DRAFT

Sampling and Analysis Plan

Prepared for

Thomson Development Inc.

October 2015

WEST YOST ASSOCIATES
Consulting Engineers

595-04-14-01

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Peter Dellavalle, PG

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1.0 INTRODUCTION

On behalf of Thompson Development, Inc. (TDI), West Yost Associates (West Yost) has prepared a Sampling and Analysis Plan (SAP) for the Hamilton Square Parcel (Site), 970 C Street, Novato, California, see Figures 1, 2, and 3. This SAP was prepared to support TDI's new residential development plan. Prior remedial action at the Site was conducted to meet the cleanup goals for a commercial site. The prior remedial action is described in Section 2.1 below.

This SAP provides proposed project sampling strategies for the subsurface investigation using site-specific information. The sampling strategies include the proposed sampling rationale and methods, and field, laboratory analytical and Quality Assurance/Quality Control (QA/QC) methods.

1.1 Site Area Background

The Site is located at a former Navy Exchange (NEX) gas station that was in use from the mid-1970s to the early 1990s and operated underground storage tanks (USTs) that stored gasoline. At the time the gas station was closed, the three USTs that had supported the NEX gas station (UST 970-1, UST 970-2, and UST 970-3) and one waste oil UST (UST-Waste Oil) were removed. Groundwater at the Site was subsequently found to be impacted by fuel releases from the NEX gas station. In addition, hydrocarbons were detected in soil beneath the station building during a subsurface investigation beneath the building subsequent to the removal of three hydraulic lifts and associated subsurface features.

1.2 Site Location

The Site is located at the northwest corner of Main Gate Road and C Street in Novato, California, see Figure 1. The Site comprises an area of approximately 2.7 acres (see Figure 2).

1.3 Project Organization

West Yost is performing this work for the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB), the California Department of Toxic Substances Control (DTSC), and the Department of the Navy (DON) under contract with the Site owner, TDI.

1.4 Project Overview

The goal of the remedial action at this Site is to improve Site subsurface soil and groundwater conditions to meet residential human health standards in preparation for redevelopment. Proposed remedial action in support of this goal consists of conducting secondary source removal in the vicinity of the former station building, pumps islands and UST excavations. Work will be performed under a soil and groundwater management plan and a Site-specific health and safety plan, which are presented under separate cover. The remedial action will prepare the Site for a future risk assessment that will be conducted to determine conformity with residential human health standards. When residential standards are met, the land use covenant (LUC) may be removed to allow for residential development.

2.0 BACKGROUND

2.1 Previous Investigations/Regulatory Involvement

A detailed description of previous investigations and regulatory involvement is presented in Section 2.3 of the Remedial Action Plan (RAP) dated April 10, 2015. In summary, the four former USTs were removed from the Site in 1995 and 1996, at which time petroleum hydrocarbon releases were discovered. Extensive investigations were completed for the DON to characterize the extent of petroleum hydrocarbon impacts primarily to groundwater. Active groundwater remediation using air sparging and soil vapor extraction was operated at the Site from 1998 until 2009. The remediation activities were terminated because petroleum hydrocarbon constituents in groundwater were decreased to below remediation goals with the exception of some residual methyl tert-butyl ether (MTBE). The DON continues to monitor groundwater on an annual basis to document continued MTBE reduction through natural attenuation.

2.2 Statement of the Specific Problems

The remediation work completed by the DON was sufficient for industrial uses of the Site, with the result that a LUC is attached to the property that precludes certain uses. TDI would like to redevelop the property for residential purposes which would require that the LUC be removed from the title. To accomplish this it is necessary to remove some limited residual soil impacts associated with the former USTs and releases beneath the station building at the Site. The RAP was developed to address residual soil contamination as described in Section 5.0 of the RAP.

This SAP is developed to support the confirmation sampling program that follows excavation activities proposed in the RAP.

2.3 Sampling Area Description

The sampling areas include sidewalls and floors of the proposed excavations shown on Figure 4. The sampling program includes discrete samples from pre-excavation characterization trenches, and a soil compositing system for the larger excavation that conforms to the Interstate Technology Regulatory Council's (ITRC) Incremental Sampling Methodology (ISM) Technical and Regulatory Guidance Document, (February 2012) ISM. The specifics of this sampling rationale are discussed in Section 4.0.

