a clean 250-mL volumetric flask on an analytical balance and tare.

7.2.1.3.2. Measure the appropriate mass of each salt into the flask. Tare the balance between each weighing.

7.2.1.3.3. Add 100–200 mL of reagent water and, while holding the neck of the flask, swirl the contents until the solids have dissolved completely.

7.2.1.3.4. Dilute to 250 mL with additional reagent water.

7.2.1.3.5. Cap the flask and invert a minimum of three times to mix thoroughly.

7.2.1.4. The stock standard solution 1 must be stored under dark and refrigerated conditions, and replaced after six months or sooner.

7.2.1.5. The stock standard solution 2 must be stored under dark and refrigerated conditions, and replaced after one month or sooner.

7.2.2. Spike Standard Solution

7.2.2.1. Use the second source stock standards 1 and 2 as the spike standard solutions 1 and 2, respectively.

7.2.2.2. The spike standards are used to prepare quality control (QC) check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

7.2.2.3. The anions for the spike standards must be of a source differing from that used for the initial seven-point calibration. If it is of the same source, then it must be of different lot.

7.2.2.4. Add 25 µL of each spike standard to each 10.0-mL aliquot of aqueous MS/MSD and LCS/LCSD sample prior to filtration.

7.2.2.5. Add 250 µL of each spike standard to each 10.0-mL aliquot of refinery aqueous MS/MSD and LCS/LCSD sample prior to peroxide pretreatment.

7.2.2.6. Add 250 µL of each spike standard to each 10.0-g aliquot of solid MS/MSD and LCS/LCSD sample prior to extraction.

7.2.3. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

8. CALIBRATION AND STANDARDIZATION

8.1. Top Loading Balance

8.1.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights.

8.1.2. Calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If the values are not within these limits, recalibrate the balance.

8.2. Pipetter

8.2.1. Calibrate the pipetter according to the procedure outlined in the current revision of SOP-T043, "Support Equipment – Calibration, Verification, Monitoring."

9. PROCEDURE

9.1. Aqueous Sample Preparation

9.1.1. Allow an aqueous sample to reach ambient temperature, and the suspended particulates, if any, in the aqueous sample to settle.

9.1.1.1. Suspended particulates may be removed by centrifuging at 2000 rpm for 10–20 minutes.

9.1.2. Measure at least 10.0 mL of the aqueous sample into a clean specimen container. Record the specimen container identification number.

9.1.2.1. For MB/LCS/LCSD, measure exactly 10.0 mL of clean reagent water.

9.1.2.2. For MS/MSD, measure exactly 10.0 mL of aqueous sample in each analytical batch selected for spiking.

9.1.3. Add 25 µL of each spike standard solution to all matrix spikes and laboratory control samples.

9.1.3.1. If nitrite and/or ortho-phosphate are not the analyte(s) of interest, add 25 µL of the spike standard solution 1 to all matrix spikes and laboratory control samples.

9.1.3.2. If nitrite and/or ortho-phosphate are the only analyte(s) of interest, add 25 µL of the spike standard solution 2 to all matrix spikes and laboratory control samples.

9.1.4. Pull the plunger of a syringe and draw the aqueous sample from the specimen container into the barrel. Record the syringe identification number.

9.1.5. Attach a clean 0.45-µm membrane filter and press the plunger to filter the sample. Discard the first few drops of the filtrate. Record the membrane filter identification number.

9.1.5.1. Slowly push down on the plunger until the sample begins to pass through the filter. Do not use excessive force as the filter may rupture.

9.1.6. Collect approximately 10 mL of the aqueous sample filtrate in a clean test tube and label appropriately. Record the test tube identification number.

9.1.7. If the filtrate appears to be turbid or colored, assemble the syringe filtration apparatus with a clean 0.20-µm membrane filter. Filter and collect the filtrate.

9.1.8. If water dip is known to be interfering with the integration of fluoride peaks at lower concentration levels, add 0.1 mL of the anion eluent concentrate per 10.0-mL aliquot of each blank, standard, and sample filtrate.

9.1.9. Cover the test tube with parafilm.

9.1.10. Transfer an aliquot of the filtrate into a clean autosampler vial immediately prior to analysis.

9.1.11. Process the MB/LCS/LCSD/MS/MSD in the same manner (Section 9.1.4. through Section 9.1.10. of this appendix) as the associated aqueous samples.

9.2. Refinery Aqueous Sample Preparation

9.2.1. Allow a refinery aqueous sample to reach ambient temperature, and the suspended particulates, if any, in the refinery aqueous sample to settle.

9.2.1.1. Suspended particulates may be removed by centrifuging at 2000 rpm for 10–20 minutes.

9.2.2. Measure exactly 10.0 mL of the aqueous sample into a clean round bottom flask.

9.2.2.1. For MB/LCS/LCSD, measure exactly 10.0 mL of clean reagent water.

9.2.2.2. For MS/MSD, measure exactly 10.0 mL of refinery aqueous sample in each analytical batch selected for spiking.

9.2.3. Add 250 µL of each spike standard solution to all matrix spikes and laboratory control samples.

9.2.3.1. If nitrite and/or ortho-phosphate are not the analyte(s) of interest, add 250 µL of the spike standard solution 1 to all matrix spikes and laboratory control samples.

9.2.3.2. If nitrite and/or ortho-phosphate are the only analyte(s) of interest, add 250 µL of the spike standard solution 2 to all matrix spikes and laboratory control samples.

9.2.4. Add 90 mL of reagent water and 1.0 mL of 30% hydrogen peroxide to the round bottom flask.

9.2.4.1. Yellow color in the solution indicates the presence of sulfide.

9.2.5. Assemble the purging apparatus and purge the diluted sample with nitrogen for a minimum of 12 hours or until the solution remains colorless.

9.2.5.1. If the yellow color persists, add 5 drops of 30% hydrogen peroxide periodically (i.e., every 2–4 hours), and continue purging until the solution remains colorless.

9.2.6. Verify the absence of sulfide by transferring a drop of the purged sample onto a lead acetate test strip. A white color indicates the absence of sulfide, and a black color indicates the presence of sulfide.

9.2.6.1. If sulfide is still present, add 5 drops of 30% hydrogen peroxide periodically (i.e., every 2–4 hours), and continue purging until sulfide is completely removed.

9.2.7. Transfer the purged sample into a clean specimen container, and adjust the volume to 100 mL with reagent water.

9.2.8. Cap the specimen container and shake to mix the purged sample.

9.2.9. Pull the plunger of a syringe and draw the purged sample from the specimen container into the barrel. Record the syringe identification number.

9.2.10. Attach a clean 0.45-µm membrane filter and press the plunger to filter the sample. Discard the first few drops of the filtrate. Record the membrane filter identification number.

9.2.10.1. Slowly push down on the plunger until the sample begins to pass through the filter. Do not use excessive force as the filter may rupture.

9.2.11. Collect approximately 10 mL of the refinery aqueous sample filtrate in a clean test tube and label appropriately. Record the test tube identification number.

9.2.12. If the filtrate appears to be turbid or colored, assemble the syringe filtration apparatus with a clean 0.20-µm membrane filter. Filter and collect the filtrate.

9.2.13. If water dip is known to be interfering with the integration of fluoride peaks at lower concentration levels, add 0.1 mL of the anion eluent concentrate per 10.0-mL aliquot of each blank, standard, and sample filtrate.

9.2.14. Cover the test tube with parafilm.

9.2.15. Transfer an aliquot of the filtrate into a clean autosampler vial immediately prior to analysis.

9.2.16. Process the MB/LCS/LCSD/MS/MSD in the same manner (Section 9.2.4. through Section 9.2.15. of this appendix) as the associated refinery aqueous samples.

9.3. Solid Sample Preparation

9.3.1. Homogenize a solid, soil, or sediment sample as outlined in the current revision of SOP-M230.

9.3.2. Measure 10.0 ± 0.1 g (wet weight) of the homogenized solid sample into a clean specimen container. Record the specimen container identification number.

9.3.2.1. For MB/LCS/LCSD, measure 10.0 ± 0.1 g (wet weight) of washed sea sand. Record the washed sea sand identification number.

9.3.2.2. For MS/MSD, measure 10.0 ± 0.1 g (wet weight) of solid sample in each analytical batch selected for spiking.

9.3.3. Add 250 µL of each spike standard solution to all matrix spikes and laboratory control samples.

9.3.3.1. If nitrite and/or ortho-phosphate are not the analyte(s) of interest, add 250 µL of the spike standard solution 1 to all matrix spikes and laboratory control samples.

9.3.3.2. If nitrite and/or ortho-phosphate are the only analyte(s) of interest, add 250 µL of the spike standard solution 2 to all matrix spikes and laboratory control samples.

9.3.4. Add 100 mL of reagent water to the specimen container.

9.3.5. Cap the specimen container and shake to mix the slurry.

9.3.6. Place the specimen container in the ultrasonic bath and sonicate the slurry for 30 minutes at ambient temperature.

9.3.6.1. The aqueous phase of the slurry is the solid sample extract.

9.3.7. Allow the solid phase and the suspended particulates, if any, in the extract to settle.

9.3.7.1. Suspended particulates may be removed by centrifuging at 2000 rpm for 10–20 minutes.

9.3.8. Pull the plunger of a syringe and draw the extract from the specimen container into the barrel. Record the syringe identification number.

9.3.9. Attach a clean 0.45-µm membrane filter and press the plunger to filter the extract. Discard the first few drops of the filtrate. Record the membrane filter identification number.

9.3.9.1. Slowly push down on the plunger until the extract begins to pass through the filter. Do not use excessive force as the filter may rupture.

9.3.10. Collect approximately 10 mL of the solid sample filtrate in a clean test tube and label appropriately. Record the test tube identification number.

9.3.11. If the filtrate appears to be turbid or colored, assemble the syringe filtration apparatus with a clean 0.20-µm membrane filter. Filter and collect the filtrate.

9.3.12. If water dip is known to be interfering with the integration of fluoride peaks at lower concentration levels, add 0.1 mL of the anion eluent concentrate per 10.0-mL aliquot of each blank, standard, and sample filtrate.

9.3.13. Cover the test tube with parafilm.

9.3.14. Transfer an aliquot of the filtrate into a clean autosampler vial immediately prior to analysis.

9.3.15. Process the MB/LCS/LCSD/MS/MSD in the same manner (Section 9.3.4. through Section 9.3.14. of this appendix) as the associated solid samples.

9.4. Aqueous LLOQ Check Sample Preparation

9.4.1. Measure the appropriate volume(s) of the stock standard(s) into a clean 100-mL volumetric flask.

9.4.1.1. If chloride, bromide, nitrate, and/or sulfate are the analytes of interest, measure 5.0 µL of the stock standard 1.

9.4.1.2. If fluoride, nitrite, and/or ortho-phosphate are the analytes of interest, measure 10.0 µL each of the stock standards 1 and 2.

9.4.2. Dilute to 100 mL with reagent water.

9.4.3. Cap the flask and invert a minimum of three times to mix thoroughly.

9.4.3.1. The solution is the LLOQ check sample.

9.4.4. Measure at least 10.0 mL of the check sample into a clean specimen container. Record the specimen container identification number.

9.4.5. Process the check sample in the same manner (Section 9.1.4. through Section 9.1.10. of this appendix) as the associated aqueous samples.

9.5. Refinery Aqueous LLOQ Check Sample Preparation

9.5.1. Measure the appropriate volume(s) of the stock standard(s) into a clean 100-mL volumetric flask.

9.5.1.1. If chloride, bromide, nitrate, and/or sulfate are the analytes of interest, measure 50 µL of the stock standard 1.

9.5.1.2. If fluoride, nitrite, and/or ortho-phosphate are the analytes of interest, measure 100 µL each of the stock standards 1 and 2.

9.5.2. Dilute to 100 mL with reagent water.

9.5.3. Cap the flask and invert a minimum of three times to mix thoroughly.

9.5.3.1. The solution is the LLOQ check sample.

9.5.4. Measure exactly 10.0 mL of the check sample into a clean round bottom flask.

9.5.5. Process the check sample in the same manner (Section 9.2.4. through Section 9.2.15. of this appendix) as the associated refinery aqueous samples.

9.6. Solid LLOQ Check Sample Preparation

9.6.1. Measure 10.0 ± 0.1 g (wet weight) of washed sea sand into a clean specimen container. Record the specimen container and the washed sea sand identification numbers.

9.6.2. Measure the appropriate volume(s) of the stock standard(s) into the same specimen container.

9.6.2.1. If chloride, bromide, nitrate, and/or sulfate are the analytes of interest, measure 50 µL of the stock standard 1.

9.6.2.2. If fluoride, nitrite, and/or ortho-phosphate are the analytes of interest, measure 100 µL each of the stock standards 1 and 2.

9.6.3. Add 100 mL of reagent water to the specimen container.

9.6.4. Cap the specimen container and shake to mix the slurry.

9.6.4.1. The solid phase of the slurry is the LLOQ check sample.

9.6.5. Process the check sample in the same manner (Section 9.3.6. through Section 9.3.14. of this appendix) as the associated solid samples.

9.7. Thoroughly document all aspects of the sample preparation on the sequence table printout (for aqueous matrix) or in the Anion Sample Preparation Logbook (for refinery aqueous matrix or solid matrix). The sample preparation logbook includes, but is not limited to:

9.7.1. Batch preparation date, start time, and end time.

9.7.2. Sample matrix, initial volume or mass, and final volume.

9.7.3. Reagent and supply identification numbers.

9.7.4. Standard identification number, concentration, and volume added.

9.7.5. Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.

10. MODIFICATIONS

10.1. The following modifications from EPA Method 300.0 are noted.

10.1.1. Reagents and Standards

10.1.1.1. Eluent and standard preparations are modified.

10.1.2. Procedure

10.1.2.1. Solid sample extraction device and time are modified.

10.2. The following modifications from EPA Method 9056 are noted.

10.2.1. Reagents and Standards

10.2.1.1. Eluent and standard preparations are modified.

Appendix B

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 9056, Determination of Inorganic Anions by Ion Chromatography – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. DETECTION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. STANDARDS

4.1. The spike standard solutions shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. QUALITY CONTROL

5.1. Method Detection Limit (MDL)

5.1.1. MDL study shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, and following a change in instrumentation that affects the sensitivity of the analysis thereafter.

5.1.2. MDL verification must be performed immediately following an MDL study and quarterly thereafter.

5.1.2.1. MDL verification sample shall be prepared by spiking an appropriate matrix at approximately 2–3 times the detection limit for a single-analyte standard, or 1–4 times the detection limit for a multiple-analyte standard.

5.1.2.2. MDL verification is deemed valid if the apparent signal-to-noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., retention time, pattern recognition, etc.).

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the MDL study and verification at a higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive MDL verifications at a higher concentration. Set the MDL at the higher concentration.

5.1.3. No samples shall be analyzed without a valid MDL.

5.2. Initial Calibration (IC)

5.2.1. The IC is deemed valid if the correlation coefficient, r, for linear least squares regression is ≥ 0.995.

5.3. Initial Calibration Verification (ICV)

5.3.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 10%.

5.4. Continuing Calibration Verification (CCV)

5.4.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 10%.

5.4.2. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.5. Retention Time Window

5.5.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a low-to-midpoint CCV standard at the beginning of an analytical sequence.

5.5.1.1. When initial calibration is performed, daily retention time window for each analyte is the retention time of the analyte in the midpoint calibration standard ± 3S.

5.5.1.2. When initial calibration is <u>not</u> performed, daily retention time window for each analyte is the retention time of the analyte in the low-to-midpoint CCV standard ± 3S.

5.6. Event Based Quality Control (LCS/LCSDs and MBs)

5.6.1. Method Blanks (MBs)

5.6.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.6.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, <u>and</u> is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.6.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, <u>and</u> is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.6.1.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

5.6.1.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the MDL.

5.6.1.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.7. Matrix Based Quality Control (MS/MSDs and Sample Duplicates)

5.7.1. Matrix Spikes (MS/MSDs)

5.7.1.1. The lower and upper acceptance limits for %REC of each MS/MSD anion are 80% and 120%, respectively. The RPD is ≤ 15%.

5.7.2. Sample Duplicates

5.7.2.1. The RPD is ≤ 10%.

5.7.2.2. If the RPD of the duplicate anions are not within the established acceptance limits, reprocess the sample and the associated sample duplicate in a subsequent preparation batch.

5.7.2.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (J-flag) for the specific analyte(s) in the sample duplicate.

6. PROCEDURE

6.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 samples or portion thereof within a 12-hour shift, and at the end of sequence.

6.2. Standard and sample vials are loaded in the following or other logical order:

1) Instrument Blank (IB)
2) Continuing Calibration Verification (CCV)
3) Continuing Calibration Blank (CCB)
4) LLOQ Check (per client request or project specific DQOs)
5) Method Blank (MB)
6) Laboratory Control Sample (LCS)
7) Laboratory Control Sample Duplicate (LCSD)
8) Samples (up to 10 per batch, including QC check samples and MBs)
9) Sample Duplicate
10) CCV
11) CCB
12) Matrix Spike (MS)
13) Matrix Spike Duplicate (MSD)

14) Samples (up to 10 per batch, including QC check samples and MBs)
15) Sample Duplicate
16) Ending CCV
17) Ending CCB

6.2.1. The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.2.1.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.2.2. The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

7. REFERENCES

7.1. Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.2, October 25, 2010.

Title : **SM 2540 C / EPA METHOD 160.1, TOTAL DISSOLVED SOLIDS (FILTERABLE RESIDUE, GRAVIMETRIC)**

Document No. : SOP-M713
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Revision 2.5 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 2/15/10
MANAGEMENT **DATE**

_____ 02-15-10
QA DEPARTMENT **DATE**

ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

1. METHOD IDENTIFICATION

1.1. ► SM 2540 C / EPA Method 160.1, Total Dissolved Solids (Filterable Residue, ***Gravimetric***).

2. APPLICABLE MATRICES

2.1. ►This method is applicable to drinking, surface and saline waters, domestic and industrial wastewaters. It is also applicable to soil and solid wastes as a modified method.

3. DETECTION LIMITS

3.1. ►The estimated quantitation limits (EQLs) for this method are as follows:

Concentration (mg/L or mg/kg) in Sample	EQL (mg/L or mg/kg)
≤999	1.0
> 999 and ≤9,999	10
> 9,999 and ≤99,999	100
> 99,999	1000

4. ►SCOPE AND APPLICATION

4.1. ***SM 2540 C / EPA Method 160.1*** are used to determine the total dissolved solids.

4.2. This method is restricted to use by ***or under the supervision of*** analysts experienced in the use of the ***equipment*** and apparatus required to execute the analysis and skilled in the interpretation of the outputs.

4.2.1. Each analyst must demonstrate the ability to generate acceptable results with this method and be approved by the applicable Group Leader prior to analyzing billable samples.

5. METHOD SUMMARY

5.1. A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated ***in weighed beaker*** and dried to a constant weight at 180°C. ***The increase in weight of the beaker represents the total dissolved solids.***

5.2. ***The filtrate from the determination of total suspended solids (non-filterable residue) may be used for this method.***

6. ►DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.10. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.11. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.12. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.13. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.14. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.15. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.16. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.17. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.18. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.19. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.20. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.21. Terms Specific to Solids Analysis

6.21.1. ***Total*** Dissolved Solids: The portion of ***total*** solids that passes through a filter of 2.0-µm (or smaller) nominal pore size under specified conditions.

6.21.2. ***Total Solids: Material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids include total dissolved solids and total suspended solids.***

6.21.3. ***Total Suspended Solids: The portion of total solids retained on a filter of 2.0-µm nominal pore size under specified conditions.***

7. ►INTERFERENCES

7.1. ***Sampling, subsampling, and pipeting two-phase or three-phase samples may introduce serious errors. Make and keep such samples homogeneous during transfer. Use special handling to insure sample integrity when subsampling.***

7.1.1. ***Mix small samples with a magnetic stirrer. Avoid using a magnetic stirrer if the samples contain magnetic particles.***

7.1.2. ***If suspended solids are present, pipet with wide-bore pipets.***

7.1.3. ***If part of a sample adheres to the sample container, document it in the logbook when evaluating and reporting results.***

7.2. ***Some samples may dry with the formation of a crust that prevents water evaporating.***

7.2.1. ***Limit sample to no more than 200 mg residue to prevent water-trapping crust.***

7.3. ***Weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, gases from heat-induced chemical decomposition, and weight gains due to oxidation depend on the temperature and heating time at which the residue is dried.***

7.3.1. ***Each sample requires close attention to desiccation after drying. Minimize opening the desiccator to prevent moist air from entering.***

7.3.2. ***Some samples may be stronger desiccants than those used in the desiccator and may take on water.***

7.4. ***Residue dried at 180 ± 2°C will lose almost all mechanically occluded water. Some water of crystallization may remain, especially if sulfates are present. Organic matter may be lost by volatilization, but not completely destroyed. Loss of carbon dioxide may convert bicarbonate to carbonate, and carbonates may be decomposed partially to oxides or basic salts. Some chloride and nitrate salts may be lost.***

7.4.1. ***In general, evaporating and drying water samples at 180°C yields values for dissolved solids closer to those obtained from summation of individually determined mineral species than the dissolved solids values secured through drying at the lower temperature.***

7.5. ***Residues high in oil or grease may yield questionable results because of the difficulty of drying to constant weight in a reasonable time.***

7.5.1. ***Disperse visible floating oil and grease with a blender before withdrawing a sample aliquot for analysis.***

7.6. Highly mineralized water with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing.

7.7. Samples containing high concentrations of bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate.

8. ►SAFETY

8.1. ***Beakers are heated in an oven and will be hot upon removal. Use tongs to handle the weighing dishes when removing from the oven.***

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. ►EQUIPMENT AND SUPPLIES

9.1. ***Specimen containers, 4.5-oz (120-mL), with lids, high density polyethylene (HDPE) or polypropylene, disposable.***

9.2. Graduated cylinders, ***25-mL***, 50-mL, ***100-mL, or other capacity***, glass, Class A.

9.2.1. ***Class A graduated cylinder is utilized to measure sample volume.***

9.3. ***Graduated cylinders, 50-mL, glass, Class B.***

9.3.1. ***Class B graduated cylinder is utilized to collect sample filtrate.***

9.4. ***Blender or homogenizer.***

9.5. ***Magnetic stirrer.***

9.6. ***Stir bars, Teflon coated.***

9.7. ***Stir bar retriever, magnetic.***

9.8. ***Transfer pipets, wide-bore, glass or plastic, disposable.***

9.9. ***Spatula, stainless steel.***

9.10. ***Vacuum filtration apparatus:***

9.10.1. Vacuum apparatus.

9.10.2. ***Buchner funnel, 100-mm diameter, 320-mL capacity, porcelain with fixed perforated plate, capable of supporting a 90-mm diameter filter, CoorsTek Fixed Plate Buchner Funnel or equivalent.***

9.10.3. Filtration flask, 1000-mL ***or other capacity***, glass, ***with tubulation***.

9.10.4. Filter paper, ***1.5-µm effective pore size***, 90-mm diameter, ***borosilicate glass microfiber, binder free***, Whatman Grade 934-AH ***Glass Microfiber Filter or equivalent***.

9.11. Beakers, 50-mL or 150-mL, glass.

9.12. Drying oven, ***thermostatically controlled, forced draft***, capable of maintaining 180 ± ***2***°C.

9.13. Hot plate, capable of maintaining 80−100°C.

9.14. ***Muffle furnace, capable of maintaining 550 ± 50°C.***

9.15. Thermometer, ***calibrated, capable of monitoring temperatures at 90 ± 10°C and 180 ± 2°C***.

9.16. Desiccator, ***containing indicating-type desiccant***.

9.17. ***Forceps or tongs, stainless steel.***

9.18. ***Gloves, heat resistant.***

9.19. Wash bottle, ***500-mL, 1000-mL, or other capacity, low density polyethylene (LDPE)***.

9.20. Balance, analytical, ***calibrated***, capable of weighing to the nearest 0.1 mg.

9.21. ***Ultrasonic bath, VWR Scientific Aquasonic Model 550T or equivalent.***

9.22. ***Paper towels.***

9.23. ***Tray, plastic.***

10. ►REAGENTS AND STANDARDS

10.1. ***Reagents***

10.1.1. Reagent water, interferant free, deionized.

10.1.2. Sand, washed, ***sea or standard Ottawa***.

10.1.3. ***All reagents (except reagent water) must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.***

10.2. ***Standards***

10.2.1. ***None.***

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. ***Aqueous*** samples should be collected in ***1-L pre-cleaned high density polyethylene (HDPE) or clear glass*** containers with Teflon-lined closures.

11.1.1. No preservation chemicals are required.

11.2. ***Solid samples should be collected in 4-oz or 8-oz pre-cleaned clear glass wide-mouth jars (preferable), or 6-in decontaminated stainless steel or brass sleeves with Teflon-lined closures.***

11.3. ***Samples should be maintained in a chill state (≤4°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).***

11.4. ***Upon receipt, the samples are stored in a 0–6°C cooler.***

11.4.1. ***Aqueous and solid*** samples shall be analyzed as soon as feasible ***to minimize microbiological decomposition of solids***. The maximum holding time is within 7 days of sample collection.

11.5. Additional sample handling information can be found in the Sample Control SOPs.

12. ►QUALITY CONTROL

12.1. ***Event Based Quality Control (MBs)***

12.1.1. ***Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB).***

12.1.2. ***Ideally, the concentration of target analyte in an MB should be less than the respective reporting limit (RL). If the concentration of target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated.***

12.2. ***Matrix Based Quality Control (Sample Duplicates)***

12.2.1. ***Matrix based quality control consists of QC samples processed using actual environmental samples. This consists of a sample duplicate.***

12.2.1.1. ***A sample duplicate is a selected field sample re-processed and re-analyzed under the same analytical conditions as the associated samples.***

12.2.2. The acceptance criteria for duplicate analyte are as follows:

12.2.2.1. The RPD is ≤***10***%.

12.2.2.1.1. ***For EPA Region 9 requirement, the RPD is < 20%.***

12.2.2.2. ***When the RPD of the duplicate analyte is at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of***

the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.

12.2.2.3. ***If the RPD of the duplicate analyte is not within the established acceptance limits, the analytical system performance shall be suspect.***

12.2.3. ***Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. Determine the cause of the problem and effect corrective action.***

12.3. ***If the RPD of the sample duplicate is unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.***

12.4. ***Additional information regarding internal quality control check is provided*** in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Analytical Balance

13.1.1. Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights.

13.1.2. ►Calibration shall be within ***± 0.1% or 0.05 mg, whichever is greater***. If the values are not within these limits, recalibrate the balance.

13.2. Thermometer

13.2.1. Calibrate the thermometer using an NIST certified thermometer. The calibration procedure shall adhere to the current revision of SOP-T042, "Thermometer Calibration."

14. ►PROCEDURE

14.1. Conductivity Determination

14.1.1. Determine the conductivity of an aqueous sample as outlined in the current revision of SOP-M702. ***Record the conductivity to 3 significant figures*** in the Comments section of the ***Gravimetric Logbook for Total Dissolved Solids***.

14.1.2. ***Conductivity measurement is used to estimate the concentration (in mg/L) of total dissolved solids in an aqueous sample by multiplying conductivity (in µmho/cm) by an empirical factor. This factor may vary from 0.55 to 0.90, depending on the soluble components of the water and on the temperature of measurement.***

14.1.2.1. ***Relatively high factors may be required for saline or boiler waters, whereas lower factors may apply where considerable hydroxide of free acid is present.***

14.1.2.2. ***The factor of 0.6 is applied to all aqueous samples received at the laboratory.***

14.2. Beaker Preparation

14.2.1. ***Using a fine point Sharpie, write an identification number on a clean 50-mL beaker.***

14.2.1.1. ***Handle beaker using clean forceps or tongs throughout the course of beaker preparation.***

14.2.1.2. ***Do not use fingers. Oils or other contaminants from fingers or gloves may change the mass of the beaker and skew the mass of the residue.***

14.2.2. Heat the clean, labeled beaker in an oven at 180°C ± ***2***°C for one hour.

14.2.2.1. ***If volatile solids are to be measured, heat the beaker in a muffle furnace at 550°C ± 50°C for 15 minutes instead.***

14.2.3. ***Remove the beaker from the oven, transfer to*** a desiccator, and allow to cool.

14.2.4. ***When cool to ambient temperature, and immediately prior to sample preparation, weigh the beaker on a calibrated analytical balance. Record the beaker identification number and the mass to the nearest 0.1 mg (or 0.0001 g).***

14.2.4.1. ***Shut all access doors on the balance and tare. Open a single access door, remove a beaker from the desiccator, and place on the balance pan. Shut the access door and allow the digital readout to stabilize before recording the mass.***

14.2.4.2. ***Place the beaker in a tray lined with clean paper towels for immediate use.***

14.3. ***Filter Paper*** Preparation

14.3.1. ***If total suspended solids is to be determined in conjunction with this method, prepare filter paper as outlined in the current revision of SOP-M714.***

14.4. ***Aqueous Sample Preparation***

14.4.1. ***Allow an aqueous sample to reach ambient temperature.***

14.4.2. ***Homogenize the aqueous sample by shaking the sample thoroughly. Invert the sample container at least three times while shaking.***

14.4.2.1. ***Sample may be homogenized by stirring with a magnetic stirrer at a speed to shear large particles.***

14.4.3. Quickly measure 20.0 ***± 1.0 mL of the homogenized aqueous sample into a Class A graduated cylinder. Excess volume may be removed***

with a disposable transfer pipet. Record the volume to the nearest 0.1 mL or 3 significant figures.

14.4.3.1. ***For MB, measure exactly 20.0 mL of clean reagent water.***

14.4.3.2. The sample volume shall yield between 2.5-mg and 200-mg dried residue. If the volume filtered fails to meet the minimum yield, increase the sample volume. ***If complete filtration takes more than 10 minutes, increase the filter diameter or decrease the sample volume.***

14.4.4. ***Proceed to Section 14.6. for filtration procedure.***

14.5. ***Solid Sample Preparation***

14.5.1. ***Allow a solid sample to reach ambient temperature.***

14.5.2. ***Homogenize the solid sample as outlined in the current revision of SOP-M230.***

14.5.3. ***Measure 3.00 ± 0.15 g of the homogenized solid sample into a clean specimen container. Record the mass to the nearest 0.01 g or 3 significant figures.***

14.5.3.1. ***For MB, measure exactly 3.00 g of washed sea sand. Record the washed sea sand identification number.***

14.5.3.2. ***The sample mass shall yield between 2.5-mg and 200-mg dried residue. If complete filtration takes more than 10 minutes, increase the filter diameter or decrease the sample mass.***

14.5.4. ***Add 20.0 mL of clean reagent water to the solid sample. Cap the specimen container and shake vigorously.***

14.5.5. ***Place the specimen container in an ultrasonic bath, and sonicate the solid sample for at least 30 minutes.***

14.5.6. ***Proceed to Section 14.6. for filtration procedure.***

14.6. Assemble a vacuum filtration apparatus ***with a clean filtration flask and Buchner funnel***.

14.7. ***Place a filter paper in the Buchner funnel and*** apply vacuum.

14.7.1. ***Handle filter paper using clean forceps throughout the course of sample preparation and analysis.***

14.8. ***Using wash bottle, wet the filter paper with a small volume of reagent water to seat it on the funnel, then rinse the filter paper with three successive 20-mL portions of reagent water.***

14.8.1. ***If the filter paper was pre-prepared for the determination of total suspended solids, no rinsing with three successive 20-mL portions of reagent water is required.***

14.9. ***Continue to apply vacuum until all traces of water have been removed. Turn the vacuum pump off and discard the washings.***

14.10. ***Place a clean, dry 50-mL Class A or B graduated cylinder in the filtration flask to collect filtrate.***

14.11. ***Apply vacuum and carefully decant the measured sample onto and*** through the filter paper ***without splashing. Continue filtration with the vacuum operating.***

14.12. ***Using wash bottle***, rinse the filter paper thoroughly with ***three successive 10-mL portions of reagent*** water. ***Allow complete drainage between washings, and continue to apply vacuum for about 3 minutes after filtration is complete or until all visible water is removed***.

14.13. ***Turn the vacuum pump off. Carefully remove the graduated cylinder from the filtration flask using clean forceps or tongs.***

14.13.1. ***Do not splash or spill the contents of the graduated cylinder.***

14.14. Pour the filtrate (with washings) into a pre-weighed beaker.

14.14.1. ***Handle beaker using clean forceps or tongs throughout the course of sample preparation and analysis.***

14.15. Place the beaker on a hot plate set at 80−100°C.

14.15.1. ***Monitor the hot plate temperature with a calibrated thermometer.***

14.16. Evaporate the filtrate on the hot plate until all traces of water have been removed.

14.16.1. Evaporating on a hot plate ensures observation that no sample splattering occurs.

14.17. ***Once dry***, transfer the beaker to an oven designated for the analysis.

14.17.1. ***Check the oven temperature prior to placing the beaker inside. The acceptable temperature range is 178−182°C.***

14.17.2. ***Check the temperature log and/or the actual thermometer to be sure the oven is in proper working condition.***

14.18. Dry the residue and the filter paper in the oven at 180 ± 2°C for at least one hour.

14.19. ***Remove the beaker from the oven, transfer to a desiccator and allow to cool.***

14.20. ***When cool to ambient temperature, weigh the beaker including the dried residue on a calibrated analytical balance. Record the mass to the nearest 0.1 mg (or 0.0001 g).***

14.20.1. Repeat the drying cycle ***(Section 14.18. to Section 14.19.)*** until a constant mass is obtained. ***The mass change shall be less than 4% of the previous mass or 0.5 mg, whichever is less.***

14.21. ***Samples are filtered one at a time in the following or other logical order:***

1) ***Method Blank (MB)***
2) ***Samples (up to 20 per batch, excluding MBs)***

3) ***Sample Duplicate***

14.21.1. ***Item 1: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.***

14.21.1.1. ***For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of washed sea sand.***

14.21.1.2. ***One MB is required every day preparatory procedures (i.e., filtrations, dryings, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.***

14.21.2. ***Item 2: Up to 20 samples (excluding method blanks) per batch.***

14.21.3. ***Item 3: The sample duplicate is a selected field sample re-processed and re-analyzed under the same analytical conditions. The sample duplicate is processed concurrently with the associated samples. In the processing of the sample duplicate, reagents and procedures identical to those for actual samples are used.***

14.21.3.1. ***The purpose of the sample duplicate is to access the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.1.***

14.21.3.2. ***One sample duplicate is required for every batch of 10 samples per matrix or portion thereof processed concurrently.***

14.21.3.2.1. ***For EPA Region 9 requirement, one sample duplicate is required for every batch of 20 samples per matrix or portion thereof processed concurrently.***

14.22. ***Thoroughly document all aspects of the preparatory procedures in the Gravimetric Logbook for Total Dissolved Solids. This logbook includes, but is not limited to:***

14.22.1. ***Preparation and analysis dates.***

14.22.2. ***Sample volume or mass.***

14.22.3. ***Beaker and dried residue masses.***

14.22.4. ***Analyst comments which include encountered problems, pertinent observations, or conditions that could potentially impact data quality.***

14.23. ***Data Interpretation***

14.23.1. ***Determine the total dissolved solids of a sample from the sample volume or mass, and the beaker masses before and after sample filtration. The formulas for calculating the concentration of total dissolved solids are listed in Section 15.3. and Section 15.4.***

15. ►CALCULATIONS

15.1. The relative percent difference is calculated as follows:

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

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of total dissolved solids in measurement 1.
C_2 = concentration of total dissolved solids in measurement 2.

Note: Concentrations must be in equivalent units.

15.2. ***The preparation factor for a solid sample is calculated as follows:***

$$P = \frac{V_w}{W_S}$$

where: P = preparation factor for solid sample in mL/g.
V_w = volume of reagent water used prior to sonication in mL. Unless specified otherwise, V_w = 20.
W_S = mass of solid sample sonicated in g.

15.3. ***The target analyte concentration for an aqueous sample is calculated as follows:***

$$C_{TDS} = \frac{(M_f - M_i) \times 1000}{V_A}$$

where: C_{TDS} = concentration of total dissolved solids (TDS) in mg/L.
M_f = mass of beaker and oven-dried residue in mg.
M_i = mass of beaker in mg.
V_A = volume of aqueous sample filtered in mL.

15.4. ***The target analyte concentration for a solid sample is calculated as follows:***

$$C_{TDS} = \frac{(M_f - M_i) \times 1000}{V_x} \times P$$

where: C_{TDS} = ***concentration of total dissolved solids (TDS) in mg/kg.***
M_f = ***mass of beaker and oven-dried residue in mg.***
M_i = ***mass of beaker in mg.***
V_x = ***volume of sonicated solid sample filtered in mL. Unless specified otherwise, V_x = 20.***
P = ***preparation factor for solid sample in mL/g.***

15.5. All concentrations shall be reported in mg/L (ppm) for aqueous samples and mg/kg (ppm) for solid samples.

15.6. Report TDS concentrations which are < 100 ppm to 2 significant figures, and TDS concentrations which are ≥100 ppm to 3 significant figures.

15.7. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009 unless specified otherwise.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentration of target analyte in an MB should be less than the respective reporting limit (RL). If the concentration of target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.1.1. If the target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and/or re-analyzed.

18.2. ***The acceptance criteria for duplicate analyte are predetermined. The RPD is ≤ 10%.***

18.2.1. ***For EPA Region 9 requirement, refer to Section 12.2.2.1.1. for acceptance criteria.***

18.2.2. ***When the RPD of the duplicate analyte is at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.***

18.2.3. ***If the RPD of the duplicate analyte is not within the established acceptance limits, the analytical system performance shall be suspect.***

18.3. ***Unacceptable RPD values are typically caused by sample inhomogeneity or poor technique. Determine the cause of the problem and effect corrective action.***

18.4. Additional information regarding internal quality control checks is provided in SOP-T020.

18.5. All concentrations shall be reported in mg/L (ppm) for aqueous samples and mg/kg (ppm) for solid samples.

18.6. Report TDS concentrations which are < 100 ppm to 2 significant figures, and TDS concentrations which are ≥100 ppm to 3 significant figures.

18.7. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009 unless specified otherwise.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. ►REFERENCES

22.1. *2540 C. Total Dissolved Solids Dried at 180°C*, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998.

22.2. ***2540 C. Total Dissolved Solids Dried at 180°C, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.***

22.3. ***2510 A. Conductivity, Introduction, Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.***

22.4. *EPA Method 160.1: Residue, Filterable (Gravimetric, Dried at 180°C)*, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, USEPA, March 1983.

22.5. ***Total Dissolved Solids (TDS), EPA Method 160.1 (Gravimetric, Dried at 180°C, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, November 1999.***

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. ***None.***

24. ►MODIFICATIONS

24.1. ***The following modifications from SM 2540 C. are noted.***

24.1.1. ***Quality Control***

24.1.1.1. ***The RPD control limit is modified.***

24.1.2. ***Procedure***

24.1.2.1. ***The filtrate evaporation procedure is modified.***

24.2. ***The following modifications from EPA Method 160.1 are noted.***

24.2.1. ***Quality Control***

24.2.1.1. ***EPA Region 9 requirements on contract required detection limit (CRDL), analytical balance check acceptance criteria, and mineral reference sample analyses are not applied.***

24.2.2. ***Procedure***

24.2.2.1. ***The volume of an aqueous sample filtered is modified.***

24.2.2.2. ***The filtrate evaporation procedure is modified.***

Title: **STANDARD METHOD 5220D / EPA METHOD 410.4 / 410.4M, CHEMICAL OXYGEN DEMAND (COD) BY CLOSED REFLUX, COLORIMETRIC TECHNIQUE**

Document No. : SOP-M724
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Revision 2.1 changes (other than NELAC Formatting) are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 07/19/06
MANAGEMENT **DATE**

_____ 07-19-06
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. Standard Methods 5220D / EPA method 410.4 / 410.4M, Chemical Oxygen Demand (COD) by closed reflux, colorimetric technique

2. APPLICABLE MATRICES

2.1. This method covers the determination of COD in surface waters, ground waters, domestic/industrial wastewaters and soils, sediments and similar materials.

3. DETECTION LIMITS

3.1. ►The estimated quantitation limits EQLs for this method are 5 or ***20 mg/L (low or high* range)** for aqueous samples and 50 ***to 200 mg/kg (low or high* range),** wet weight, for soil or solid waste. The EQLs will be proportionally higher for samples that require dilution.

4. SCOPE AND APPLICATION

4.1. The applicable range of the method is ***5 to 900 mg/L for aqueous samples and 50 to 9000 mg/kg for soil or solid waste.***

4.2. The Chemical Oxygen Demand (COD) test determines the quantity of oxygen required for oxidation of reduced species including organic matter in a water or solid sample using a specific oxidizing agent, temperature and time of reaction.

5. METHOD SUMMARY

5.1. Samples, blanks and standards in sealed tubes are heated in a COD reactor in the presence of dichromate at 150°C. After two hours, the tubes are removed from the COD reactor, cooled, and measured spectrophotometrically at 600 nm.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An

analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Continuing Calibration Verification (CCV): Solution prepared with the same conditions used as the initial calibration solution. The CCV contains each target compound, including surrogates and internal standards where applicable. The CCV must be prepared from a source other than that used for preparing the initial calibration solution.

6.7. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.8. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.9. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.10. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.11. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.12. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.13. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.14. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.15. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.16. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.17. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.18. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.19. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.20. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.21. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.22. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.23. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.24. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.25. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.26. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.27. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. INTERFERENCES

7.1. Chlorides are among the reduced species oxidized by dichromate and will cause erroneously high COD values if over 2000 mg/L Cl and not complexed. Therefore, sufficient mercuric sulfate is added to the reagents to complex chloride before the chloride reacts with the dichromate.

7.2. Volatile straight-chain aliphatic compounds are not oxidized to any appreciable extent, and; therefore, Silver sulfate is added as a catalyst to enhance the oxidation of volatile straight-chain aliphatic compounds.

7.3. Nitrite may cause a positive interference if present in appreciable amount. Sulfamic acid is added to eliminate this positive interference of nitrite.

8. SAFETY

8.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled as a potential health hazard.

8.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current Calscience Health & Safety Manual. In general, safety apparel and eyewear (i.e., lab coats and glasses) are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDS's) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Spectronic 20D spectrophotometer (Milton Roy Company) or equivalent.

9.2. HACH COD Reactor Model 16500-10 or equivalent.

10. REAGENTS AND STANDARDS

10.1. Stock potassium acid phthalate: Dissolve 0.850 g in 800 mL of distilled water and dilute to 1 liter. The KHP must have been pre-dried at 120° C. 1 ml=1 mg COD.

10.1.1. ► ***Prepare COD working standard solutions for Low Range analysis of 5, 10, 20, 50, 100 and 150 ppm by diluting appropriate volumes of the stock standard.***

10.1.2. ►Prepare COD working standard solutions ***for High Range analysis*** of ***20, 50, 200, 400, 600 and 900 ppm*** by diluting appropriate volumes of the stock standard.

10.2. Premixed COD reagents in screw-cap vials containing 76% sulfuric acid, 0.20% potassium dichromate, 0.40% silver sulfate, 0.60% mercuric sulfate and 0.002% sulfamic acid.

10.3. Mercuric sulfate for chloride pretreatment.

10.4. Concentrated sulfuric acid for chloride pretreatment.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Collect the samples in glass bottles if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers. Recommended sample container size is 250 ml for aqueous samples and 2 oz jars with teflon-lined caps for soil/solid samples.

11.2. Aqueous samples should be preserved with sulfuric acid to a pH < 2 and maintained at 4°C until analysis. Solid samples should be maintained at 4°C until analysis.

11.3. The holding time for aqueous samples preserved with sulfuric acid is 28 days and for solid samples is 14 days.

12. QUALITY CONTROL

12.1. The laboratory must, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control.

12.2. All quality control data should be maintained and available for easy reference and inspection.

12.3. General acceptance criteria and corrective actions can be found in SOP-T020, Internal Quality Control Checks SOP. The QC policies set forth in SOP-T020 should be adhered, unless superseded in this document.

12.4. Method blank and sample duplicate are performed every twenty samples or a portion thereof.

12.5. SUMMARY OF QC CHECKS

12.5.1. Initial Calibration

12.5.1.1. ►A seven-point initial calibration ***(including the instrument blank) must be established and the linear curve of Absorbance AU versus Concentration must have an R squared correlation coefficient of ≥0.995.***

12.5.1.2. A new calibration curve must be prepared for each new lot of COD vials or when the daily CCV (as follows) is deemed unacceptable.

12.5.2. Continuing Calibration Verification (midpoint)

12.5.2.1. Following establishment of a valid initial calibration, a CCV (midpoint) standard must be analyzed following every 20 samples thereafter and at the end of the run sequence. If the percent difference (%D) is < 5%, the initial calibration is deemed valid and sample analysis may resume.

12.5.2.2. If this criterion is not met, the CCV is deemed unacceptable for sample analysis to resume. Reanalyze the CCV. If it remains unacceptable, effect corrective action and recheck calibration.

12.5.3. Matrix-based Quality Control (Sample Duplicate) or (Matrix Spike / Matrix Spike Duplicate).

12.5.4. One sample duplicate is analyzed for every 20 samples, or portion thereof. The Reported Percent Difference (RPD) for the duplicate is 0–25 percent.

12.5.4.1. Under certain project programs a Matrix Spike (MS) / Matrix Spike Duplicate (MSD) are required. These are used in lieu of a batch Sample Duplicate.

12.5.4.2. If there is insufficient sample volume to perform a sample duplicate, a LCS/LCSD shall be performed.

12.5.4.3. The acceptance criteria for sample duplicates are as follows:

12.5.4.3.1. When the relative percent difference (RPD) of the sample duplicate is at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method. The sample duplicate data shall be reported with the corresponding sample data.

12.5.4.3.2. If the RPD is not within the established acceptance limits, the analytical system performance shall be suspect.

12.5.4.3.3. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.5.4.4. The acceptance criteria for MS / MSDs are referenced in section 18.4

12.5.5. Event-based Quality Control (LCS/LCSDs and MBs)

12.5.5.1. If there is insufficient sample to prepare a sample duplicate or if the RPD is not acceptable, a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) shall be analyzed for every 20 samples, or portion thereof.

12.5.5.2. If the LCS/LCSD is not acceptable, the problem must be identified, corrected and associated samples re-prepared and re-analyzed.

12.5.5.3. The acceptance criteria for LCS / LCSD are referenced in section 18.1.

12.5.5.4. One method blank is analyzed with every 20 samples, or portion thereof.

12.5.5.5. Ideally, the concentration of the MB should be less than the reporting limit (RL). If the concentration exceeds the RL, the source of contamination must be investigated and, if possible, eliminated. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and re-analyzed if the MB criterion is not met.

12.5.5.6. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Turn on spectrophotometer and allow to "warm-up" for 15 minutes. Set the wavelength at 600 nanometers (nm).

13.2. Prepare calibration standards as in section 10.

13.3. Preheat the COD reactor to 150°C.

13.4. Remove the cap from the COD vial. Carefully add 2.5ml of the standard down the side of the vial such that if forms a layer on top of the reagents. Carefully replace the cap and tighten moderately. Thoroughly mix the contents of the sealed vial by shaking. Repeat for each standard.

13.5. Place the vials in the COD reactor for 2 hours.

13.6. Turn off the the COD reactor and allow vials to cool to room temperature.

13.7. Carefully wipe the outside surface of the vial clean with a Kimwipe or equivalent.

13.8. ►Insert each vial into the spectrophotometer and read and record the absorbance of each standard into the ***COD Excel spreadsheet calculator program, see example in Appendix 23.1.***

13.9. ***►Add the standard concentration and observed absorbance from each standard vial to the spreadsheet and note this into the COD logbook. Check that the R^2 value for the linear curve is ≥0.995. If not re-prepare the standards.***

14. PROCEDURE

14.1. Preheat the COD reactor to 150° C.

14.2. If sample has a chloride concentration > 2000 mg/L then follow the steps below. Otherwise, proceed to step 8.3.

14.2.1. Place 30 ml of the sample into an Erlenmeyer flask.

14.2.2. Add 10 mg mercuric sulfate for every mg of Cl present in the sample.

14.2.3. Carefully add 5 ml of concentrated sulfuric acid with stirring to the contents of the flask and mix thoroughly.

14.3. ►Remove the cap from a ***High Range (20 – 900 mg/L)*** COD vial. Carefully add 2.5 ml of aqueous sample or 0.25gm of solid sample down the side of the vial such that it forms a layer on top of the reagents. Carefully replace the cap and tighten moderately.

14.4. Thoroughly mix the contents of the sealed vial by shaking.

14.5. Process the standards and blanks exactly as the samples.

14.6. Place the vials in the COD reactor for 2 hours.

14.7. Turn off COD reactor and allow vials to cool to room temperature.

14.8. Carefully wipe the outside surface of the vial clean with a Kimwipe or equivalent.

14.9. ►***Read the observed absorbance and note into the COD logbook.***

14.10. ►***After all the samples are analyzed, input the absorbance for each sample into the COD Excel spreadsheet calculator program.***

14.11. ►***Record the calculated concentration from the spreadsheet for each sample into the COD logbook.***

14.12. ►***Print and retain the COD Excel spreadsheet and place into a sequentially arranged 3-ring notebook.***

14.13. ►***If any samples are noted below the High Range reporting level of 20 mg/L, re-analyze using Low Range vials that have a reporting level of 5 mg/L.***

15. CALCULATIONS

15.1. The percent difference (%D) is calculated as follows:

$$\%D = \frac{|C_P - C_M|}{C_P} \times 100$$

where: %D = percent difference
C_P = concentration as prepared
C_M = concentration as measured

Note: Concentrations must be in equivalent units

15.2. The relative percent difference (RPD) is calculated as follows:

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

where: %RPD = relative percent difference
C_1 = original sample concentration
C_2 = duplicate sample concentration

Note: Concentrations must be in equivalent units

15.3. Results shall be reported to two significant figures in mg/L for aqueous samples and mg/kg for solid samples.

15.4. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13, "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The upper and lower acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ±3S. All LCS/LCSD compounds must be within acceptance limits. If one or more LCS/LCSD compounds are not acceptable, the problem must be identified and corrected.

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentration of target analytes in a MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.2.3. If methylene chloride is found in the MB, no positive sample results should be reported unless the concentration of the compound in the sample exceeds 10 times the MB level. Report the data with qualification indicating the analyte was present in the corresponding MB.

18.3. The acceptance criteria for surrogate spike compound recoveries vary depending upon historical data. The upper and lower acceptance limits for each surrogate spike compound is based upon the historical average recovery ± 3S.

18.3.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

18.3.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.3. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.3.1. Check the internal standard and surrogate spiking solutions for degradation and contamination.

18.3.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same sample or extract should be re-analyzed.

18.3.3.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-extracted and/or re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.1. If, upon re-extraction and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-extracted and re-analyzed.

18.3.4. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSDs are as follows:

18.4.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically causes unacceptable % REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L(ppb) for water samples and µg/kg(ppb) for oil, soil and solid waste samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set is then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries are subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries an MS/MSD data set is does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. REFERENCE

22.1. Standard Methods for the Examination of Water and Wastewater, 18th Edition, Method 5220D.

22.2. Methods for Chemical Analysis of Water and Wastes (MCAWW), EPA/600/4-79-020, Revised March 1983.

22.3. Bioscience, Inc., Twist-cap vial Method for Chemical Oxygen Demand (Spectrophotometric Method).

23. APPENDIX

23.1. ►***Example: Excel Spreadsheet Calculator***

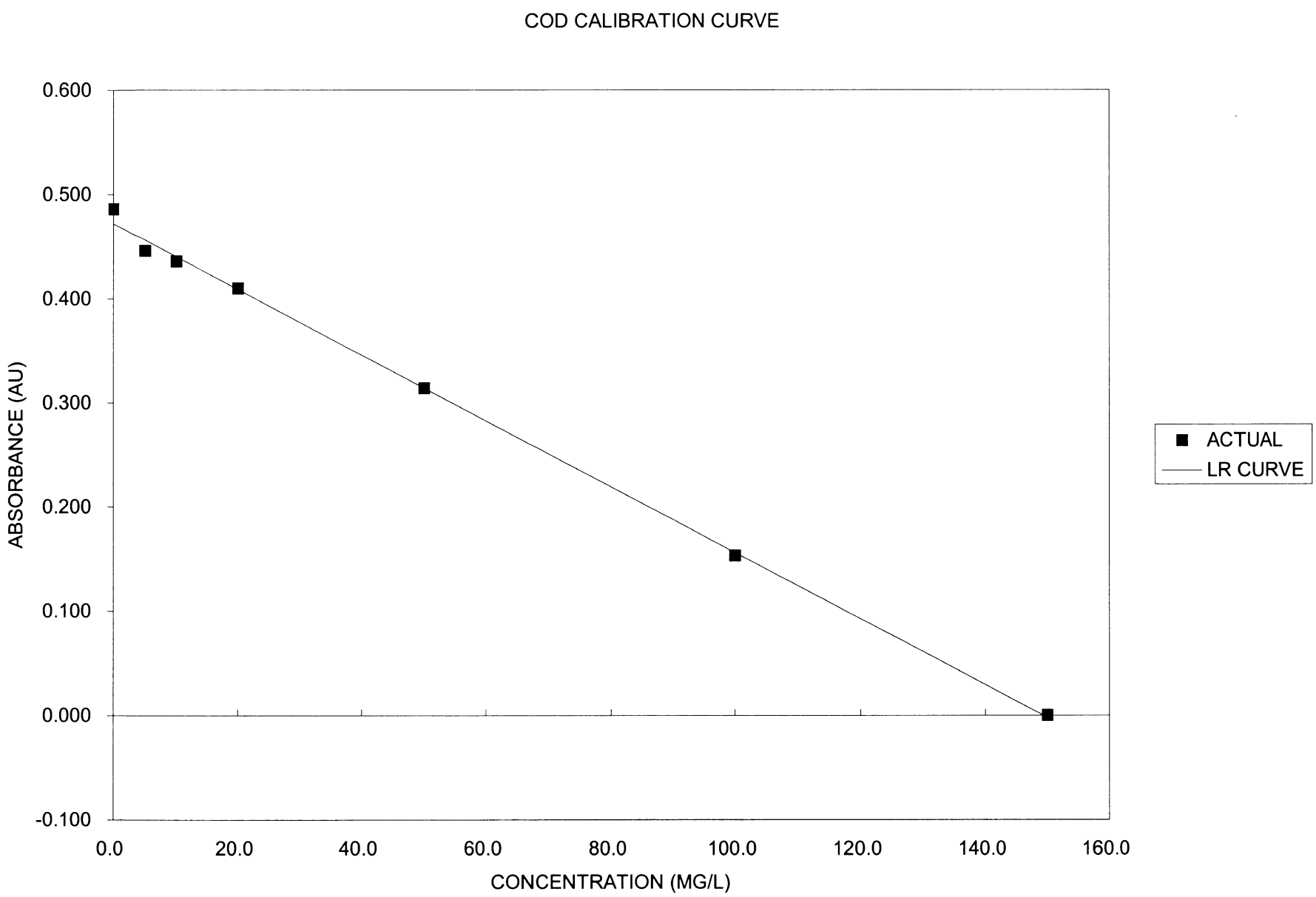
CALCULATION OF COD
Date: 7/12/2006
Tech: Eleo Ng
CALIBRATION
LOW RANGE

STANDARD (MG/L)	ABSORBANCE	REGRESS. LINE	APPARENT CONC.
0.0	0.486	0.472	-4.40
5.0	0.446	0.456	8.24
10.0	0.436	0.440	11.41
20.0	0.410	0.409	19.63
50.0	0.314	0.314	49.98
100.0	0.153	0.156	100.89
150.0	0.000	-0.002	149.26

Regression Output:

Constant		0.4720702
Std Err of Y Est		0.0081692
R Squared		0.9982915
No. of Observations		7
Degrees of Freedom		5
X Coefficient(s)	-3.16E-03	
Std Err of Coef.	5.8512E-05	

SAMPLE ID	ABSORBANCE	COD(MG/L)	DILUTION	RESULT
Method Blank	0.485	-4	1	-4
LCS	0.311	51	1	51
LCSD	0.305	53	1	53
06-07-0010-1	0.444	9	1	9
06-07-0010-2	0.111	114	1	114
06-07-0010-3	0.213	82	1	82
06-07-0010-4	0.335	43	2	87
06-07-0010-5	0.212	82	1	82
06-07-0010-6	0.389	26	1	26
06-07-0010-7	0.111	114	1	114
06-07-0010-8	0.160	99	1	99
06-07-0010-8-DUP	0.163	98	1	98
CCV	0.313	50	1	50


COD CALIBRATION CURVE
0.600
0.500
0.400
0.300
0.200
0.100
0.000
-0.100
ABSORBANCE (AU)
0.0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
160.0
CONCENTRATION (MG/L)
ACTUAL
LR CURVE

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Title : **SM 5310 B/D / EPA METHOD 415.1, TOTAL ORGANIC CARBON (TOC)**

Document No. : SOP-M726
Revision No. : 1.1
Supersedes : 1.0

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Revision 1.1 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 7/21/10
MANAGEMENT **DATE**

_____ 07-21-10
QA DEPARTMENT **DATE**

ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

1. METHOD IDENTIFICATION

1.1. SM 5310 B/D / EPA Method 415.1, Total Organic Carbon (TOC).

2. APPLICABLE MATRICES

2.1. This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes.

3. DETECTION LIMITS

3.1. The estimated quantitation limits EQLs for this method are approximately 0.5mg/L for aqueous samples. The EQLs will be proportionally higher for samples which require dilution.

4. SCOPE AND APPLICATION

4.1. This method is applicable only to samples which can be prepared homogeneously and loaded onto the TOC analyzer reproducibly.

5. METHOD SUMMARY

5.1. Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector. The amount of CO_2 in a sample is directly proportional to the concentration of carbonaceous material in the sample.

5.2. Catalytic Combustion:

5.2.1. The sample is homogenized and diluted as necessary and a microportion is injected into a heated reaction chamber packed with an oxidative catalyst (i.e. platinum group metals). The water is vaporized and the organic carbon is oxidized to CO_2 and H_2O. The CO_2 from oxidation of organic and inorganic carbon is transferred in the carrier-gas streams and is measured separately by means of a non-dispersive infrared (NDIR) detector. The NDIR detector is calibrated to display the mass of CO_2 detected.

5.2.2. Because total carbon is measured, inorganic carbon must be removed by acidification and sparging and the TOC obtained by difference. This is typically done automatically by the instrument based upon whether the TIC or TOC option is selected.

5.3. Wet Chemical Oxidation:

5.3.1. The sample is acidified with phosphoric acid to convert carbonate and bicarbonate ions into dissolved CO_2. This CO_2 is purged from solution, concentrated by trapping, then desorbed and carried into a non-dispersive infrared (NDIR) analyzer which has been calibrated to directly display the

mass of CO_2 detected. This mass is equivalent to the mass of total inorganic carbon (TIC) in the sample.

5.3.2. After the sample has been acidified and purged of TIC, sodium persulfate ($Na_2S_2O_8$), a strong oxidizer, is added. $Na_2S_2O_8$ quickly reacts with organic carbon in the sample at 100°C to form CO_2. When the oxidation reaction is complete, the CO_2 is purged from the solution, concentrated by trapping, and detected similarly as in the determination for TIC. The resulting carbon mass in the form of CO_2 is equivalent to the mass of total organic carbon (TOC) originally present in the sample.

6. DEFINITIONS

6.1. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.2. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same matrix, meeting the above mentioned criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.3. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.4. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.5. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.6. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.7. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.8. Laboratory Control Sample: A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or

analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.9. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.10. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.11. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.12. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.13. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.14. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.15. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.16. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.17. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets user needs.

6.18. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.19. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes

which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.20. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.21. TERMS SPECIFIC TO TOC ANALYSIS

6.21.1. Total Carbon (TC): All of the carbon in a sample, including inorganic, organic, and volatile carbon.

6.21.2. Total Inorganic Carbon (TIC): All of the carbon in a sample that is converted to carbon dioxide after sample acidification. TIC includes all dissolved carbon dioxide, bicarbonate, and carbonate species.

6.21.3. Total Organic Carbon (TOC): All of the carbon in a sample including purgeable compounds that is converted to carbon dioxide by oxidation. TOC is determined by acidifying the sample to remove the TIC and oxidizing the remaining carbon.

7. INTERFERENCES

7.1. Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

7.2. Method interferences, which are positive biases, may be caused by contaminants in the gas, dilution water, reagents, glassware, or other sample processing equipment. All of these materials must be routinely demonstrated to be free from interference under the conditions of analysis by running reagent blanks.

8. ►SAFETY

8.1. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals and samples.

8.2. ***Dilute acids are prepared in this procedure. Wear appropriate glasses, coats and gloves when handling acids and always add acid to water to limit the exothermic reaction. Heat will be generated.***

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. ►EQUIPMENT AND SUPPLIES

9.1. Total Organic Carbon Analyzer: OI Analytical Model 1010 TOC Analyzer configured with Model 1051 Autosampler and PC based data system or equivalent.

9.1.1. Sample loop, 5-mL.

9.1.2. Autosampler vial, clear glass, 40mL (95.25mm × 27mm), disposable. Vial is equipped with open-hole screw cap and Teflon-faced septum.

9.2. Total Organic Carbon Analyzer: OI Analytical Model 1020A TOC Analyzer configured with Model 1051 Autosampler and PC based data system or equivalent.

9.2.1. Sample loop, 200-µL (nominal).

9.2.2. Autosampler vial, clear glass, 40mL (95.25mm × 27mm), disposable. Vial is equipped with open-hole screw cap and Teflon-faced septum.

9.3. ***Calibrated*** analytical balance, capable of weighing to 0.1 mg.

9.4. Drying oven ***capable of maintaining a temperature of 110°C (for drying the KHP)***.

9.5. Volumetric flask, Class "A", 10-mL, 50-mL, 100-mL, 250-mL, and 1-L, or other volumes as needed.

9.6. Pipetter.

9.7. Weighing paper.

9.8. ***Calibrated*** dispenser, set volume to 1 mL or 2 mL.

9.9. Magnetic stirrer.

9.10. Wash bottle, 250-mL.

10. ►REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, distilled or deionized.

10.1.2. Sodium persulfate ($Na_2S_2O_8$), 100-g/L, reagent grade.

10.1.2.1. Prepare the solution by adding 100 g of $Na_2S_2O_8$ into a 1-L volumetric flask and diluting to volume with reagent water.

10.1.3. Phosphoric acid (H_3PO_4), 5% (v/v), reagent grade.

10.1.3.1. Prepare the solution by volume by adding 59 mL of 85% H_3PO_4 into a 1-L volumetric flask and diluting to volume with reagent water.

10.1.4. Sulfuric acid (H_2SO_4), 1:1, reagent grade.

10.1.4.1. ***Dilute equal volumes of concentrated sulfuric Acid with reagent water to reach a 1:1 solution. Add the acid to the water and use caution as heat will be generated.***

10.2. Standards

10.2.1. Potassium biphthalate (KHP) ***stock standard***, 1000 mg/L of carbon.

10.2.1.1. Add 2.128 g of KHP (previously dried to constant mass at 110°C) to a 1-L volumetric flask and dilute to volume with reagent water.

10.2.1.2. ***Prepare the calibration standards by diluting the 1000-ppm stock standard with reagent water to achieve the necessary concentrations of 0.5, 2.5, 5.0, 10 or 20ppm for the low level curve, or 0.5, 1.0, 10.0, 100 and 1000ppm for the high level curve. Use volumetric glassware to make the dilutions.***

10.2.1.3. ***For the CCV, partially fill a 1000-mL volumetric flask with reagent water, spike 10.0 mL of the 1000-ppm stock standard the flask (or add 5.0 mL for the low level analysis) and dilute to volume with reagent water to make a 5-ppm or 10-pmm CCV standard.***

10.2.2. Second source standards, 1000 mg/L of carbon. ***The salts used to make these standards are from a different vendor, or are different lot #s from the same vendor. The second source standard is used to prepare ICV, LCS/LCSD and MS/MSD by diluting the second source stock standard with reagent water. Use volumetric glassware to make the dilutions.***

10.2.2.1. ***For ICV and the LCS/LCSD, partially fill a 1000-mL volumetric flask with reagent water, spike 10.0 mL (or add 5.0 mL for the low level analysis) of the 1000-ppm second source stock standard into the flask and bring to volume with reagent water.***

10.2.2.2. ***For MS/MSD, partially fill a 100-mL volumetric flask with the client sample, spike 1.0 mL (or add 0.5 mL for the low level analysis) of the 1000-ppm second source stock standard into the flask and bring to volume with additional sample.***

10.2.2.3. ***ICV/LCS/LCSD, MS/MSD – Low Level TOC = 5-ppm standard.***

10.2.2.4. ***ICV/LCS/LCSD, MS/MSD – High Level TOC = 10-ppm standard.***

10.2.3. Sodium carbonate (Na_2CO_3), 1000 mg/L of carbon. This standard is applicable to Total Inorganic Carbon (TIC) analysis only.

10.2.3.1. Prepare a stock solution by adding 8.826 g of Na_2CO_3 (previously dried to constant mass at 110°C) into a 1-L volumetric flask and diluting to volume with reagent water.

10.2.3.2. ***Calibration standards and spikes would be prepared as for the TOC standards. Refer to Sections 10.2.1 and 10.2.2 for further information on standard preparation schemes.***

10.3. Gases

10.3.1. ***Nitrogen gas, 4.5 grade or better.***

10.3.2. ***Oxygen gas, Ultra high purity.***

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. ***A 250-mL amber bottle preserved with H_2SO_4 and no headspace is preferred.***

11.1.1. For most accurate analyses, sampling containers should be free of organic contaminants. ***Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible <u>if</u> it is established that the containers do not contribute contaminating organics to the samples.*** Sampling and storage of samples in amber glass bottles is preferable over plastic.

11.2. To limit oxidation and/or bacterial decomposition, samples should be maintained in a chilled state at 4 ± 2°C and protected from sunlight and atmospheric oxygen prior to analysis.

11.3. In instances where analysis cannot be performed within 2 hours from time of sampling, the sample must be acidified to pH ≤2 with H_2SO_4.

11.3.1. ***SM 5310 D (Section 1.d): Acid preservation invalidates any inorganic carbon determination on the samples. If Total Inorganic Carbon (TIC) is required, collect a separate unpreserved aliquot.***

11.4. Samples should be analyzed within 28 days from collection.

12. ►QUALITY CONTROL

12.1. ***Replicate Injections***

12.1.1. ***Each standard or sample is introduced a minimum of two times and the percent relative standard deviation (%RSD) must be calculated.***

12.1.1.1. ***In order for the injections to be acceptable and analysis to continue, the calculated %RSD between replicate injections must be ≤10%. If the %RSD criteria are met, report the average of the replicates.***

12.1.2. ***In the event that the first two replicates do not result in a %RSD ≤ 10%, the sample must be reanalyzed in duplicate. Again, calculate the %RSD between these duplicate injections. If the %RSD criteria are met, report the average of the replicates.***

12.1.3. ***If the second set of replicates does not meet criteria, analyze a third set of duplicate samples. Again, calculate the %RSD between these duplicate injections. If the %RSD criteria are met, report the average of the replicates. If the criteria are not met, proceed as follows:***

12.1.3.1. ***Review all three sets of data for the lowest %RSD, be sure all associated quality control is within criteria for that data set and report the average of the replicates. Note on the Chemist's bench sheet that the %RSD was outside criteria. The data will need to be flagged and the PM will need to address the issue in the narrative.***

12.1.4. ***If it is taking several replicate injections to meet the %RSD criteria for calibration standards and/or the LCS, stop the analysis, perform maintenance and recalibrate the instrument.***

12.2. Initial Calibration (ICAL)

12.2.1. An acceptable initial calibration must be established prior to the processing of samples.

12.2.2. The calibration curve consists of a calibration blank and five calibration standards which define the calibration range.

12.2.3. The ICAL is deemed valid if the correlation coefficient of the calibration curve is ≥0.995.

12.2.4. If this criterion is not met, then the ICAL is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.5. ***At a minimum, an initial calibration must be performed annually.***

12.3. Initial Calibration Verification (ICV)

12.3.1. ***An ICV is analyzed immediately following the initial calibration standards and is used to validate the acceptance of the ICAL.*** The ICAL is deemed valid if the %D of TOC ***in the ICV*** is ≤15%.

12.3.2. If this criterion is not met, the ICAL is deemed unacceptable for sample analysis. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Investigate, effect corrective action, which may include re-preparation of standard solutions, and recalibrate, if necessary.

12.3.2.1. ***Recalibration will be necessary if repreparation and reanalysis of a new ICV solution does not meet acceptance criteria.***

12.4. Initial Calibration Blank (ICB)

12.4.1. ***The ICB is used to monitor the instrument baseline for carryover and/or contamination and is analyzed immediately following the ICV.*** The ***ICB*** is deemed satisfactory if no contaminants are detected.

12.4.2. If this criterion is not met, the analytical system is deemed unacceptable for sample analysis to begin. Determine and eliminate the source of contamination. Reanalyze the ICB. If the ICB criterion remains unacceptable, effect corrective action and recalibrate.

12.5. Continuing Calibration Verification (CCV)

12.5.1. Following the establishment of a valid ICAL, a CCV standard must be analyzed daily prior to sample analysis, every batch of 20 samples or portion thereof, and at the end of sequence.

12.5.2. The ICAL is deemed valid if the %D of TOC ***in the CCV*** is ≤5%.

12.5.3. If this criterion is not met, the ICAL is deemed unacceptable for sample analysis to resume. Reanalyze the CCV. If the CCV criterion remains unacceptable, effect corrective action and recalibrate.

12.5.3.1. ***Following recalibration and the analysis of the ICV/ICB,*** reanalyze all samples analyzed since the last acceptable CCV.

12.5.3.2. If a failed CCV is the first of the day, corrective action must be effected prior to analyzing any samples.

12.6. Continuing Calibration Blank (CCB)

12.6.1. ***CCBs are used to monitor the instrument baseline for carryover and/or contamination and are analyzed immediately following the CCVs.*** The CCBs are analyzed daily prior to sample analysis, every batch of 20 samples or portion thereof, and at the end of sequence.

12.6.2. The instrument baseline is deemed satisfactory if no TOC is detected in the blank above the RL or other project defined criteria.

12.6.3. If this criterion is not met, the analytical system is deemed unacceptable for sample analysis to resume. Determine and eliminate the source of contamination. Reanalyze the CCB. If the CCB criterion remains unacceptable, effect corrective action and recalibrate.

12.7. Event Based Quality Control (LCS/LCSDs and MBs)

12.7.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample, laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.7.2. The acceptance criteria for LCS/LCSD compound(s) are as follows:

12.7.2.1. ***The lower and upper acceptance limits for %REC of TOC in the LCS/LCSD are 80% and 120% respectively. The RPD is ≤20%.***

12.7.3. Ideally, the concentration of the target analyte in an MB should be less than the respective reporting limit (RL). If the concentration of the target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.7.3.1. If the target analyte is found in the MB, but not in the associated samples, report the sample and MB without qualification.

12.7.3.2. If the target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment must be exercised to determine if the data should be qualified, or rejected and the samples re-analyzed.

12.8. Matrix Based Quality Control (MS/MSDs)

12.8.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD).

12.8.2. The acceptance criteria for MS/MSD compound(s) are as follows:

12.8.2.1. ***The lower and upper limits for %REC of TOC in the MS/MSD are 75% and 125% respectively. The RPD is ≤25%.***

12.8.2.2. When the %REC and RPD of the MS/MSD compound are at or within acceptance limits, the analytical system is deemed to be in control for the particular sample and/or matrix.

12.8.2.3. If the %REC and/or RPD of the MS/MSD compound are not within the established acceptance limits, the analytical system performance shall be suspect.

12.8.2.4. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance. Unacceptable RPD values are typically caused by sample in-homogeneity or poor instrument performance. To evaluate the performance of the analytical system, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference in the associated MS/MSD.

12.9. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data is invalidated and all associated samples re-analyzed.

12.10. Additional information regarding internal QC checks is provided in SOP-T020.

13. ►CALIBRATION AND STANDARDIZATION

13.1. Calibrate the instrument according to the instrument manufacturer's recommended procedures, using the calibration standard solutions. To minimize erratic readings, the system is programmed to average duplicate readings.

13.1.1. ***Replicate injections must have an RSD of ≤10%.***

13.1.2. Prior to the analysis of samples, a valid initial five-point calibration curve must be established. ***There are two curves, one for high-level samples***

and one for low-level samples. In both cases a calibration blank must also be analyzed and included in the curve.

13.1.2.1. The calibration blank standard of 0.0ppm carbon is obtained by analyzing a calibration blank. The calibration blank consists of reagent water.

13.1.2.2. The concentrations of the calibration standards are ***0.5,*** 2.5, 5.0, 10.0, and 20.0ppm of carbon for low-concentration analysis.

13.1.2.3. The concentrations of the calibration standards are ***0.5,*** 1.0, 10.0, 100, and 1000ppm of carbon for high-concentration analysis.

13.1.3. Using linear regression curve fitting, calculate the correlation coefficient (*r*). The calibration curve is deemed acceptable if $r \geq 0.995$.

13.2. A CCV is used to verify the acceptance of the initial five-point calibration on a continuing basis. An acceptable CCV is required ***daily*** prior to sample analysis, every batch of 20 samples or portion thereof, and at the end of sequence.

13.2.1. More frequent (e.g., every 10 samples) calibration verification may be useful to minimize the number of sample re-analyses that would be required in the event of an unacceptable CCV.

13.3. Analytical Balance

13.3.1. Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights.

13.3.2. Calibration shall be within ± 10% at 2 mg (± 0.2 mg), or within ± 2% at 1 g (± 0.02 g) and at 100 g (± 2 g). If the values are not within these limits, recalibrate the balance.

13.4. ***Pipetter***

13.4.1. ***Calibrate the pipetter according to the procedure outlined in the Pipetter Calibration Check Logbook.***

13.5. ***Dispenser***

13.5.1. ***Calibrate the dispenser according to the procedure outlined in the Dispenser Calibration Check Logbook.***

14. ►PROCEDURE

14.1. Clean Water Recycling

14.1.1. Clean water recycling must be performed daily prior to sample analysis to eliminate carbon contamination. To do this, load ten (10) autosampler vials containing reagent water onto the sample tray and commence the clean water recycling sequence.

14.2. Fill each autosampler vial with the appropriate instrument or sample QC.

14.2.1. For ICV (when calibrating), fill the vial with the appropriate spiked sample.

14.2.2. For CCV, fill the vial with the appropriate spiked sample.

14.2.3. For IB / CCB / MB, fill the vial with reagent water.

14.2.4. For LCS / LCSD, fill the vial with the appropriate spiked sample.

14.2.5. For MS / MSD, fill the vial with the appropriate spiked sample.

14.3. The autosampler vials are loaded onto the sample tray and analyzed in the following or other logical order:

Instrument Blank

****Calibration standard 1***

****Calibration standard 2***

****Calibration standard 3***

****Calibration standard 4***

****Calibration standard 5***

****Initial Calibration Verification (ICV)***

****Initial Calibration Blank (ICB)***

Continuing Calibration Verification (CCV)

Continuing Calibration Blank (CCB)

Method Blank (MB)

Laboratory Control Sample (LCS)

Laboratory Control Sample Duplicate (LCSD)

Samples (up to 20 per batch)

Matrix Spike (MS)

Matrix Spike Duplicate (MSD)

Ending (or bracketing) CCV

Ending (or bracketing) CCB

14.3.1. ***An instrument blank is analyzed prior to the analysis of any samples or standards to show that the instrument baseline is clean and stable.***

14.3.2. ****ICAL standards 1-5, ICV and ICB are analyzed whenever the instrument needs calibration due to failing CCVs and or major instrument maintenance that results in recalibration being necessary.***

14.3.3. A CCV is used to verify the acceptance of the initial four-point calibration on a continuing basis. An acceptable CCV is required prior to sample analysis, every 20 samples thereafter, and at the end of every sequence.

14.3.3.1. More frequent (e.g., every 10 samples) calibration verification may be useful to minimize the number of sample re-analyses that would be required in the event of an unacceptable CCV.

14.3.4. A CCB is used to verify the acceptability of instrument baseline and to isolate sources of contamination in the MB that may occur. An acceptable CCB is required prior to sample analysis, every 20 samples thereafter, and at the end of every sequence.

14.3.5. The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used. The MB consists of reagent water.

14.3.5.1. One MB is required for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.3.6. An LCS is a known matrix which has been spiked with a known concentration of the target analyte. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used. The LCS consists of the target analyte spiked into reagent water.

14.3.7. An LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.4.

14.3.7.1. One LCS/LCSD pair is required for every batch of 20 samples per matrix or portion thereof.

14.3.8. Up to 20 samples per batch. If the instrument response is or suspected to be above its calibration range, samples should be sufficiently diluted to ensure that the TOC analyzer is not contaminated. In diluting, increased reporting limits may result.

14.3.9. An MS is the actual matrix spiked with a known concentration of the target analyte. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.3.9.1. The purpose of an MS is to assess the effect of a sample matrix on the recovery of the target analyte (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.3.

14.3.9.2. One MS is required for every batch of 20 samples per matrix or portion thereof analyzed concurrently. This approach is considered “closed batch” as opposed to “open batch.”

14.3.10. An MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.3.11. An acceptable CCV and CCB are required at the completion of every analytical sequence.

14.4. Set up the TOC analyzer in preparation for the analytical sequence.

14.5. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record the pertinent information in the run logbook and the raw data form (Section 23.1.).

14.6. Initiate the sequence.

14.7. Data Interpretation

14.7.1. Instrument detector response factor (RF) is in micrograms of carbon per thousand area counts.

14.7.2. Quantitation of the target analyte is based on a reproducible response of the detector within the calibration range and a direct proportionality of the RF readings in the sample and the calibration standards.

14.7.2.1. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak can be determined.

14.7.2.2. Determine the TOC concentration of a sample based on the difference in the TC and TIC concentrations obtained from the sample.

14.7.2.3. If the instrument response exceeds the calibration range, dilute the sample and reanalyze to maintain the carbon concentration within the 1000ppm carbon range ***for high level samples or 20ppm for low level samples***.

15. CALCULATIONS

15.1. Response factors are calculated as follows:

$$RF = \frac{M}{A_s - A_b} \times 1000$$

where: RF = response factor for TOC being measured.
M = TOC mass of the sample in µg of carbon.
A_s = peak area of the sample in thousand counts.
A_b = peak area of the calibration blank in thousand counts.

15.2. The percent difference of CCV is calculated as follows:

$$\%D = \frac{|C_{prepared} - C_{measured}|}{C_{prepared}} \times 100$$

where: %D = percent difference of TOC in CCV.
$C_{prepared}$ = TOC concentration prepared.
$C_{measured}$ = TOC concentration measured.

Note: Concentrations must be in equivalent units.

15.3. The recovery of LCS/LCSD is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of TOC in LCS (or LCSD).
$C_{recovered}$ = TOC concentration recovered.
C_{added} = TOC concentration added.

Note: Concentrations must be in equivalent units.

15.4. The recovery of the MS/MSD is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of TOC in MS (or MSD).
$C_{recovered}$ = TOC concentration recovered.
C_{sample} = TOC concentration in the sample used.
C_{added} = TOC concentration added.

Note: Concentrations must be in equivalent units.

15.5. The relative percent difference is calculated as follows:

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

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = TOC concentration recovered in measurement 1.
C_2 = TOC concentration recovered in measurement 2.

Note: Concentrations must be in equivalent units.

15.6. TOC concentration in the sample is calculated as follows:

$$C = \frac{M}{V} \times DF \times 1000$$

where: C = TOC concentration of the sample in mg/L of carbon.
M = TOC mass of the sample in µg of carbon.
V = volume of the sample in mL.
DF = dilution factor.

15.7. All concentrations shall be reported in mg/L (ppm) of carbon.

15.8. Report total-organic-carbon concentrations which are < 10 mg/L to 2 significant figures, and total-organic-carbon concentrations which are ≥10 mg/L to 3 significant figures.

15.9. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13, "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD vary depending upon historical data. The upper and lower acceptance limits for %REC of LCS/LCSD are based upon the historical average recovery ± 3S. The RPD of the LCS/LCSD is $\leq$20%. The LCS/LCSD must be within acceptance limits. If the LCS/LCSD is not acceptable, the problem must be identified and corrected.

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentration of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.3. The acceptance criteria for MS/MSDs are as follows:

18.3.1. When the %REC of the MS/MSD is at or within the established acceptance limits, and the RPD is $\leq$25%, the analytical system is deemed to be

compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.3.2. If the %REC and/or RPD of the MS/MSD are not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. Matrix effects or poor instrument performance/technique typically causes unacceptable % REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.5. Additional information regarding internal quality control checks is provided in SOP-T020.

18.6. Report total-organic-carbon concentrations which are < 10mg/L to 2 significant figures, and total-organic-carbon concentrations which are ≥10mg/L to 3 significant figures.