2.4 Geologic Information

2.4.1 Site Geology

According to Battelle (2002), heterogeneous soil conditions predominate throughout the property. Surface soils consist mostly of a sandy "alluvial fill" material to depths ranging from 1.5 to about 9.5 feet below ground surface (ft bgs); a sandy clay fill encountered from about 5 to 7 ft bgs; and, sandy soils encountered at depths ranging from 7 to 15 ft bgs. These sandy soils are part of the aquifer zone and generally consist of clayey to gravelly sands, with clay lenses present throughout the aquifer zone. The underlying Cretaceous Franciscan bedrock, which is generally encountered from 15 to 20 ft bgs, is generally hard, massive, and slightly fractured.

Regional groundwater flow in the aquifer is toward the north and is primarily controlled by the topography of the bedrock, which dips gently toward the north. The groundwater gradient beneath the Site calculated from Battelle's 2013 Annual Site Status Report (Battelle, 2014) was approximately 0.3 of a foot per foot toward the north.

Surface water is primarily limited to Pacheco Creek, which extends along the west side of the Site. The soil and bedrock geology and the hydrogeology of the Site are discussed in more detail in the Conceptual Site Model, Section 4.0 of the RAP.

2.4.2 Groundwater

The depth to groundwater at the Site, and the resulting thickness of the unsaturated (vadose) zone, varies seasonally by approximately five feet (Battelle, 2002). Groundwater is unconfined across the Site. Higher groundwater elevations are evident during the late winter/early spring months, with the highest elevation in early spring (ECON and Blankinship & Associates, 2007). According to Battelle (2002), groundwater recharge in the alluvial aquifer originates primarily from precipitation. In addition, there is a significant amount of groundwater flux from portions of the aquifer that are upgradient in this bedrock valley. Based on the recharge conditions during the current drought, groundwater is likely to be encountered in the maximum range of depths in the summer and fall of 2015, until recharge begins with winter precipitation.

2.5 Environmental and/or Human Impact During Site Work

ECON and Blankinship & Associates (2007) developed a flow chart for their conceptual site model of the adjacent Site to the north of the Site, which has similar subsurface conditions and is also impacted with hydrocarbons in subsurface soil and groundwater. The flow chart depicts complete exposure pathways for on-site trench workers (outdoor air). Exposure pathways and potential receptors are discussed in greater detail in Section 4.6 of the RAP. For the purposes of this SAP, exposure pathways for dermal contact, soil ingestion and inhalation, and dermal contact for Site construction workers applies and will be mitigated through the Site Specific Health and Safety Plan.

3.0 PROJECT DATA QUALITY OBJECTIVES (DQOs)

The DQO process determines the level of data quality needed for specific data collection activities during sampling and analysis. The process begins with defining the problem at the Site, moves into a decision-making process that defines options and decision-making input, defines both temporal and physical study boundaries, develops a decision rule, and specifies limits on decision errors, all in order to optimize the plan design.

3.1 Project Tasks

The goals for the sampling and analysis described in this SAP are to provide data for a future human health risk assessment and to confirm that the excavation remedial action has reduced soil constituents of concern (COC) concentrations to below regulatory screening levels. To achieve these goals, West Yost will conduct three tasks, as follows:

- Pre-excavation potholing to characterize the subsurface in areas where data gaps have been found and for waste characterization;
- Excavation guidance using field screening methods and a mobile laboratory; and
- Post-excavation confirmation sampling.

3.2 Data Quality Objectives

Table 1 lists the COCs that were determined based on previous investigation work. The table also lists the applicable regulatory standards to which the data will be compared. Unless otherwise noted, COC concentrations are compared to SFBRWQCB Final Environmental Screening Levels (ESLs) which are screening levels for substances commonly found in soil at sites where releases of hazardous substances have occurred. Remediation goals for the site are set to Table A-1 "Residential Land Use (Groundwater is a Current or Potential Source of Drinking Water)" The Site is proposed for redevelopment into a residential/commercial mixed use development and therefore the category of "Residential Land Use" is appropriate to use for the Site. Remediation goals were set to EPA Regional Screening Level (RSL) Summary Table - Resident Soil Screening Levels when that value was more stringent.

The COCs in soil at the Site are petroleum hydrocarbons and related compounds, tetraethyl lead from gasoline, and lead from lead-based paint. The residential ESLs for the COCs are listed in Table 1. It should be noted that Total Petroleum Hydrocarbons (TPH) as hydraulic oil (TPHo) and Total Oil and Grease (TOG) have been detected in soil at the Site, but there are no ESLs for them; therefore, the screening level for TPH as motor oil (TPHmo) will be used in their place.