18.7. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set is does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that

analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. "Organic Carbon, Total, Method 415.1 (Combustion or Oxidation)," Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, USEPA, March 1983.

22.2. "5310 B. High-Temperature Combustion Method," Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998.

22.3. "5310 D. Wet-Oxidation Method," Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Total Organic Carbon Raw Data Form.

Figure 23.1

Calscience Environmental Laboratories
Total Organic Carbon Raw Data Form

MBMSLCS

Analyte: Total Organic Carbon

Method:_____ MB/LCS/LCSD Batch No.:_____ Date Prepared:_____

Matrix:_____ MS/MSD Batch No.:_____ Date Analyzed:_____

Concentration Units:_____ Instrument Name:_____ Analyst:_____

Work Order Number	CEL I.D. #	Init. Conc.	DF	Final Conc.	RL	Qual	Comments
Method Blank	MB						

QA/QC

Sample Used	Sample Result	Spike Added	MS Result	%REC	MSD Result	% REC	Control Limits	RPD	Control Limits
							75 - 125		0 - 25
Dilution Factors									

LCS		Conc. Added	LCS Result	%REC	LCSD Result	% REC	Control Limits	RPD	Control Limits
Laboratory Control Sample							80 - 120		0 - 20
Dilution Factors									

A copy of the supporting raw data must be attached.

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Title : **RSK-175(M), DISSOLVED GASES IN GROUND WATER BY GC HEADSPACE EQUILIBRATION TECHNIQUE**

Document No. : SOP-M386
Revision No. : 2.3
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ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
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1. METHOD IDENTIFICATION

1.1. RSK-175(M), Dissolved Gases in Ground Water by GC Headspace Equilibration Technique.

2. APPLICABLE MATRICES

2.1. This method is applicable to ground water and other water matrices.

3. DETECTION LIMITS

3.1. The estimated quantitation limits (EQLs) for this method are as follows:

Hydrocarbon	EQL (µg/L)
C_1 (Methane)	1.0
C_2 (Ethane/Ethene)	1.0

3.2. The EQLs will be proportionally higher for samples which require dilution.

4. SCOPE AND APPLICATION

4.1. Method RSK-175(M) is applicable to the preparation of water samples for determination of dissolved gases. The concentration of dissolved gas in the water before equilibration is calculated after the gas is equilibrated into the prepared headspace.

4.1.1. The measurement of dissolved gases such as methane, ethane, and ethylene in ground water is utilized to determine the occurrence of intrinsic bioremediation in a fuel- or solvent-contaminated aquifer, and to detect biodegradation processes in contaminated aquifers.

4.2. This method is specifically designed to determine dissolved methane, ethane, ethane, and carbon dioxide.

4.3. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph (GC) and skilled in the interpretation of gas chromatograms.

5. METHOD SUMMARY

5.1. Water sample is collected without headspace in an appropriate sample container. Prior to analysis, a headspace is prepared by displacing a portion of the water sample with high purity nitrogen. After shaking the sample container for 10 minutes, an aliquot of the headspace sample is withdrawn from the headspace and injected onto a gas chromatographic column where the gaseous components are separated. Detection is achieved using a flame ionization detector (FID).

5.2. The concentration of each dissolved gas in the original water sample is calculated by using the Henry's law constant, the concentration of the gas in the headspace, the container volume, and the temperature of the sample.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-

laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.12. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.13. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.14. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.15. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.16. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.17. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.18. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.19. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.20. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the

appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.21. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.22. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

7. INTERFERENCES

7.1. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high level samples should be diluted and then analyzed at the end of the sequence to prevent carryover contamination. The analysis of non-humidified high-purity helium blanks after high concentration samples is encouraged.

7.2. Interference can also occur when "dirty" samples leave residue in the analytical column. The analytical column can be "baked" after such samples.

7.3. Methane is a very common contaminant and occurs naturally in the atmosphere. Furthermore, automobile exhaust contains high levels of the target analytes. Hence, care should be taken to prevent contamination in transport.

8. SAFETY

8.1. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.2. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Hewlett Packard 5890 Series II Gas Chromatograph, Agilent 6890N Gas Chromatograph, or equivalent configured with the following components:

9.1.1. One 10-port valve.

9.1.2. PC based data system, Hewlett Packard GC ChemStation, Agilent GC ChemStation, or equivalent.

9.2. Primary Detection Channel

9.2.1. Detector: Flame ionization detector (FID).

9.2.2. Analytical Column: 6-ft (1.83-m) × ⅛-in OD × 2.1-mm ID, 80-100 mesh particle size, packed, uncoated Hayesep A porous polymer, stainless steel tubing, Supelco HayeSep® A 13105-U or equivalent.

9.2.3. Analytical Column: 6-ft (1.83-m) × ⅛-in OD × 2.1-mm ID, 80-100 mesh particle size, packed, uncoated Hayesep Q porous polymer, stainless steel tubing, Supelco HayeSep® Q 13801 or equivalent.

9.3. Carrier/Makeup Gas: Helium, He, 99.995%, compressed, Praxair 4.5 grade or equivalent.

9.4. FID Fuel Gas: Hydrogen, H_2, 99.995%, compressed, Praxair 4.5 grade or equivalent.

9.5. FID Combustion/Oxidation Gas: Air, 19.5%–23.5% of O_2, compressed, Praxair Extra Dry grade or equivalent.

9.6. VOA vials, 28-mm × 95-mm (40-mL capacity), clear glass or amber glass, with Teflon or aluminum foil lined screw-caps, EPA VOA Vial or equivalent.

9.7. Bottles, 125-mL, narrow-mouth Boston round open top, amber glass, with Teflon-lined closures, EPA certified or equivalent.

9.8. Shaker, 30–750-rpm variable speed, 0–60-min mechanical timer, 4-position side arms, Thermo Scientific Lab-Line Multi-Wrist Shaker Model 3589 or equivalent.

9.9. Sample loops, 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, 1-mL, 2-mL, and 10-mL, stainless steel or equivalent.

9.10. Syringes, 10-mL, gastight, SampleLock (SL) with Removable Needle (RN) termination, Hamilton 1000 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.11. Syringes, 50-mL, gastight, SampleLock (SL) termination, Hamilton 1000 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.12. Needle, 2-in, 18-gauge, point style AS or equivalent for efficient septum penetration without coring.

9.13. Needle, 2-in, 16-gauge, point style 5 or equivalent for efficient septum penetration without coring.

9.13.1. The 16-gauge needle is used to withdraw water sample during headspace generation.

9.14. Tubing, 18-gauge, appropriate length, PTFE or equivalent.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free.

10.1.2. Hydrochloric acid, HCl, 36.5–38.0% (v/v), concentrated, colorless to pale yellow liquid, reagent grade or equivalent.

10.1.3. Hydrochloric acid, HCl, 1:1 (v/v).

10.1.3.1. Prepare the 1:1 HCl solution by slowly adding concentrated HCl to equal volume of reagent water.

10.1.4. Helium, He, 99.995%, compressed, Praxair 4.5 grade or equivalent.

10.1.5. Nitrogen, N_2, 99.998%, compressed, Praxair 4.8 grade or equivalent.

10.1.6. All reagents (except He and N_2) must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Pre-certified and NIST traceable stock standard gas mixtures, each in sealed cylinders, containing various concentrations of methane (CH_4), ethane (C_2H_6), and ethene or ethylene (C_2H_4) in helium (He) balance are used as the calibration standards.

10.2.1.1. The stock standards are as follows:

Analyte	Nominal Standard Gas Concentration (ppm)
methane ethane	100
methane	5000
ethene	100

10.2.1.2. Analyze the appropriate stock standards using a sample loop with the appropriate size for initial calibration. Draw approximately 10-mL aliquot of the stock standard using a clean 50-mL gastight syringe for direct injection analysis.

Calibration Level (ppm)		Nominal Standard Gas Concentration (ppm)	Sample Loop Size
C_1	C_2		
1	1	100	25 µL
2	2	100	100 µL
5	5	100	500 µL
100	100	100	2 mL
500	500	100	10 mL
2500		5000	1 mL

Note: $C_1 = CH_4$; C_2–$C_6 = C_2H_6$ or C_2H_4

10.2.1.3. The 100-ppm stock standards are also used as the continuing calibration verification (CCV) standards.

10.2.1.4. Analyze the CCV standard using a 2-mL sample loop for continuing calibration verification. Draw approximately 10-mL

aliquot of the CCV standard using a clean 50-mL gastight syringe for direct injection analysis.

Calibration Verification Level (ppm)		Nominal Standard Gas Concentration (ppm)	Sample Loop Size
C_1	C_2		
100	100	100	2 mL

Note: $C_1 = CH_4$; C_2–$C_6 = C_2H_6$ or C_2H_4

10.2.2. Pre-certified and NIST traceable second source stock standard gas mixtures, each in sealed cylinders, containing 100 ppm (nominal) each of methane, ethane, and ethene in nitrogen (N_2) balance are used as the check standards. The standard must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.2.1. The second source stock standards are as follows:

Analyte	Nominal Standard Gas Concentration (ppm)
methane ethane	100
ethene	100

10.2.2.2. The second source stock standards are used as the initial calibration verification (ICV) standards and quality control (QC) check samples such as laboratory control samples (LCS/LCSDs).

10.2.2.3. Analyze the ICV standard using a 2-mL sample loop for initial calibration verification or quality control check. Draw approximately 10-mL aliquot of the ICV standard using a clean 50-mL gastight syringe for direct injection analysis.

Calibration Verification Level (ppm)		Nominal Standard Gas Concentration (ppm)	Sample Loop Size
C_1	C_2		
100	100	100	2 mL

Note: $C_1 = CH_4$; C_2–$C_6 = C_2H_6$ or C_2H_4

10.2.3. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Water samples should be collected in 125-mL pre-cleaned amber glass bottles, or 40-mL pre-cleaned amber glass or clear glass VOA vials with Teflon-lined closures.

For 125-mL bottles, collect all samples in duplicate. For 40-mL vials, collect all samples in triplicate.

11.1.1. Collect a water sample by gently adding the sample down the side of the container in order to reduce agitation. Care should be taken to avoid the creation of bubbles or headspace in the container.

11.1.2. Adjust the pH of the water sample to < 2 by adding 1:1 HCl solution while stirring.

11.1.3. Completely fill and hermetically seal the sample container such that when the container is inverted, no headspace is visible.

11.1.3.1. It is possible for the sample to generate some headspace in the form of micro bubbles during storage. The bubbles should not exceed ¼ in or 6 mm in diameter.

11.2. Samples shall be maintained in a chilled state (≤ 4°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.3. Upon receipt, the samples are stored in a 0–6°C cooler.

11.3.1. Water samples with acid preservation (pH < 2) must be analyzed within 14 days of sample collection.

11.3.2. Water samples without acid preservation (pH ≥ 2) must be analyzed within 7 days of sample collection.

12. QUALITY CONTROL

12.1. Initial Calibration (IC)

12.1.1. The initial multi-point calibration must be established prior to the processing of samples.

12.1.2. The IC is deemed valid if the %RSD for each analyte is ≤ 20%.

12.1.3. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.1.3.1. If the problem appears to be associated with a single calibration level, then that one level may be reanalyzed once within the same analytical shift prior to sample analysis.

12.2. Initial Calibration Verification (ICV)

12.2.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.2.2. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like gases from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the gases is no longer intact (representative of the stated concentration). Document the unacceptable result and reanalyze the ICV within 2 hours

after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective action, which may include replacement of standard gases, and recalibrate.

12.3. Continuing Calibration Verification (CCV)

12.3.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 24-hour shift, and at the end of sequence.

12.3.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.3.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.4. Retention Time Window

12.4.1. Establishment of retention time window position is accomplished by using the midpoint calibration level once per initial calibration.

12.4.1.1. The midpoint calibration level is obtained by analyzing the 100-ppm stock standard using a 2-mL sample loop.

12.4.1.2. Absolute retention time window for each analyte is the retention time of the analyte in the midpoint calibration level ± $0.2T_R$ (where T_R is the retention time of that analyte in the midpoint calibration level).

12.4.1.3. Document the serial number of the analytical column associated with the retention time window.

12.4.1.4. Record the retention time in minutes for each analyte to three decimal places.

12.4.2. Retention time window for each analyte is verified as follows:

12.4.2.1. All CCV standards must fall within the absolute retention time window established by the midpoint calibration level.

12.4.2.2. If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window position, if necessary.

12.5. Event Based Quality Control (LCS/LCSDs and MBs)

12.5.1. Event based quality control consists of QC samples analyzed under the same analytical conditions as the actual environmental samples. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.5.2. The acceptance criteria for LCS/LCSD ***compounds are as follows***:

12.5.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 80% and 120%, respectively. The RPD is ≤ 20%.

12.5.2.2. All LCS/LCSD compounds must be within acceptance limits. If the LCS/LCSD compounds are not acceptable, determine the cause of the problem and effect corrective action.

12.5.3. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.5.3.1. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.5.3.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-analyzed.

12.6. Matrix Based Quality Control (Sample Duplicates)

12.6.1. Matrix based quality control consists of QC samples processed using actual environmental samples. This consists of a sample duplicate.

12.6.1.1. A sample duplicate is a selected field sample re-analyzed under the same analytical conditions as the associated samples. It is only required per client request or project specific DQOs.

12.6.2. The acceptance criteria for duplicate compounds are as follows:

12.6.2.1. The RPD is ≤ 25%.

12.6.2.2. When the RPD of the duplicate compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.

12.6.2.3. If the RPD of the duplicate compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.6.3. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.7. If the %REC or RPD of the LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples reanalyzed.

12.8. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Initial Calibration

13.1.1. Establish an acceptable multi-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.1.

13.1.1.1. Recalibration is required for the following maintenance procedures.

13.1.1.1.1. Change, replace, or reverse the analytical column.

13.1.1.1.2. Change the FID jet.

13.1.2. After obtaining an acceptable multi-point calibration curve and prior to processing field or QC samples, an ICV standard must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.2.

13.1.3. The initial multi-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

14. PROCEDURE

14.1. Instrument Setup

14.1.1. Use the following GC operating conditions as guidance to establish the GC temperature program necessary to separate the analytes of interest. For GC hardware without constant pressure setting, adjust the pressure manually to achieve the optimal operating conditions, and record the pressure in the instrument run logbook.

Description	GC Operating Condition 1
Carrier gas flow rate	20 mL/min
Hydrogen flow rate	35 mL/min
Air flow rate	400 mL/min
Detector temperature	250°C
Initial temperature	60°C, hold 2.00 min
Temperature program	60°C to 180°C at 40.00°C/min
Final temperature	180°C, hold 11.00 min

Description	GC Operating Condition 2
Carrier gas flow rate	50 mL/min at 20.00 psi
Hydrogen flow rate	40 mL/min
Air flow rate	400 mL/min
Detector temperature	250°C
Initial temperature	60°C
Temperature program	60°C to 180°C at 60.00°C/min
Final temperature	180°C, hold 15.00 min

14.1.2. Install a sample loop with the appropriate size.

14.1.2.1. Use a 2-mL sample loop for daily field and QC sample analysis.

14.1.2.2. Use a smaller sample loop to dilute samples with concentrations exceeding the highest calibration level.

14.1.3. Program the data system to integrate the total resolved and unresolved peak area.

14.1.4. Check the carrier gas cylinder pressure prior to sample analysis.

14.1.4.1. If the pressure is less than 200 psi, replace the carrier gas cylinder to minimize impurities.

14.2. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 24-hour shift, and at the end of sequence. If the QC and retention time window criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.3. and Section 12.4.2.

14.2.1. If a failed CCV is the first of the day, effect corrective action prior to analyzing any samples.

14.2.2. If a failed CCV is <u>not</u> the first of the day, effect corrective action and reanalyze all samples since the last acceptable CCV.

14.3. Nitrogen Gas Cylinder Setup

14.3.1. Connect an 18-gauge needle and PTFE tubing to the nitrogen gas cylinder flow controller.

14.3.2. Set the nitrogen gas flow to 5 mL/min or less.

14.3.3. Open the valve when sample containers are ready for headspace generation.

14.4. Multi-Wrist Shaker Setup

14.4.1. Turn the speed rotary dial to 6, and the timer rotary dial to 10.

14.5. Water Sample Preparation

14.5.1. Allow a water sample to reach room temperature.

14.5.1.1. Keep the sample container inverted throughout the course of sample preparation except when drawing the headspace sample for direct injection analysis.

14.5.2. Attach a 16-gauge needle to a 10-mL gastight syringe designated for headspace generation.

14.5.3. Insert the needle attached to the syringe through the septum of the sample container.

14.5.4. Insert the needle connected to the nitrogen gas cylinder through a different part of the septum.

14.5.5. Generate a headspace by allowing the nitrogen gas to force the water sample out of the sample container and into the syringe.

14.5.5.1. For a 125-mL bottle, remove 10.0 mL of the water sample.

14.5.5.2. For a 40-mL vial, remove 6.0 mL of the water sample.

14.5.6. After headspace generation, pull both needles from the septum. Discard the water sample in the syringe into a waste container.

14.5.6.1. If the needle is partially clogged, gently flush the syringe with reagent water. If the needle is completely clogged, use a needle cleaning wire to dislodge any foreign materials, and gently flush the syringe with reagent water.

14.5.7. Hold the sample container in place with the clamps on the side arm of the multi-wrist shaker, and agitate the water sample at 450 rpm for 10 minutes to allow the gases to equilibrate between the gas phase (headspace) and the liquid phase (water).

14.5.8. Attach an 18-gauge needle to a clean 10-mL gastight syringe designated for direct injection analysis.

14.5.9. Draw approximately 2.5-mL aliquot of the headspace sample from the sample container using the 10-mL gastight syringe for direct injection analysis.

14.5.9.1. For MB, draw approximately 2.5-mL aliquot of high purity nitrogen using a clean 10-mL gastight syringe.

14.5.9.2. For LCS/LCSD, draw approximately 10-mL aliquot of the 100-ppm second source stock standard using a clean 50-mL gastight syringe.

14.5.9.3. If sample dilution is required, the volume of the headspace sample drawn for analysis should be at least 0.5 mL greater than the sample loop size.

14.5.10. If necessary, fill and flush the syringe with high purity helium at least 3 times between each use to prevent cross contamination.

14.6. Standards and samples are injected manually and analyzed one at a time in the following or other logical order:

1) Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Laboratory Control Sample Duplicate (LCSD)
4) Method Blank (MB)
5) Samples (up to 20 per batch, excluding QC check samples and MBs)
6) Sample Duplicate (per client request or project specific DQOs)
7) Ending CCV

14.6.1. Items 1 and 7: A CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every batch of 20 samples or portion thereof within a 24-hour shift, and at the end of sequence.

14.6.1.1. More frequent (e.g., every 10 samples) calibration verification may be useful to minimize the number of sample re-analyses that would be required in the event of an unacceptable CCV.

14.6.2. Item 2: The LCS is a known matrix containing known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.6.2.1. For gaseous samples, the LCS consists of a standard gas mixture containing the specified compounds.

14.6.2.2. One LCS is required daily for every batch of 20 samples or portion thereof, whichever is more frequent.

14.6.3. Item 3: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.6.4. Item 4: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

14.6.4.1. For gaseous samples, the MB consists of high-purity nitrogen.

14.6.4.2. One MB is required daily for every batch of 20 samples or portion thereof, whichever is more frequent.

14.6.5. Item 5: Up to 20 samples (excluding QC check samples and method blanks) per batch. High concentration samples should be sufficiently diluted by using a smaller sample loop for analysis. Dilution of samples will result in increased reporting limits. The formula for calculating the appropriate sample loop size is listed in Section 15.6.

14.6.6. Item 6: The sample duplicate is a selected field sample re-analyzed under the same analytical conditions. The sample duplicate is processed

concurrently with the associated samples. In the processing of the sample duplicate, reagents and procedures identical to those for actual samples are used.

14.6.6.1. The purpose of the sample duplicate is to access matrix effects. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.5.

14.6.6.2. To comply with client request or project specific data quality objectives (DQOs), one sample duplicate is required daily for every batch of 20 samples or portion thereof, whichever is more frequent.

14.6.7. Instrument blanks consisting of non-humidified high-purity helium may be added elsewhere in the sequence, as necessary (i.e., after suspected high level samples), to check for potential carryover or cross-contamination.

14.7. Edit the sample information in the data system and record pertinent information in the instrument run logbook.

14.8. Data Interpretation

14.8.1. Establish the absolute retention time window for each analyte (see Section 12.4.1.2.).

14.8.1.1. Tentative identification of an analyte occurs when the peak of the analyte from a sample falls within the analyte's absolute retention time window.

14.8.1.2. Use the CCV standards analyzed throughout the course of an analytical sequence within a 24-hour shift to evaluate retention time stability (see Section 12.4.2.). If any analyte(s) in the CCV standard fall outside of their absolute retention time window(s), determine the cause of the problem and effect appropriate corrective action.

14.8.1.2.1. If any analyte(s) in the CCV standard fall outside of their absolute retention time window(s), then all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed.

14.8.1.3. Tentative identification of an analyte in a diluted sample occurs when the peak of the analyte from the diluted sample falls within the analyte's reference retention time window.

14.8.1.3.1. Reference retention time window for each analyte in a diluted sample is the retention time of the analyte in the calibration standard analyzed using the same size sample loop ± $0.2T_{R'}$ (where $T_{R'}$ is the retention time of that analyte in the calibration standard analyzed using the same size sample loop).

14.8.2. Quantitation of a target analyte in the gas phase (headspace) is based on a reproducible response of the detector within the calibration range and a direct proportionality of the magnitude of response between peaks in the sample and the calibration standards.

14.8.2.1. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak(s) can be determined.

14.8.2.2. Determine the concentration based on the initial calibration curve.

14.8.2.2.1. Calculate the concentration of each target analyte in the gas phase (headspace) using the average of the initial RFs and the area of the characteristic peak(s). The formula for calculating concentration is listed in Section 15.8.

14.8.2.2.2. The data system is programmed to perform the calculation of concentration.

14.8.2.3. If the instrument response exceeds the calibration range, dilute the sample and reanalyze.

14.8.3. Quantitation of a target analyte in the original water sample is derived from Henry's law and the concentration in the gas phase (headspace).

14.8.3.1. Obtain the concentration of each target analyte in the gas phase (headspace) from the gas chromatogram.

14.8.3.2. Calculate the concentration of each target analyte in the liquid phase (water) from the concentration in the gas phase (headspace).

14.8.3.2.1. Program a Microsoft Excel spreadsheet to apply the appropriate formulas and Henry's law constants at 293 K (20°C) for calculation. The formulas are listed in Section 15.9.

14.8.3.2.2. The Henry's law constant at 293 K (20°C) and molecular weight of each target analyte are as follows:

Analyte	Henry's Law Contant (atm/mol·fraction)	Molecular Weight (g/mol)
methane	37,600	16.04
ethane	26,300	30.07
ethene	10,200	28.05

14.8.3.3. Calculate the concentration of each target analyte in the original water sample by summing the concentrations in the gas and liquid phases.

14.8.3.3.1. Program the same Microsoft Excel spreadsheet to apply the appropriate formulas for calculation. The formulas are listed in Section 15.10.

14.8.3.3.2. The EPA-defined standard conditions are as follows:

Description	Condition
Standard pressure	101.325 kPa
Standard temperature	293.15 K (20°C)

14.8.3.3.3. The actual water sample volume, the gas phase (headspace) volume, and the liquid phase (water) volume of each container are as follows:

Container (Bottle/Vial)	Volume (mL)		
	Water Sample	Gas Phase	Liquid Phase
125-mL	128.0	10.0	118.0
40-mL	42.5	6.0	36.5

14.8.4. Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.

15. CALCULATIONS

15.1. The response factor is calculated as follows:

$$RF = \frac{A_x}{C_x}$$

where: RF = response factor for target analyte being measured.
A_x = area of the characteristic peak(s) for target analyte being measured.
C_x = concentration of target analyte being measured in ppm (v/v).

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RFs for the target analyte.
RF_{ave} = mean of the 5 or 6 initial RFs for the target analyte.

15.3. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RF_{ave} - RF_{daily}|}{RF_{ave}} \times 100$$

where: %D = percent difference.
RF_{daily} = daily RF for the target analyte.
RF_{ave} = mean of the 5 or 6 initial RFs for the target analyte.

15.4. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.5. The relative percent difference is calculated as follows:

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

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.
C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.6. The sample loop size is calculated as follows:

$$L \leq \frac{CL \times RF_{ave} \times 2000}{A_x}$$

where: L = sample loop size in µL.
CL = upper limit of the calibration level for the target analyte in ppm (v/v).
RF_{ave} = mean of the 5 or 6 initial RFs for the target analyte.
A_x = area of the characteristic peak(s) for the target analyte.

15.7. The dilution factor is calculated as follows:

15.7.1. If sample loop is used for dilution, the dilution factor is calculated as follows:

$$D = \frac{2000}{L}$$

where: D = dilution factor.
L = sample loop size in µL.

15.7.2. If syringe is used for dilution, the dilution factor is calculated as follows:

$$D = \frac{V_f}{V_i}$$

where: D = dilution factor.
V_f = volume of sample after dilution in mL.
V_i = volume of sample before dilution in mL.

15.8. The target analyte concentration in the gas phase (headspace) is calculated as follows:

$$C_x = \frac{A_x}{RF_{ave}} \times D$$

where: C_x = concentration of target analyte in gas phase in ppm (v/v).
A_x = area of the characteristic peak(s) for target analyte.
RF_{ave} = mean of the 5 or 6 initial RFs for the target analyte.
D = dilution factor, if the sample was diluted prior to analysis. If no dilution was made, D = 1.

15.9. The target analyte concentration in the liquid phase (water) is calculated as follows in the order presented:

15.9.1. The target analyte partial pressure is calculated as follows:

$$P_x = \frac{C_x}{1000000} \times P_t$$

where: P_x = partial pressure of target analyte in atm.
C_x = concentration of target analyte in gas phase in ppm (v/v).
P_t = total pressure in atm. Assume $p_t = 1$.

15.9.2. The target analyte mole fraction is calculated as follows:

$$F_x = \frac{P_x}{H}$$

where: F_x = mole fraction of dissolved target analyte at equilibrium in mol·fraction (mole/mole).
P_x = partial pressure of target analyte in atm.
H = Henry's law constant for target analyte in atm/mol·fraction.

15.9.3. The target analyte molar concentration (molarity) in one liter of water is calculated as follows:

$$F_x = \frac{n_x}{n_x + n_w}$$

$$n_x = F_x \times (n_x + n_w)$$

$$n_x << n_w$$

$$n_x \approx F_x \times n_w = \frac{P_x}{H} \times n_w$$

where: F_x = mole fraction of dissolved target analyte at equilibrium in mol·fraction (mole/mole).
n_x = molar concentration of target analyte in mol/L.
n_w = molar concentration of water molecule in mol/L. For one liter of water, n_w = 55.5.
P_x = partial pressure of target analyte in atm.
H = Henry's law constant for target analyte in atm/mol·fraction.

15.9.4. The target analyte concentration in the liquid phase (water) is calculated as follows:

$$C_w = n_x \times MW \times 1000 = \frac{P_x}{H} \times n_w \times MW \times 1000$$

where: C_w = concentration of target analyte in liquid phase in mg/L.
n_x = molar concentration of target analyte in mol/L.
MW = molecular weight of target analyte in g/mol.
P_x = partial pressure of target analyte in atm.
H = Henry's law constant for target analyte in atm/mol·fraction.
n_w = molar concentration of water molecule in mol/L. For one liter of water, n_w = 55.5.

15.10. The target analyte concentration in the original water sample is calculated as follows in the order presented:

15.10.1. The target analyte density under standard conditions is calculated as follows:

$$\rho = \frac{MW}{V} \times \frac{273}{T} \times 1000$$

where: ρ = density of target analyte in mg/L.
MW = molecular weight of target analyte in g/mol.
V = molar volume of target analyte in L/mol. For one mole of an ideal gas, V = 22.4.
T = temperature of water sample in K. Assume T = 293.

15.10.2. The target analyte concentration partitioned into the gas phase (headspace) from the original water sample.

$$C_h = \frac{V_h}{V_w} \times \frac{C_x}{1000000} \times \rho$$

where: C_h = concentration of target analyte partitioned into gas phase from original water sample in mg/L.
V_h = volume of gas phase in mL.
V_w = volume of liquid phase in mL.
C_x = concentration of target analyte in gas phase in ppm (v/v).
ρ = density of target analyte in mg/L.

15.10.3. The target analyte concentration in the original water sample is calculated as follows:

$$C_t = (C_w + C_h) \times 1000$$

where: C_t = concentration of target analyte in original water sample in µg/L.
C_w = concentration of target analyte in liquid phase in mg/L.
C_h = concentration of target analyte partitioned into gas phase from original water sample in mg/L.

15.11. All concentrations shall be reported in µg/L for water samples.

15.12. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD compounds are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 80% and 120%, respectively. The RPD is ≤ 20%. All LCS/LCSD compounds must be within acceptance limits.

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-analyzed.

18.3. The acceptance criteria for duplicate compounds are predetermined. The RPD is ≤ 25%.

18.3.1. When the RPD of the duplicate compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the precision requirement of the method for the particular matrix. The duplicate data shall be reported with the corresponding sample data.

18.3.2. If the RPD of the duplicate compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.4. Matrix effects or poor instrument performance/technique typically causes unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.5. Additional information regarding internal quality control checks is provided in SOP-T020.

18.6. All concentrations shall be reported in µg/L for water samples.

18.7. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.1.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.1.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.1.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique, RSKSOP-175, USEPA Robert S. Kerr Environmental Research Laboratory, Revision 0, August 1994.

22.2. Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique, RSKSOP-175, USEPA Ground Water and Ecosystems Restoration Division, Revision 2, May 2004.

22.3. Solubilities, Perry's Chemical Engineers' Handbook, Seventh Edition, Edited by R.H. Perry and D.W. Green, Published by McGraw-Hill, 1997.

22.4. Solubilities of Gases in Liquids, International Critical Tables of Numerical Data, Physics, Chemistry and Technology, First Electronic Edition, Volume 3, Edited by E.W. Washburn, Published by Knovel, 2003.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Procedure for Dissolved Carbon Dioxide in Ground Water by GC Headspace Equilibration Technique.

23.2. Appendix B: RSK-175(M) C_1–C_2 Hydrocarbons and CO_2 Quality Control Data Form.

23.3. Appendix C: Additional Quality Control Criteria for BP Project.

24. MODIFICATIONS

24.1. The following modifications from Method RSK-175 (Revision 0) are noted.

24.1.1. Equipment and Supplies

24.1.1.1. The syringe needle specification is modified.

24.1.2. Procedure

24.1.2.1. The shaker speed and time are modified.

Appendix A

PROCEDURE FOR DISSOLVED CARBON DIOXIDE IN GROUND WATER BY GC HEADSPACE EQUILIBRATION TECHNIQUE

1. METHOD IDENTIFICATION

1.1. RSK-175(M), Dissolved Carbon Dioxide in Ground Water by GC Headspace Equilibration Technique.

2. DETECTION LIMITS

2.1. The estimated quantitation limit (EQL) for this method is as follows:

Analyte	EQL (µg/L)
CO_2 (Carbon Dioxide)	1.7

2.2. The EQLs will be proportionally higher for samples which require dilution.

3. SCOPE AND APPLICATION

3.1. The procedure described herein either supersedes or is in addition to the standard procedure.

4. EQUIPMENT AND SUPPLIES

4.1. Gas Chromatograph: Hewlett Packard 5890 Series II Gas Chromatograph or equivalent configured with the following components:

4.1.1. Two 6-port valves and one 4-port valve.

4.1.2. Oxidation catalyst system (oxidizer), capable of oxidizing CH_4 to CO_2 with at least 95% efficiency.

4.1.3. Reduction catalyst system (methanizer), capable of reducing CO_2 to CH_4 with at least 95% efficiency.

4.1.4. Flame-out buffer, 6-ft × ⅛-in OD, 80-100 mesh particle size, packed, uncoated Hayesep Q porous polymer, stainless steel tubing, Supelco HayeSep® Q 13801 or equivalent.

4.1.4.1. An empty stainless steel column can be used as a substitute for flame-out buffer.

4.1.5. PC based data system, Hewlett Packard GC ChemStation, Agilent GC ChemStation, or equivalent.

4.2. Primary Detection Channel

4.2.1. Detector: Flame ionization detector (FID).

4.2.2. Analytical Column: 6-ft × ⅛-in OD, 80-100 mesh particle size, packed, uncoated Chromosorb porous polymer, stainless steel tubing, Supelco Chromosorb® 106 or equivalent.

4.2.3. Analytical Column: 6-ft × ⅛-in OD, 80-100 mesh particle size, packed, uncoated Tenax porous polymer, stainless steel tubing, Supelco Tenax® TA or equivalent.

4.3. Sample loops, 100-µL, 200-µL, and 1-mL, stainless steel or equivalent.

5. STANDARDS

5.1. Pre-certified and NIST traceable stock standard gas mixtures, each in sealed cylinders, containing various concentrations of carbon dioxide (CO_2) in helium (He) or nitrogen (N_2) balance are used as the calibration standards.

5.1.1. The stock standards are as follows:

Analyte	Nominal Standard Gas Concentration (ppm)
carbon dioxide	5
carbon dioxide	300
carbon dioxide	5000

5.1.2. Analyze the appropriate stock standards using a sample loop with the appropriate size for initial calibration. Draw approximately 10-mL aliquot of the stock standard using a clean 50-mL gastight syringe for direct injection analysis.

Calibration Level (ppm) CO_2	Nominal Standard Gas Concentration (ppm)	Sample Loop Size
1	5	200-µL
5	5	1-mL
300	300	1-mL
5000	5000	1-mL

5.1.3. The 300-ppm stock standard is also used as the continuing calibration verification (CCV) standard.

5.1.4. Analyze the CCV standard using a 1-mL sample loop for continuing calibration verification. Draw approximately 10-mL aliquot of the CCV standard using a clean 50-mL gastight syringe for direct injection analysis.

Calibration Verification Level (ppm) CO_2	Nominal Standard Gas Concentration (ppm)	Sample Loop Size
300	300	1-mL

5.2. Pre-certified and NIST traceable second source stock standard gas mixture, in a sealed cylinder, containing 5000 ppm (nominal) of carbon dioxide (CO_2) in nitrogen (N_2) balance is used as the check standard. The standard must be of a source differing from that used for the initial four-point calibration. If it is of the same source, then it must be of different lot.

5.2.1. The second source stock standard is as follows:

Analyte	Nominal Standard Gas Concentration (ppm)
carbon dioxide	5000 (or 0.5%)

5.2.2. The second source stock standard is used as the initial calibration verification (ICV) standard and quality control (QC) check samples such as laboratory control samples (LCS/LCSDs).

5.2.3. Analyze the ICV standard using a 100-uL sample loop for initial calibration verification or quality control check. Draw approximately 10-mL aliquot of the ICV standard using a clean 50-mL gastight syringe for direct injection analysis.

Calibration Verification Level (ppm) CO_2	Nominal Standard Gas Concentration (ppm)	Sample Loop Size
500	5000	100-µL

5.3. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

6. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

6.1. Water samples should be collected in 125-mL pre-cleaned amber glass bottles, or 40-mL pre-cleaned amber glass or clear glass VOA vials with Teflon-lined closures. For 125-mL bottles, collect all samples in duplicate. For 40-mL vials, collect all samples in triplicate.

6.1.1. No preservation chemicals are required. Do not add any acid to the water samples. Acid may convert inorganic carbon to carbon dioxide.

6.2. Samples shall be maintained in a chilled state (≤ 4°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

6.3. Upon receipt, the samples are stored in a 0–6°C cooler.

6.3.1. Water samples must be analyzed within 7 days of sample collection.

7. QUALITY CONTROL

7.1. Retention Time Window

7.1.1. Establishment of retention time window position is accomplished by using the midpoint calibration level once per initial calibration.

7.1.1.1. The midpoint calibration level is obtained by analyzing the 300-ppm stock standard using a 1-mL sample loop.

7.1.1.2. Absolute retention time window for the analyte is the retention time of the analyte in the midpoint calibration level ± 0.500 minute.

7.1.1.3. Document the serial number of the analytical column associated with the retention time window.

7.1.1.4. Record the retention time in minutes for the analyte to three decimal places.

7.1.2. Retention time window for the analyte is verified as follows:

7.1.2.1. All CCV standards must fall within the absolute retention time window established by the midpoint calibration level.

7.1.2.2. If these criteria are not met, determine the cause of the problem, effect corrective action, and re-establish the retention time window position, if necessary.

8. PROCEDURE

8.1. Instrument Setup

8.1.1. Use the following GC operating conditions as guidance to establish the GC temperature program necessary to separate the analytes of interest. For GC hardware without constant pressure setting, adjust the pressure manually to achieve the optimal operating conditions.

Description	GC Operating Condition
Carrier gas flow rate	20 mL/min
Hydrogen flow rate	35 mL/min
Air flow rate	400 mL/min
Detector temperature	250°C
Initial temperature	32°C, hold 15.00 min
Temperature program	32°C to 100°C at 25.0°C/min
Final temperature	100°C, hold 10.00 min

8.1.2. Install a sample loop with the appropriate size.

8.1.2.1. Use a 1-mL sample loop for daily field and QC sample analysis.

8.1.2.2. Use a smaller sample loop to dilute samples with concentrations exceeding the highest calibration level.

8.2. Data Interpretation

8.2.1. Establish the absolute retention time window for the analyte (see Section 7.1.1.2. of this appendix).

8.2.1.1. Tentative identification of an analyte occurs when the peak of the analyte from a sample falls within the analyte's absolute retention time window.

8.2.1.2. Use the CCV standards analyzed throughout the course of an analytical sequence within a 24-hour shift to evaluate retention time stability (see Section 7.1.2. of this appendix). If the analyte in the CCV standard falls outside of its absolute retention time window, determine the cause of the problem and effect appropriate corrective action.

8.2.1.2.1. If the analyte in the CCV standard falls outside of its absolute retention time window, then all samples analyzed since the last acceptable CCV should be invalidated, corrective action effected, and the affected samples re-analyzed.

8.2.2. The Henry's law constant at 293 K (20°C) and molecular weight of the target analyte are as follows:

Analyte	Henry's Law Contant (atm/mol·fraction)	Molecular Weight (g/mol)
carbon dioxide	1,420	44.01

9. CALCULATIONS

9.1. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RFs for the target analyte.
RF_{ave} = mean of the 4 initial RFs for the target analyte.

9.2. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RF_{ave} - RF_{daily}|}{RF_{ave}} \times 100$$

where: %D = percent difference.
RF_{daily} = daily RF for the target analyte.
RF_{ave} = mean of the 4 initial RFs for the target analyte.

9.3. The sample loop size is calculated as follows:

$$L \leq \frac{CL \times RF_{ave} \times 1000}{A_x}$$

where: L = sample loop size in µL.
CL = upper limit of the calibration level for the target analyte in ppm (v/v).
RF_{ave} = mean of the 4 initial RFs for the target analyte.
A_x = area of the characteristic peak(s) for the target analyte.

9.4. The dilution factor is calculated as follows:

9.4.1. If sample loop is used for dilution, the dilution factor is calculated as follows:

$$D = \frac{1000}{L}$$

where: D = dilution factor, if the sample was diluted prior to analysis. If no dilution was made, D = 1.
L = sample loop size in µL.

9.4.2. If syringe is used for dilution, the dilution factor is calculated as follows:

$$D = \frac{V_f}{V_i}$$

where: D = dilution factor, if the sample was diluted prior to analysis. If no dilution was made, D = 1.
V_f = volume of sample after dilution in mL.
V_i = volume of sample before dilution in mL.

9.5. The target analyte concentration in the gas phase (headspace) is calculated as follows:

$$C_x = \frac{A_x}{RF_{ave}} \times D$$

where: C_x = concentration of target analyte in gas phase in ppm (v/v).
A_x = area of the characteristic peak(s) for target analyte.
RF_{ave} = mean of the 4 initial RFs for the target analyte.
D = dilution factor, if the sample was diluted prior to analysis. If no dilution was made, D = 1.

Appendix B

RSK-175(M) C_1–C_2 HYDROCARBONS AND CO_2 QUALITY CONTROL DATA FORM

Calscience Environmental Laboratories, Inc.