Table 1. Remediation Goals

Analyte Group	Analyte	Remediation Goal[(a)], mg/kg
TPH	TPHg	100
	TPHd	100
	TPHmo	100
VOCs	MTBE	0.023
	Benzene	0.044
	Toluene	2.9
	Ethylbenzene	3.3
	Xylene, m-/p-	2.3 (total xylenes)
	Xylene, o-	2.3 (total xylenes)
Metals	Cadmium	12
	Chromium	100
	Lead	80
	Nickel	150
	Zinc	600
PCBs	Aroclor1016	0.22
	Aroclor1221	0.17[(b)]
	Aroclor1232	0.17[(b)]
	Aroclor1242	0.22
	Aroclor1248	0.22
	Aroclor1254	0.22
	Aroclor1260	0.22
	Aroclor1262	0.22
	Aroclor1268	0.22
PAHs	Acenaphthene	16
	Acenaphthlyene	13
	Anthracene	2.8
	Benzo(a)anthracene	0.16[(b)]
	Benzo(a)pyrene	0.016[(b)]
	Benzo(b)fluoranthene	0.16[(b)]
	Benzo(g,h,i) perylene	27
	Benzo(k)fluoranthene	0.38
	Chrysene	3.8
	Dibenz(a,h)anthracene	0.016[(b)]
	Fluoranthene	40
	Fluorene	8.9
	Indeno[1,2,3-cd]pyrene	0.16[(b)]
	Methylnaphthalene, 1-	18[(b)]
	Methylnaphthalene, 2-	0.025[(b)]
	Naphthalene	1.2
	Phenanthrene	11
	Pyrene	85
Other	Tetraethyl Lead	0.0078[(b)]

Source: Analytical by Eurofins Calscience, Inc.

(a) Unless otherwise noted, remediation goals are Final ESLs from SFBRWQCB Table A-1 Shallow Soil Screening Levels (≤ 3m bgs), Residential Land Use (groundwater is a current or potential drinking water resource), December 2013

(b) Remediation goals from EPA Regional Screening Level Summary Table (TR=1E-6, HQ=1), June 2015 (revised)

mg/kg = milligrams/kilogram
TPHg,d,mo = Total Petroleum Hydrocarbons as gasoline, diesel, and motor oil
MTBE = Methyl Tert-Butyl Ether
VOCs = Volatile organic compounds
PCBs= Polychlorinated Biphenyls
PAHs = Polynuclear aromatic hydrocarbons

3.3 Data Quality Indicators (DQIs)

The purpose of QA/QC procedures is to produce data of known and expected quality by satisfying certain DQIs of precision, accuracy, representativeness, comparability, and completeness. The performance criteria for laboratory analysis for the constituents of concern can be found in the USEPA Region 9 DQI Tables (various tables with various revision dates between 1999 and 2001).

Indicators of data quality as part of the QA/QC program include data precision, accuracy, representativeness, comparability, and completeness, as summarized in the following sections.

3.3.1 Precision

Precision is the degree to which the analytical measurement is reproducible (i.e. that there is agreement between replicate measurements made under similar conditions for the same property). This is a measure of random error and can result from problems with sampling procedures, preservation, storage, shipment, preparation or analysis. Reproducibility among duplicate samples provides a determination of precision, which can be expressed as the relative percent difference in the amount of detected compounds between the original and duplicate samples. Relative percent difference (RPD) is quantified by the following equation:

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

where:

RPD = Relative percent difference
C1 = Larger of the two observed values
C2 = Smaller of the two observed values

Precision will be tracked by the analytical laboratory, Eurofins Calscience, Inc., of Garden Grove, California, using spiked matrix samples. Table 2 outlines the reference methods and measurement quality objectives for the anticipated analyses.

3.3.2 Accuracy

Accuracy is the evaluation of how close the analytical measurement is to the true value. Accuracy is a combination of random error (precision) and systematic error (bias). Accuracy for laboratory analytes is determined by comparing measured concentrations in a sample matrix against the measured concentration in a matrix spiked with a known amount. The formula for determining accuracy from matrix spike samples is:

$$\text{Percent Recovery (\%)} = \frac{(B - A) \times 100}{T}$$

where:

B = measured concentration of spiked samples;
A = measured concentration of unspiked samples; and
T = true spiked concentration.

Samples will be spiked at mid calibration curve when possible.

Table 2. Analytes, Reference Methods, and Measurement Quality Objectives

Analyte Group	Analyte	Analytical Method	Sample Preparation	Analytical Instrumentation	Detection Limit, mg/kg	Reporting Limit, mg/kg	Remediation Goal[(a)], mg/kg	RPD Precision Objective Standard,%	PR Accuracy Objective Range, %
TPH	TPHg	8015B	5035	GC-FID	.050	.25	100	0-25	70-130
	TPHd	8015B	3550	GC-FID	1.3	5.0	100	0-15	64-130
	TPHmo	8015B	3550	GC-FID	.93	5.0	100	0-15	64-130
VOCs	MTBE	8260B	5035	GC-MS	0.0003	.002	.023	0-33	61-145
	Benzene	8260B	5035	GC-MS	0.00013	0.001	.044	0-41	31-145
	Toluene	8260B	5035	GC-MS	0.00052	0.001	2.9	0-52	39-141
	Ethylbenzene	8260B	5035	GC-MS	0.00015	0.001	3.3	0-61	32-146
	Xylene, m-/p-	8260B	5035	GC-MS	0.00027	0.002	2.3 total xylenes	0-30	70-130
	Xylene, o-	8260B	5035	GC-MS	0.00056	0.0001	2.3 total xylenes	0-30	70-130
Metals	Cadmium	6010B	3050	ICP-AES	0.135	0.50	12	0-20	75-125
	Chromium	6010B	3050	ICP-AES	0.142	0.25	100	0-20	75-125
	Lead	6010B	3050	ICP-AES	0.132	0.50	80	0-20	75-125
	Nickel	6010B	3050	ICP-AES	0.145	0.25	150	0-20	75-125
	Zinc	6010B	3050	ICP-AES	0.178	1.0	600	0-20	75-125
PCBs	Aroclor1016	8082	3540, 3550, or 3545	GC	0.021	0.050	.22	0-20	50-135
	Aroclor1221	8082	3540, 3550, or 3545	GC	0.042	0.050	.17 [b]		
	Aroclor1232	8082	3540, 3550, or 3545	GC	0.025	0.050	.17 [b]		
	Aroclor1242	8082	3540, 3550, or 3545	GC	0.037	0.050	.22		
	Aroclor1248	8082	3540, 3550, or 3545	GC	0.032	0.050	.22		
	Aroclor1254	8082	3540, 3550, or 3545	GC	0.032	0.050	.22		
	Aroclor1260	8082	3540, 3550, or 3545	GC	0.03	0.050	.22	0-20	50-135
	Aroclor1262	8082	3540, 3550, or 3545	GC	0.035	0.050	.22		
	Aroclor1268	8082	3540, 3550, or 3545	GC	0.033	0.050	.22		
PAHs	Acenaphthene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0024	0.010	16	0-28	29-137
	Acenaphthlyene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0018	0.010	13	0-32	29-131
	Anthracene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0035	0.010	2.8	0-27	26-134
	Benzo(a)anthracene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0022	0.010	.16 [b]	0-24	24-150
	Benzo(a)pyrene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0018	0.010	.016 [b]	0-22	29-149
	Benzo(b)fluoranthene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0027	0.010	.16 [b]	0-26	21-153
	Benzo(g,h,i) perylene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0015	0.010	27	0-27	20-148
	Benzo(k)fluoranthene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0028	0.010	.38	0-26	28-148
	Chrysene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0022	0.010	3.8	0-28	25-145
	Dibenz(a,h)anthracene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.002	0.010	.016 [b]	0-26	20-132
	Fluoranthene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0018	0.010	40	0-26	20-151
	Fluorene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0031	0.010	8.9	0-27	36-132
	Indeno[1,2,3-cd]pyrene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0016	0.010	.16 [b]	0-25	20-154
	Methylnaphthalene, 1-	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0023	0.010	18 [b]	0-29	34-136
	Methylnaphthalene, 2-	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0023	0.010	.025 [b]	0-31	29-137
	Naphthalene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0035	0.010	1.2	0-33	20-150
	Phenanthrene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0022	0.010	11	0-27	20-144
	Pyrene	8270C-SIM	3510C, 3520C, or 3545A	GC-MS in SIM	0.0022	0.010	85	0-32	20-150
Other	Tetraethyl Lead	8270C	3540C, 3550C, or 3454A	GC-MS	0.011	0.050	.0078 [b]	0-20	50-150