Calscience Environmental Laboratories
RSK-175(M) C_1–C_2 Hydrocarbons and CO_2 Quality Control Data Form

Method: ☐ RSK-175(M), Methane (CH_4), Ethane (C_2H_6), and Ethene (C_2H_4)
☐ RSK-175(M), Carbon Dioxide (CO_2)
☐ Other (Specified) _____

Reviewed by: _____
Date: ____ / ____ / ____

WORK ORDER #	INSTRUMENT ID	BATCH NUMBER	COMMENTS
		C_1–C_2: MB/LCS/LCSD:	
		CO_2: MB/LCS/LCSD:	

STANDARD ID #	CONC UNIT(S)	DATE	COMMENTS
C_1–C_2 CCV	☐ ppm (v/v), ☐ other _____		
Ethene CCV			
CO_2 CCV			
C_1–C_2 LCS/LCSD			
Ethene LCS/LCSD			
CO_2 LCS/LCSD			

Flame Ionization Detector (FID) Analysis - CCV

ANALYTE(S)	AVERAGE RF (n.nn × 10^0)	DAILY RF (n.nn × 10^0)	%D	CONTROL LIMIT	ANALYST	COMMENTS
Methane (CH_4)				0 – 15		
Ethane (C_2H_6)				0 – 15		
Ethene (C_2H_4)				0 – 15		
Carbon Dioxide (CO_2)				0 – 15		
				0 – 15		

Flame Ionization Detector (FID) Analysis - LCS/LCSD

ANALYTE(S)	ADDED CONC	LCS		LCSD		CONTROL LIMIT	RPD	CONTROL LIMIT	ANALYST	COMMENTS
		RECOVERED CONC	%REC	RECOVERED CONC	%REC					
Methane (CH_4)						80 – 120		0 – 20		
Ethane (C_2H_6)						80 – 120		0 – 20		
Ethene (C_2H_4)						80 – 120		0 – 20		
Carbon Dioxide (CO_2)						80 – 120		0 – 20		

Appendix C

ADDITIONAL QUALITY CONTROL CRITERIA FOR BP PROJECT

1. METHOD IDENTIFICATION

1.1. RSK-175(M), Dissolved Gases in Ground Water by GC Headspace Equilibration Technique – Additional Quality Control Criteria for BP Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The use of a standard from a second lot as the second source standard is acceptable if written warranties demonstrating that the standards from two different lots are not prepared from the same reference materials are obtained from the manufacturer. "Manufacturer" refers to the producer of the standard, not the vendor.

4. QUALITY CONTROL

4.1. Method Detection Limit (MDL)

4.1.1. MDL study should be performed annually for each analyte and matrix.

4.1.2. MDL verification must be performed immediately following an MDL study.

4.1.2.1. MDL verification sample must be spiked at the calculated MDL value.

4.1.2.2. MDL verification is deemed valid if all analytes in the verification sample are recovered.

4.1.3. At a minimum, the MDL study shall be performed on a single instrument, and the calculated MDL value must be confirmed by analyzing an MDL verification sample on all instruments used to analyze BP samples.

4.2. Continuing Calibration Verification (CCV)

4.2.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every 10 injections or portion thereof within a 24-hour shift, and at the end of sequence.

4.2.2. Documentation for multiple (more than one) injection trials of CCV standards must include the reason for the multiple trials, the corrective action and which trial was used and why.

4.3. Event Based Quality Control (MBs)

4.3.1. Method Blanks (MBs)

4.3.1.1. Contamination observed in the MB at a concentration greater than 1/2 of the RL is acceptable if either one of the following conditions is met.

4.3.1.1.1. No contaminant is detected in the associated samples.

4.3.1.1.2. The concentration of the contaminant in the associated samples is greater than 10 times the concentration in the MB.

5. PROCEDURE

5.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every 10 injections or portion thereof within a 24-hour shift, and at the end of sequence. If the QC and retention time window criteria are met, the initial calibration is assumed to be valid and sample analysis may resume.

5.2. Standards and samples are injected manually and analyzed one at a time in the following or other logical order:

1) Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Laboratory Control Sample Duplicate (LCSD)
4) Method Blank (MB)
5) Samples (up to 10 injections, including QC check samples and MBs)
6) Middle CCV
7) Samples (up to 10 injections, including QC check samples and MBs)
8) Ending CCV

5.2.1. Items 1, 6, and 8: A CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis, after every 10 injections or portion thereof within a 24-hour shift, and at the end of sequence.

5.2.2. Item 2: The LCS is a known matrix containing known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

5.2.2.1. For gaseous samples, the LCS consists of a standard gas mixture containing the specified compounds.

5.2.2.2. One LCS is required daily for every batch of 20 samples or portion thereof, whichever is more frequent.

5.2.3. Item 3: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to

assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD).

5.2.4. Item 4: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

5.2.4.1. For gaseous samples, the MB consists of high-purity nitrogen.

5.2.4.2. One MB is required every daily for every batch of 20 samples or portion thereof, whichever is more frequent.

5.2.5. Items 5 and 7: Up to 10 (including QC check sample and method blank) injections. High concentration samples should be sufficiently diluted by using a smaller sample loop for analysis. Dilution of samples will result in increased reporting limits.

5.2.5.1. In order for a sample dilution analysis to be acceptable, the highest concentration of a target analyte must be in the upper half of the calibration curve. If the highest concentration of a target analyte is not in the upper half of the calibration curve, a more concentrated analysis must be performed.

6. REFERENCES

6.1. Technical Requirements for Environmental Laboratory Analytical Services, BP Laboratory Management Program (LaMP), Revision 09, July 30, 2007.

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Title : **EPA METHOD 5030C, PURGE-AND-TRAP FOR AQUEOUS SAMPLES**

Document No. : SOP-M212
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_____ **QA DEPARTMENT** 11-10-11 **DATE**

ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

1. METHOD IDENTIFICATION

1.1. EPA Method 5030**C**, Purge-and-Trap for Aqueous Samples.

2. APPLICABLE MATRICES

2.1. This method is applicable to aqueous samples, water miscible liquid samples, and high concentration soil and waste sample extracts prepared in EPA Method 5035A. It is also applicable to soil and waste samples not prepared via EPA Method 5035A as a modified method.

3. DETECTION LIMITS

3.1. Refer to the determinative (analytical) method for detection limit data.

4. SCOPE AND APPLICATION

4.1. EPA Method 5030C describes a purge-and-trap procedure for the analysis of volatile organic compounds (VOCs) in aqueous samples and water miscible liquid samples. It also describes the analysis of high concentration soil and waste sample extracts prepared in EPA Method 5035A. The gas chromatographic determinative steps are found in EPA Methods 8015C, 8021B, and 8260C.

4.1.1. This method in conjunction with EPA Method 8015C may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons (gasoline).

4.1.2. This method and EPA Method 8021B may be used for the analysis of the aromatic fraction (BTEX).

4.1.3. A total determinative analysis of gasoline fractions may be obtaining using EPA Method 8021B in series with EPA Method 8015C.

4.2. EPA Method 5030C can be used for most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, quantitation limits via GC or GC/MS analysis in some cases are approximately ten times higher with erratic precision due to poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a coated capillary column. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

4.2.1. The purging efficiency can be improved for water soluble analytes (e.g. ketones and alcohols) when purging at an elevated temperature of 80°C as compared to 20°C or 40°C.

4.3. Problems are often encountered with the analysis of fuel oxygenated compounds, both with the effectiveness of the determinative methods and the evaluation of the resulting data.

4.3.1. The fuel oxygenated compounds generally include methyl t-butyl ether (MTBE), ethyl t-butyl ether (ETBE), t-amyl methyl ether (TAME), diisopropyl ether (DIPE), and t-butyl alcohol (TBA). These oxygenated compounds can be classified as volatile organics based on their boiling points and vapor pressures. However, due to the high solubility of some of these oxygenated compounds in water, using purge-and-trap procedures that have been optimized for less water-soluble volatiles can potentially lead to significantly underestimating the oxygenate concentrations in the same samples.

4.3.2. Purging at an elevated temperature of 80°C and proper analytical column can improve the low-level concentration recoveries of the oxygenate compounds.

4.4. Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by direct injection of the sample into the chromatographic system or by dilution of the sample prior to the purge-and-trap process. Samples for the analysis of the following compounds can be prepared by this method:

acetone
acetonitrile
acrolein
acrylonitrile
allyl chloride
t-amyl methyl ether (TAME)
benzene
bromochloromethane
bromodichloromethane
bromoform
bromomethane
2-butanone
t-butyl alcohol (TBA)
carbon disulfide
carbon tetrachloride
chlorobenzene
chloroethane
2-chloroethyl vinyl ether
chloroform
chloromethane
chloroprene
1,2-dibromo-3-chloropropane
1,2-dibromoethane
dibromomethane
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
t-1,4-dichloro-2-butene
dichlorodifluoromethane
1,1-dichloroethane
1,2-dichloroethane
1,1-dichloroethene
c-1,2-dichloroethene
t-1,2-dichloroethene
1,2-dichloropropane
c-1,3-dichloropropene
t-1,3-dichloropropene
diethyl ether
diisopropyl ether (DIPE)
1,4-dioxane
ethylbenzene
ethyl methacrylate
ethyl t-butyl ether (ETBE)
hexachloro-1,3-butadiene
2-hexanone
iodomethane
isobutyl alcohol
isopropylbenzene
methacrylonitrile
methyl t-butyl ether (MTBE)
methylene chloride
methyl methacrylate
4-methyl-2-pentanone (MIBK)
naphthalene
propionitrile
styrene
1,1,1,2-tetrachloroethane
1,1,2,2-tetrachloroethane
tetrachloroethene
toluene
1,2,4-trichlorobenzene
1,1,1-trichloroethane
1,1,2-trichloroethane
trichloroethene
trichlorofluoromethane
1,2,3-trichloropropane
vinyl acetate
vinyl chloride
o-xylene
p/m-xylenes

4.5. This method is restricted to use by or under the supervision of analysts/technicians experienced in the use of purge-and-trap system and apparatus required to execute the procedure.

5. METHOD SUMMARY

5.1. For aqueous sample analysis, an inert gas is bubbled through a portion of the aqueous sample at ambient temperature or an elevated temperature depending on the desired target analytes, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.

5.2. For high concentration extract analysis, an aliquot of the methanol extract prepared in EPA Method 5035A is combined with organic-free reagent water and transferred to the purging chamber. The combined solution is then analyzed by purge-and-trap GC or GC/MS following the normal aqueous method.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.13. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.14. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.15. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.16. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.17. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.18. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.19. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.20. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.21. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.22. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.23. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.24. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.25. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.26. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

7. INTERFERENCES

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

7.1.1. Field and trip blanks prepared from an organic-free matrix and sample container, and carried through sampling and handling protocols serve as checks on such contamination.

7.2. Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

7.2.1. The use of high purity solvents, reagents and pre-conditioning of disposables that come in contact with the sample help to minimize interference problems.

7.3. Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems.

7.3.1. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials may out-gas organic components which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

7.3.2. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks.

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

7.4.1. To reduce the potential for carryover, the sample purging devices must be thoroughly rinsed between samples with an appropriate solvent. Purge and trap devices or headspace devices should be thoroughly baked out between samples.

7.4.2. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination.

7.4.2.1. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent sample(s), the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are <u>not</u> present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

7.4.3. Suspected high-concentration samples should be diluted and analyzed at the end of the sequence to prevent carryover contamination.

7.5. The laboratory where volatile analysis is performed should be complete free of solvents except limited amount of methanol.

7.5.1. Special precautions must be taken when analyzing for methylene chloride. The analytical and sample storage area should be isolated ***from all***

atmospheric sources of methylene chloride. Otherwise random background levels can result.

7.5.2. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing.

7.5.3. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid-liquid extraction procedures can contribute to sample contamination.

7.5.4. The presence of other organic solvents in the laboratory where volatile organics are analyzed can also lead to random background levels and the same precautions must be taken.

7.6. Contamination on an autosampler position can also occur. If an autosampler position is suspected of containing a sample with unusually high concentrations of analytes, an instrument blank or solvent blank should be placed on that position and the following position. Analyze and evaluate the blank for contamination prior to analyzing the remaining samples.

7.7. Refer to the determinative method for other potential interferences.

8. SAFETY

8.1. Processes that promote vaporization of volatile chemicals into the work area should be performed in a fume hood vented to the exterior of the laboratory

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Purge-and-Trap System: System configured with a purging chamber and the following components:

9.1.1. Purge-and-trap concentrator, equipped with a 5-mL or 25-mL fritted glass sparger, a trap, and a heater, EST Analytical Encon Purge and Trap Concentrator, OI Analytical Eclipse 4660 Purge-and-Trap Sample Concentrator, Teledyne Tekmar-Dohrmann 3100 Sample Concentrator, Teledyne Tekmar Velocity XPT Accelerated Purge and Trap System, Teledyne Tekmar Stratum PTC Purge and Trap Concentrator, or equivalent.

9.1.1.1. Condition a new trap according to manufacturer's instructions prior to initial use.

9.1.2. Purge-and-trap autosampler, EST Analytical Archon Water/Soil Autosampler, Teledyne Tekmar 2016/2032 Autosampler, Teledyne Tekmar SOLATek 72 Multi-Matrix Vial Autosampler, Varian Archon Purge and Trap Autosampler, or equivalent.

9.1.3. Trap packing material, Tenax® GC/Silica Gel/Charcoal adsorbents, Tenax® GC/Silica Gel/Carbosieve™ S-III adsorbents, Carbopack™ B/Carboxen™ 1000/ Carboxen™ 1001 adsorbents, Carbopack™ C/Carbopack™ B/Carboxen™ 1000/ Carboxen™ 1001 adsorbents, or equivalent.

9.2. Purge Gas: Helium, He, or nitrogen, N_2, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.3. Carrier Gas: Helium, He, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.4. Culture tubes, 18-mm × 150-mm (30-mL capacity), borosilicate glass, disposable.

9.4.1. The culture tubes are used as purge vessels.

9.5. VOA vials, 28-mm × 95-mm (40-mL capacity), screw top, clear or amber glass, with Teflon-lined open top or closed top screw caps and Teflon-lined septa, EPA VOA Vial or equivalent.

9.5.1. Bake VOA vials in an oven at 90°C for 24 hours prior to use.

9.5.2. The VOA vials may be used as purge vessels.

9.6. Storage vials, 15-mm × 45-mm (4-mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.

9.7. Volumetric flasks, 25-mL, 50-mL, or other capacity, glass, Class A.

9.8. Dispensers, 1–10-mL, 2.5–25-mL, and 5–50-mL, analog display, adjustable volume.

9.9. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certification.

9.10. Syringes, 1-mL, 5-mL, and 25-mL, gastight, Removable Needle (RN), Teflon Luer Lock (TLL), or SampleLock (SL) termination, Hamilton 1000 Series or equivalent with NIST Traceable Certification.

9.11. pH indicator paper, narrow range (0.0 – 3.0).

9.12. Spatula, stainless steel.

9.13. Balance, top loading, capable of weighing to the nearest 0.01 g.

9.14. Drying oven, capable of maintaining 90°C.

9.15. Gloves, heat resistant.

9.16. Refer to the specific SOPs of the determinative methods for additional equipment and supplies.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, nano-pure.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. Sodium thiosulfate, $Na_2S_2O_3$, anhydrous, white solid, reagent grade or equivalent.

10.1.4. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v).

10.1.4.1. Prepare the 10% $Na_2S_2O_3$ solution by dissolving 100 g of anhydrous $Na_2S_2O_3$ in reagent water and dilute to 1 L with additional reagent water.

10.1.5. Hydrochloric acid, HCl, 36.5–38.0% (v/v), concentrated, colorless to pale yellow liquid, reagent grade or equivalent.

10.1.6. Hydrochloric acid, HCl, 1:1 (v/v).

10.1.6.1. Prepare the 1:1 HCl solution by slowly adding concentrated HCl to equal volume of reagent water.

10.1.7. Sodium phosphate, tribasic, Na_3PO_4, dodecahydrate, white crystalline powder, reagent grade or equivalent.

10.1.8. Methanol, CH_3OH, clear colorless liquid, purge and trap grade or equivalent.

10.1.9. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Refer to the specific SOPs of the determinative methods for standards.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 40-mL pre-cleaned amber glass or clear glass VOA vials with Teflon-lined closures. Collect all samples in triplicate.

11.1.1. If the aqueous sample contains residual chlorine, collect the sample in a 125-mL amber glass container containing 4 drops of the 10% $Na_2S_2O_3$ solution. Gently swirl to mix the sample, and transfer to pre-cleaned amber glass or clear glass VOA vials.

11.1.1.1. Aqueous sample containing greater than 5 mg/L of residual chlorine may require additional amount of the dechlorinating agent.

11.1.2. Adjust the pH of the aqueous sample to < 2 by adding 1:1 HCl solution while stirring.

11.1.2.1. If a dechlorinating agent and acid are both added as preservatives, the aqueous sample must be dechlorinated first and then acidified.

11.1.2.2. Reactive compounds (e.g., acrolein, acrylonitrile, 2-chloroethyl vinyl ether, styrene, and vinyl chloride) are unstable at low pH. It is recommended that a second set of the aqueous sample without acid preservative be collected.

11.1.2.3. If fuel oxygenated compounds are the only analytes of interest, and the aqueous sample will be purged at an elevated temperature of 80°C, no acid preservation is required.

11.1.2.4. If carbonaceous materials are present, the aqueous sample should not be acid preserved due to possible effervescence and loss of volatile organic compounds.

11.1.3. Completely fill and hermetically seal the sample vial such that when the vial is inverted, no headspace is visible.

11.1.3.1. It is possible for the sample to generate some headspace in the form of micro bubbles during storage. The bubbles should not exceed ¼ in or 6 mm in diameter.

11.2. Solid samples should be collected in 4-oz or 8-oz pre-cleaned clear glass wide-mouth jars or 6-in decontaminated stainless steel or brass sleeves with Teflon-lined closures.

11.3. Oil samples should be collected in 40-mL pre-cleaned clear glass VOA vials with Teflon-lined closures.

11.4. Mobility-procedure extracts should be collected in 4-mL pre-cleaned clear glass storage vials with Teflon-lined closures.

11.4.1. If the mobility-procedure extract will not be analyzed within 24 hours, collect the mobility-procedure extract in a 40-mL pre-cleaned amber glass or clear glass VOA vial, and adjust the pH to < 2 by adding 1:1 HCl solution while stirring.

11.4.1.1. If effervescence (bubbling, hissing, or foaming of liquid as gas escapes) is observed upon adding 1:1 HCl solution, do not acid preserve the mobility-procedure extract.

11.4.2. Completely fill and hermetically seal the sample vial such that when the vial is inverted, no headspace is visible.

11.4.2.1. It is possible for the sample to generate some headspace in the form of micro bubbles during storage. The bubbles should not exceed ¼ in or 6 mm in diameter.

11.5. Samples shall be maintained in a chilled state (≤ 4°C) post sample collection until received at the laboratory. Samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.6. Upon receipt, the samples are stored in 0~6°C coolers.

11.6.1. Aqueous samples with acid preservation (pH < 2) must be analyzed within 14 days of sample collection.

11.6.2. Aqueous samples without acid preservation (pH ≥ 2) must be analyzed within 7 days of sample collection.

11.6.2.1. If reactive compounds are the analytes of interest, the aqueous samples should be analyzed as soon as possible.

11.6.3. Solid samples must be analyzed within 14 days of sample collection.

11.6.3.1. Solid samples may also be stored in a −10~−20°C freezer if solids content determination is not required.

11.6.3.1.1. Freezing solid samples within 48 hours of collection can minimize biodegradation of aromatic hydrocarbons (e.g. benzene, toluene, ethylbenzene, and xylenes).

11.6.4. High concentration (> 200 µg/kg) solid samples must be preserved with methanol and analyzed within 14 days of sample collection.

11.6.4.1. Methanol extracts shall be stored in a 0~6°C cooler with a minimum contact time of 24 hours between the solid sample and methanol prior to analysis.

11.6.5. Oil samples must be preserved with methanol and analyzed within 14 days of sample collection.

11.6.5.1. Methanol extracts shall be stored in a 0~6°C cooler with a minimum contact time of 24 hours between the oil sample and methanol prior to analysis.

11.6.6. Mobility-procedure extracts with acid preservation (pH < 2) must be analyzed within 14 days post mobility extraction for aqueous samples, or within 7 days post mobility extraction for solid samples.

11.6.6.1. Mobility-procedure extracts shall be stored in a 0~6°C cooler post mobility extraction if analysis is not to be performed within 24 hours.

11.6.7. Mobility-procedure extracts without acid preservation (pH ≥ 2) must be analyzed within 24 hours post mobility extraction.

11.7. Refer to the specific SOPs of the mobility extraction and determinative methods for additional information on sample preservation and holding times.

12. QUALITY CONTROL

12.1. Event Based Quality Control (LCS/LCSDs and MBs)

12.1.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory

control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.1.2. One LCS consisting of the specified compounds spiked into clean reagent water or washed sea sand is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent. The LCSD is handled identically to the LCS.

12.1.3. One MB consisting of clean reagent water or washed sea sand is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

12.1.4. The MB/LCS/LCSD is processed concurrently with the associated samples. In the processing of the MB/LCS/LCSD, reagents and procedures identical to those for actual samples are used (e.g., surrogates, internal standards, etc.).

12.2. Matrix Based Quality Control (Surrogates and MS/MSDs)

12.2.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD) and surrogates added to each sample.

12.2.2. One MS consisting of the actual sample matrix spiked with known concentrations of specific target analytes is required for every batch of 20 samples per matrix or portion thereof extracted concurrently. The MSD is handled identically to the MS.

12.2.3. The sample which is spiked for the MS/MSD is processed concurrently with the associated samples. In the processing of the MS/MSD, reagents and procedures identical to those for actual samples are used (e.g., surrogates, internal standards, etc.).

12.3. Refer to the specific SOPs of the determinative methods for additional information on quality control.

13. CALIBRATION AND STANDARDIZATION

13.1. Top Loading Balance

13.1.1. Calibrate the top loading balance at 1 g and 100 g using Class 2 weights.

13.1.2. Calibration shall be within ± 2% or ± 0.02 g, whichever is greater. If the values are not within these limits, recalibrate the balance.

13.2. Dispenser

13.2.1. Calibrate the dispenser according to the procedure outlined in the Dispenser Calibration Check Logbook.

14. ►PROCEDURE

14.1. Purge-and-Trap System Setup

14.1.1. Condition (heat) the trap daily for 10 minutes while backflushing at 180°C with the analytical column at 220°C prior to purge-and-trap extraction.

14.1.2. For EPA Method 8015C, use the following purge-and-trap operating parameters as guidance to purge and trap blank, standard, or sample.

Description	Purge-and-Trap Operating Parameter	
	Aqueous	Solid
Dry purge time	1 min	1 min
Purge gas flow rate	40 mL/min	40 mL/min
Purge time	11.0 ± 0.1 min	11.0 ± 0.1 min
Purge temperature	40°C	40°C
Desorb pre-heat temperature	245°C	245°C
Desorb gas flow rate	10 mL/min	10 mL/min
Desorb time	4 min	4 min
Desorb temperature	250°C	250°C
Backflush inert gas flow rate	20–60 mL/min	20–60 mL/min
Trap stand-by temperature	40°C	40°C
Bake time	10 min	10 min
Bake temperature	260°C	260°C

14.1.3. For EPA Method 8021B, use the following purge-and-trap operating parameters as guidance to purge and trap blank, standard, or sample.

Description	Purge-and-Trap Operating Parameter	
	Aqueous	Solid
Dry purge time	1 min	1 min

Description	Purge-and-Trap Operating Parameter	
	Aqueous	Solid
Purge gas flow rate	40 mL/min	40 mL/min
Purge time	11.0 ± 0.1 min	11.0 ± 0.1 min
Purge temperature	ambient	ambient
Desorb pre-heat temperature	245°C	245°C
Desorb gas flow rate	10 mL/min	10 mL/min
Desorb time	4 min	4 min
Desorb temperature	250°C	250°C
Backflush inert gas flow rate	20–60 mL/min	20–60 mL/min
Trap stand-by temperature	40°C	40°C
Bake time	10 min	10 min
Bake temperature	260°C	260°C

14.1.3.1. Using a wide-bore capillary column, the backflush inert gas flow rate will optimize at approximately 10–15 mL/min.

14.1.4. For EPA Method 8260C, use the following purge-and-trap operating parameters as guidance to purge and trap blank, standard, or sample.

Description	Purge-and-Trap Operating Parameter	
	Aqueous	Solid
Dry purge time	0.5–2.0 min	0.5–2.0 min
Purge gas flow rate	40 mL/min	40 mL/min
Purge time	11.0 ± 0.1 min	11.0 ± 0.1 min
Purge temperature	ambient or 40°C	40°C
Desorb pre-heat temperature	245°C	245°C
Desorb gas flow rate	10 mL/min	10 mL/min
Desorb time	0.5–2.0 min	0.5–2.0 min
Desorb temperature	250°C	250°C
Backflush inert gas flow rate	20–60 mL/min	20–60 mL/min
Trap stand-by temperature	40°C	40°C
Bake time	8 min	8 min
Bake temperature	280°C	280°C

14.1.4.1. The purge temperature may be set at 80°C for analyzing fuel oxygenated compounds.

14.1.4.2. The dry purge time and desorb time are set according to the manufacturer's recommendations.

14.1.5. Proper dry purge time and trap stand-by temperature depend on the trap packing material. Consult instructions from both the manufacturer of the purge-and-trap system and the supplier of the trap packing material.

14.1.6. If cross contamination and memory effects of later eluting compounds from a high concentration sample or even a standard become a problem, adjust the bake time and temperature or replace the trap packing material.

14.2. Precaution

14.2.1. The process of opening a sample or extract vial and taking an aliquot for purge-and-trap extraction destroys the integrity of the sample or extract for future analysis. Hence, employ one of the following techniques to maintain sample or extract integrity for re-analysis.

14.2.1.1. Use a sample or extract vial that was never opened for each analysis.

14.2.1.2. Take a second aliquot of the sample or extract at the same time and prepare it for re-analysis within 24 hours.

14.2.1.3. Draw an aliquot of the sample or extract by puncturing the septum of a sample or extract vial using a syringe equipped with a needle.

14.3. Calibration and Calibration Verification Standard Preparation

14.3.1. Allow working standard solution(s) to reach ambient temperature.

14.3.2. Pull the plunger of a 5-mL syringe and draw slightly more than 5 mL of clean reagent water.

14.3.3. Slowly dispense the excess reagent water while eliminating trapped air.

14.3.4. Adjust the volume of the reagent water in the barrel to exactly 5.00 mL.

14.3.5. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.3.6. Measure the appropriate volume (refer to the determinative method) of each working standard solution using a different syringe.

14.3.7. Transfer the working standard solution(s) into the same purge vessel.

14.3.7.1. The resulting solution is the calibration or calibration verification standard solution.

14.3.8. For EPA Methods 8015C and 8021B, if autosampler is not configured to inject surrogate standard solution(s) automatically, add the appropriate volume(s) of the surrogate standard solution(s) listed in the determinative method to all calibration and calibration verification standard solutions.

14.3.9. For EPA Method 8260C, if autosampler is not configured to inject surrogate and internal standard solution(s) automatically, add the appropriate volume(s) of the surrogate and internal standard solution(s) listed in the determinative method to all calibration and calibration verification standard solutions.

14.3.10. If the purge vessel is a VOA vial, seal it with a septum and an open top screw cap.

14.3.10.1. Improperly sealed purge vessel may cause leakage through the septum and low surrogate and internal standard recoveries.

14.3.11. Proceed to Section 14.11. for purge-and-trap extraction procedure.

14.4. Calibration and Calibration Verification Standard Preparation for EPA Method 8260C Lower Limits of Quantitation

14.4.1. Allow working standard solution(s) to reach ambient temperature.

14.4.2. Pull the plunger of a 25-mL syringe and draw slightly more than 20 mL of clean reagent water.

14.4.3. Slowly dispense the excess reagent water while eliminating trapped air.

14.4.4. Adjust the volume of the reagent water in the barrel to exactly 20.0 mL.

14.4.5. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.4.6. Measure the appropriate volume (refer to the determinative method) of each working standard solution using a different syringe.

14.4.7. Transfer the working standard solution(s) into the same purge vessel.

14.4.7.1. The resulting solution is the calibration or calibration verification standard solution.

14.4.8. If autosampler is not configured to inject surrogate and internal standard solution(s) automatically, add the appropriate volume(s) of the surrogate

and internal standard solution(s) listed in the determinative method to all calibration and calibration verification standard solutions.

14.4.9. If the purge vessel is a VOA vial, seal it with a septum and an open top screw cap.

14.4.9.1. Improperly sealed purge vessel may cause leakage through the septum and low surrogate and internal standard recoveries.

14.4.10. Proceed to Section 14.11. for purge-and-trap extraction procedure.

14.5. Aqueous Sample Preparation

14.5.1. If an aqueous sample containing MTBE, ETBE, TAME, or other fuel oxygenated ethers have been acid preserved with 1:1 HCl solution, and will be purged at an elevated temperature, adjust the pH of the aqueous sample to > 10 with $Na_3PO_4 \cdot 12H_2O$.

14.5.1.1. Adjust the pH of each associated QC sample with $Na_3PO_4 \cdot 12H_2O$ to the same pH.

14.5.2. Allow an aqueous sample to reach ambient temperature, and the suspended particulates, if any, in the aqueous sample to settle.

14.5.2.1. Do not subsample the suspended particulates.

14.5.3. For a suspected high concentration aqueous sample, estimate the volume of the aqueous sample to be diluted.

14.5.3.1. To prevent excessive dilution, the highest instrument response of a target analyte in the diluted sample must be in the upper half of the calibration range.

14.5.3.2. Extremely high concentration aqueous sample may be serially diluted, if necessary.

14.5.4. If no dilution is required, prepare the aqueous sample as follows:

14.5.4.1. Pull the plunger of a 5-mL syringe and draw slightly more than 5 mL of the aqueous sample.

14.5.4.1.1. For MB/LCS/LCSD, draw slightly more than 5 mL of clean reagent water.

14.5.4.1.2. For MS/MSD, draw slightly more than 5 mL of aqueous sample in each analytical batch selected for spiking.

14.5.4.2. Slowly dispense the excess aqueous sample while eliminating trapped air.

14.5.4.3. Adjust the volume of the aqueous sample in the barrel to exactly 5.00 mL. Record the volume to the smallest graduation.

14.5.4.3.1. For MB/LCS/LCSD, adjust the volume of the reagent water to exactly 5.00 mL.

14.5.4.3.2. For MS/MSD, adjust the volume of the aqueous sample to exactly 5.00 mL.

14.5.4.4. Transfer the aqueous sample into a clean purge vessel and label the purge vessel with a sharpie.

14.5.5. If dilution is required, and the estimated volume of the aqueous sample to be diluted is greater than or equal to 50 µL, prepare the aqueous sample as follows:

14.5.5.1. Pull the plunger of a 5-mL syringe and draw the appropriate volume of clean reagent water.

14.5.5.1.1. For MB/LCS/LCSD, draw slightly more than 5 mL of clean reagent water.

14.5.5.1.2. For MS/MSD, draw the appropriate volume of clean reagent water.

14.5.5.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.5.5.3. Adjust the volume of the reagent water in the barrel such that the total volume of the reagent water and the aqueous sample to be diluted is 5.00 mL.

14.5.5.3.1. For MB/LCS/LCSD, adjust the volume of the reagent water to exactly 5.00 mL.

14.5.5.3.2. For MS/MSD, adjust the volume of the reagent water such that the total volume of the reagent water and the aqueous sample to be diluted is 5.00 mL.

14.5.5.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.5.5.5. Measure the appropriate volume of the aqueous sample using a different syringe. Record the volume to the smallest graduation.

14.5.5.5.1. For MS/MSD, measure the same volume of aqueous sample in each analytical batch selected for spiking.

14.5.5.6. Transfer the aqueous sample into the same purge vessel.

14.5.5.6.1. The resulting solution is the diluted sample.

14.5.6. If dilution is required, and the estimated volume of the aqueous sample to be diluted is less than 50 µL, prepare the aqueous sample as follows:

14.5.6.1. Pull the plunger of a 5-mL syringe and draw slightly more than 5 mL of clean reagent water.

14.5.6.1.1. For MB/LCS/LCSD/MS/MSD, draw slightly more than 5 mL of clean reagent water.

14.5.6.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.5.6.3. Adjust the volume of the reagent water in the barrel to exactly 5.00 mL.

14.5.6.3.1. For MB/LCS/LCSD/MS/MSD, adjust the volume of the reagent water to exactly 5.00 mL.

14.5.6.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.5.6.5. Measure the appropriate volume of the aqueous sample using a different syringe. Record the volume to the smallest graduation.

14.5.6.5.1. For MS/MSD, measure the same volume of aqueous sample in each analytical batch selected for spiking.

14.5.6.6. Transfer the aqueous sample into the same purge vessel.

14.5.6.6.1. The resulting solution is the diluted sample.

14.5.7. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spikes and laboratory control samples.

14.5.8. For EPA Methods 8015C and 8021B, if autosampler is not configured to inject surrogate standard solution(s) automatically, add the appropriate volume(s) of the surrogate standard solution(s) listed in the determinative method to all samples, matrix spikes, laboratory control samples, and method blanks.

14.5.9. For EPA Method 8260C, if autosampler is not configured to inject surrogate and internal standard solution(s) automatically, add the appropriate volume(s) of the surrogate and internal standard solution(s) listed in the determinative method to all samples, matrix spikes, laboratory control samples, and method blanks.

14.5.10. If the purge vessel is a VOA vial, seal it with a septum and an open top screw cap.

14.5.10.1. Improperly sealed purge vessel may cause leakage through the septum and low surrogate and internal standard recoveries.

14.5.11. Proceed to Section 14.11. for purge-and-trap extraction procedure.

14.6. Aqueous Sample Preparation for EPA Method 8260C Lower Limits of Quantitation

14.6.1. If an aqueous sample containing MTBE, ETBE, TAME, or other fuel oxygenated ethers have been acid preserved with 1:1 HCl solution, and will be purged at an elevated temperature, adjust the pH of the aqueous sample to > 10 with $Na_3PO_4 \cdot 12H_2O$.

14.6.1.1. Adjust the pH of each associated QC sample with $Na_3PO_4 \cdot 12H_2O$ to the same pH.

14.6.2. Allow an aqueous sample to reach ambient temperature, and the suspended particulates, if any, in the aqueous sample to settle.

14.6.2.1. Do not subsample the suspended particulates.

14.6.3. For a suspected high concentration aqueous sample, estimate the volume of the aqueous sample to be diluted.

14.6.3.1. To prevent excessive dilution, the highest instrument response of a target analyte in the diluted sample must be in the upper half of the calibration range.

14.6.3.2. Extremely high concentration aqueous sample may be serially diluted, if necessary.

14.6.4. If no dilution is required, prepare the aqueous sample as follows:

14.6.4.1. Pull the plunger of a 25-mL syringe and draw slightly more than 20 mL of the aqueous sample.

14.6.4.1.1. For MB/LCS/LCSD, draw slightly more than 20 mL of clean reagent water.

14.6.4.1.2. For MS/MSD, draw slightly more than 5 mL of aqueous sample in each analytical batch selected for spiking.

14.6.4.2. Slowly dispense the excess aqueous sample while eliminating trapped air.

14.6.4.3. Adjust the volume of the aqueous sample in the barrel to exactly 20.0 mL. Record the volume to the smallest graduation.

14.6.4.3.1. For MB/LCS/LCSD, adjust the volume of the reagent water to exactly 20.0 mL.

14.6.4.3.2. For MS/MSD, adjust the volume of the aqueous sample to exactly 20.0 mL.

14.6.4.4. Transfer the aqueous sample into a clean purge vessel and label the purge vessel with a sharpie.

14.6.5. If dilution is required, and the estimated volume of the aqueous sample to be diluted is greater than or equal to 250 µL, prepare the aqueous sample as follows:

14.6.5.1. Pull the plunger of a 25-mL syringe and draw the appropriate volume of clean reagent water.

14.6.5.1.1. For MB/LCS/LCSD, draw slightly more than 20 mL of clean reagent water.

14.6.5.1.2. For MS/MSD, draw the appropriate volume of clean reagent water.

14.6.5.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.6.5.3. Adjust the volume of the reagent water in the barrel such that the total volume of the reagent water and the aqueous sample to be diluted is 20.0 mL.

14.6.5.3.1. For MB/LCS/LCSD, adjust the volume of the reagent water to exactly 20.0 mL.

14.6.5.3.2. For MS/MSD, adjust the volume of the reagent water such that the total volume of the reagent water and the aqueous sample to be diluted is 20.0 mL.

14.6.5.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.6.5.5. Measure the appropriate volume of the aqueous sample using a different syringe. Record the volume to the smallest graduation.

14.6.5.5.1. For MS/MSD, measure the same volume of aqueous sample in each analytical batch selected for spiking.

14.6.5.6. Transfer the aqueous sample into the same purge vessel.

14.6.5.6.1. The resulting solution is the diluted sample.

14.6.6. If dilution is required, and the estimated volume of the aqueous sample to be diluted is less than 250 µL, prepare the aqueous sample as follows:

14.6.6.1. Pull the plunger of a 25-mL syringe and draw slightly more than 20 mL of clean reagent water.

14.6.6.1.1. For MB/LCS/LCSD/MS/MSD, draw slightly more than 20 mL of clean reagent water.

14.6.6.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.6.6.3. Adjust the volume of the reagent water in the barrel to exactly 20.0 mL.

14.6.6.3.1. For MB/LCS/LCSD/MS/MSD, adjust the volume of the reagent water to exactly 20.0 mL.

14.6.6.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.6.6.5. Measure the appropriate volume of the aqueous sample using a different syringe. Record the volume to the smallest graduation.

14.6.6.5.1. For MS/MSD, measure the same volume of aqueous sample in each analytical batch selected for spiking.

14.6.6.6. Transfer the aqueous sample into the same purge vessel.

14.6.6.6.1. The resulting solution is the diluted sample.

14.6.7. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spikes and laboratory control samples.

14.6.8. If autosampler is not configured to inject surrogate and internal standard solution(s) automatically, add the appropriate volume(s) of the surrogate and internal standard solution(s) listed in the determinative method to all samples, matrix spikes, laboratory control samples, and method blanks.

14.6.9. If the purge vessel is a VOA vial, seal it with a septum and an open top screw cap.

14.6.9.1. Improperly sealed purge vessel may cause leakage through the septum and low surrogate and internal standard recoveries.

14.6.10. Proceed to Section 14.11. for purge-and-trap extraction procedure.

14.7. Solid Sample Preparation

14.7.1. Label a clean VOA vial with a sharpie. Add a clean stir bar to the VOA vial and tare.

14.7.1.1. If the purge-and-trap autosampler employs a means of stirring sample other than a magnetic stirrer (e.g., sonication or other mechanical means), the stir bar may be omitted.

14.7.1.2. The VOA vial is used as the purge vessel.

14.7.2. Allow a solid sample to reach ambient temperature.

14.7.3. Composite the solid sample as outlined in the current revision of SOP-M230.

14.7.4. If sample result is to be reported on a dry weight basis, weigh a second portion of the solid sample and determine the solids content as outlined in the current revision of SOP-M700.

14.7.5. If the highest instrument response of a target analyte is suspected to exceed the calibration range, weigh and prepare a second portion of the solid sample according to Section 14.8.

14.7.6. For EPA Methods 8015C and 8021B, measure 1.00 ± 0.10 g (wet weight) of the solid sample into the tared purge vessel. Record the mass to the nearest 0.01 g.

14.7.6.1. For MB/LCS/LCSD, measure exactly 1.00 g of washed sea sand. Record the washed sea sand identification number in the sample preparation logbook.

14.7.6.2. For MS/MSD, measure exactly 1.00 g of solid sample in each analytical batch selected for spiking.

14.7.7. For EPA Method 8260C, measure 5.00 ± 0.50 g (wet weight) of the solid sample into the tared purge vessel. Record the mass to the nearest 0.01 g.

14.7.7.1. For MB/LCS/LCSD, measure exactly 5.00 g of washed sea sand. Record the washed sea sand identification number in the sample preparation logbook.

14.7.7.2. For MS/MSD, measure exactly 5.00 g of solid sample in each analytical batch selected for spiking.

14.7.8. Add 5 mL of reagent water to the purge vessel and seal it with a septum and an open top screw cap.

14.7.8.1. Improperly sealed purge vessel may cause leakage through the septum and low surrogate and internal standard recoveries.

14.7.9. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spikes and laboratory control samples just prior to analysis.

14.7.9.1. Introduce the spike standard solution into the purge vessel by puncturing the septum using a syringe equipped with a small-gauge needle.

14.7.10. For EPA Methods 8015C and 8021B, if autosampler is not configured to inject surrogate standard solution(s) automatically, add the appropriate volume(s) of the surrogate standard solution(s) listed in the determinative method to all samples, matrix spikes, laboratory control samples, and method blanks just prior to analysis.

14.7.10.1. Introduce the surrogate standard solution into the purge vessel by puncturing the septum using a syringe equipped with a small-gauge needle.

14.7.11. For EPA Method 8260C, if autosampler is not configured to inject surrogate and internal standard solution(s) automatically, add the appropriate volume(s) of the surrogate and internal standard solution(s) listed in the determinative method to all samples, matrix spikes, laboratory control samples, and method blanks just prior to analysis.

14.7.11.1. Introduce the surrogate and internal standard solution into the purge vessel by puncturing the septum using a syringe equipped with a small-gauge needle.

14.7.12. Proceed to Section 14.11. for purge-and-trap extraction procedure.

14.8. High Concentration Solid or Oil Sample Preparation

14.8.1. Label a clean VOA vial with a sharpie and tare.

14.8.2. Allow a solid or oil sample to reach ambient temperature.

14.8.3. Composite the solid sample as outlined in the current revision of SOP-M230.

14.8.4. If sample result is to be reported on a dry weight basis, weigh a second portion of the solid sample and determine the solids content as outlined in the current revision of SOP-M700.

14.8.5. For EPA Methods 8015C and 8021B, measure 1.00 ± 0.10 g (wet weight) of the solid or oil sample into the tared VOA vial. Record the mass to the nearest 0.01 g.

14.8.5.1. For MB/LCS/LCSD, measure exactly 1.00 g of washed sea sand. Record the washed sea sand identification number in the sample preparation logbook.

14.8.5.2. For MS/MSD, measure exactly 1.00 g of solid or oil sample in each analytical batch selected for spiking.

14.8.6. For EPA Method 8260C, measure 5.00 ± 0.50 g (wet weight) of the solid or oil sample into the tared VOA vial. Record the mass to the nearest 0.01 g.

14.8.6.1. For MB/LCS/LCSD, measure exactly 5.00 g of washed sea sand. Record the washed sea sand identification number in the sample preparation logbook.

14.8.6.2. For MS/MSD, measure exactly 5.00 g of solid or oil sample in each analytical batch selected for spiking.

14.8.7. Add 10 mL of methanol to the VOA vial and seal it with a septum and an open top screw cap.

14.8.7.1. Improperly sealed VOA vial may cause leakage through the septum.

14.8.8. Proceed to Section 14.10. for methanol extract preparation procedure.

14.9. Mobility-Procedure Extract Preparation

14.9.1. If a mobility-procedure extract containing MTBE, ETBE, TAME, or other fuel oxygenated ethers have been acid preserved with 1:1 HCl solution, and will be purged at an elevated temperature, adjust the pH of the mobility-procedure extract to > 10 with $Na_3PO_4 \cdot 12H_2O$.

14.9.1.1. Adjust the pH of each associated QC mobility-procedure extract with $Na_3PO_4 \cdot 12H_2O$ to the same pH.

14.9.2. Allow a mobility-procedure extract to reach ambient temperature, and the suspended particulates, if any, in the mobility-procedure extract to settle.

14.9.2.1. Do not subsample the suspended particulates.

14.9.3. Estimate the volume of the mobility-procedure extract to be diluted.

14.9.3.1. To prevent excessive dilution, the highest instrument response of a target analyte in the diluted mobility-procedure extract must be in the upper half of the calibration range.

14.9.3.2. Extremely high concentration mobility-procedure extract may be serially diluted, if necessary.

14.9.4. If the estimated volume of the mobility-procedure extract to be diluted is greater than or equal to 50 µL, prepare the mobility-procedure extract as follows:

14.9.4.1. Pull the plunger of a 5-mL syringe and draw the appropriate volume of clean reagent water.

14.9.4.1.1. For MB/LCS/LCSD/MS/MSD, draw the appropriate volume of clean reagent water.

14.9.4.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.9.4.3. Adjust the volume of the reagent water in the barrel such that the total volume of the reagent water and the mobility-procedure extract to be diluted is 5.00 mL.

14.9.4.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.9.4.5. Measure the appropriate volume of the mobility-procedure extract using a different syringe. Record the volume to the smallest graduation.

14.9.4.5.1. For MB/LCS/LCSD, measure the same volume of mobility-procedure extract designated as MB/LCS/LCSD. Refer to the mobility extraction method for information.

14.9.4.5.2. For MS/MSD, measure the same volume of mobility-procedure extract designated as MS/MSD. Refer to the mobility extraction method for information.

14.9.4.6. Transfer the mobility-procedure extract into the same purge vessel.

14.9.4.6.1. The resulting solution is the diluted mobility-procedure extract.

14.9.5. If the estimated volume of the mobility-procedure extract to be diluted is less than 50 µL, prepare the mobility-procedure extract as follows:

14.9.5.1. Pull the plunger of a 5-mL syringe and draw slightly more than 5 mL of clean reagent water.

14.9.5.1.1. For MB/LCS/LCSD/MS/MSD, draw slightly more than 5 mL of clean reagent water.

14.9.5.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.9.5.3. Adjust the volume of the reagent water in the barrel to exactly 5.00 mL.

14.9.5.3.1. For MB/LCS/LCSD/MS/MSD, adjust the volume of the reagent water to exactly 5.00 mL.

14.9.5.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.9.5.5. Measure the appropriate volume of the mobility-procedure extract using a different syringe. Record the volume to the smallest graduation.

14.9.5.5.1. For MB/LCS/LCSD, measure the same volume of mobility-procedure extract designated as MB/LCS/LCSD. Refer to the mobility extraction method for information.

14.9.5.5.2. For MS/MSD, measure the same volume of mobility-procedure extract designated as MS/MSD. Refer to the mobility extraction method for information.

14.9.5.6. Transfer the mobility-procedure extract into the same purge vessel.

14.9.5.6.1. The resulting solution is the diluted mobility-procedure extract.

14.9.6. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spike and laboratory control sample mobility-procedure extracts.

14.9.7. For EPA Methods 8015C and 8021B, if autosampler is not configured to inject surrogate standard solution(s) automatically, add the appropriate volume(s) of the surrogate standard solution(s) listed in the determinative method to all sample, matrix spike, laboratory control sample, and method blank mobility-procedure extracts.

14.9.8. For EPA Method 8260C, if autosampler is not configured to inject surrogate and internal standard solution(s) automatically, add the appropriate volume(s) of the surrogate and internal standard solution(s) listed in the determinative method to all sample, matrix spike, laboratory control sample, and method blank mobility-procedure extracts.

14.9.9. If the purge vessel is a VOA vial, seal it with a septum and an open top screw cap.

14.9.9.1. Improperly sealed purge vessel may cause leakage through the septum and low surrogate and internal standard recoveries.

14.9.10. Proceed to Section 14.11. for purge-and-trap extraction procedure.

14.10. Methanol Extract Preparation

14.10.1. Allow a methanol extract to reach ambient temperature, and the suspended particulates, if any, in the methanol extract to settle.

14.10.1.1. Do not subsample the suspended particulates.

14.10.2. Estimate the volume of the methanol extract to be diluted.

14.10.2.1. To prevent excessive dilution, the highest instrument response of a target analyte in the diluted methanol extract must be in the upper half of the calibration range.

14.10.2.2. Extremely high concentration methanol extract may be serially diluted, if necessary.

14.10.3. If the estimated volume of the methanol extract to be diluted is greater than or equal to 50 µL, prepare the methanol extract as follows:

14.10.3.1. Pull the plunger of a 5-mL syringe and draw the appropriate volume of clean reagent water.

14.10.3.1.1. For MB/LCS/LCSD/MS/MSD, draw the appropriate volume of clean reagent water.

14.10.3.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.10.3.3. Adjust the volume of the reagent water in the barrel such that the total volume of the reagent water and the methanol extract to be diluted is 5.00 mL.

14.10.3.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.10.3.5. Measure the appropriate volume of the methanol extract using a different syringe. Record the volume to the smallest graduation.

14.10.3.5.1. For MB/LCS/LCSD, measure the same volume of methanol extract designated as MB/LCS/LCSD.

14.10.3.5.2. For MS/MSD, measure the same volume of methanol extract designated as MS/MSD.

14.10.3.6. Transfer the methanol extract into the same purge vessel.

14.10.3.6.1. The resulting solution is the diluted methanol extract.

14.10.4. If the estimated volume of the methanol extract to be diluted is less than 50 µL, prepare the methanol extract as follows:

14.10.4.1. Pull the plunger of a 5-mL syringe and draw slightly more than 5 mL of clean reagent water.

14.10.4.1.1. For MB/LCS/LCSD/MS/MSD, draw slightly more than 5 mL of clean reagent water.

14.10.4.2. Slowly dispense the excess reagent water while eliminating trapped air.

14.10.4.3. Adjust the volume of the reagent water in the barrel to exactly 5.00 mL.

14.10.4.3.1. For MB/LCS/LCSD/MS/MSD, adjust the volume of the reagent water to exactly 5.00 mL.

14.10.4.4. Transfer the reagent water into a clean purge vessel and label the purge vessel with a sharpie.

14.10.4.5. Measure the appropriate volume of the methanol extract using a different syringe. Record the volume to the smallest graduation.

14.10.4.5.1. For MB/LCS/LCSD, measure the same volume of methanol extract designated as MB/LCS/LCSD.

14.10.4.5.2. For MS/MSD, measure the same volume of methanol extract designated as MS/MSD.

14.10.4.6. Transfer the methanol extract into the same purge vessel.

14.10.4.6.1. The resulting solution is the diluted methanol extract.

14.10.5. Add the appropriate volume(s) of the spike standard solution(s) listed in the determinative method to all matrix spike and laboratory control sample methanol extracts.

14.10.6. For EPA Methods 8015C and 8021B, if autosampler is not configured to inject surrogate standard solution(s) automatically, add the appropriate volume(s) of the surrogate standard solution(s) listed in the determinative method to all sample, matrix spike, laboratory control sample, and method blank methanol extracts.

14.10.7. For EPA Method 8260C, if autosampler is not configured to inject surrogate and internal standard solution(s) automatically, add the appropriate volume(s) of the surrogate and internal standard solution(s) listed in the determinative method to all sample, matrix spike, laboratory control sample, and method blank methanol extracts.

14.10.8. If the purge vessel is a VOA vial, seal it with a septum and an open top screw cap.

14.10.8.1. Improperly sealed purge vessel may cause leakage through the septum and low surrogate and internal standard recoveries.

14.10.9. Proceed to Section 14.11. for purge-and-trap extraction procedure.

14.11. Load the purge vessels into the purge-and-trap autosampler, set up the GC or GC/MS operating conditions as specified in the determinative method, and start purge-and-trap extraction and analysis.

14.12. Thoroughly document all aspects of the purge-and-trap sample preparation and extraction in a sample preparation logbook and an instrument run logbook, or on an instrument run sequence table.

14.13. Data Interpretation

14.13.1. If the result of a solid sample is to be reported on the dry weight basis, calculate the solids content. The formula for calculating solids content is listed in Section 15.2.

14.13.2. If the result of a methanol extracted solid or oil sample is to be reported on the wet weight basis, calculate the preparation factor without moisture correction. The formula for calculating preparation factor without moisture correction is listed in Section 15.4.

14.13.3. If the result of a methanol extracted solid sample with less than or equal to 10% of moisture content is to be reported on the dry weight basis, calculate the preparation factor without methanol/water dilution factor correction. The formula for calculating preparation factor without methanol/water dilution factor correction is listed in Section 15.5.

14.13.4. If the result of a methanol extracted solid sample with greater than 10% of moisture content is to be reported on a dry weight basis, calculate the preparation factor with methanol/water dilution factor correction. The formula for calculating preparation factor with methanol/water dilution factor correction is listed in Section 15.6.

14.14. Refer to the determinative method for additional information on instrument setup, analytical procedure, and data interpretation.

15. CALCULATIONS

15.1. The dilution factor is calculated as follows:

$$D = \frac{V_f}{V_i}$$

where: D = dilution factor.
V_f = volume of sample or extract after dilution in mL.
V_i = volume of sample or extract before dilution in mL.

15.2. The solids content for a sample is calculated as follows:

$$C_{ss} = \frac{M_2 - M_0}{M_1 - M_0} \times 100$$

where: C_{ss} = solids content in %.
M_2 = mass of weighing dish and oven-dried sample in g.
M_0 = mass of weighing dish in g.
M_1 = mass of weighing dish and as-received sample in g.

15.3. The moisture content for a sample is calculated as follows:

$$C_w = \frac{M_1 - M_2}{M_1 - M_0} \times 100 \qquad C_w = 100\% - C_{ss}$$

where: C_w = moisture content in %.
M_1 = mass of weighing dish and as-received sample in g.

M_2 = mass of weighing dish and oven-dried sample in g.
M_0 = mass of weighing dish in g.

15.4. The preparation factor without moisture correction for a methanol extracted solid (or oil) sample is calculated as follows:

$$P_1 = \frac{V_m}{W_S}$$

where: P_1 = preparation factor without moisture correction for methanol extracted solid (or oil) sample in mL/g.
V_m = volume of methanol added in mL.
Unless specified otherwise, V_m = 10.
W_S = mass of solid (or oil) sample methanol extracted in g.

15.5. The preparation factor <u>without</u> methanol/water dilution factor correction for a methanol extracted solid sample is calculated as follows:

$$P_2 = \frac{V_m}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: P_2 = preparation factor without methanol/water dilution factor correction for methanol extracted solid sample in mL/g.
V_m = volume of methanol added in mL.
Unless specified otherwise, V_m = 10.
W_S = mass of solid sample methanol extracted in g.
C_{ss} = solids content in %.

15.6. The preparation factor <u>with</u> methanol/water dilution factor correction for a methanol extracted solid sample is calculated as follows:

$$P_3 = \frac{V_m + \left(\frac{C_w}{100} \times W_S \times \rho\right)}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: P_3 = preparation factor with methanol/water dilution factor correction for methanol extracted solid sample in mL/g.
V_m = volume of methanol added in mL.
Unless specified otherwise, V_m = 10.
C_w = moisture content in %.
W_S = mass of solid sample methanol extracted in g.
ρ = density of water in mL/g. Assume ρ = 1.
C_{ss} = solids content in %.

15.7. Refer to the mobility extraction and determinative methods for additional calculations.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Refer to the determinative method for data assessment and acceptance criteria.

18.2. Additional information regarding internal quality control checks is provided in SOP-T020.

18.3. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Refer to the determinative method for contingencies for out-of-control or unacceptable data.

20.2. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. Purge-and-Trap for Aqueous Samples, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 5030C, USEPA, Revision 3, May 2003.

22.2. Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 5035A, USEPA, Revision 1, July 2002.

22.3. Determinative Chromatographic Separations, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000C, USEPA, Revision 3, March 2003.

22.4. Quality Control, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.5. Choosing the Correct Procedure, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.6. Organic Analytes, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, February 2007.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Additional Quality Control Criteria for Department of Defense Project.

23.2. Appendix B: Additional Quality Control Criteria for BP Project.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 5030C are noted.

24.1.1. Sample Collection, Preservation, Containers and Holding Times

24.1.1.1. The concentration and the volume of the dechlorinating agent used for aqueous sample preservation are modified.

24.1.2. Procedure

24.1.2.1. The purge temperature and desorb temperature are modified.

24.1.2.2. The sample preparation and dilution techniques are modified.

24.1.2.3. The sample volume required for purge-and-trap extraction via EPA Method 8260C lower limits of quantitation is modified.

Appendix A

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

1. METHOD IDENTIFICATION

1.1. EPA Method 5030C, Purge-and-Trap for Aqueous Samples – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

4. QUALITY CONTROL

4.1. Matrix Based Quality Control (MS/MSDs)

4.1.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

5. REFERENCES

5.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.1, April 2009.

Appendix B

ADDITIONAL QUALITY CONTROL CRITERIA FOR BP PROJECT

1. METHOD IDENTIFICATION

1.1. EPA Method 5030C, Purge-and-Trap for Aqueous Samples – Additional Quality Control Criteria for BP Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The use of a standard from a second lot as the second source standard is acceptable if written warranties demonstrating that the standards from two different lots are not prepared from the same reference materials are obtained from the manufacturer. "Manufacturer" refers to the producer of the standard, not the vendor.

3.2. For solid sample to be extracted with methanol, add the spike standard and surrogate standard prior to the addition of methanol.

4. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

4.1. All solid samples must be preserved within 48 hours of sample collection, and analyzed within 48 hours or 14 days of sample collection based on the preservation method chosen.

5. QUALITY CONTROL

5.1. Event Based Quality Control (LCS/LCSDs and MBs)

5.1.1. One LCS consisting of the specified compounds spiked into clean reagent water is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent, within an 8-hour preparation/extraction event. The LCSD is handled identically to the LCS.

5.1.2. One MB consisting of clean reagent water is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent, within an 8-hour preparation/extraction event.

5.2. Matrix Based Quality Control (MS/MSDs)

5.2.1. One MS consisting of the actual sample matrix spiked with known concentrations of specific target analytes is required for every batch of 20 samples per matrix or portion thereof extracted concurrently within an 8-hour preparation/extraction event. The MSD is handled identically to the MS.

5.2.2. The sample selected for spiking must be one of the samples collected for the specific BP project. If 10 or less BP samples are received, and no MS is designated, then a non-BP sample may be used.

5.2.3. Samples identified as trip or field blanks cannot be used for MS/MSD.

6. PROCEDURE

6.1. Organic extracts must be stored in the same type of vials (amber glass or clear glass) as the associated standards at the appropriate storage temperature.

7. REFERENCES

7.1. Technical Requirements for Environmental Laboratory Analytical Services, BP Laboratory Management Program (LaMP), Revision 09, July 30, 2007.

Title : **EPA METHOD 8260B, VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY / MASS SPECTROMETRY (GC/MS)**

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QA DEPARTMENT **DATE**

ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

1. METHOD IDENTIFICATION

1.1. EPA Method 8260B, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS).

2. APPLICABLE MATRICES

2.1. This method is applicable for ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

3. DETECTION LIMITS

3.1. The estimated quantitation limits (EQLs) for this method are as follows:

	Soil	Water	Oil
VOCs	5.0~250 µg/kg (wet-weight)	0.5~100 µg/L	500~25000 µg/kg
Lower-QL VOCs		0.5~50.0 µg/L	

3.2. The EQLs will be proportionally higher for samples which require dilution or reduced sample size.

4. SCOPE AND APPLICATION

4.1. EPA Method 8260B is used to determine the concentrations of most volatile organic compounds (VOCs) that have boiling points below 200°C and are insoluble or slightly soluble in water.

4.2. The following compounds are routinely determined by this method. Compounds with poor chromatographic behavior, poor purging efficiency, or other difficulties are indicated with the "*" symbol.

acetone*
t-amyl methyl ether (TAME)
benzene
bromobenzene
bromochloromethane
bromodichloromethane
bromoform
bromomethane*
2-butanone*
t-butyl alcohol (TBA)
n-butylbenzene
s-butylbenzene
t-butylbenzene
carbon disulfide
carbon tetrachloride
chlorobenzene
chloroethane
chloroform
chloromethane*
2-chlorotoluene
4-chlorotoluene
dibromochloromethane
1,2-dibromo-3-chloropropane
1,2-dibromoethane (EDB)
dibromomethane
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
dichlorodifluoromethane*
1,1-dichloroethane
1,2-dichloroethane
1,1-dichloroethene
c-1,2-dichloroethene
t-1,2-dichloroethene
1,2-dichloropropane
1,3-dichloropropane
2,2-dichloropropane
1,1-dichloropropene
c-1,3-dichloropropene
t-1,3-dichloropropene
diisopropyl ether (DIPE)
ethanol*
ethylbenzene
ethyl t-butyl ether (ETBE)
hexachloro-1,3-butadiene
2-hexanone*
isopropylbenzene
p-isopropyltoluene
methyl t-butyl ether (MTBE)
methylene chloride
4-methyl-2-pentanone (MIBK)*
naphthalene
n-propylbenzene
styrene

1,1,1,2-tetrachloroethane	1,2,4-trichlorobenzene	1,2,4-trimethylbenzene
1,1,2,2-tetrachloroethane	1,1,1-trichloroethane	1,3,5-trimethylbenzene
tetrachloroethene	1,1,2-trichloroethane	vinyl acetate
tetrahydrofuran	trichloroethene	vinyl chloride
toluene	trichlorofluoromethane	o-xylene
1,2,3-trichlorobenzene	1,2,3-trichloropropane	p/m-xylenes

4.3. The following compounds may also be determined by this method. Compounds with poor chromatographic behavior, poor purging efficiency, or other difficulties are indicated with the "*" symbol. Compounds requiring an unpreserved aqueous sample aliquot for analysis are denoted with the "**" symbol.

acetonitrile	hexane
acrolein	iodomethane
acrylonitrile	isobutyl alcohol
allyl chloride	isopropanol*
1,3-butadiene	methacrylonitrile
2-chloroethyl vinyl ether**	methyl acetate
chloroprene	methyl methacrylate
1-chloropropane	methylcyclohexane
2-chloropropane	propanedinitrile
cyclohexane	propionitrile
t-1,4-dichloro-2-butene	thiophene
diethyl ether	1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)
1,4-dioxane*	2,2,4-trimethyl pentane
ethyl methacrylate	

4.4. Upon client request, additional target analytes may be added to this analysis. However, it needs to be demonstrated that any added compounds lend themselves to EPA Method 8260B determination, either by regulatory reference or validation studies.

4.5. Most volatile organic compounds may be introduced into the GC/MS system via purge-and-trap method (EPA Method 5030C) and closed system purge-and-trap method (EPA Method 5035A). Water soluble compounds, including low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides, can be included in this analytical technique by the use of azeotropic distillation method (EPA Method 5031) or closed system vacuum distillation method (EPA Method 5032).

4.6. This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph / mass spectrometer (GC/MS) and skilled in the interpretation of mass spectra.

5. METHOD SUMMARY

5.1. EPA Method 8260B describes chromatographic procedures that will allow for the separation of volatile organic compounds and their qualitative and quantitative analysis by gas chromatography and mass spectrometry. Detection is achieved using a mass selective detector (MSD).

5.2. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample.

5.2.1. Volatile organic compounds in a sample are introduced into the gas chromatograph via the appropriate purge-and-trap method. The analytes are introduced directly to a wide-bore capillary column. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

5.3. Acceptable preparatory methods include, but are not limited to, the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Purge-and-Trap for Aqueous Samples	5030C	SOP-M212
Closed System Purge-and-Trap for Soil/Waste Samples	5035A	SOP-M213
TCLP	1311	SOP-M226
SPLP	1312	SOP-M227
STLC (California Code of Regulations)	CCR T22.11.5.A-II	SOP-M228

5.4. Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator. Identification of target analytes is accomplished by comparing their mass spectra with the mass spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using an appropriate calibration curve for the intended application.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

6.5. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.6. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.7. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.8. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.9. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.10. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.11. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.12. Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

6.13. Matrix Spike Duplicate (spiked sample or fortified sample duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

6.14. Method Blank: A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.15. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.16. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality

indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.17. Preservation: Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

6.18. Pure Reagent Water: Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method.

6.19. Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

6.20. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.21. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.22. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.23. Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

6.24. Standard: The document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies.

6.25. Standard Operating Procedure (SOP): A written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

6.26. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes.

6.27. Term Specific to GC/MS Analysis

6.27.1. Mass-to-Charge Ratio (m/z): The dimensionless quantity formed by dividing the mass of an ion in unified atomic mass units by its charge number (regardless of sign).

7. INTERFERENCES

7.1. Samples can become contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage.

7.1.1. Trip blanks prepared from both reagent water (when associated with aqueous samples) and methanol (when associated with soil/sediment samples) should be carried through sampling and subsequent storage and handling to serve as a check on such contamination. Refer to the current revision of SOP-T011, "Field QA/QC Samples" for guidance.

7.2. Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

7.2.1. The use of high purity solvents, reagents and pre-conditioning of disposables that come in contact with the sample help to minimize interference problems.

7.3. Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The laboratory where the analysis is to be performed should be free of solvents other than water and methanol.

7.3.1. Many common solvents, most notably acetone and methylene chloride, are frequently found in the laboratory air at low levels. The sample receiving chamber should be loaded in an environment that is clean enough to eliminate the potential for contamination from ambient sources.

7.4. The use of non-polytetrafluoroethylene (non-PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation.

7.4.1. Analyses of reagent blanks provide information about the presence of contaminants. However, subtracting blank values from sample results is not permitted.

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

7.5.1. Sample syringe and/or purging device should be thoroughly rinsed with organic-free reagent water between samples.

7.5.2. Analysis of a suspected high level sample should be followed by an analysis of organic-free reagent water to check for cross-contamination.

7.5.3. For volatile samples containing high concentrations of water-soluble materials, suspended solids, or high boiling-point compounds, it may be necessary to clean purging device, rinse it with organic-free reagent water, and then dry in an oven at 105°C between analyses.

7.6. Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing.

7.7. Use of sensitive mass spectrometers to achieve lower quantitation levels will increase the potential to detect laboratory contaminants as interferences.

7.8. Co-elution of the p- and m-xylene isomers may occur.

7.9. Refer to the preparatory method for other potential interferences.

8. SAFETY

8.1. The following compounds covered by this method have been tentatively classified as known or suspected human carcinogens: benzene, bromodichloromethane, bromoform, carbon tetrachloride, chloroform, dibromochloromethane, 1,4-dichlorobenzene, 1,1-dichloroethane, 1,2-dichloroethane, methylene chloride, 1,1,2,2-tetrachloroethane, and vinyl chloride. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when analysts handle high concentrations of these compounds.

8.2. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

8.4. Refer to the preparatory methods for additional safety issues.

9. EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Agilent 6890Series/6890N/7890A Gas Chromatograph or equivalent configured with the following components:

9.1.1. Purge-and-trap system (see the appropriate preparatory method).

9.2. Mass Spectrometer: Agilent 5973N/5975B/5975C Mass Selective Detector (MSD) or equivalent capable of scanning from 35 to 270 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron-impact ionization (EI) mode, and configured with the following components:

9.2.1. Electron-ionization ion source.

9.2.2. Hyperbolic quadrupole mass filter.

9.2.3. High energy dynode (HED) electron multiplier detector.

9.2.4. PC based data system, Agilent MSD ChemStation or equivalent equipped with NIST mass spectral library.

9.3. Analytical Column: 25-m × 0.2-mm ID, 1.12-µm film thickness, mid-polar, low bleed, wide-bore, capillary, fused silica, J&W Scientific DB-624 or equivalent.

9.4. Purge Gas: Helium, He, or nitrogen, N_2, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.5. Carrier Gas: Helium, He, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.6. VOA vials, 28-mm × 95-mm (40-mL capacity), screw top, clear or amber glass, with Teflon-lined open top or closed top screw caps and Teflon-lined septa, EPA VOA Vial or equivalent.

9.6.1. Bake VOA vials in an oven at 90°C for 24 hours prior to use.

9.7. Storage vials, 15-mm × 45-mm (4-mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.

9.8. Volumetric flasks, 25-mL, 50-mL, or other capacity, glass, Class A.

9.9. Syringes, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, and 500-µL, gastight, Cemented Needle (N) termination, Hamilton 1700 Series or equivalent with NIST Traceable Certification.

9.10. Syringes, 1-mL, 5-mL, and 25-mL, gastight, Removable Needle (RN), Teflon Luer Lock (TLL), or SampleLock (SL) termination, Hamilton 1000 Series or equivalent with NIST Traceable Certificate or equivalent documentation.

9.11. Refer to the specific SOPs of the preparatory methods for additional equipment and supplies.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Reagent water, interferant free, nano-pure.

10.1.2. Sand, washed, sea or standard Ottawa.

10.1.3. Methanol, CH_3OH, purge-and-trap grade or equivalent.

10.1.4. Sodium thiosulfate, $Na_2S_2O_3$, anhydrous, white solid, reagent grade or equivalent.

10.1.5. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v).

10.1.5.1. Prepare the 10% $Na_2S_2O_3$ solution by dissolving 100 g of anhydrous $Na_2S_2O_3$ in reagent water and dilute to 1 L with additional reagent water.

10.1.6. Hydrochloric acid, HCl, 36.5–38.0% (v/v), concentrated, colorless to pale yellow liquid, reagent grade or equivalent.

10.1.7. Hydrochloric acid, HCl, 1:1 (v/v).

10.1.7.1. Prepare the 1:1 HCl solution by slowly adding concentrated HCl to equal volume of reagent water.

10.1.8. Sodium bisulfate, $NaHSO_4$, monohydrate, colorless crystals, reagent grade or equivalent.

10.1.9. Methanol, CH_3OH, clear colorless liquid, purge and trap grade or equivalent.

10.1.10. Refer to the specific SOPs of the preparatory methods for additional reagents.

10.1.11. All reagents must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2. Standards

10.2.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing 2000 ppm of each gaseous volatile organic target analyte are used to prepare calibration and check standards.

10.2.1.1. The gaseous target analytes are dichlorodifluoromethane (CFC-12), chloromethane (methyl chloride), vinyl chloride, bromomethane (methyl bromide), chloroethane (ethyl chloride), and trichlorofluoromethane (CFC-11).

10.2.1.2. Prepare each 50-ppm gaseous volatile organic working standard solution by diluting 1.25 mL of the 2000-ppm gaseous volatile organic stock standard to 50.0 mL with methanol.

10.2.1.3. The 50-ppm gaseous volatile organic working standard solutions must be stored under dark and refrigerated conditions, and replaced after two weeks or sooner if comparison with check standards indicates a problem.

10.2.1.4. Prepare the 0.5-ppm gaseous volatile organic working standard solution by diluting 10 µL of the 50-ppm gaseous volatile organic working standard to 1.00 mL with methanol.

10.2.1.5. The 0.5-ppm gaseous volatile organic working standard solution must be prepared fresh on the day of calibration.

10.2.2. Pre-certified stock standard solutions, each in sealed glass ampules, containing 50 ppm of each non-gaseous volatile organic target analyte (except acrolein, t-butyl alcohol, 1,4-dioxane, ethanol, and isopropanol),

100 ppm of acrolein, 250 ppm of t-butyl alcohol, 500 ppm of 1,4-dioxane, 500 ppm of ethanol, and 250 ppm of isopropanol are used to prepare calibration and check standards.

10.2.2.1. Prepare the 0.5-ppm non-gaseous volatile organic working standard solution by diluting the appropriate volume of the non-gaseous volatile organic stock standard to 1.00 mL with methanol.

10.2.2.2. The 0.5-ppm non-gaseous volatile organic working standard is prepared as follows:

	Initial		Final	
Analyte	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
volatile organics	50	10	0.5	1.00
acrolein	100		1.0	
t-butyl alcohol	250		2.5	
1,4-dioxane	500		5.0	
ethanol	500		5.0	
isopropanol	250		2.5	

10.2.2.3. The 0.5-ppm non-gaseous volatile organic working standard solution must be prepared fresh on the day of calibration.

10.2.3. Pre-certified stock standard solutions, each in sealed glass ampules, containing 2500/12500 ppm of each surrogate, 2500/12500 ppm of each internal standard (except TBA-d_9), and 12500/62500 ppm of TBA-d_9 are used to prepare surrogate and internal standard working standards.

10.2.3.1. The surrogates are 1,4-bromofluorobenzene (BFB), di-bromofluoromethane, 1,2-dichloroethane-d_4, and toluene-d_8. The internal standards are t-butyl alcohol-d_9 (TBA-d_9), chlorobenzene-d_5, 1,4-dichlorobenzene-d_4, 1,4-difluoro-benzene, and pentafluorobenzene.

10.2.3.1.1. The internal standards selected should permit most analytes of interest in a chromatogram to have relative retention times of 0.80−1.20.

10.2.3.2. Prepare the 50-ppm and 250-ppm surrogate and internal standard working standard solutions by diluting the appropriate volumes of the surrogate and internal standard stock standards to 50 mL with methanol.

10.2.3.3. The 50-ppm surrogate and internal standard working standard is prepared as follows:

Surrogate and Internal Standard	Initial		Final	
	Conc. (ppm)	Volume (mL)	Conc. (ppm)	Volume (mL)
1,4-bromofluorobenzene	2500	1.0	50	50
dibromofluoromethane	2500		50	
1,2-dichloroethane-d_4	2500		50	
toluene-d_8	2500		50	
TBA-d_9	12500	1.0	250	
chlorobenzene-d_5	2500		50	
1,4-dichlorobenzene-d_4	2500		50	
1,4-difluorobenzene	2500		50	
pentafluorobenzene	2500		50	

10.2.3.4. The 250-ppm surrogate and internal standard working standard is prepared as follows:

Surrogate and Internal Standard	Initial		Final	
	Conc. (ppm)	Volume (mL)	Conc. (ppm)	Volume (mL)
1,4-bromofluorobenzene	12500	1.0	250	50
dibromofluoromethane	12500		250	
1,2-dichloroethane-d_4	12500		250	
toluene-d_8	12500		250	
TBA-d_9	62500	1.0	1250	
chlorobenzene-d_5	12500		250	
1,4-dichlorobenzene-d_4	12500		250	
1,4-difluorobenzene	12500		250	
pentafluorobenzene	12500		250	

10.2.4. Tuning standard solution containing 50 ppm of 1,4-bromofluorobenzene (BFB) in methanol.

10.2.4.1. Use the 50-ppm surrogate and internal standard working standard solution as the tuning standard solution.

10.2.4.2. Add 1.0 µL of the tuning standard to 5.0 mL of reagent water, and purge and trap for hardware turning.

10.2.5. Calibration standard solutions containing various concentrations of target analytes, surrogates, and internal standards in methanol.

10.2.5.1. Add the appropriate volumes of the working and stock standards and the appropriate volume of the 250-ppm surrogate and internal standard working standard to 5.0 mL of reagent water, and purge and trap for initial calibration.

10.2.5.1.1. For lower limit of quantitation, add the appropriate volumes of the working and stock standards and the appropriate volume of the 50-ppm surrogate and internal standard working standard to 20 mL of reagent water.

10.2.5.1.2. If samples are preserved with sodium bisulfate, and the presence of the preservative affects the purging efficiencies of the analytes, it is recommended that the same amount (~1.00 g) of sodium bisulfate be added to the reagent water after adding the standards.

10.2.5.2. Use the following calibration levels as guidance to prepare the calibration standards.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
0.5	1.0	2.5	5.0	50	0.5~5.0	250	5.0	1.0
1.0	2.0	5.0	10	50	0.5~5.0	250	10.0	1.0
10	20	50	100	50	50~500	250	1.0	1.0
20	40	100	200	50	50~500	250	2.0	1.0
50	100	250	500	50	50~500	250	5.0	1.0
100	200	500	1000	50	50~500	250	10.0	1.0
200	400	1000	2000	50	50~500	250	20.0	1.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein;
A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate;
IS = Internal Standard; A = A1 + A2 + A3 + A4;
Calibration Level of TBA-d_9 = 250 ppb;
Initial Concentration of TBA-d_9 = 1250 ppm

10.2.5.3. Use the following calibration levels as guidance to prepare the calibration standards for lower limit of quantitation.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
0.5	1.0	2.5	5.0	10	0.5~5.0	50	20.0	4.0
2.0	4.0	10	20	10	0.5~5.0	50	80.0	4.0
5.0	10	25	50	10	50~500	50	2.0	4.0
10	20	50	100	10	50~500	50	4.0	4.0
20	40	100	200	10	50~500	50	8.0	4.0
30	60	150	300	10	50~500	50	12.0	4.0
40	80	200	400	10	50~500	50	16.0	4.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein;
A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate;
IS = Internal Standard; A = A1 + A2 + A3 + A4;
Calibration Level of TBA-d_9 = 50 ppb;
Initial Concentration of TBA-d_9 = 250 ppm

10.2.5.4. The midpoint standard is also used as the continuing calibration verification solutions.

10.2.6. Initial calibration verification (ICV) solution containing the appropriate concentrations of each target analyte, surrogate, and internal standard in reagent water. The ICV solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.6.1. Add the appropriate volumes of the second source working and stock standards and the appropriate volume of the 250-ppm surrogate and internal standard working standard to 5.0 mL of reagent water, and purge and trap for initial calibration verification.

10.2.6.1.1. For lower limit of quantitation, add the appropriate volumes of the second source working and stock standards and the appropriate volume of the 50-ppm surrogate and internal standard working standard to 20 mL of reagent water.

10.2.6.1.2. If samples are preserved with sodium bisulfate, and the presence of the preservative affects the purging efficiencies of the analytes, it is recommended that the same amount (~1.00 g) of sodium bisulfate be added to the reagent water after adding the standards.

10.2.6.2. Use the following calibration level as guidance to prepare the ICV solution.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
50	100	250	500	50	50~500	250	5.0	1.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein;
A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate;
IS = Internal Standard; A = A1 + A2 + A3 + A4;
Calibration Level of TBA-d_9 = 250 ppb;
Initial Concentration of TBA-d_9 = 1250 ppm

10.2.6.3. Use the following calibration level as guidance to prepare the ICV solution for lower limit of quantitation.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
10	20	50	100	10	50~500	50	4.0	4.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein;
A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate;
IS = Internal Standard; A = A1 + A2 + A3 + A4;
Calibration Level of TBA-d_9 = 50 ppb;

Initial Concentration of TBA-d_9 = 250 ppm

10.2.7. Continuing calibration verification (CCV) solution containing the appropriate concentrations of each target analyte, surrogate, and internal standard in reagent water. The CCV solution is of a source same as that used for the initial multi-point calibration.

10.2.7.1. Add the appropriate volumes of the working and stock standards and the appropriate volume of the 250-ppm surrogate and internal standard working standard to 5.0 mL of reagent water, and purge and trap for continuing calibration verification.

10.2.7.1.1. For lower limit of quantitation, add the appropriate volumes of the working and stock standards and the appropriate volume of the 50-ppm surrogate and internal standard working standard to 20 mL of reagent water.

10.2.7.1.2. If samples are preserved with sodium bisulfate, and the presence of the preservative affects the purging efficiencies of the analytes, it is recommended that the same amount (~1.00 g) of sodium bisulfate be added to the reagent water after adding the standards.

10.2.7.2. Use the following calibration level as guidance to prepare the CCV solution.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
50	100	250	500	50	50~500	250	5.0	1.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein;
A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate;
IS = Internal Standard; A = A1 + A2 + A3 + A4;
Calibration Level of TBA-d_9 = 250 ppb;
Initial Concentration of TBA-d_9 = 1250 ppm

10.2.7.3. Use the following calibration level as guidance to prepare the CCV solution for lower limit of quantitation.

Calibration Level (ppb)					Initial Conc (ppm)		Initial Volume (µL)	
A1	A2	A3	A4	S / IS	A	S / IS	A	S / IS
10	20	50	100	10	50~500	50	4.0	4.0

Note: A1 = Volatile Organic Analyte; A2 = Acrolein;
A3 = TBA or Isopropanol; A4 = 1,4-Dioxane or Ethanol; S = Surrogate;
IS = Internal Standard; A = A1 + A2 + A3 + A4;
Calibration Level of TBA-d_9 = 50 ppb;

Initial Concentration of TBA-d_9 = 250 ppm

10.2.8. Surrogate and internal standard working standard solutions containing 50/250 ppm of each surrogate, 50/250 ppm of each internal standard (except TBA-d_9), and 250/1250 ppm of TBA-d_9 in methanol.

10.2.8.1. If autosampler is <u>not</u> capable of injecting standard solution automatically, manually add 5.0 µL of the 50-ppm surrogate and internal standard working standard to each 5.0-mL aliquot of sample including each calibration standard, calibration verification standard, quality control (QC) check sample, and method blank prior to purge-and-trap extraction.

10.2.8.1.1. For lower limit of quantitation, manually add 4.0 µL of the 50-ppm surrogate and internal standard working standard to each 20-mL aliquot of sample including each calibration standard, calibration verification standard, QC check sample, and method blank.

10.2.8.2. If autosampler is capable of injecting standard solution automatically, configure the autosampler to inject 1.0 µL of the 250-ppm surrogate and internal standard working standard into each 5.0-mL aliquot of sample including each calibration standard, calibration verification standard, QC check sample, and method blank prior to purge-and-trap extraction.

10.2.8.2.1. For lower limit of quantitation, configure the autosampler to inject 4.0 µL of the 50-ppm surrogate and internal standard working standard into each 20-mL aliquot of sample including each calibration standard, calibration verification standard, QC check sample, and method blank.

10.2.9. Spike standard solutions containing various concentrations of target analytes in methanol. The spike standard solution must be of a source differing from that used for the initial multi-point calibration. If it is of the same source, then it must be of different lot.