Source: *Analytical by Eurofins Calscience, Inc.*

(a) Unless otherwise noted, remediation goals are Final ESLs from SFBRWQCB Table A-1 Shallow Soil Screening Levels (≤ 3m bgs), Residential Land Use (groundwater is a current or potential drinking water resource), December 2013

(b) Remediation goals from EPA Regional Screening Level Summary Table (TR=1E-6, HQ=1), June 2015 (revised)

mg/kg = milligrams/kilogram
RPD = Relative percent difference
PR = Percent recovery
TPHg,d,mo = Total Petroleum Hydrocarbons gasoline, diesel fuel, motor oil
MTBE = Methyl Tert-Butyl Ether
VOCs = Volatile organic compounds
PCBs= Polychlorinated Biphenyls
PAHs = Polynuclear aromatic hydrocarbons
GC = gas chromatograph
GC-FID = gas chromatograph-flame ionization detector
GC-MS = gas chromatograph mass spectrometer
SIM = Selected ion monitoring
ICP-AES = Inductively coupled plasma– atomic emission spectrometry

3.3.3 Representativeness

Representativeness is a qualitative term describing the degree to which sample data typifies the characteristic of interest at the point of interest accurately and precisely. Representativeness of data from field sites is a function of the sampling process design and the sampling procedures discussed in Sections 4.0 and 6.0, which are designed to optimize the potential for obtaining samples that reflect the true state of the environment while maintaining practicability. All sampling methods follow standard protocols and are documented in Standard Operating Procedures (Appendix A). Sample types, frequency of collection, holding time and volumes are described in Table 3.

3.3.4 Comparability

Comparability is a qualitative term to describe the ability and appropriateness of taking two or more data sets to make collective conclusions. Issues to be considered include variables that could affect the descriptive value of the data for specific parameters at specific times using specific methods.

Considerations include:

- Variables of interest included;
- Common units used;
- Similarity of methods and QA;
- Time frames;
- Season;
- Pesticide/herbicide use
- Weather; and
- Equipment used.

This SAP addresses these issues by describing the project objectives and planned activities under the project.

3.3.5 Completeness

Completeness describes the percentage of valid data achieved versus what was planned by a measurement system. Most importantly, enough data should be generated to draw correct conclusions. There are two components of data completeness: (1) the percentage of usable field samples taken of the samples planned; and (2) the valid (within QC objectives) data percentage of the total tests conducted. All data collected within the QA/QC limits set by this SAP for the project will be of value and can thus be used to draw conclusions concerning the impact of past uses on the Site.

Table 3. Analytical SOP Requirements Table

Analyte/Analyte Group	Matrix	Analytical Method	SOP Document	Preparation Method	Containers	Minimum Sample Volume	Preservation	Preparation Holding Time	Analytical Holding Time
TPH, Purgeable	Solid	8015B - TOTAL PETROLEUM HYDROCARBONS BY GC/FID	SOP-M507 Revision No. 1.2	EPA METHOD 5035	Teflon-lined glass containers, or similar, provided by laboratory; Methanol at a 1/1 ratio to sample volume	2 ounces	0°C - 6°C	N/A	14 days
TPH, Extractable	Solid	8015B - TOTAL PETROLEUM HYDROCARBONS BY GC/FID	SOP-M507 Revision No. 1.2	EPA METHOD 3550	Teflon-lined glass containers, or similar, provided by laboratory	2 ounces	0°C - 6°C	14 days	40 days
VOCs	Sold	8260B - VOLATILE ORGANIC COMPUNDS BY GC/MS	SOP-M311 Revision No. 0.4	EPA METHOD 5035	Terra Core or En Core Samplers, or equivalent	5 grams	0°C - 6°C	N/A	14 days
Metals	Solid	6010B - INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETRY	SOP-M601 Revision No. 6.1	EPA METHOD 3050	Glass, brass, or stainless steel jars or sleeves with Teflon-lined closures, or similar, provided by laboratory	4 ounces	0°C - 6°C	180 days	180 days
PCBs	Solid	8082 - POLYCHLORINATED BIPHENYLS (PCBs) AS AROCLORS BY GAS CHROMATOGRAPHY (GC)	SOP-M407 Revision No. 4.1	EPA METHOD 3540, 3550, or 3545	Glass, brass, or stainless steel jars or sleeves with Teflon-lined closures, or similar, provided by laboratory	4 ounces	0°C - 6°C	14 days	40 days
PAHs	Solid	8270C - SIM - SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MIS) - SELECTED ION MONITORING (SIM) MODE	SOP-M404 Revision No. 4.9	EPA METHOD 3501C, 3520C, or 3545A	Wide-mouth clear glass jars with Teflon-lined closures, or similar, provided by laboratory	4 ounces	0°C - 6°C	7 days	40 days
Tetraehtyl Lead	Solid	8270C - SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MIS)	SOP-M404 Revision No. 4.9	EPA METHOD 3501C, 3520C, or 3545A	Wide-mouth clear glass jars with Teflon-lined closures, or similar, provided by laboratory	4 ounces	0°C - 6°C	7 days	40 days
Sample Preparation	Solid	MULTI-INCREMENTAL SAMPLING (MIS)	SOP-M235 Revision No. 2.1		Ziploc, or similar, sealable container	Analytical method dependent	0°C - 6°C		