10.2.9.1. Use the second source 50-ppm gaseous volatile organic working standard solution as the gaseous spike standard solution. Use the second source non-gaseous volatile organic stock standard solution as the non-gaseous spike standard solution.

10.2.9.2. The spike standards are used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

10.2.9.3. Add 5.0 µL of the gaseous spike standard and 5.0 µL of the non-gaseous spike standard to each 5.0-mL aliquot of MS/MSD and LCS/LCSD sample prior to purge-and-trap extraction.

10.2.9.3.1. For lower limit of quantitation, add 4.0 µL of the gaseous spike standard and 4.0 µL of the non-gaseous spike standard to each 20-mL aliquot of MS/MSD and LCS/LCSD sample.

10.2.10. All working standards must be replaced after three months (unless specified otherwise) or sooner if comparison with check standards indicates a problem.

10.2.10.1. Store all working standards with minimal headspace under dark and refrigerated condition.

10.2.10.2. Return the working standards to the refrigerator or freezer as soon as possible after use to prevent the loss of volatile organic compounds.

10.2.10.3. Check all working standards frequently for signs of degradation or evaporation.

10.2.11. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2.11.1. Return the stock standards to the refrigerator or freezer as soon as possible after use to prevent the loss of volatile organic compounds.

10.2.11.2. Check all opened stock standards frequently for signs of degradation or evaporation.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Aqueous samples should be collected in 40-mL pre-cleaned amber glass or clear glass VOA vials with Teflon-lined closures. Collect all samples in triplicate.

11.1.1. If the aqueous sample contains residual chlorine, collect the sample in a 125-mL amber glass container containing 4 drops of the 10% $Na_2S_2O_3$ solution. Gently swirl to mix the sample, and transfer to pre-cleaned amber glass or clear glass VOA vials.

11.1.1.1. Aqueous sample containing greater than 5 mg/L of residual chlorine may require additional amount of the dechlorinating agent.

11.1.2. Adjust the pH of the aqueous sample to < 2 by adding 1:1 HCl solution while stirring.

11.1.2.1. If a dechlorinating agent and acid are both added as preservatives, the aqueous sample must be dechlorinated first and then acidified.

11.1.2.2. Reactive compounds (e.g., acrolein, acrylonitrile, 2-chloroethyl vinyl ether, styrene, and vinyl chloride) are unstable at low pH.

It is recommended that a second set of the aqueous sample without acid preservative be collected.

11.1.2.3. If fuel oxygenated compounds are the only analytes of interest, and the aqueous sample will be purged at an elevated temperature of 80°C, no acid preservation is required.

11.1.2.4. If carbonaceous materials are present, the aqueous sample should not be acid preserved due to possible effervescence and loss of volatile organic compounds.

11.1.2.5. If aromatic and biologically active compounds are the analytes of interest, acid preservation is necessary.

11.1.3. Completely fill and hermetically seal the sample vial such that when the vial is inverted, no headspace is visible.

11.1.3.1. It is possible for the sample to generate some headspace in the form of micro bubbles during storage. The bubbles should not exceed ¼ in or 6 mm in diameter. In the event that the headspace greater than 6 mm is evident, and the vial is used for analysis, the data should be qualified.

11.1.4. A reagent water trip blank, preserved in the same manner as the field samples, should accompany each batch of aqueous samples.

11.2. Solid samples for EPA Method 5030C purge-and-trap extraction should be collected in 4-oz or 8-oz pre-cleaned clear glass wide-mouth jars or 6-in decontaminated stainless steel or brass sleeves with Teflon-lined closures.

11.2.1. A reagent water trip blank should accompany each batch of solid samples.

11.3. Solid samples for EPA Method 5035A closed system purge-and-trap extraction should be collected in Terra Core Samplers, En Core® Samplers, or equivalent. Collect all samples in triplicate.

11.3.1. Solid samples collected using the Terra Core or equivalent coring device shall be immediately extruded into a pre-weighed 40-mL amber glass or clear glass VOA vial containing 5 mL of sodium bisulfate solution and a magnetic stirring bar, or 10 mL of methanol, and sealed with a Teflon-lined septum and screw cap by client field personnel.

11.3.2. If sample result is to be reported on a dry weight basis, one additional solid sample should be collected in a 4-oz pre-cleaned clear glass wide-mouth jar with a Teflon-lined closure, and labeled specifically for solids content determination.

11.3.3. If MS/MSD analyses are required, collect one sample in quintuplicate.

11.3.4. A reagent water trip blank should accompany each batch of solid samples.

11.4. Oil samples should be collected in 40-mL pre-cleaned clear glass VOA vials with Teflon-lined closures.

11.4.1. A reagent water trip blank should accompany each batch of oil samples.

11.5. Mobility-procedure extracts should be collected in 4-mL pre-cleaned clear glass storage vials with Teflon-lined closures.

11.5.1. If the mobility-procedure extract will not be analyzed within 24 hours, collect the mobility-procedure extract in a 40-mL pre-cleaned amber glass or clear glass VOA vial, and adjust the pH to < 2 by adding 1:1 HCl solution while stirring.

11.5.1.1. If effervescence (bubbling, hissing, or foaming of liquid as gas escapes) is observed upon adding 1:1 HCl solution, do not acid preserve the mobility-procedure extract.

11.5.2. Completely fill and hermetically seal the sample vial such that when the vial is inverted, no headspace is visible.

11.5.2.1. It is possible for the sample to generate some headspace in the form of micro bubbles during storage. The bubbles should not exceed ¼ in or 6 mm in diameter.

11.6. Samples shall be maintained in a chilled state (≤ 4°C) post sample collection until received at the laboratory. Aqueous and oil samples should not be frozen (e.g., do not use dry ice as the refrigerant). Solid samples may be frozen to −7°C if solids content determination is not required. Freezing of solid samples may require contract approval.

11.6.1. Freezing solid samples within 48 hours of sample collection can minimize biodegradation of aromatic hydrocarbons (e.g., benzene, toluene, ethylbenzene, and xylenes).

11.7. Upon receipt, the samples are stored in a 0~6°C cooler. Solid samples may be stored in a −10~−20°C freezer if solids content determination is not required.

11.7.1. Aqueous samples with acid preservation (pH < 2) must be analyzed within 14 days of sample collection.

11.7.2. Aqueous samples without acid preservation (pH ≥ 2) must be analyzed within 7 days of sample collection.

11.7.2.1. Aqueous samples containing highly reactive compounds (e.g., acrolein, acrylonitrile, 2-chloroethyl vinyl ether, styrene, vinyl chloride, etc.) as target analytes should be analyzed as soon as possible.

11.7.3. Solid samples collected in jars or sleeves must be analyzed within 14 days of sample collection.

11.7.4. High concentration (> 200 µg/kg) solid samples collected in jars or sleeves must be preserved with methanol and analyzed within 14 days of sample collection.

11.7.4.1. Methanol extracts shall be stored in a 0~6°C cooler with a minimum contact time of 24 hours between the solid sample and methanol prior to analysis.

11.7.5. Solid samples collected in Terra Core Samplers, En Core® Samplers, or equivalent must be preserved with sodium bisulfate solution and analyzed within 14 days of sample collection.

11.7.5.1. Solid samples collected using the En Core® or equivalent coring/transport device shall be preserved within 48 hours of sample collection. Refer to the current revision of SOP-M213 for preservation procedure.

11.7.5.2. Solid samples may also be analyzed within 48 hours of sample collection without sodium bisulfate preservation.

11.7.6. High concentration (> 200 µg/kg) solid samples collected in Terra Core Samplers, En Core® Samplers, or equivalent must be preserved with methanol and analyzed within 14 days of sample collection.

11.7.6.1. High concentration solid samples collected using the En Core® or equivalent coring/transport device shall be preserved within 48 hours of sample collection. Refer to the current revision of SOP-M213 for preservation procedure.

11.7.6.2. Methanol extracts shall be stored in a 0~6°C cooler with a minimum contact time of 24 hours between the solid sample and methanol prior to analysis.

11.7.7. Oil samples must be preserved with methanol and analyzed within 14 days of sample collection.

11.7.7.1. Methanol extracts shall be stored in a 0~6°C cooler with a minimum contact time of 24 hours between the oil sample and methanol prior to analysis.

11.7.8. Mobility-procedure extracts with acid preservation (pH < 2) must be analyzed within 14 days post mobility extraction for aqueous samples, or within 7 days post mobility extraction for solid samples.

11.7.8.1. Mobility-procedure extracts shall be stored in a 0~6°C cooler post mobility extraction if analysis is not to be performed within 24 hours.

11.7.9. Mobility-procedure extracts without acid preservation (pH ≥ 2) must be analyzed within 24 hours post mobility extraction.

11.7.10. Storage blanks consisting of clean reagent water should be used to monitor potential cross-contamination of samples due to improper storage conditions.

12. QUALITY CONTROL

12.1. Hardware Tuning

12.1.1. Prior to running the calibration standards, the tuning standard solution must be analyzed and meet the defined acceptance criteria.

12.1.2. The following criteria must be demonstrated every 12 hours.

m/z	Relative Abundance Criteria
50	15 – 40% of m/z 95
75	30 – 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 – 9% of m/z 95
173	< 2% of m/z 174
174	> 50% of m/z 95
175	5 – 9% of m/z 174
176	> 95% but < 101% of m/z 174
177	5 – 9% of m/z 176

12.1.3. If these criteria are not met, then the analytical system is deemed unacceptable for sample analysis to begin. Effect corrective action and re-tune the system.

12.2. Initial Calibration (IC)

12.2.1. The initial multi-point calibration must be established prior to the processing of samples.

12.2.1.1. The calibration curve is established with a minimum of five calibration standards, but may contain six or seven calibration standards.

12.2.2. The IC is deemed valid if the %RSD for each analyte (except CCC) is ≤ 15%, the %RSD for each CCC is ≤ 30%, and the average relative response factor (RRF) for each SPCC is as follows:

SPCC	Average RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

12.2.2.1. The calibration check compounds (CCCs) are chloroform, ethylbenzene, 1,1-dichloroethene, 1,2-dichloropropane, toluene, and vinyl chloride.

12.2.2.2. The system performance check compounds (SPCCs) are bromoform, chlorobenzene, chloromethane, 1,1-dichloroethane, and 1,1,2,2-tetrachloroethane.

12.2.3. If the %RSD for an analyte is ≤ 15%, the RRF is assumed to be constant over the calibration range, and the average RRF may be used for quantitation.

12.2.4. In those instances where the %RSD for one or more target analytes exceeds 15%, the initial calibration remains acceptable if the mean of the %RSD values for all analytes in the calibration is ≤ 15%. This approach (i.e., the average of all %RSD values ≤ 15%) is referred to as the grand mean approach.

12.2.4.1. The mean %RSD is calculated by summing the %RSD value for each analyte and dividing by the total number of analytes.

12.2.4.1.1. The mean %RSD criterion applies to all analytes in the calibration standards, regardless of whether or not they are of interest for a specific project. In other words, if the analyte is part of the calibration standard, its %RSD value is included in the evaluation.

12.2.4.2. If the grand mean approach is utilized, the average RRF with %RSD > 15% may be used for quantitation.

12.2.4.2.1. Per client request or project specific data quality objectives (DQOs), a summary of the initial calibration data or a specific list of the target analytes for which the %RSD exceeded 15%, and the results of the mean %RSD calculation must be included in the data package.

12.2.4.3. The use of the grand mean approach will lead to greater uncertainty for those analytes for which the %RSD is > 15%. Review the associated quality control results carefully, with particular attention to the matrix spike and laboratory control sample results, to determine if the calibration linearity poses a significant concern.

12.2.4.3.1. If the grand mean approach is not acceptable due to client or project specific requirements, employ one of the other calibration options (see Section 12.2.5.), or adjust instrument operating conditions and/or the calibration range until the %RSD is ≤ 15%.

12.2.5. Other calibration options are as follows:

12.2.5.1. The first calibration option is linear least squares regression with equal weighting factor. The IC is deemed valid if the correlation coefficient, r, is ≥ 0.99.

12.2.5.2. The section calibration option is quadratic least squares regression with equal weighting factor. The IC is deemed valid if the coefficient of determination, r^2, is ≥ 0.99.

12.2.5.2.1. This option requires at least six calibration levels.

12.2.6. The relative retention time (RRT) of each analyte in each calibration standard should agree to within ± 0.06 RRT units.

12.2.7. If these criteria are not met, then the calibration is unacceptable for sample analysis to begin. Effect corrective action and recalibrate.

12.2.7.1. If the problem appears to be associated with a single calibration standard, then that one standard may be reanalyzed once within the same analytical shift prior to sample analysis.

12.3. Initial Calibration Verification (ICV)

12.3.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%, and the daily RRF for each SPCC is as follows:

SPCC	Daily RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

12.3.1.1. If the calibration option is average relative response, the %D is the percent difference.

12.3.1.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

12.3.2. The %D of each non-CCC is evaluated only per client request or project specific DQOs.

12.3.2.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, the initial calibration is deemed valid if the %D for each non-CCC is ≤ 25%.

12.3.3. The internal standard response and retention time for the ICV must be evaluated during or immediately after data acquisition.

12.3.3.1. If the extracted ion current profile (EICP) area of any internal standard in an ICV standard changes by a factor of two (−50% to +100%) from that in the midpoint calibration standard for the most recent initial calibration, the mass spectrometer must be inspected for malfunctions and corrective action effected.

12.3.3.2. If the retention time of any internal standard in an ICV standard changes by more than 30 seconds from that in the midpoint calibration standard for the most recent initial calibration, the gas chromatograph must be inspected for malfunctions and corrective action effected.

12.3.4. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to begin. An unacceptable ICV result indicates either a disagreement between like solutions from separate sources or a change in instrument conditions. Normally, this is caused when at least one of the solutions is no longer intact (representative of the stated concentration). Document the unacceptable result and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective actions, which may include re-preparation of standard solutions or instrument maintenance, and recalibrate.

12.4. Continuing Calibration Verification (CCV)

12.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and every 12 hours thereafter at the beginning of an analytical batch.

12.4.2. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%, and the daily RRF for each SPCC is as follows:

SPCC	Daily RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

12.4.2.1. If the calibration option is average relative response, the %D is the percent difference.

12.4.2.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

12.4.3. For EPA Region 9 requirement, the initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.4.4. The %D of each non-CCC is evaluated only per client request or project specific DQOs.

12.4.4.1. Project-specific control limits shall be applied. If project-specific control limits are unavailable, the initial calibration is deemed valid if the %D for each non-CCC is ≤ 25%.

12.4.5. The internal standard response and retention time for the CCV must be evaluated during or immediately after data acquisition.

12.4.5.1. If the EICP area of any internal standard in a CCV standard changes by a factor of two (−50% to +100%) from that in the midpoint calibration standard for the most recent initial calibration, the mass spectrometer must be inspected for malfunctions and corrective action effected.

12.4.5.2. If the retention time of any internal standard in a CCV standard changes by more than 30 seconds from that in the midpoint calibration standard for the most recent initial calibration, the gas chromatograph must be inspected for malfunctions and corrective action effected.

12.4.5.3. Following corrective action, reanalysis of samples analyzed while the system was malfunctioning is required.

12.4.6. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective action and recalibrate.

12.5. Event Based Quality Control (LCS/LCSDs and MBs)

12.5.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) and a method blank (MB).

12.5.2. The acceptance criteria for LCS/LCSD compounds are as follows:

12.5.2.1. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.5.2.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each LCS/LCSD compound are 80% and 120%, respectively. The RPD is ≤ 20%.

12.5.2.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each LCS/LCSD compound in a water sample are 70% and 130%, respectively. The RPD is ≤ 30%.

12.5.2.1.3. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each LCS/LCSD compound in a soil sample are 65% and 135%, respectively. The RPD is ≤ 50%.

12.5.2.2. All LCS/LCSD compounds must be within acceptance limits. However, if a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside of control limits. This may not indicate that the system is out of control; therefore, corrective action may not be necessary. Lower and upper marginal exceedance (ME) limits can be established to determine when corrective action is necessary.

12.5.2.3. ME is defined as being beyond the LCS control limit (3 standard deviations), but within the ME limits. ME limits are between 3 and 4 standard deviations around the mean.

12.5.2.4. The number of allowable marginal exceedances is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and corrective action is necessary. This marginal exceedance approach is relevant for methods with long lists of analytes. It will not apply to target analyte lists with fewer than 11 analytes.

12.5.2.5. The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number of Analytes Allowed in ME of the LCS Control Limit
> 90	5

Number of Analytes in LCS	Number of Analytes Allowed in ME of the LCS Control Limit
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

12.5.2.6. Marginal exceedances must be random. If the same analyte exceeds the LCS control limit 2 out of 3 consecutive LCS, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

12.5.3. Ideally, the concentration of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

12.5.3.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

12.5.3.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified, or rejected and the samples re-processed and re-analyzed.

12.6. Matrix Based Quality Control (Surrogates, Internal Standards, and MS/MSDs)

12.6.1. Matrix based quality control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicate (MS/MSD), and surrogates and internal standards added to each sample.

12.6.2. The acceptance criteria for surrogate compounds are as follows:

12.6.2.1. The lower and upper acceptance limits for %REC of each surrogate compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.2.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each surrogate compound are 70% and 130%, respectively.

12.6.2.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of the surrogate compound in a water sample are 85% and 115%, respectively.

12.6.2.1.3. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of the surrogate

compound in a soil sample are 70% and 125%, respectively.

12.6.2.2. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

12.6.2.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration or a problem may have occurred during extraction. The data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.6.2.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.6.2.4.1. Check the surrogate and internal standard solutions for degradation and contamination.

12.6.2.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same sample should be re-processed and re-analyzed.

12.6.2.4.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-processed and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.2.4.3.1. If, upon re-extraction and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.2.4.3.2. If the MB surrogates are unacceptable, all associated sample data must invalidated and all associated samples re-processed and re-analyzed.

12.6.2.5. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

12.6.3. The acceptance criteria for internal standard compounds are as follows:

12.6.3.1. It is recommended that the internal standard responses (area counts) and retention times for each standard, sample, and blank be monitored for method performance, injection execution, system/instrument maintenance, analytical errors, or interferences.

12.6.3.2. The area count of each internal standard peak in a standard, sample, or blank should be within 50% to 200% of that in the midpoint calibration standard for the most recent initial calibration.

12.6.3.3. The retention time of each internal standard peak in a standard, sample, or blank should be within ± 30 seconds of that in the midpoint calibration standard for the most recent initial calibration.

12.6.4. The acceptance criteria for MS/MSDs compounds are as follows:

12.6.4.1. The lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.6.4.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each MS/MSD compound are 70% and 130%, respectively. The RPD is ≤ 30%.

12.6.4.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each MS/MSD compound in a water sample are 65% and 135%, respectively. The RPD is ≤ 30%.

12.6.4.1.3. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each MS/MSD compound in a soil sample are 50% and 150%, respectively. The RPD is ≤ 50%.

12.6.4.2. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

12.6.4.3. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

12.6.5. Unacceptable %REC values are typically caused by matrix effects or poor instrument performance/technique. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

12.7. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.8. Additional information regarding internal quality control checks is provided in SOP-T020.

13. CALIBRATION AND STANDARDIZATION

13.1. Prior to initial calibration and the analysis of field or QC samples, the GC/MS system must be hardware tuned such that the analysis of 50 ng or less of BFB meets the tuning criteria. The acceptance criteria for the tune are listed in Section 12.1.

13.1.1. Obtain the mass spectrum of BFB as follows:

13.1.1.1. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired within 20 scans of the elution of BFB.

13.1.1.1.1. The background subtraction should be designed only to eliminate column bleed or instrument background ions.

13.1.1.1.2. Do not subtract part of the BFB peak or any other discrete peak that does not coelute with BFB.

13.1.2. All subsequent standards, samples, and blanks associated with a specific tune must use identical mass spectrometer operating conditions.

13.1.3. Whenever invasive maintenance of the hardware is performed, the system must be re-tuned.

13.2. Initial Calibration

13.2.1. Establish an acceptable multi-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.2.

13.2.1.1. Recalibration is required for the following maintenance procedures.

13.2.1.1.1. Change, replace, or reverse the analytical column.

13.2.1.1.2. Replace the trap on a purge-and-trap system.

13.2.1.1.3. Change the entrance lens, draw-out lens, or repeller.

13.2.1.1.4. Change the electron multiplier and/or ion source chamber.

13.2.1.1.5. Clean the ion source and/or quadrupole rods.

13.2.2. After obtaining an acceptable multi-point calibration curve and prior to processing field or QC samples, an ICV standard must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.3.

13.2.3. The initial multi-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

14. PROCEDURE

14.1. Instrument Setup

14.1.1. Refer to the current revision of SOP-M212 or SOP-M213 for purge-and-trap system setup.

14.1.2. Use the following GC/MS operating conditions as guidance to establish the GC/MS temperature program and flow rate necessary to separate the analytes of interest.

Description	GC/MS Operating Condition
Mode	split
Split ratio	100 : 1
Split flow rate	48.9 mL/min
Inlet pressure	7.41 psi
Total flow rate	52.5 mL/min
Initial temperature	40°C, hold 4.00 min
Temperature program	40°C to 190°C at 12.00°C/min 190°C, hold 0.50 min 190°C to 230°C at 45.00°C/min
Final temperature	230°C, hold 3.11 min
Transfer line temperature	260°C
Scan range	35~270 amu
Detector threshold	150

14.1.3. The sampling rate shall result in at least five full mass spectra across the chromatographic peak, and within 1 second or less per mass spectrum.

14.2. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and every 12 hours thereafter at the beginning of an analytical batch. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume. The acceptance criteria are listed in Section 12.4.

14.2.1. If a CCV fails, effect corrective action prior to analyzing any samples.

14.3. Following purge-and-trap preparation by the method specified in Section 5.2., the QC and actual environmental samples are received in purge vessels. The purge vessels are then loaded onto the purge-and-trap system.

14.4. Standard and sample purge vessels are loaded in the following or other logical order:

1) Tuning Standard
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) Samples (up to 20 per batch, excluding QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)

14.4.1. Item 1: An acceptable tune demonstrates satisfactory hardware performance. A tune meeting the acceptance criteria is required daily prior to sample analysis and every 12 hours thereafter during analysis.

14.4.2. Item 2: A CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. An acceptable CCV is required daily prior to sample analysis and every 12 hours thereafter at the beginning of an analytical batch.

14.4.3. Item 3: The LCS is a known matrix that has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

14.4.3.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid samples, the LCS consists of the specified compounds spiked into washed sea sand. For mobility-procedure extracts, the LCS consists of the specified compounds spiked into the mobility-procedure extract designated as LCS. For methanol extracts, the LCS consists of the specified compounds spiked into the methanol extract designated as LCS.

14.4.3.2. One LCS is required every day preparatory methods (i.e., methanol extractions, purge-and-trap extractions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.4. Item 4: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is

expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.8.

14.4.5. Item 5: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used (e.g., surrogates, internal standards, etc.).

14.4.5.1. For aqueous samples, the MB consists of clean reagent water. For solid samples, the MB consists of washed sea sand. For mobility-procedure extracts, the MB consists of the mobility-procedure extract designated as MB. For methanol extracts, the MB consists of the methanol extract designated as MB.

14.4.5.2. One MB is required every day preparatory methods (i.e., methanol extractions, purge-and-trap extractions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.6. Item 6: Up to 20 samples (excluding QC check samples and method blanks) per batch. High concentration samples should be sufficiently diluted to ensure that instrument is not contaminated. Dilution of samples will result in increased reporting limits.

14.4.6.1. All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

14.4.7. Item 7: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

14.4.7.1. The purpose of the MS is to assess the effect of a sample matrix on the recovery of target analytes (i.e., assess the accuracy of the analytical measurements of the matrix). The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.7.

14.4.7.2. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently. This approach is considered "closed batch" as opposed to "open batch."

14.4.8. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15.8.

14.4.9. Solvent blanks may be added elsewhere in the sequence, as necessary (i.e., after suspected high concentration samples), to check for potential carryover or cross-contamination.

14.5. Ensure that a sufficient amount of the appropriate surrogate and internal standard working standard solution is present in the autosampler standard vial(s) if the autosampler is configured to inject standard solution automatically, and that a sufficient unused volume exists in the autosampler waste containers at the beginning of the sequence.

14.6. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the instrument run logbook or on the sequence table printout.

14.7. Initiate the sequence.

14.8. Data Interpretation

14.8.1. Evaluate the response (area count) and retention time of each internal standard compound in each standard, sample, and blank (see Section 12.6.3.).

14.8.2. Qualitative identification of each analyte/surrogate is based on retention time of the sample component, and on comparison of the sample mass spectrum, after background correction, with the characteristic ions in a reference mass spectrum.

14.8.2.1. The reference mass spectrum must be generated using the same conditions of this method.

14.8.2.2. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum.

14.8.2.3. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte.

14.8.2.3.1. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

14.8.3. Target analytes are identified as present when the following criteria are met.

14.8.3.1. The intensities of the characteristic ions of an analyte maximize in the same scan or within one scan of each other.

14.8.3.1.1. Selection of a peak by a data system target analyte search routine where the search is based on the

presence of a target chromatographic peak containing ions specific for the target analyte at an analyte-specific retention time will be accepted as meeting this criterion.

14.8.3.2. The RRT of the sample analyte is within ± 0.06 RRT units of the RRT of the standard analyte.

14.8.3.3. The relative intensities of the characteristic ions in the sample spectrum agree within ± 30% of the relative intensities of these ions in the reference spectrum.

14.8.3.4. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times.

14.8.3.4.1. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

14.8.3.5. Examination of extracted ion current profiles (EICPs) of appropriate ions can aid in the selection of spectra and in qualitative identification of analytes.

14.8.3.5.1. When analytes coelute, the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting analyte.

14.8.4. Tentative identification of a non-target analyte can be accomplished by using the data system library search. Refer to SOP-T025 for procedure.

14.8.4.1. The search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

14.8.4.2. The guidelines for making tentative identifications are as follows:

14.8.4.2.1. Relative intensities of major ions (ions greater than 10% of the most abundant ion) in the reference spectrum should be present in the sample spectrum.

14.8.4.2.2. Relative intensities of major ions in the sample spectrum should agree within ± 20% of those in the reference spectrum.

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

14.8.4.2.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting analytes.

14.8.4.2.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from sample spectrum due to background contamination or coeluting analytes. Data system library reduction program can sometimes create these discrepancies.

14.8.5. Quantitation of a target analyte is based on the integrated abundance from the EICP of the primary characteristic ion.

14.8.5.1. Proper quantitation requires the appropriate selection of a baseline and integration from which the area of the characteristic ion peak can be determined.

14.8.5.2. Determine the concentration based on the initial calibration curve.

14.8.5.2.1. Calculate the concentration of each target analyte in a sample extract using the average of the initial RRFs, the area of the characteristic ion peak, and the internal standard concentration and ion peak area. The formula for calculating concentration is listed in Section 15.9.

14.8.5.2.2. The data system is programmed to perform the calculation of concentration.

14.8.5.3. If the instrument response exceeds the calibration range, dilute the sample and reanalyze.

14.8.5.4. For any non-target analyte identified in a sample extract, estimate the concentration as follows:

14.8.5.4.1. Obtain the area of the characteristic ion peak for the non-target analyte and the internal standard ion peak area from the total ion chromatogram.

14.8.5.4.2. Assume the average of the initial RRFs for the non-target analyte to be 1.

14.8.5.4.3. Calculate and report the concentration as an estimated value.

14.8.6. Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.

14.8.6.1. When the instrument software produces proper integrations, it is highly recommended to use the integrations produced by the instrument software for consistency.

14.8.6.2. When the instrument software does not produce proper integrations (e.g., selecting an improper baseline, missing the correct peak, integrating a coelution, partially integrating a peak, etc.), manual integrations performed by the analyst are necessary.

14.8.6.3. Manual integration should be minimized by properly maintaining the instrument, updating the retention times, and configuring the peak integration parameters.

15. CALCULATIONS

15.1. The relative response factor is calculated as follows:

$$RRF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

where:
- RRF = relative response factor for target analyte being measured.
- A_x = area of the characteristic ion for target analyte being measured.
- C_{is} = concentration of internal standard in µg/L.
- A_{is} = area of the characteristic ion for internal standard.
- C_x = concentration of target analyte being measured in µg/L.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RRF_{ave}} \times 100$$

where:
- %RSD = percent relative standard deviation.
- SD = standard deviation of the RRFs for the target analyte.
- RRF_{ave} = mean of the 5, 6, or 7 initial RRFs for the target analyte.

15.3. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|RRF_{ave} - RRF_{daily}|}{RRF_{ave}} \times 100$$

where:
- %D = percent difference.
- RRF_{daily} = daily RRF for the target analyte.
- RRF_{ave} = mean of the 5, 6, or 7 initial RRFs for the target analyte.

15.4. The percent drift of each analyte is calculated as follows:

$$\%D = \frac{|C_{expected} - C_{measured}|}{C_{expected}} \times 100$$

where: %D = percent drift.
$C_{expected}$ = concentration of target analyte expected.
$C_{measured}$ = concentration of target analyte measured.

Note: Concentrations must be in equivalent units.

15.5. The relative retention time of each target analyte is calculated as follows:

$$RRT = \frac{RT_x}{RT_{is}}$$

where: RRT = relative retention time of target analyte.
RT_x = retention time of target analyte.
RT_{is} = retention time of internal standard.

Note: Retention times are in minutes to three decimal places.

15.6. The recovery of each LCS compound is calculated as follows:

$$\%REC_{LCS} = \frac{C_{recovered}}{C_{added}} \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.7. The recovery of each MS compound is calculated as follows:

$$\%REC_{MS} = \frac{C_{recovered} - C_{sample}}{C_{added}} \times 100$$

where: $\%REC_{MS}$ = percent recovery of target analyte in MS (or MSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{sample} = concentration of target analyte in environmental sample used.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.8. The relative percent difference is calculated as follows:

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

where: RPD = relative percent difference between two measurements (C_1 and C_2).
C_1 = concentration of target analyte in measurement 1.

C_2 = concentration of target analyte in measurement 2.

Note: Concentrations must be in equivalent units.

15.9. The target analyte concentration for a sample extract is calculated as follows:

$$C_{ex} = \frac{A_x \times C_{is}}{A_{is} \times RRF_{ave}}$$

where:
C_{ex} = concentration of target analyte in extract in µg/L.
A_x = area of the characteristic ion for target analyte.
C_{is} = concentration of internal standard in µg/L.
A_{is} = area of the characteristic ion for internal standard.
RRF_{ave} = mean of the 5, 6, or 7 initial RRFs for the target analyte.

15.10. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_p \times D}{V_A}$$

where:
C_A = concentration of target analyte in aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, $V_p = 5$.
For lower limit of quantitation, $V_p = 20$.
V_A = volume of aqueous sample purge-and-trap extracted in mL.
D = dilution factor, if the aqueous sample was serially diluted prior to purge-and-trap extraction. If no dilution was made, D = 1.

15.11. The target analyte concentration for a solid sample is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p}{W_S}$$

where:
C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, $V_p = 5$.
W_S = mass of solid sample purge-and-trap extracted in g.

15.12. The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, $V_p = 5$.
W_S = mass of solid sample purge-and-trap extracted in g.
C_{ss} = solids content in %.

15.13. The target analyte concentration for a methanol extracted solid (or oil) sample without moisture correction is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p \times P_1}{V_S}$$

where: C_S = concentration of target analyte in solid (or oil) sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, $V_p = 5$.
V_S = volume of methanol extract purge-and-trap extracted in mL.
P_1 = preparation factor without moisture correction for methanol extracted solid (or oil) sample in mL/g.

15.14. The target analyte concentration for a methanol extracted solid sample <u>without</u> methanol/water dilution factor correction is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p \times P_2}{V_S}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, $V_p = 5$.
V_S = volume of methanol extract purge-and-trap extracted in mL.
P_2 = preparation factor without methanol/water dilution factor correction for methanol extracted solid sample in mL/g.

15.15. The target analyte concentration for a methanol extracted solid sample <u>with</u> methanol/water dilution factor correction is calculated as follows:

$$C_S = \frac{C_{ex} \times V_p \times P_3}{V_S}$$

where: C_S = concentration of target analyte in solid sample in µg/kg.
C_{ex} = concentration of target analyte in extract in µg/L.
V_p = purge volume in mL.
Unless specified otherwise, $V_p = 5$.
V_S = volume of methanol extract purge-and-trap extracted in mL.
P_3 = preparation factor with methanol/water dilution factor correction

for methanol extracted solid sample in mL/g.

15.16. The target analyte concentration for a mobility-procedure extract is calculated as follows:

$$C_{MP} = \frac{C_{ex} \times V_p \times D}{V_{MP}}$$

where: C_{MP} = concentration of target analyte in mobility-procedure extract in mg/L.
C_{ex} = concentration of target analyte in extract in mg/L.
V_p = purge volume in mL.
Unless specified otherwise, $V_p = 5$.
V_{MP} = volume of mobility-procedure extract purge-and-trap extracted in mL.
D = dilution factor, if the mobility-procedure extract was serially diluted prior to purge-and-trap extraction.
If no dilution was made, D = 1.

15.17. Refer to the preparatory method(s) for additional calculations.

15.18. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and µg/kg (ppb) for oil, soil and solid waste samples.

15.18.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

15.19. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13., "Calibration and Standardization," shall be followed.

16.3. Proficiency test sample results shall be used to evaluate the ability to produce accurate results.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In

general, protective eyewear (e.g. safety glasses or goggles), and protective apparel (e.g. lab coats) and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually. All LCS/LCSD compounds must be within acceptance limits (see Section 12.5.2. for additional information).

18.1.1. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.1.2. The LCSD is only reported when the MS/MSD is unacceptable due to matrix interference effects, or when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity.

18.2. Ideally, the concentrations of target analytes in an MB should be less than the respective reporting limits (RLs). If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs are as follows:

18.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-processed and re-analyzed.

18.3. The acceptance criteria for surrogate compound recoveries vary depending upon historical data. The lower and upper acceptance limits for %REC of each surrogate compound are based upon the historical average recovery ± 3S that is updated at least annually.

18.3.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

18.3.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analysis. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.3.3. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.3.1. Check the surrogate and internal standard solutions for degradation and contamination.

18.3.3.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same sample should be re-processed and re-analyzed.

18.3.3.3. If incorrect procedures or degraded/contaminated standard solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-processed and re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.1. If, upon re-extraction and re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.3.3.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

18.3.4. Where sample dilution is required, depending on the dilution factor, the surrogate recovery will be low or not detected. This is an expected occurrence and reference should be made to the MB surrogate recovery which must be reported to the client.

18.4. The acceptance criteria for MS/MSD compounds vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each MS/MSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

18.4.1. When the %REC and RPD of the MS/MSD compounds are at or within the established acceptance limits, the analytical system is deemed to be compliant with the accuracy and precision requirement of the method for the particular matrix. The MS/MSD data shall be reported with the corresponding sample data.

18.4.2. If the %REC and/or RPD of the MS/MSD compounds are not within the established acceptance limits, the analytical system performance shall be suspect.

18.5. Matrix effects or poor instrument performance/technique typically cause unacceptable %REC values. Unacceptable RPD values are typically caused by sample inhomogeneity or poor instrument performance/technique. To properly evaluate the performance of the analytical system in these situations, refer to the LCS/LCSD. Specifically, an acceptable LCS/LCSD usually supports matrix interference.

18.6. Additional information regarding internal quality control checks is provided in SOP-T020.

18.7. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and µg/kg (ppb) for oil, soil and solid waste samples.

18.7.1. For EPA Region 9 requirement, report all concentrations in µg/L (ppb) for water samples, and µg/kg (ppb) on a dry-weight basis for soil samples.

18.8. The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set are then subject to reanalysis, depending upon the QC type in question.

20.1.1. MS/MSD: Acceptability of the MS/MSD recoveries is subject to the matrix and any anomalies associated with the subject batch. Failure of recoveries of an MS/MSD data set does not constitute an automatic reanalysis of the batch samples. Rather, it is acceptable to defer to the LCS/LCSD recoveries, to determine acceptance of the sample results.

20.1.2. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptance criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.2.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.2.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.2.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Unused or remaining soil or liquid samples and all other solid or liquid wastes resulting from our laboratory operations are considered hazardous for disposal purposes.

21.3. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal.

21.4. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste.

21.5. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly.

21.6. In order to maintain accountability for all samples received by Calscience, when a sample is used in its entirety for analysis, the empty container(s) are returned to Sample Control for placement in analytical storage.

21.7. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Wastes."

22. REFERENCES

22.1. *Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS)*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8260B, USEPA, Revision 2, December 1996.

22.2. *Determinative Chromatographic Separations*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000B, USEPA, Revision 2, December 1996.

22.3. *Quality Control*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter One, USEPA, Revision 1, July 1992.

22.4. *Choosing the Correct Procedure*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Two, USEPA, Revision 4, February 2007.

22.5. *Organic Analytes*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, February 2007.

22.6. *Volatile Organic Compounds (VOCs)*, SW-846 Method 8260, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, December 1999.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: List of Primary and Secondary Ions of Target Analytes, Surrogates, and Internal Standards.

23.2. Appendix B: Additional Quality Control Criteria for Department of Defense Project.

23.3. Appendix C: Control Limits for Department of Defense Project.

23.4. Appendix D: Additional Quality Control Criteria for BP Project.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 8260B are noted.

24.1.1. Quality Control

24.1.1.1. The requirement of providing the data user a summary of the initial calibration data or a specific list of the target analytes for which the %RSD exceeded the specified limit, and the results of the mean %RSD calculation is modified.

Appendix A

LIST OF PRIMARY AND SECONDARY IONS OF TARGET ANALYTES, SURROGATES, AND INTERNAL STANDARDS

Calscience Environmental Laboratories, Inc.

Appendix A

Primary and Secondary Ions

Compound Name	Characteristic Ion(s)	
	Primary	Secondary
acetone	58.10	43.00
acetonitrile	41.10	40.10 , 39.00
acrolein	56.10	55.00 , 58.00
acrylonitrile	53.10	52.10 , 51.00
allyl chloride	76.00	41.10 , 39.00 , 78.00
tert-amyl methyl ether (TAME)	73.10	87.10 , 55.10
benzene	78.10	
bromobenzene	156.00	77.10 , 158.00
bromochloromethane	128.00	130.00 , 49.00
bromodichloromethane	83.00	85.00 , 127.00
1,4-bromofluorobenzene (surrogate)	95.10	174.00 , 176.00
bromoform	173.00	175.00 , 254.00
bromomethane	94.00	96.00
1,3-butadiene	54.10	53.10 , 39.10
2-butanone	72.00	43.00
tert-butyl alcohol (TBA)	59.10	57.10 , 41.10
tert-butyl alcohol-d_9 (internal standard)	65.00	66.00
n-butylbenzene	91.10	92.10 , 134.20
sec-butylbenzene	105.10	134.10
tert-butylbenzene	119.10	91.10 , 134.10
carbon disulfide	76.00	78.00
carbon tetrachloride	117.00	119.00
chlorobenzene	112.00	77.00 , 114.00
chlorobenzene-d_5 (internal standard)	117.00	
chloroethane	64.00	66.00
2-chloroethyl vinyl ether	63.10	65.10 , 106.10
chloroform	83.00	85.00
chloromethane	50.00	52.00
chloroprene	53.10	88.00 , 90.00 , 51.00
1-chloropropane	42.10	41.10 , 39.10
2-chloropropane	43.10	41.10 , 39.10 , 63.00
2-chlorotoluene	91.10	126.10
4-chlorotoluene	91.10	126.10
cyclohexane	84.10	56.10 , 41.10 , 55.10
dibromochloromethane	129.00	208.00 , 206.00
1,2-dibromo-3-chloropropane	75.00	155.00 , 157.00

Appendix A

Primary and Secondary Ions (Cont.)

Compound Name	Characteristic Ion(s)	
	Primary	Secondary
1,2-dibromoethane	107.00	109.00 , 188.00
dibromofluoromethane (surrogate)	113.00	
dibromomethane	93.00	95.00 , 174.00
1,2-dichlorobenzene	146.00	111.00 , 148.00
1,3-dichlorobenzene	146.00	111.00 , 148.00
1,4-dichlorobenzene	146.00	148.00 , 111.00
1,4-dichlorobenzene-d_4 (internal standard)	152.00	115.00 , 150.00
trans-1,4-dichloro-2-butene	53.10	88.10 , 75.00
dichlorodifluoromethane	85.00	87.00
1,1-dichloroethane	63.00	65.00 , 83.00
1,2-dichloroethane	62.00	98.00
1,2-dichloroethane-d_4 (surrogate)	65.00	102.00 , 67.00
1,1-dichloroethene	96.00	61.00 , 63.00
cis-1,2-dichloroethene	96.00	98.00 , 61.00
trans-1,2-dichloroethene	96.00	98.00 , 61.00
1,2-dichloropropane	63.00	112.00
1,3-dichloropropane	76.00	78.00
2,2-dichloropropane	77.00	97.00
1,1-dichloropropene	75.00	110.00 , 77.00
cis-1,3-dichloropropene	75.00	77.00 , 39.00
trans-1,3-dichloropropene	75.00	77.00 , 39.00
diethyl ether	74.00	45.00 , 59.00
1,4-difluorobenzene (internal standard)	114.10	
diisopropyl ether (DIPE)	45.10	87.10
1,4-dioxane	88.10	58.10 , 43.00 , 57.00
ethanol	45.00	46.10 , 43.10
ethylbenzene	91.10	106.10
ethyl tert-butyl ether (ETBE)	59.10	87.10
ethyl methacrylate	69.00	41.00 , 99.00 , 114.00
hexachloro-1,3-butadiene	224.90	222.90 , 226.90
hexane	57.10	56.10 , 43.10 , 41.10
2-hexanone	43.00	58.00 , 57.00 , 100.00
iodomethane	142.00	127.00 141.00
isobutyl alcohol (iso-butanol)	43.10	41.10 , 42.10 , 74.10
isopropanol (2-propanol)	45.10	59.20
isopropylbenzene	105.10	120.10

Appendix A

Primary and Secondary Ions (Cont.)

Compound Name	Characteristic Ion(s)	
	Primary	Secondary
p-isopropyltoluene	119.10	91.10 , 134.10
methacrylonitrile	41.00	67.10 , 52.00 , 66.00
methyl acetate	43.10	74.10 , 59.00
methyl tert-butyl ether (MTBE)	73.10	57.10
methyl methacrylate	69.00	41.00 , 100.00 , 39.00
methylcyclohexane	83.10	55.10 , 98.20 , 41.10
methylene chloride	84.00	86.00 , 49.00
4-methyl-2-pentanone (MIBK)	100.00	43.00 , 58.00 , 85.00
naphthalene	128.10	
pentafluorobenzene (internal standard)	168.00	
propanedinitrile	66.10	38.10 , 39.00 , 65.00
propionitrile	54.10	52.00 , 55.00 , 40.00
n-propylbenzene	91.10	120.10
styrene	104.10	78.10
1,1,1,2-tetrachloroethane	131.00	133.00 , 119.00
1,1,2,2-tetrachloroethane	83.00	131.00 , 85.00
tetrachloroethene	164.00	129.00 , 131.00 , 166.00
tetrahydrofuran	42.10	41.10 , 71.10 , 72.10
thiophene	84.00	58.00 , 45.00
toluene	92.00	91.00
toluene-d_8 (surrogate)	98.00	
1,2,3-trichlorobenzene	180.00	182.00 , 145.00
1,2,4-trichlorobenzene	180.00	182.00 , 145.00
1,1,1-trichloroethane	97.00	61.00 , 99.00
1,1,2-trichloroethane	83.00	97.00 , 85.00
trichloroethene	95.00	97.00 , 130.00 , 132.00
trichlorofluoromethane	101.00	103.00
1,2,3-trichloropropane	75.00	77.00
1,1,2-trichloro-1,2,2-trifluoroethane	101.00	151.00 , 153.00
2,2,4-trimethyl pentane	57.10	56.10 , 41.10
1,2,4-trimethylbenzene	105.10	120.10
1,3,5-trimethylbenzene	105.10	120.10
vinyl acetate	43.00	86.00
vinyl chloride	62.00	64.00
o-xylene	106.00	91.00
p/m-xylenes	106.00	91.00

Appendix B

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8260B, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. DETECTION LIMITS

2.1. The quantitation limit must be set within the calibration range.

3. SCOPE AND APPLICATION

3.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

4. STANDARDS

4.1. The spike standard solutions shall contain all anticipated target analytes.

4.2. The use of a standard from a second lot as the second source standard is acceptable when only one manufacturer of the calibration standard exists. "Manufacturer" refers to the producer of the standard, not the vendor.

5. QUALITY CONTROL

5.1. Method Detection Limit (MDL)

5.1.1. MDL study shall be performed at the initial test method setup, following a change in the test method that affects how the test is performed, or when a change in instrumentation that affects the sensitivity of the analysis.

5.1.2. MDL verification must be performed immediately following an MDL study and quarterly thereafter.

5.1.2.1. MDL verification sample shall be prepared by spiking an appropriate matrix at approximately 2–3 times the detection limit for single-analyte test, or 1–4 times the detection limit for multiple-analyte test.

5.1.2.2. MDL verification is deemed valid if the apparent signal to noise ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification (e.g., ion abundance, etc.).

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the MDL study and verification at a higher concentration. Set the MDL at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive MDL verifications at a higher concentration. Set the MDL at the higher concentration.

5.1.3. No samples shall be analyzed without a valid MDL.

5.2. Initial Calibration (IC)

5.2.1. The IC is deemed valid if the %RSD for each analyte (except CCC) is ≤ 15%, the %RSD for each CCC is ≤ 30%, and the average RRF for each SPCC is as follows:

SPCC	Average RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

5.2.2. If the %RSD criterion for an analyte is not met, employ one of the following calibration options.

5.2.2.1. The first calibration option is linear least squares regression with equal weighting factor. The IC is deemed valid if the correlation coefficient, r, is ≥ 0.995.

5.2.2.1.1. Calibration may not be forced through the origin.

5.2.2.2. The second calibration option is quadratic least squares regression with equal weighting factor. The IC is deemed valid if the coefficient of determination, r^2, is ≥ 0.990.

5.2.2.2.1. This option requires at least six calibration levels.

5.3. Initial Calibration Verification (ICV)

5.3.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

5.4. Continuing Calibration Verification (CCV)

5.4.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%, and the daily RRF for each SPCC is as follows:

SPCC	Daily RRF
bromoform	≥ 0.10
chlorobenzene	≥ 0.30
chloromethane	≥ 0.10
1,1-dichloroethane	≥ 0.10
1,1,2,2-tetrachloroethane	≥ 0.30

5.4.2. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.5. Retention Time Window

5.5.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration, and by using a low-to-midpoint CCV standard at the beginning of an analytical sequence.

5.5.1.1. When initial calibration is performed, daily retention time window for each analyte/surrogate is determined from the elution time of the analyte/surrogate in the midpoint calibration standard.

5.5.1.2. When initial calibration is not performed, daily retention time window for each analyte/surrogate is determined from the elution time of the analyte/surrogate in the low-to-midpoint CCV standard.

5.5.1.3. Document the serial number of the analytical column associated with the retention time window.

5.5.1.4. Record the retention time in minutes for each analyte/surrogate to three decimal places.

5.6. Event Based Quality Control (LCS/LCSDs and MBs)

5.6.1. Laboratory Control Samples (LCS/LCSDs)

5.6.1.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound in aqueous and solid matrices are listed in Appendix C.

5.6.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.6.1.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.6.1.3. All project-specific analytes of concern must be within control limits. No marginal exceedance is allowed for any project-specific analyte of concern. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.6.2. Method Blanks (MBs)

5.6.2.1. The MB is considered to be contaminated if one of the following conditions is met.

5.6.2.1.1. The concentration of any target analyte in the MB exceeds 1/2 the RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.6.2.1.2. The concentration of any common laboratory contaminant in the MB exceeds RL, and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater).

5.6.2.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

5.6.2.2. If the MB is contaminated, reprocess the samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the MDL.

5.6.2.2.1. If insufficient sample volume remains for reprocessing, the results shall be reported with the appropriate data qualifier (B-flag) for the specific analyte(s) in all samples associated with the failed MB.

5.7. Matrix Based Quality Control (Surrogates, Internal Standards, and MS/MSDs)

5.7.1. Surrogates

5.7.1.1. The lower and upper acceptance limits for %REC of each surrogate compound in aqueous and solid matrices are listed in Appendix C.

5.7.1.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.7.2. Internal Standards

5.7.2.1. If the EICP area of any internal standard in each standard and sample is not within −50% to +100% from that in the midpoint calibration standard for the most recent initial calibration, the mass spectrometer must be inspected for malfunctions and corrective action effected.

5.7.2.2. If the retention time of any internal standard in each standard and sample is not within ± 30 seconds from that in the midpoint calibration standard for the most recent initial calibration, the gas chromatograph must be inspected for malfunctions and corrective action effected.

5.7.2.3. Following corrective action, reanalysis of samples analyzed while the system was malfunctioning is required.

5.7.2.4. If corrective action fails in a field sample, the results shall be reported with the appropriate data qualifier (Q-flag) for the specific analyte(s) associated with the failed internal standard.

5.7.3. Matrix Spikes (MS/MSDs)

5.7.3.1. The lower and upper acceptance limits for %REC of each MS/MSD compound in aqueous and solid matrices are listed in Appendix C. The RPD is ≤ 30%.

5.7.3.2. Project-specific control limits shall be applied. If project-specific control limits are unavailable, DoD generated control limits shall be applied. If DoD generated control limits are unavailable, laboratory's in-house control limits shall be applied.

5.7.3.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

6. PROCEDURE

6.1. Standard and sample purge vessels are loaded in the following or other logical order:

1) Tuning Standard
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) Samples (up to 20 per batch, excluding QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)

6.1.1. Item 7: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.1.1.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.1.2. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

7. REFERENCES

7.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 25, 2010.

Appendix C

CONTROL LIMITS FOR DEPARTMENT OF DEFENSE PROJECT

Calscience Environmental Laboratories, Inc.

Appendix C

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Aqueous Matrix

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
1,1,1,2-Tetrachloroethane	80	130	75	135
1,1,1-Trichloroethane	65	130	55	145
1,1,2,2-Tetrachloroethane	65	130	55	140
1,1,2-Trichloroethane	75	125	65	135
1,1-Dichloroethane	70	135	60	145
1,1-Dichloroethene	70	130	55	140
1,1-Dichloropropene	75	130	65	140
1,2,3-Trichlorobenzene	55	140	45	155
1,2,3-Trichloropropane	75	125	65	130
1,2,4-Trichlorobenzene	65	135	55	145
1,2,4-Trimethylbenzene	75	130	65	140
1,2-Dibromo-3-chloropropane	50	130	35	145
1,2-Dibromoethane	80	120	75	125
1,2-Dichlorobenzene	70	120	60	130
1,2-Dichloroethane	70	130	60	140
1,2-Dichloropropane	75	125	65	135
1,3,5-Trimethylbenzene	75	130	65	140
1,3-Dichlorobenzene	75	125	65	130
1,3-Dichloropropane	75	125	65	135
1,4-Dichlorobenzene	75	125	65	130
2,2-Dichloropropane	70	135	60	150
2-Butanone	30	150	10	170
2-Chlorotoluene	75	125	65	135
2-Hexanone	55	130	45	140
4-Chlorotoluene	75	130	65	135
4-Methyl-2-pentanone (MIBK)	60	135	45	145
Acetone	40	140	20	160
Benzene	80	120	75	130
Bromobenzene	75	125	70	130
Bromochloromethane	65	130	55	140
Bromodichloromethane	75	120	70	130
Bromoform	70	130	60	140
Bromomethane	30	145	10	165
Carbon disulfide	35	160	15	185
Carbon tetrachloride	65	140	55	150
Chlorobenzene	80	120	75	130
Chlorodibromomethane	60	135	45	145
Chloroethane	60	135	50	145
Chloroform	65	135	50	150
Chloromethane	40	125	25	140
cis-1,2-Dichloroethene	70	125	60	135
cis-1,3-Dichloropropene	70	130	60	140

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix C

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Aqueous Matrix (Cont.)

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Dibromomethane	75	125	65	135
Dichlorodifluoromethane	30	155	10	175
Ethylbenzene	75	125	65	135
Hexachloro-1,3-butadiene	50	140	35	160
Isopropylbenzene	75	125	65	135
m,p-Xylene	75	130	65	135
Methyl tert-butyl ether (MTBE)	65	125	55	135
Methylene chloride	55	140	40	155
Naphthalene	55	140	40	150
n-Butylbenzene	70	135	55	150
n-Propylbenzene	70	130	65	140
o-Xylene	80	120	75	130
p-Isopropyltoluene	75	130	65	140
sec-Butylbenzene	70	125	65	135
Styrene	65	135	55	145
tert-Butylbenzene	70	130	60	140
Tetrachloroethene	45	150	25	165
Toluene	75	120	70	130
trans-1,2-Dichloroethene	60	140	45	150
trans-1,3-Dichloropropene	55	140	40	155
Trichloroethene	70	125	60	135
Trichlorofluoromethane	60	145	45	160
Vinyl chloride	50	145	35	165

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix C

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Solid Matrix

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
1,1,1,2-Tetrachloroethane	75	125	65	135
1,1,1-Trichloroethane	70	135	55	145
1,1,2,2-Tetrachloroethane	55	130	40	145
1,1,2-Trichloroethane	60	125	50	140
1,1-Dichloroethane	75	125	65	135
1,1-Dichloroethene	65	135	55	150
1,1-Dichloropropene	70	135	60	145
1,2,3-Trichlorobenzene	60	135	50	145
1,2,3-Trichloropropane	65	130	50	140
1,2,4-Trichlorobenzene	65	130	55	140
1,2,4-Trimethylbenzene	65	135	55	145
1,2-Dibromo-3-chloropropane	40	135	25	150
1,2-Dibromoethane	70	125	60	135
1,2-Dichlorobenzene	75	120	65	125
1,2-Dichloroethane	70	135	60	145
1,2-Dichloropropane	70	120	65	125
1,3,5-Trimethylbenzene	65	135	55	145
1,3-Dichlorobenzene	70	125	65	135
1,3-Dichloropropane	75	125	70	130
1,4-Dichlorobenzene	70	125	65	135
2,2-Dichloropropane	65	135	55	145
2-Butanone	30	160	10	180
2-Chlorotoluene	70	130	60	140
2-Hexanone	45	145	30	160
4-Chlorotoluene	75	125	65	135
4-Methyl-2-pentanone (MIBK)	45	145	30	165
Acetone	20	160	10	180
Benzene	75	125	65	135
Bromobenzene	65	120	55	130
Bromochloromethane	70	125	60	135
Bromodichloromethane	70	130	60	135
Bromoform	55	135	45	150
Bromomethane	30	160	10	180
Carbon disulfide	45	160	30	180
Carbon tetrachloride	65	135	55	145
Chlorobenzene	75	125	65	130
Chlorodibromomethane	65	130	55	140
Chloroethane	40	155	20	175
Chloroform	70	125	65	135
Chloromethane	50	130	40	140
cis-1,2-Dichloroethene	65	125	55	135
cis-1,3-Dichloropropene	70	125	65	135

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix C

DoD Control Limits of LCS/LCSD/MS/MSD Compounds in Solid Matrix (Cont.)

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Dibromomethane	75	130	65	135
Dichlorodifluoromethane	35	135	15	155
Ethylbenzene	75	125	65	135
Hexachloro-1,3-butadiene	55	140	40	155
Isopropylbenzene	75	130	70	140
m,p-Xylene	80	125	70	135
Methylene chloride	55	140	40	155
Naphthalene	40	125	25	140
n-Butylbenzene	65	140	50	150
n-Propylbenzene	65	135	50	145
o-Xylene	75	125	70	135
p-Isopropyltoluene	75	135	65	140
sec-Butylbenzene	65	130	50	145
Styrene	75	125	65	135
tert-Butylbenzene	65	130	55	145
Tetrachloroethene	65	140	55	150
Toluene	70	125	60	135
trans-1,2-Dichloroethene	65	135	55	145
trans-1,3-Dichloropropene	65	125	55	140
Trichloroethene	75	125	70	130
Trichlorofluoromethane	25	185	10	215
Vinyl chloride	60	125	45	140

Note: ME limits are applicable to LCS/LCSD compounds only.

Appendix C

DoD Control Limits of Surrogate Compounds in Aqueous Matrix

Analyte	Control Limit	
	Lower	Upper
1,2-Dichloroethane-d_4	70	120
4-Bromofluorobenzene	75	120
Dibromofluoromethane	85	115
Toluene-d_8	85	120

DoD Control Limits of Surrogate Compounds in Solid Matrix

Analyte	Control Limit	
	Lower	Upper
4-Bromofluorobenzene	85	120
Toluene-d_8	85	115

Appendix D

ADDITIONAL QUALITY CONTROL CRITERIA FOR BP PROJECT

Calscience Environmental Laboratories, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8260B, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) – Additional Quality Control Criteria for BP Project.

2. SCOPE AND APPLICATION

2.1. The quality control criteria and procedure described herein either supersede or are in addition to the standard quality control criteria and procedure.

3. STANDARDS

3.1. The spike standard solutions shall contain all anticipated target analytes.

3.2. The use of a standard from a second lot as the second source standard is acceptable if written warranties demonstrating that the standards from two different lots are not prepared from the same reference materials are obtained from the manufacturer. "Manufacturer" refers to the producer of the standard, not the vendor.

4. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

4.1. Holding time begins at the date and time the sample is collected as documented on the chain of custody record.

4.2. Organic extracts must be stored in the same type of vials (amber glass or clear glass) as the associated standard solutions at the appropriate storage temperatures.

4.3. Properly labeled (e.g., date installed, cold storage unit number, etc.) storage blanks must be initiated and analyzed on a bi-weekly basis for each cold storage unit (refrigerator and freezer) used to store BP samples.

4.3.1. Any field and/or trip blanks submitted by BP must be stored in the same cold storage unit units as the samples that they are intended to be associated with (even if the matrices are different).

5. QUALITY CONTROL

5.1. Method Detection Limit (MDL)

5.1.1. MDL study should be performed annually for each analyte and matrix.

5.1.2. MDL verification must be performed immediately following an MDL study.

5.1.2.1. MDL verification sample must be spiked at the calculated MDL value.

5.1.2.2. MDL verification is deemed valid if all analytes in the verification sample are recovered.

5.1.3. At a minimum, the MDL study shall be performed on a single instrument, and the calculated MDL value must be confirmed by analyzing an MDL verification sample on all instruments used to analyze BP samples.

5.2. Initial Calibration (IC)

5.2.1. In addition to the standard initial calibration criteria, the %RSD for benzene, ethylbenzene, toluene, o-xylene, p/m-xylenes, each oxygenated compound, and each surrogate must be ≤ 15%.

5.2.1.1. The oxygenated compounds are DIPE, ETBE, MTBE, TAME, TBA, and ethanol.

5.2.2. Do not force the curve equation through zero.

5.3. Initial Calibration Verification (ICV)

5.3.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

5.4. Continuing Calibration Verification (CCV)

5.4.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and after every 10 analyses or portion thereof within a 12-hour shift.

5.4.2. Documentation for multiple (more than one) injection trials of CCV standards must include the reason for the multiple trials, the corrective action and which trial was used and why.

5.5. Minimum Relative Response Factor

5.5.1. For IC, ICV, and CCV, the RRF of benzene, ethylbenzene, toluene, o-xylene, p/m-xylenes, each oxygenated compound, and each surrogate must be evaluated.

5.5.1.1. The RRF of each of the following analytes is as follows:

Analyte	RRF
benzene	> 0.300
ethylbenzene	> 0.300
toluene	> 0.300
o-xylene	> 0.300
p/m-xylene	> 0.300
oxygenate (except TBA)	> 0.300
TBA	> 0.100
ethanol	> 0.100
surrogate	> 0.200

5.6. Event Based Quality Control (LCS/LCSDs and MBs)

5.6.1. Method Blanks (MBs)

5.6.1.1. Contamination observed in the MB at a concentration greater than 1/2 of the RL is acceptable if either one of the following conditions is met.

5.6.1.1.1. No contaminant is detected in the associated samples.

5.6.1.1.2. The concentration of the contaminant in the associated samples is greater than 10 times the concentration in the MB.

6. PROCEDURE

6.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and after every 10 analyses or portion thereof within a 12-hour shift. If the QC criteria are met, the initial calibration is assumed to be valid and sample analysis may resume.

6.2. Standard and sample purge vessels are loaded in the following or other logical order:

1) Tuning Standard
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD)
5) Method Blank (MB)
6) Samples (up to 10 analyses, excluding CCV analyses)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)

6.2.1. Item 3: The LCS is a known matrix that has been spiked with known concentrations of specific target analytes. The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCS is processed concurrently with the associated samples. In the processing of the LCS, reagents and procedures identical to those for actual samples are used.

6.2.1.1. One LCS is required every day preparatory methods (i.e., methanol extractions, purge-and-trap extractions, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent, within an 8-hour preparation event.

6.2.2. Item 4: The LCSD is handled identically to the LCS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the LCS in combination with the LCSD can be used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD).

6.2.3. Item 5: The MB is a known matrix similar to the samples being analyzed which is processed concurrently with the associated samples. In the processing of the MB, reagents and procedures identical to those for actual samples are used.

6.2.3.1. One MB is required every day preparatory methods (i.e., methanol extractions, purge-and-trap extractions, etc.) are performed for every batch of 20 samples per matrix or portion

thereof, whichever is more frequent, within an 8-hour preparation event.

6.2.4. Item 7: The MS is the actual sample matrix spiked with known concentrations of specific target analytes. The sample which is spiked for the MS is processed concurrently with the associated samples. In the processing of the MS, reagents and procedures identical to those for actual samples are used.

6.2.4.1. One MS is required for every batch of 20 samples per matrix or portion thereof processed concurrently within an 8-hour preparation event.

6.2.4.2. The sample selected for spiking must be one of the samples collected for the specific BP project. If 10 or fewer BP samples are received, and no sample is designated for MS/MSD analyses, then a non-BP sample may be used.

6.2.5. Item 8: The MSD is handled identically to the MS discussed in the previous section. In addition to assessing the accuracy of the analytical measurement, the MS in combination with the MSD can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

6.2.6. If solvent, instrument, or rinse blanks are placed in the sequence, the appropriate surrogate and internal standard working standard solution shall be injected or manually added to the aforementioned blanks.

6.3. Data Interpretation

6.3.1. Qualitative identification of each analyte/surrogate is based on retention time of the sample component, and on comparison of the sample mass spectrum, after background correction, with the characteristic ions in a reference mass spectrum.

6.3.1.1. All ions for an analyte/surrogate that are present in the reference spectrum at a relative intensity greater than 10% must be present in the sample spectrum.

6.3.1.1.1. The relative intensity of the most abundant ion in the reference spectrum is 100%.

6.3.2. Target analytes are identified as present when the following criteria are met.

6.3.2.1. The intensities of the characteristic ions of an analyte maximize within one scan of each other.

6.3.2.2. The relative intensities of the characteristic ions in the sample spectrum agree within ± 30% of the relative intensities of these ions in the reference spectrum.

6.3.3. Apply methanol/water dilution factor correction for the calculation of the target analyte concentration for a methanol extracted solid sample reported on an "as-received" basis.

7. REFERENCES

7.1. Technical Requirements for Environmental Laboratory Analytical Services, BP Laboratory Management Program (LaMP), Revision 09, July 30, 2007.

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Title : **EPA METHODS TO-14A/15, VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY / MASS SPECTROMETRY (GC/MS) IN AIR USING SUMMA® CANISTERS OR TEDLAR™ BAGS**

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APPROVED FOR RELEASE BY: _____ 5/4/11
MANAGEMENT **DATE**

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ANNUAL SOP REVIEW

YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE
YEAR	GROUP LEADER	DATE	QA MANAGER	DATE

1. METHOD IDENTIFICATION

1.1. EPA Method TO-14A and EPA TO-15 Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry in Air using Summa® canisters or Tedlar™ bags.

2. APPLICABLE MATRICES

2.1. This method is applicable for air/vapor matrices.

3. ►DETECTION LIMITS

3.1. The estimated quantitation limits (EQLs) for these methods are approximately 0.5 ppbv.

3.2. The estimated quantitation limits (EQLs) generated for the compounds determined using the SIM method are approximately 0.025 ppbv. The EQLs will be proportionally higher for samples that require dilution.

3.3. ***Please refer to Appendix 2 for standard TO-15 analyte, reporting and method detection limits.***

4. SCOPE AND APPLICATION

4.1. The TO-14A/15 methods are used to determine the concentration of a large number of volatile organic compounds (VOCs) having a vapor pressure greater than 10^{-1} torr at 25°C at standard pressure. Low concentrations of analytes may also be determined by selective ion monitoring (SIM) mode. Samples are collected in Summa® polished canisters, MiniCans or Tedlar™ bags.

4.2. The following compounds are determined by this method:

TO-14A Target List

Dichlorodifluoromethane
Chloromethane
Chloroform
Vinyl Chloride
Bromomethane
Chloroethane
Trichlorofluoromethane
1,1-Dichloroethene
Methylene Chloride
Tetrachloroethene
1,1,2-Trichloro-1,2,2-Trifluoroethane
1,1-Dichloroethane
1,2-Dichloro-1,1,2,2-tetrafluoroethane
c-1,2-Dichloroethene
1,2-Dichloroethane
1,1,1-Trichloroethane
Benzene
Carbon Tetrachloride
1,2-Dichloropropane
trichloroethene
c-1,3-Dichloropropene
t-1,3-Dichloropropene
1,1,2-Trichloroethane
Toluene
Chlorobenzene
1,2-Dichlorobenzene
Ethylbenzene
p/m-Xylenes
Styrene
1,1,2,2-Tetrachloroethane
o-Xylene
1,3,5-Trimethylbenzene
1,2,4-Trimethylbenzene
Benzyl Chloride
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dibromoethane
1,2,4-Trichlorobenzene
Hexachloro-1,3-Butadiene

TO-15 Target List

Dichlorodifluoromethane
Chloromethane
Chloroform
Vinyl Chloride
Bromomethane
Chloroethane
Trichlorofluoromethane
1,1-Dichloroethene
Methylene Chloride
1,2-Dibromomethane
1,1,2-Trichloro-1,2,2-Trifluoroethane
1,1-Dichloroethane
cis-1,2-Dichloroethene
1,2-Dichloro-1,1,2,2-Tetrafluoroethane
Acetone
trans-1,2-Dichloroethene
2-Butanone
Dibromochloromethane
1,2-Dichloroethane
1,1,1-Trichloroethane
Benzene
Carbon Tetrachloride
1,2-Dichloropropane
trichloroethene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
1,1,2-Trichloroethane
Toluene
Bromodichloromethane
Tetrachloroethene
Carbon Disulfide
Methyl-t-butyl Ether
4-Methyl-2-pentanone
Bromoform
Ethylbenzene
p/m-Xylenes
Styrene
1,1,2,2-Tetrachloroethane
o-Xylene
1,3,5-Trimethylbenzene
1,2,4-Trimethylbenzene
Benzyl Chloride
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
1, 2,4-Trichlorobenzene
Hexachloro-1,3-Butadiene
Chlorobenzene
Vinyl Acetate
2-Hexanone
4-Ethyltoluene

Additional Calibrated Compounds (by Request):

Acrylonitrile
1,3-Butadiene
tert-Butyl Alcohol (TBA)
Cyclohexane
1,1-Difluoroethane
Diisopropyl Ether (DIPE)
1,4-Dioxane
Ethyl-tert-butyl Ether (ETBE)
Ethyl Acetate
Ethanol
Heptane
Hexane
Methanol
Napthalene
tert-Amyl Methyl Ether (TAME)
Propene
iso-Propanol
Tetrahydrofuran
1,2,3-Trichloropropane

TO-14A/15 SIM Target List

Benzene
Bromodichloromethane
Carbon tetrachloride
Chloroform
Dibromochloromethane
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
c-1,2-Dichloroethene
t-1,2-Dichloroethene
Ethylbenzene
Hexachloro-1,3-butadiene
Methylene chloride
1,1,2,2-Tetrachlorethane
Tetrachloroethene
Toluene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
Vinyl chloride
p/m-Xylenes
o-Xylene

4.3. This method is restricted to use by or under the supervision of analysts and supervisors who are experienced in the use of GC/MS and skilled in the interpretation of mass spectra.

5. METHOD SUMMARY

5.1. EPA Methods TO-14A and 15 describe chromatographic procedures that will allow for the separation of volatile organic compounds and their qualitative and quantitative analysis by mass spectrometry. Detection is achieved using a mass selective detector. Method TO-15 is significant in that it extends Method TO-14A capabilities in the following ways.

5.1.1. Method TO-15 requires the use of a GC/MS which results in more scientifically defensible data.

5.1.2. Method TO-15 establishes method performance and quality control criteria for acceptance of data.

5.2. A known volume of sample is directed from the container (Summa® canister, MiniCan or Tedlar™ bag) through a solid multi-module (glass beads, tenex, cryofocuser) concentrator. A very minimal portion of the water vapor in the sample may break through the concentrator during sampling. Dry purging the concentrator with helium, while retaining target analytes can further reduce the water content of the sample. Post concentration, the VOCs are thermally desorbed onto a gas chromatographic column for separation. Detection is by mass selective detector.

6. DEFINITIONS

6.1. Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in requirement documents.

6.2. Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

6.3. Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

6.4. Calibration: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

6.5. Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

6.6. Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

6.7. Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

6.8. Internal Standard: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.9. Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.10. Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

6.11. Method Blank: A sample of a matrix similar to the batch of associated samples that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.

6.12. Method Detection Limit: The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

6.13. Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

6.14. Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

6.15. Quantitation Limits: Levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specific degree of confidence.

6.16. Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.17. Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for QC purposes.

7. INTERFERENCES

7.1. Performance of this method is restricted to analysts experienced in the use of the instruments and apparatus required in executing this method and interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results and quality control prior to the analysis of billable samples.

7.2. Resulting from widespread concentration levels among various air samples, a TPH pre-determination for the purpose of determining injection volume is performed. This will help minimize instrument contamination.

7.3. Contamination by carryover can occur whenever high and low concentration level samples are analyzed sequentially. Suspected high level samples should be diluted and then analyzed at the end of the sequence to prevent carryover contamination. The analysis of blanks after high concentration samples is encouraged.

7.4. Interference can also occur when "dirty" samples leave residue in the column. The column can be "baked" after such samples.

7.5. The following provides information regarding possible interferences and target analyte anomalies during analytic processing:

7.5.1. Very volatile compounds such as Chloromethane and Vinyl Chloride can display peak broadening and co-elution with other species if the compounds are not delivered to the column in a small volume or carrier gas. Refocusing of the sample after collection on the primary trap, either on a separate focusing trap or at the head of the column, mitigates this problem.

7.5.2. Interferences in canister samples may result from improper use or from contamination of: 1) the canisters themselves due to poor manufacturing, 2) the canister cleaning apparatus, or 3) the sampling or analytical system. Attention to the following details will help to minimize the possibility of contamination of canisters.

7.5.2.1. New canisters should be filled with humidified zero air and then analyzed, after "aging" for 24 hours, to determine cleanliness. Pending analysis, canisters should be stored in a contaminant-free location.

7.5.2.2. Impurities in the calibration dilution gas and carrier gas, organic compounds out-gassing from system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system itself must be demonstrated free of contamination by the periodic analysis of humidified zero air blanks.

7.5.3. Best efforts must be taken to maintain the analytical areas free of all contaminants that include target analytes that are common solvents or reagents in other areas of the laboratory. This can be minimized by restricting entry of these solvents or solvent-contaminated items (e.g., laboratory coats) into the VOC laboratory and proper management / maintenance of laboratory ventilation.

7.5.4. Other major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-Polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber BUNA-N components should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should locate and remove the source of contamination before proceeding with calibration and analysis.

7.5.5. Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from chromatographic grade stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean since clothing previously exposed to methylene chloride fumes during SVOC extraction procedures may contribute to sample contamination.

7.6. Summa Canister Cleaning is referenced under SOP T-016.

8. SAFETY

8.1. Exposure to hazardous chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current version of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses and laboratory coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.2. The following compounds covered by this method have been tentatively classified as known or suspected human carcinogens: benzene, methylene chloride, chloroform, Bromoform, Bromodichloromethane, Chlorodibromomethane, and Vinyl Chloride. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when analysts handle high concentrations of these compounds.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph:

9.1.1. Hewlett-Packard 6890 Gas Chromatograph configured with a PC based data system or equivalent.

9.2. Entech 7016 Autosampler or equivalent

9.3. Entech 7100 Cryogenic Concentrator or equivalent

9.4. Mass Spectrometer:

9.4.1. HP 5973 Mass Selective Detector (MSD) or equivalent capable of scanning from 35 to 300amu every one second or less, using 70 volts nominal electron energy in the EI mode or equivalent. The MSD must be capable of producing a mass spectrum for BFB that meets all of the criteria in Section 12.1 below, when 100ppbv of BFB is injected.

9.4.2. Alternatively, the MSD may be used in Selective Ion Monitoring (SIM) mode.

9.5. Chromatographic Column:

9.5.1. Restek RTX-1, 60M x 0.32mm ID, 1.0μ film thickness or equivalent.

9.6. Environics Series 2000 Computerized Multi-Component Gas Mixer.

9.7. 2-stage regulators capable of handling pressures up to 4000psi and 200psi

9.8. Stainless steel or inert teflon tubing with Swagelock fittings, or equivalent

9.9. Syringes:

9.9.1. Hamilton 702N gas tight Leurlock type w/ on-off valves or equivalent, sizes 1mL, 2.5mL, 5mL, 25mL, 50mL, and 100mL.

10. ►REAGENTS AND STANDARDS

10.1. REAGENTS

10.1.1. Zero Air

10.1.2. Reagent grade water for humidifying Summa canisters

10.2. STANDARDS

10.2.1. Tuning standard containing 100ppbv of 4-bromofluorobenzene (BFB) in zero air. The tuning standard also contains internal standards and surrogate standards.

10.2.1.1. ***100***mL of the tuning standard is injected into the concentrator.

10.2.2. Internal and Surrogate standards – 1 canister:

10.2.2.1. Internal Standards: Bromochloromethane, Chlorobenzene-d_5 and 1,4-Difluorobenzene each at a nominal concentration of 100ppbv.

10.2.2.1.1. 100mL of Internal/Surrogate standard is injected with every sample, QC sample, and method blank.

10.2.2.1.2. For the lower concentrations used in the SIM mode, the internal standards are at 2.0ppbv.

10.2.2.2. Surrogates: 1,4-Bromoflurobenzene (also used as the tuning standard), 1,2-Dichloroethane-d_4 and Toluene-d_8 each at a nominal concentration of 100ppbv.

10.2.2.2.1. 100mL of Internal/Surrogate standard is injected with every sample, QC sample, and method blank.

10.2.2.2.2. For the lower concentrations used in the SIM mode, the surrogates are at 2.0ppbv.

10.2.3. Primary Calibration Standards in 2 canisters containing each target analyte at a nominal concentration of 1000ppbv.

10.2.4. Working Initial Calibration Standards:

10.2.4.1. Three working calibration mixes (1.25, 25 and 50ppbv) are prepared by using the gas mixer. The other standards are made from these three.

10.2.4.1.1. ***Press RECALL and 04 followed by START or UPDATE on the Environics Series 2000 Computerized Multi-Component Gas Mixer. The Primary standard canisters are hooked up to the gas mixer and are ready for use. Input the appropriate volumes of the standards and the zero air to make up the working standards.***

10.2.4.2. The 50ppbv calibration mix is made by blending 40mL/min with 720mL of zero air in an evacuated canister. Inject 400mL onto the instrument.

10.2.4.2.1. The 100ppbv calibration standard is made by injecting 800mL of the 50ppbv standard onto the instrument.

10.2.4.3. The 25ppbv calibration mix (tert-Butyl Alcohol at 50ppbv, and Ethanol at 200ppbv) is made by blending 20ml/min of each canister with 760ml/min of zero air in an evacuated Summa® canister. Inject 400mL onto the instrument.

10.2.4.3.1. This standard is also used for the daily CCV.

10.2.4.4. The 12.5ppbv is made by injecting 200mL of the 25ppbv standard onto the instrument.

10.2.4.5. The 6.25 standard is made by injecting 100mL of the 25ppbv standard onto the instrument.

10.2.4.6. The 1.25ppbv standard is made by blending 50mL of the 25ppbv standard with 950mL of zero air into an evacuated canister.

10.2.4.7. The 05ppbv standard is made by injecting 160mL of the 1.25ppbv standard onto the instrument.

10.2.4.7.1. For SIM analysis, the 25ppbv standard is blended as in 10.2.4.3, then 100ml/min of the resulting standard is blended with 900ml/min of zero air to create a 1ppbv standard.

10.2.5. Second Source Verification Standard (ICV/LCS)- 1 canister:

10.2.5.1. The second source standard is made from a different canister by blending 20ml/min of the second source with 780ml/min of zero air in a Summa® canister.

10.2.5.1.1. For SIM analysis the 25ppbv standard is blended as in 10.2.5.1, then 100ml/min of the resulting standard is blended with 900ml/min of zero air to create a 1ppbv standard.

10.2.5.2. Press RECALL 06 followed by START or UPDATE on the Environics Series 2000 Computerized Multi-Component Gas Mixer. The secondary source standard canisters are hooked up to the gas mixer and are ready for use. Input the appropriate volume of the standard and the zero air to make up the working ICV/LCS standard.

10.2.5.3. Attach and fill the evacuated LCS Summa® Canister.

11. SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Air samples collected in Summa® canisters or MiniCans must be analyzed within 30 days of collection. Preservation is not required (store at ambient temperature). Regulatory agencies may require shorter hold times than 30 days. It is the responsibility of the Calscience Project Manager to relay differing requirements as appropriate.

11.2. Air samples collected in Tedlar™ bags must be analyzed with 3 days of collection. Preservation is not required (store at ambient temperature out of sunlight). When analyzed in Tedlar™ bags, the report results will include a comment since the EPA TO-15 method makes no reference to Tedlar™ bags as a sampling medium.

12. ►QUALITY CONTROL

12.1. Hardware Tuning

12.1.1. An acceptable tune demonstrates satisfactory hardware performance. A tune meeting the acceptance criteria is required and MUST be recorded prior to any ICAL, CCV, QC or sample analyses.

12.1.2. Prior to running the calibration standard(s) or CCVs, the GC/MS BFB tuning standard must be analyzed and meet the following acceptance criteria:

Mass	Ion Abundance Criteria
50	15 - 40% of mass 95
75	30 - 60% of mass 95
95	Base peak, 100% relative abundance[Note 1]
96	5 - 9% of mass 95
173	< 2% of mass 174
174	> 50% to 120% of mass 95
175	5 - 9% of mass 174
176	Greater 95% but less than 101% of mass 174
177	5 - 9% of mass 176

Note 1: All ion abundances must be normalized to mass 95, the nominal base peak, even though the ion abundance of mass 174 may be up to 120% of mass 95.

12.1.3. These criteria must be demonstrated initially and, at a minimum, every 24 hours thereafter.

12.1.4. If a tune does not meet the acceptance criteria, correct the problem and re-tune the system.

12.1.5. Whenever invasive maintenance of the GC/MS hardware is performed, the system must be re-tuned.

12.2. Initial Calibration

12.2.1. A minimum of a five point, usually seven point, initial calibration must be established prior to the processing of samples.

12.2.2. The initial calibration is deemed valid if:

12.2.2.1. The %RSD for the RF for each target analyte is <30% with, at most, two exceptions up to a limit of 40%.

12.2.2.2. The %RSD for the RRT for each target analyte at each concentration level is within 0.06 RRT units of the mean RRT of the target analyte.

12.2.2.3. The area response Y at each calibration level is within 40% of the mean Y over the initial calibration range for each internal standard.

12.2.2.4. The retention time shift for each of the internal standards at each calibration level is within 20 seconds of the mean retention time over the initial calibration range for each internal standard.

12.3. ***Initial Calibration Verification (ICV)***

12.3.1. Immediately following establishment of a valid initial calibration, an ICV standard must be analyzed. The ICV is the second source standard used for the LCS/LCSD.

12.3.1.1. The ICV is deemed valid if the %D for each target analyte contained in the standard is ±30%, with the exception of three analytes, up to ±40%D. Analytes not contained in the standard (non-method specified) are not evaluated in the ICV.

12.3.1.1.1. Up to three analytes outside of the 30%D criteria but within the 40%D criteria should be noted on the chemists data review sheet as bias high or bias low and the corresponding sample data flagged as needed.

12.3.1.2. If these criteria are not met, the ICV/LCS is deemed unacceptable for sample analysis to resume. Reanalyze the ICV/LCS. If the ICV/LCS criteria remain unacceptable, effect corrective action and re-tune/recalibrate. If acceptable, proceed with sample analysis.

12.3.1.3. The internal standard area responses and retention times in the ICV must be evaluated after data acquisition. If the retention time for any internal standard changes by more than 20 seconds from the mean retention time in the initial calibration, the chromatographic system must be inspected for malfunctions and corrective action must be effected.

12.3.1.4. If the area response for any internal standard changes by +/- 40% (Range: 60% to 140%) from the mean area response in the initial calibration, the system must be inspected for malfunctions and corrective action effected. Following corrective action, reanalyze the ICV. If still out, recalibrate.

12.4. ***Continuing*** Calibration Verification (***C***CV)

12.4.1. Following establishment of a valid initial calibration and every 24 hours thereafter, a ***C***CV standard must be analyzed.

12.4.1.1. The ***C***CV is deemed valid if the %D for each target analyte is ±30%.

12.4.1.1.1. Non-method specified compounds are not subject to the ±30%D criteria.

12.4.1.2. If these criteria are not met, the ***C***CV is deemed unacceptable for sample analysis to resume. Reanalyze the ***C***CV. If the ***C***CV criteria remain unacceptable, effect corrective action and re-tune/recalibrate.

12.4.1.3. The internal standard area responses and retention times in the ***C***CV must be evaluated after or during data acquisition. If the retention time for any internal standard changes by more than 20 seconds from the last ***C***CV (24 hours), the chromatographic system must be inspected for malfunctions and corrective action must be effected.

12.4.1.4. If the area response for any internal standard changes by +/- 40% (Range: 60% to 140%) from mean area response from the initial calibration, the system must be inspected for malfunctions and corrective action effected. Following corrective action, re-analysis of samples analyzed while the system was malfunctioning is required.

12.4.1.5. If these criteria are not met then all samples analyzed since the last acceptable ***C***CV should be invalidated, corrective action effected, and the affected samples re-analyzed. If a failed ***C***CV is the first of the day, corrective action must be effected prior to analyzing any samples.

12.4.1.6. It is a useful diagnostic tool to monitor internal standard retention times and area counts in all samples, spikes, blanks, and standards to check drifting method performance and monitor system trends.

12.5. Event Based Quality Control (MB, BB and LCS/LCSD)

12.5.1. Method Blank: (MB):

12.5.1.1. The MB is a Summa canister pressurized with humidified Zero Air that is processed concurrently with the associated samples. In the processing of the MB, surrogates, internal standards and procedures identical to those for actual samples are used.

12.5.1.1.1. One method blank is required every 20 samples. Method blanks on a more frequent basis (e.g., after high concentration samples) is strongly encouraged.

12.5.1.1.2. A MB shall be contained in a Summa® canister used only for MBs. The MB can NEVER be run before a CCV and MUST be run before any samples.

12.5.1.1.3. For SIM analysis the method blank is an instrument blank analyzed directly from the autosampler.

12.5.1.2. Ideally, the concentration of target analytes in a MB should be less than the respective reporting limits (RLs). ***(Less than ½ the RL for DOD work)*** If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

12.5.1.2.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

12.5.1.2.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-analyzed.

12.5.1.3. Internal Standard Retention Times (RT) must be +/- 0.33 minutes.

12.5.1.4. The area response for each internal standard in the method blank must be within ±40% (Range: 60% to 140%) of the mean area response of the internal standards in the most recent initial calibration.

12.5.2. Tedlar Bag Blank (BB):

12.5.2.1. Samples received in Summa canisters will often require dilution to account for high levels of hydrocarbons, non-target and target analytes. These dilutions are performed in tedlar bags.

12.5.2.2. To monitor potential contamination from the tedlar bags, a Bag Blank (BB) is analyzed. A Summa canister method blank (MB) is analyzed per standard procedure and the bag blank is analyzed as a sample within the batch.

12.5.2.3. The acceptance and reporting criteria for the bag blank are as follows.

12.5.2.3.1. If no target analytes are detected, batch all sample analyses with the MB and file the BB raw data with the QC paperwork.

12.5.2.3.2. If target analytes are detected in the BB but not in the dilution samples, batch all sample analyses with the MB and file the BB raw data with the QC paperwork.

12.5.2.3.3. If target analytes are detected in the BB and in the corresponding sample dilutions, batch the dilutions with the BB and file the BB raw data with the QC paperwork.

12.5.2.3.3.1. Create separate batches for the MB and the BB. Summa analyses are batched with the MB. Tedlar dilutions are batched with the BB. Flag results as needed.

12.5.2.4. Internal Standard Retention Times (RT) must be +/- 0.33 mins.

12.5.2.5. The area response for each internal standard in the method blank must be within ±40% (Range: 60% to 140%) of the mean area response of the internal standards in the most recent initial calibration.

12.5.3. Lab Control Sample (LCS/LCSD):

12.5.3.1. The LCS is a known gaseous matrix containing a known concentration of specific target analytes (25ppbv). The purpose of the LCS is to demonstrate that the entire analytical process and systems are in control. The LCSD is a duplicate of the LCS. The LCS/LCSD is obtained by injecting 400mL of the ICV/LCS/LCSD working standard.

12.5.3.2. The LCS/LCSD is processed concurrently with the associated samples. In the processing of the LCS/LCSD, reagents and procedures identical to those for actual samples are used. The LCS/LCSD should be run after the CCV.

12.5.3.2.1. A LCS/LCSD is required for every batch of 20 samples or portion thereof, whichever is more frequent.

12.5.3.3. In addition to assessing the accuracy of the analytical measurement, the LCSD, in combination with the LCS, is used to assess the precision of the analytical process. The measurement is expressed as relative percent difference (RPD). The formula for calculating RPD is listed in Section 15, Calculations.

12.5.3.4. The acceptance criteria for LCS/LCSD compounds vary depending upon historical data. The upper and lower acceptance limits for each LCS/LCSD compound are based upon the historical average recovery ±3S.

12.5.3.5. All LCS/LCSD compounds must be within the current historical control limits. If one or more LCS/LCSD compounds are not acceptable, the problem must be identified and corrected.

12.5.3.6. Internal Standard Retention Times (RT) must be +/- 0.33 minutes.

12.5.3.7. Internal Standard Retention Areas must be +/- 40% (Range: 60% to 140%) of initial calibration

12.5.3.8. See the following table for the current historically derived control limits for the analytes reported in the LCS/LCSD:

Analyte	*% Recovery*	*% RPD*
Benzene	*60-156*	*0-40*
Carbon Tetrachloride	*64-154*	*0-32*
1,2-Dibromomethane	*54-144*	*0-36*
1,2-Dichlorobenzene	*34-160*	*0-47*
1,2-Dichloroethane	*69-153*	*0-30*
1,2-Dichloropropane	*67-157*	*0-35*
1,4-Dichlorobenzene	*38-156*	*0-47*
cis-1,3-Dichloropropene	*61-157*	*0-35*
Ethylbenzene	*52-154*	*0-38*
Naphthalene	*40-190*	*0-30*
o-Xylene	*52-148*	*0-38*
m/p-Xylene	*42-156*	*0-41*
Tetrachloroethene	*56-152*	*0-40*
Toluene	*56-146*	*0-43*
Trichloroethene	*63-159*	*0-34*
1,1,2-Trichloroethane	*65-149*	*0-37*
Vinyl Chloride	*45-177*	*0-36*

12.6. Sample Based Quality Control (Surrogates)

12.6.1. The acceptance criteria for surrogate spike compound recoveries vary depending upon historical data. The upper and lower acceptance limits for each surrogate spike compound is based upon the historical average recovery ± 3S. ***The % recovery criteria for standard reporting is as follows:***

Analyte	*% Recovery*
1,4-Bromofluorobenzene	*57-129*
1,2-Dichloroethane-d4	*47-137*
Toluene-d8	*78-156*

12.6.1.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

12.6.1.2. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration or a problem may have occurred during extraction.

12.6.1.3. The data alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

12.6.1.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.6.1.4.1. Check the internal standard and surrogate spiking mixtures for degradation and contamination.

12.6.1.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the sample should be re-analyzed.

12.6.1.4.3. If incorrect procedures or degraded/contaminated spiking mixtures are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.1.4.3.1. If, upon re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.6.1.4.3.2. If the MB surrogates are unacceptable, all associated sample data must invalidated and all associated samples re-analyzed.

12.6.2. Sample Based Quality Control (Internal Standards)

12.6.2.1. Internal Standard Retention Times (RT) must be +/- 0.33 minutes.

12.6.2.2. Internal Standard Retention Areas must be +/- 40% (Range: 60% to 140%) of initial calibration

12.7. ***Method Detection Limit (MDL):***

12.7.1. An MDL must be established prior to the analysis of samples, whenever major instrument changes are made, or annually following the procedures outlined in SOP-T006, Determination of Detection Limits.

12.7.2. The formula for calculating the MDL is listed Section 15.6.

12.7.3. MDLs should be verified immediately following the establishment of the MDL at 1 -4x the MDL value for each analyte.

12.7.3.1. MDL's may be verified more frequently as required by project or client requirements.

12.8. ***Demonstration of Capability***

12.8.1. Prior to beginning the analysis, analysts are required to initially demonstrate method competence by generating 4 LCSs that meet the acceptance criteria for the method.

12.8.2. Additionally, analysts are required to generate continuing demonstrations of capability on an annual basis to show continued proficiency in the method.

12.9. Additional information regarding internal quality control checks is provided in SOP-T020.

13. ►CALIBRATION AND STANDARDIZATION

13.1. Prior to the analysis of samples or QC samples, the GC/MS system must be hardware tuned and an initial ***seven***-point calibration established. The acceptance criteria for the tuning parameters are listed in Section 12.1.

13.2. Tuning:

13.2.1. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required and must be accomplished using a single scan no more than 20 scans prior to the elution of the BFB. Do not background subtract part of the BFB peak.

13.2.2. Additionally, baseline separation of Benzene and Carbon Tetrachloride is an indication of acceptable chromatographic performance and must be achieved prior to establishment of the calibration. If not, check or replace the column.

13.3. Initial and Continuing Calibration :

13.3.1. An initial seven-point calibration is obtained by injecting 0.5, 1.25, 6.25, 12.5, 25, 50, and 100ppbv standards into the GCMS.

13.3.1.1. The ICAL is acceptable if the %RSD for the RF for each target analyte is ≤30% with the exception of two target analytes, to a limit of ≤40%.

13.3.1.2. Alternatively, for the SIM mode a ***six***-point calibration is used. ***The concentrations are as follows: 0.025, 0.50, 0.10, 0.25, 0.50 and 1.0ppbv. These are made from serial dilutions starting from the 25ppbv standard. The acceptance criteria fro the ICAL is the same as for the standard TO-15 analysis.***

13.3.2. Prior to the analysis of any samples or QC samples and after obtaining an acceptable initial calibration, the ICAL must be verified by the analysis of an Initial Calibration Verification standard (ICV/LCS).

13.3.2.1. The ICV is deemed valid if the %D for each target analyte contained in the standard is ±30%, with the exception of three analytes, up to ±40%D. Analytes not contained in the standard (non-method specified analytes) are not evaluated in the ICV.

13.3.3. To verify the continued validity of the ICAL, a continuing calibration verification (CCV) must be analyzed prior to analyzing any QC or samples. This is done daily at the start of each batch, following the tuning standard.

13.3.3.1. The CCV is deemed valid if the %D for each target analyte is ±30%.

14. ►PROCEDURE

14.1. Samples should be loaded in the following order:

- Tuning Standard
- ***Continuing*** Calibration Verification (***C***CV)
- Laboratory Control Sample (LCS)
- LCS Duplicate (LCSD)
- Method Blank (MB)
- Samples (up to 20)

14.2. Perform preliminary screening of the samples via TO-3 (M) analysis. This is not necessary for samples known to be fairly clean or if there is historical data available.

14.2.1. Summa® canisters may need to be pressurized prior to analysis, reference SOP, T-016 for pressurization procedures.

14.3. Calculate and perform dilutions as needed using the gas mixer and syringes for non-chlorinated samples based upon screening level found i.e., target the diluted TPH (G) to be bracketed thusly: 3.5 ppmv < Diluted TPH (G) level < 4 ppmv.

14.4. Attach to the samples to the autosampler "tree", using inert teflon tubing for Tedlar™ bags or hang and use metal Swage-type connections for Summa® canisters.

14.5. Edit the sequence in the data system. After all correct sample information is entered, save the sequence. After saving the sequence, record pertinent information in the run logbook.

14.6. Initiate the sequence.

14.7. Data Interpretation

14.7.1. The qualitative identification of analytes determined by this method is based on the 1) elution of the sample component at the same relative retention time (RRT) as the standard component and 2) comparison of the sample mass spectrum, after background correction if necessary, with characteristic ions in a reference mass spectrum.

14.7.2. The reference mass spectrum should be obtained from the GC/MS within the same 24 hour period as the sample analysis. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum.

14.7.3. Target analytes should be identified as present when:

14.7.3.1. The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target analyte at a compound-specific retention time will be accepted as meeting this criterion.

14.7.3.2. The RRT of the sample target analyte is within ±0.06 RRT units of the RRT of the standard target analyte.

14.7.3.3. The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.

14.7.3.4. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different retention times. Sufficient resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

14.7.3.5. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one target analyte. When gas chromatographic peaks obviously represent more than one sample component, appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles (EICPs) of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes co-elute, the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting compound.

14.7.4. When a compound has been identified, the quantitation of the compound will be based on the integrated abundance of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte.

14.7.4.1. Identify and compute the concentration of each target analyte in the sample. The GC/MS data system should be programmed to perform these functions. The details provided in the below subsections are for the purpose of understanding and data system programming.

14.7.4.2. Upon request, a library search may be made for the purpose of tentative identification of compounds not associated with the calibration standards. Refer to SOP-T025.

15. ►CALCULATIONS

15.1. Response factors are calculated as follows:

$$RF = \frac{(A_x \times C_{is})}{(A_{is} \times C_x)}$$

where:
- RF = response factor for target analyte being measured.
- A_x = area of the characteristic ion for target analyte being measured.
- A_{is} = area of the characteristic ion for the applicable internal standard.
- C_{is} = concentration of the specific internal standard in ng/µL.
- C_x = concentration of the target analyte being measured in ng/µL.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where:
- %RSD = percent relative standard deviation.
- SD = standard deviation of the average RFs for the target analyte.
- RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.3. The relative retention time (RRT) is calculated as follows:

$$RRT = \frac{RT_c}{RT_{is}}$$

where:
- RRT = relative retention time of the target analyte.
- RTc = retention time of the target analyte.
- C_c = retention time of the nearest internal standard.

Note: Retention times must be in equivalent units.

15.4. The RPD between the sample and sample duplicate is calculated as follows:

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

where:
- RPD = relative percent difference between two measurements (C_1 & C_2).
- C_1 = concentration of target analyte recovered in measurement 1.
- C_2 = concentration of target analyte recovered in measurement 2.

Note: Concentrations must be in equivalent units.

15.5. The recovery of LCS compounds is calculated as follows:

$$\%REC_{LCS} = \left(\frac{C_{recovered}}{C_{added}}\right) \times 100$$

where: $\%REC_{LCS}$ = percent recovery of target analyte in LCS (or LCSD).
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.

Note: Concentrations must be in equivalent units.

15.6. ***Calculate the MDL as follows.***

$$MDL = t \times S_{n-1}$$

where: ***MDL*** = ***method detection limit.***
t = ***student's t value at a 99% confidence level with (n − 1) degrees of freedom. For seven replicate analyses, t = 3.14.***
S_{n-1} = ***standard deviation of the (n − 1) replicate analyses.***
n = ***number of replicate analyses.***

16. METHOD PERFORMANCE

16.1. A demonstration of analytical capability shall be performed initially (prior to the analysis of any samples) and with a significant change in instrument type, personnel, matrix or test method.

16.2. Calibration protocols specified in Section 13, "Calibration and Standardization," shall be followed.

17. POLLUTION PREVENTION

17.1. The toxicity, carcinogenicity and other health hazards associated with the use of most laboratory chemicals have not been precisely defined. Each chemical should be handled assuming it is a potential health hazard.

17.2. Exposure to these chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Calscience's Health, Safety, and Respiratory Protection Manual. In general, safety glasses, lab coats and gloves are required to be worn when handling chemicals.

17.3. The following additional precautions should be taken, as necessary, when handling high concentrations of hazardous materials:

17.3.1. A NIOSH approved air purifying respirator with cartridges appropriate for the chemical handled.

17.3.2. Extended length protective gloves.

17.3.3. Face shield.

17.3.4. Full-length laboratory apron.

17.4. Processes that promote vaporization of volatile chemicals should be performed in an area well ventilated to the exterior of the laboratory to prevent contamination to other areas in the laboratory.

17.5. When working with large amounts of volatile chemicals, the Coordinator must be cautious of the risk of high levels of volatile displacing the atmospheric air within the work area; therefore causing asphyxiation. Air purification respirators are ineffective in this situation and must not be used. The Coordinator must immediately vacate the area until ventilation has effectively reduced the concentration of volatiles. Alternatively, the Coordinator may utilize a self-contained breathing apparatus or other supplied air system if appropriately trained and approved by the Health and Safety Manager.

17.6. Material Safety Data Sheets (MSDSs) are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS for all chemicals to be used prior to handling.

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. ***Method Blank:***

18.1.1. Ideally, the concentration of target analytes in a MB should be less than the respective reporting limits (RLs). (less than ½ the RL for DOD work) If the concentration of any target analyte exceeds its RL, the source of contamination must be investigated and, if possible, eliminated. The acceptance criteria for MBs is as follows:

18.1.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.1.2. If a target analyte is found in the MB and in the associated samples, evaluate the analyte in question to determine the effect on the analysis of samples. Determine and eliminate the source of contamination.

18.1.1.3. Professional judgment should be exercised to determine if the data should be qualified or rejected and the samples re-extracted and/or re-analyzed.

18.2. ***LCS/LCSD:***

18.2.1. The acceptance criteria, % recovery and % RPD, for the LCS/LCSD compounds are as follows:

Analyte	*% Recovery*	*% RPD*
Benzene	*60-156*	*0-40*
Carbon Tetrachloride	*64-154*	*0-32*
1,2-Dibromomethane	*54-144*	*0-36*
1,2-Dichlorobenzene	*34-160*	*0-47*
1,2-Dichloroethane	*69-153*	*0-30*
1,2-Dichloropropane	*67-157*	*0-35*
1,4-Dichlorobenzene	*38-156*	*0-47*
cis-1,3-Dichloropropene	*61-157*	*0-35*
Ethylbenzene	*52-154*	*0-38*
Naphthalene	*40-190*	*0-30*
o-Xylene	*52-148*	*0-38*
m/p-Xylene	*42-156*	*0-41*
Tetrachloroethene	*56-152*	*0-40*
Toluene	*56-146*	*0-43*
Trichloroethene	*63-159*	*0-34*
1,1,2-Trichloroethane	*65-149*	*0-37*
Vinyl Chloride	*45-177*	*0-36*

18.2.2. All LCS/LCSD compounds must be within acceptance limits. If one or more LCS/LCSD compounds are not acceptable, the problem must be identified and corrected.

18.2.3. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.3. ***Internal Standards:***

18.3.1. Internal Standard Retention Times (RT) for Bromochloromethane, Chlorobenzene-d_5 and 1,4-Difluorobenzene in all samples and QC must be +/- 0.33 minutes.

18.3.2. The area response for each internal standard in all samples and QC must be within ±40% (Range: 60% to 140%) of the mean area response of the internal standards in the most recent initial calibration.

18.4. ***Surrogates:***

18.4.1. The acceptance criteria for surrogate spike compound recoveries vary depending upon historical data. The upper and lower acceptance limits for each surrogate spike compound is based upon the historical average recovery ± 3S. The acceptance criteria for the surrogate compounds is as follows:

Analyte	*% Recovery*
1,4-Bromofluorobenzene	*57-129*
1,2-Dichloroethane-d4	*47-137*
Toluene-d8	*78-156*

18.4.2. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

18.4.3. If one or more surrogate recoveries are not acceptable, evaluation is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high analyte concentration. This data alone cannot be used to evaluate the precision and accuracy of individual sample analyses. However, when exercising professional judgment, this data should be used in conjunction with other available QC information.

18.4.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.4.4.1. Check the internal standard and surrogate spiking mixture for degradation and contamination.

18.4.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate(s) recovery, the same sample or extract should be re-analyzed.

18.4.4.3. If incorrect procedures or degraded/contaminated spiking solutions are determined to have not caused the unacceptable surrogate recoveries, the affected sample(s) must be re-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.4.4.3.1. If, upon re-analysis, the surrogates remain unacceptable, matrix interference can be cited and reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

18.4.4.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-analyzed.

18.5. ***Additional information regarding internal quality control checks is provided in SOP-T020.***

18.6. ***All concentrations shall be reported in ppb (v/v). Units may be reported in ppm (v/v), ug/l or ug/m^3, on a project specific basis.***

18.7. ***The data reported shall adhere to the significant figures, rounding, and data reporting procedures outlined in the current revision of SOP-T009.***

19. CORRECTIVE ACTIONS

19.1. If on the basis of internal or external systems or performance audits, routine monitoring of laboratory support equipment, or QC sample analysis results, analytical systems fail to meet the established criteria, an appropriate corrective action must be implemented.

19.2. The Operations Manager, Project Manager, Quality Control Manager, Group Leader and analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected or if corrective action will impact the project budget or schedule, the action may directly involve the Laboratory Director.

19.3. Corrective actions are generally of two types, immediate and long-term actions.

19.3.1. An **immediate action** is designed to correct or repair nonconforming instruments and measurement systems. The analyst or Group Leader as a result of calibration checks and other QC sample analyses most frequently will identify the need for such an action.

19.3.2. A **long-term action** is designed to eliminate causes of nonconformance. The need for such actions is identified by systems and performance audits. The systematic nonconformances identified during the data generation process and the appropriate corrective measures taken are thoroughly documented in the Corrective Action Record. Examples of this type of action include:

19.3.2.1. Remedial training of staff in technical skills, technique or implementation of operating procedures.

19.3.2.2. Rescheduling of analytical laboratory routine to ensure analysis within holding times.

19.3.2.3. Revision of standard operating procedures.

19.3.2.4. Replacing personnel, as necessary.

19.4. For either type of corrective action, the sequential steps that compose a close-loop corrective action system are as follows:

19.4.1. Define the problem.

19.4.2. Assign responsibility for investigating the problem.

19.4.3. Investigate and determine the cause of the problem.

19.4.4. Assign and accept responsibility for implementing the corrective action.

19.4.5. Determine effectiveness of the corrective action and implement correction.

19.4.6. Verify that the corrective action has eliminated the problem.

19.5. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be properly documented on a Corrective Action Record.

20. CONTINGENCIES FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1. Out-of-control data are reviewed and verified by the technical director of the appropriate department. All samples associated with an unacceptable QC set is then subject to reanalysis, depending upon the QC type in question.

20.1.1. LCS/LCSD: Because they denote whether the analytical system is operating within control, it is imperative that the LCS recoveries obtained are within acceptability criteria. If the recoveries fail for a given reported compound, the technical director confirms the unacceptable result.

20.1.1.1. If the LCS results are verified as acceptable, no corrective action is required.

20.1.1.2. If the LCS result is verified as out-of-control, and the subject compound is to be reported in samples within that analytical batch, the samples reported with that failed compound must be reanalyzed with a valid LCS recovery for the compound.

20.1.1.3. If the LCS result is verified as out-of-control, and the subject compound is NOT to be reported in the samples within that analytical batch, the samples are not subject to reanalysis. No corrective action is required for that batch.

21. WASTE MANAGEMENT

21.1. The proper disposal of analytical samples and laboratory wastes is not only good laboratory practice, but also regulated by a variety of local, state, and federal laws. In order to remain compliant with these laws, and at the same time keep sample disposal costs at a minimum, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream, if applicable.

21.2. All laboratory personnel must be aware of the types of chemicals they are using and the appropriate procedures for their disposal, if applicable.

21.3. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These waste containers shall be used for temporary collection of residual sample from aliquotting procedures, contaminated consumables, sample extracts, purged aqueous samples, and other wastes that require disposal as hazardous waste, if applicable.

21.4. To ensure compliance with Federal RCRA regulations, the Hazardous Waste Coordinator collects and disposes of the hazardous waste at each satellite collection point no less than monthly, if applicable.

21.5. Waste management procedures shall adhere to the current revision of SOP-T005, "Disposal of Laboratory Samples and Waste."

22. REFERENCES

22.1. US EPA, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, January 1997, Method TO-14A, "Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters With Subsequent Analysis By Gas Chromatography".

22.2. US EPA, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, January 1997, Method TO-15, "The Determination of Volatile Organic Compounds (VOCs) in Air Collected in Summa® Canisters and Analyzed by Gas Chromatography/Mass Spectrometry".

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix 1: Ions for Qualitative Identification of Selected Target Compounds.

23.2. ***Appendix 2: Standard reporting and method Detection Limits for TO-15.***

APPENDIX 1

Table I : Ions for Qualitative Identification of Selected Target Compounds

Compound Name	QIon E	2nd	3rd	4th
Dichlorodifluoromethane	85	87		
Propene	41	39	42	
1,1-Difluoroethane	51	65		
Chloromethane	50	52		
1,2-Dichloro-1,1,2,2-tetrafluoroethane	101	151	103	153
Vinyl Chloride	62	64		
1,3-Butadiene	54	39	53	50
Bromomethane	94	96		
Chloroethane	64	66		
Ethanol	45	46	43	
Trichlorofluoromethane	101	103		
Acetone	58	43		
Isopropanol	45	43	41	59
1,1-Dichloroethene	61	96	98	
1,1,2-Trichloro-1,2,2-Trifluorethane	101	151	153	
Tert-Butyl alcohol (TBA)	59	57	41	
Carbon Disulfide	76	78		
Acrylonitrile	53	52	51	
Methylene Chloride	84	86		
t-1,2-Dichloroethene	96	98		
Methyl-tert-Butyl Ether	73	57		
1,1-Dichloroethane	63	65	83	
Vinyl Acetate	86	43		
Diisopropyl ether (DIPE)	45	87		
Ethyl t-butyl ether (ETBE)	59	87		
c-1,2-Dichloroethene	96	98		
Hexane	86	57	43	41
Ethyl Acetate	88	43	41	59
2-Butanone	43	72		
Bromochloromethane	130	128		
Tetrahydrofuran	42	41	71	72
Chloroform	83	85		
1,1,1-Trichloroethane	97	61	63	
Carbon Tetrachloride	117	119		
Cyclohexane	56	84	69	41
1,4-Difluorobenzene	114	88		
Benzene	78	51		
1,2-Dichloroethane	62	98	64	49

APPENDIX 1

Table I : Ions for Qualitative Identification of Selected Target Compounds

Compound Name	QIon E	2nd	3rd	4th
Tert-Amyl methyl ether	73	87	55	
Trichloroethene	95	130	132	
1,4-Dioxane	88	58	43	57
Heptane	100	43	71	57
1,2-Dichloropropane	63	112		
Dibromomethane	93	95	174	
Bromodichloromethane	83	85		
c-1,3-Dichloropropene	75	77	110	
Toluene	91	92		
4-Methyl-2-Pentanone	58	85		
Chlorobenzene-d5	117	82		
t-1,3-Dichloropropene	75	77	110	
1,1,2-Trichloroethane	83	97	85	
Tetrachloroethene	166	164	131	
2-Hexanone	58	43		
Dibromochloromethane	129	127		
1,2-Dibromoethane	107	109		
Chlorobenzene	112	114		
Ethylbenzene	91	106		
p/m-Xylene	91	106		
o-Xylene	91	106		
4-Ethyltoluene	105	120	91	77
Styrene	104	78		
Bromoform	173	175		
1,4-Bromofluorobenzene	95	174		
1,1,2,2-Tetrachloroethane	83	85		
1,3,5-Trimethylbenzene	105	120		
1,2,4-Trimethylbenzene	105	120		
Benzyl Chloride	91	126	65	
1,3-Dichlorobenzene	146	111	148	
1,4-Dichlorobenzene	146	148	111	
1,2-Dichlorobenzene	146	111	148	
1,2,4-Trichlorobenzene	180	182	145	
Hexachloro-1,3-Butadiene	225	223	227	
Naphthalene	128	127		

APPENDIX 2

Standard Analyte, Reporting and Method Detection Limits (ppbv)

Analyte	CAS Number	RL (PPBV)	MDL (PPBV)
Acetone	67-64-1	2.0	0.19
Benzene	71-43-2	0.50	0.094
Benzyl Chloride	100-44-7	1.5	0.39
Bromodichloromethane	75-27-4	0.50	0.10
Bromoform	75-25-2	0.50	0.15
Bromomethane	74-83-9	0.50	0.093
2-Butanone	78-93-3	1.5	0.099
Carbon Disulfide	75-15-0	2.0	0.099
Carbon Tetrachloride	56-23-5	0.50	0.098
Chlorobenzene	108-90-7	0.50	0.11
Chloroethane	75-00-3	0.50	0.15
Chloroform	67-66-3	0.50	0.090
Chloromethane	74-87-3	0.50	0.098
Dibromochloromethane	124-48-1	0.50	0.11
Dichlorodifluoromethane	75-71-8	0.50	0.14
1,1-Dichloroethane	75-34-3	0.50	0.10
1,1-Dichloroethene	75-35-4	0.50	0.11
1,2-Dibromoethane	106-93-4	0.50	0.11
1,2-Dichloro-1,1,2,2-tetrafluoroethane	76-14-2	2.0	0.11
1,2-DichloroBenzene	95-50-1	0.50	0.11
1,2-Dichloroethane	107-06-2	0.50	0.095
1,2-Dichloropropane	78-87-5	0.50	0.11
1,3-DichloroBenzene	541-73-1	0.50	0.13
1,4-DichloroBenzene	106-46-7	0.50	0.13
c-1,3-Dichloropropene	10061-01-5	0.50	0.14
c-1,2-Dichloroethene	156-59-2	0.50	0.13
t-1,2-Dichloroethene	156-60-5	0.50	0.19
t-1,3-Dichloropropene	10061-02-6	1.0	0.10
Ethylbenzene	100-41-4	0.50	0.11
4-Ethyltoluene	622-96-8	0.50	0.18
Hexachloro-1,3-Butadiene	87-68-3	1.5	0.18
2-Hexanone	591-78-6	1.5	0.52
Methyl-t-Butyl Ether (MTBE)	1634-04-4	2.0	0.12
Methylene Chloride	75-09-2	5.0	1.0
4-Methyl-2-Pentanone	108-10-1	1.5	0.15
Naphthalene	91-20-3	10	2.1
o-Xylene	95-47-6	0.50	0.12
P/m-Xylene	179601-23-1	2.0	0.76
Styrene	100-42-5	1.5	0.18

Analyte	CAS Number	RL (PPBV)	MDL (PPBV)
Tetrachloroethene	127-18-4	0.50	0.11
Toluene	108-88-3	0.50	0.12
Trichloroethene	79-01-6	0.50	0.11
Trichlorofluoromethane	75-69-4	1.0	0.077
1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	1.5	0.10
1,1,1-Trichloroethane	71-55-6	0.50	0.10
1,1,2-Trichloroethane	79-00-5	0.50	0.12
1,3,5-TrimethylBenzene	108-67-8	0.50	0.17
1,1,2,2-Tetrachloroethane	79-34-5	1.0	0.11
1,2,4-TrimethylBenzene	95-63-6	1.5	0.33
1,2,4-TrichloroBenzene	120-82-1	2.0	0.72
Vinyl Acetate	108-05-4	2.0	0.45
Vinyl Chloride	75-01-4	0.50	0.10

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microbialinsights
2340 Stock Creek Blvd
Rockford TN 37853

STANDARD OPERATING PROCEDURE

Quantitative Polymerase Chain Reaction (qPCR)

SOP Number:	DNA-qPCR
Revision Number:	2.0 FINAL
Revision Date:	01/10/2011
Effective Date:	01/10/2011

Reviewed by: Dora M Ogles 1/10/2011

Dora Ogles Date

Lab Director

Reviewed by: Anita Biernacki 1/10/2011

Anita Biernacki Date

Operations Manger

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PURPOSE

The purpose of this standard operating procedure (SOP) is to describe the activities involved in the preparation, handling, documentation, and analysis of samples collected from a variety of matrices (water, soil, bio-traps, etc) to enumerate target populations using quantitative Real-Time polymerase chain reaction or qPCR.

1.0 SCOPE AND APPLICATION

Quantitative Real-Time polymerase chain reaction (qPCR) is used to enumerate target populations of microorganisms. Microbial Insights, Inc. (MI) uses qPCR to target the following organisms associated with the remediation of a priority pollutants such as Tetrachloroethene (PCE) and Methyl *tert*-butyl ether (MTBE).

2.0 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

Samples are collected following the standard operating procedure developed by Microbial Insights, Inc (MI). DNA extraction and RNA extraction are performed following the extraction standard operating procedure developed by Microbial Insights, Inc. DNA is stored in 1/10 Tris-EDTA(TE) at 4ºC while RNA is stored in RNA Storage solution at -20ºC. RNA samples are converted to cDNA following (SOP-RNA ext) prior to the quantitative PCR analysis.

3.0 EQUIPMENT AND SUPPLIES

- 96-well plate (Applied Biosystems).
- Micropipettes (Gilson P-10, P-100, P-1000) and 10 ml pipettes, and appropriate sterile tips (ART). [see calibration listed in calibration log]
- Applied Biosystems SDS 7000 or 7300 instrument. [see calibration listed in calibration log]
- Sterile 0.5ml thin wall strip tubes and optical clear caps (Applied Biosystems)

4.0 REAGENTS AND POSITIVE CONTROLS

4.1 TaqMan DNA polymerase and master mix for Taqman assays (Applied Biosystems)

4.2 Sterile filtered (0.2mM) nanopure, organic-free, deionized water.

4.3 Forward and Reverse primers/Probe: these are gene/assay specific (IDT Technologies primers, Applied Biosystems FAM/TAMRA probes). See notes section for primer handling. Final concentration of probe and primers: [redacted] or adjusted as needed for each primer set. [redacted]

4.4 Positive and Negative Control DNA: DNA is purchased from ATCC or extracted and purified in-house from pure isolates. The amount of DNA used in all assays is 3µl. For negative controls, water is added in place of template DNA.

4.5 [redacted] for SYBR green assays ([redacted])

4.6 [redacted] for SYBR green assay

4.7 [redacted]

[redacted]

5.0 PROCEDURE

5.1 Preparation of Stock Primer

5.1.1 It is necessary to resuspend and dilute our primers (IDT Technologies) before we can use them for our PCR reaction. This procedure is done when new primers are received and both working stocks and solution stocks should be prepared at this time. The label on the tube will provide the oligo length and concentration.

5.1.2 To the stock tube, aseptically add 1ml of sterile PCR dH2O and vortex the tube for 1 minute to resuspend the primer. Centrifuge for 1 minute at 14,000 rpm to remove any solution from the lid then allow the tube to sit at room temperature for 5 minutes to ensure complete dissolution. This provides the solution stock.

5.1.3 To make the working stock to be used in each reaction, add the amount of nanomoles of the stock solution (listed on the stock tube) to a clean 1.5ml tube and bring this volume up to 1ml with sterile dH2O.

5.2 Mixing Reagents-Taqman Assays

5.2.1 Prepare a master mix including the appropriate amounts of each of the following: PCR water, Taqman Universal PCR mix, Primers (forward and reverse) and Probe. The appropriate amounts are listed in the MI primer list (primer.xls) prepared for each primer/probe combination.

5.2.2 Add [redacted] to each well of the 96 well plate or strip tube. Add [redacted] template DNA/cDNA to the appropriate wells. Add [redacted] positive control DNA to the appropriate wells. Add [redacted] PCR water to the negative control wells.

5.2.1 Spin the plate in the centrifuge at 3600 rpm for 2 minutes to be sure all mix is in the bottom of the tube and that no bubbles are present.

5.2.2 The plate of samples is then placed in either the ABI 7000 or 7300. The conditions of each assay will vary depending upon the primer/probe combination (see table1).

5.2.3 Upon completion of the run, export the data to an Excel worksheet to determine the number of target molecules, using an equation derived from standard curves of known numbers of target molecules.

5.2.4 Standard curves are developed from a serial dilution of a known concentration of the positive control organism. At least 4 dilutions will be used for each curve and the R^2 of each equation must be at least 0.95.

5.3 Mixing Reagents-SYBR green Assays

5.3.1 Prepare a master mix including the appropriate amounts of each of the following ingredients: PCR water, [redacted], PCR Primers (forward and reverse), [redacted] Reaction Buffer, [redacted] The appropriate amounts are listed in the excel sheets prepared for each primer combination.

5.3.2 Add [redacted] of master mix to each well of the 96 well plate or strip tube. Add [redacted] template DNA/cDNA to the appropriate wells. Add [redacted] positive control DNA to the appropriate wells. Add [redacted] PCR water to the negative control wells.

5.3.3 Spin the plate in the centrifuge at 3600 rpm for 2 minutes to be sure all mix is in the bottom of the tube and that no bubbles are present.

5.3.4 The plate of samples is then placed in either the ABI 7000 or 7300. The conditions of each assay will vary depending upon the primer/probe combination (see DNA primers xls data sheet)

5.3.5 Upon completion of the run, export the data to an Excel worksheet, then determine the number of target molecules, using an equation derived from standard curves of known numbers of target molecules. The standard curves are developed from a serial dilution of a known concentration of the positive control organism. At least 4 dilutions will be used for each curve and the R^2 of each equation must be at least 0.95.

6.0 QUALITY CONTROL

6.1 For quality control of the amplification process, positive and negative controls are always performed. The extraction blank from each set is also amplified to ensure no cross contamination of samples or solutions during the extraction process.

6.2 Ongoing calibration checks and maintenance of the instruments must be documented in the appropriate logbook.

6.3 The Laboratory Director has the responsibility to ensure that this procedure is performed by an employee who has been properly trained in its use and has the required experience to process the samples.

6.4 All deviations from this SOP must be documented in a Nonconformance Report (NCR) or using an equivalent system (i.e., database).

7.0 ANALYTICAL REPORT

7.1 All data regarding quantities are entered into a data report using the laboratory information management systems (LIMS).

7.2 All documentation pertinent to a project will be placed in the "project folder" identified with the unique LIMS Project number. Hardcopy records, data sheets, and soft copy reports will be stored for a period of three years.

8.0 DOCUMENT CORRECTIONS

Changes or corrections on any laboratory documentation will be made by crossing out the erroneous item with a single line and initialing (by the person performing the correction) and dating the correction.
The original item, although erroneous, must remain legible beneath the cross-out line. The new information should be written clearly above the crossed-out erroneous item. All information will be recorded using black or blue indelible ink.

9.0 TABLES, DIAGRAMS, AND FLOWCHARTS

[redacted]

Attachment 2

EXAMPLE CHAIN-OF-CUSTODY FORM, SAMPLE LABEL, AND CUSTODY SEAL

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Chain of Custody Record

Client Contact	Project Manager:	Site Contact:	Date:	COC No:
Your Company Name here	Tel/Fax:	Lab Contact:	Carrier:	_____ of _____ COCs
Address	Analysis Turnaround Time			Job No.
City/State/Zip	Calendar (C) or Work Days (W) _____			
(xxx) xxx-xxxx Phone	TAT if different from Below _____			
(xxx) xxx-xxxx FAX	☐ 2 weeks			SDG No.
Project Name:	☐ 1 week			
Site:	☐ 2 days			
P O #	☐ 1 day			

Sample Identification	Sample Date	Sample Time	Sample Type	Matrix	# of Cont.	Filtered Sample																			Sample Specific Notes:

Preservation Used: 1= Ice, 2= HCl; 3= H2SO4; 4=HNO3; 5=NaOH; 6= Other _____

Possible Hazard Identification

☐ *Non-Hazard* ☐ *Flammable* ☐ *Skin Irritant* *Poison B* ☐ *Unknown* ☐

Sample Disposal (A fee may be assessed if samples are retained longer than 1 month)

☐ *Return To Client* ☐ *Disposal By Lab* ☐ *Archive For _____ Months*

Special Instructions/QC Requirements & Comments:

Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:

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SAMPLE LABEL (EXAMPLE)

SAMPLE NO.:_____
PROJECT:_____
DATE:_____/_____/_____ TIME:_____HRS_____
MEDIUM: WATER_____ SOIL_____ SEDIMENT_____
OTHER_____(Specify)
TYPE: GRAB_____ COMPOSITE_____ OTHER_____
PRESERVATION:_____
ANALYSIS:_____
SAMPLED BY:_____
REMARKS:_____
_____

CUSTODY SEAL (EXAMPLE)

CUSTODY SEAL

Person Collecting Sample:_____ Sample No.:_____
(Signature)
Date Collected:_____ Time_____
_____

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