SOP = Standard Operating Procedure

TPH = Total Petroleum Hydrocarbons

VOCs = Volatile Organic Compunds

PCBs = Polychlorinated Biphenyls

PAHs = Polynuclear aromatic hydrocarbons

GC = Gas chromatography

FID = Flame ionization detector

MS = Mass spectrometer

The measurement quality objectives for sample analysis for the Site are outlined in Table 2. The objective for completeness (samples usable for analysis) will be defined as follows: for field sampling, 80 percent of soil samples. The specific number depends upon the number of samples actually collected. 100 percent of the data should meet the QA/QC objectives prescribed by this SAP. If the policies and procedures outlined in this SAP are not followed, or if the goals of the SAP are not met, re-sampling or re-testing will be performed.

3.4 Data Review and Validation

Data review and validation is the process of examining field collection and laboratory analytical procedures and the resulting data to determine how well they conform to the requirements stated by the SAP. Data validation under this project will be accomplished through routine audits and by monitoring of QC sample results. A tiered structure of validation will be accomplished as outlined below:

Tier 1: Daily summary forms review by Project Manager

Tier 2: Focused review of selected analytes by Project QA Manager

3.5 Data Management and Tier 1 Data Review

To assure that the project objectives, and more specifically the data quality objectives, are met the following series of steps will be performed in implementing this investigation:

1. The Project Manager will prepare a brief written scope of work that the Project Manager will review with the Field Representative. At this time the Project Manager will familiarize the Field Representative with the sampling locations, sampling protocols, sample handling requirements, and the overall data quality objectives.
2. The Field Representative will document all field activities, including instrument calibration, on standard field data and calibration sheets. Examples of these sheets are included in Appendix B.
3. The Field Representative will document all samples collected on a laboratory chain-of-custody record which will be transported with the samples to the laboratory.
4. The Project Manager will review the Field Representative's field notes and the chain-of-custody record within 24 hours of collecting samples. If any field sampling discrepancies are noted that require correction by field or laboratory staff, the Project Manager will address them as soon as practicable with the staff. If necessary, additional samples may have to be collected and analyzed in accordance with this SAP.
5. The Project Manager will review the analytical laboratory report within 24 hours of receipt. The goal of this Tier 1 review is to quickly provide a brief summary of key analytical issues/deficiencies which might affect data quality, and, hence, the Project Manager's decisions based on the data. Such a review may include review of the data package for completeness, review of chain of custody forms (against laboratory reported information) for signatures, sample condition upon receipt by the laboratory, sample preservation, review of holding times, review of QC summaries, review of

blank results for possible field or laboratory contamination; random checks of reported results against raw data, and random checks of raw data for interference problems or system control problems (e.g., baseline anomalies, baseline drifts, etc.). Results of the review will at a minimum be recorded in the Project Manager's log. The Project Manager may also prepare a memo summarizing the evaluated results, and/or a table of data showing data points (with associated qualifiers) that were considered to be biased or outside acceptance criteria for various DQIs by a large enough factor that use of the data might affect environmental decisions. If any discrepancies are noted, the Project Manager will address them as soon as practicable with the laboratory and if necessary, additional samples may have to be collected in accordance with this SAP.

6. The analytical data will be received in hard copy as well as electronically. After it is received and the data is validated the data will be inserted into tables to be used in the data report. The Project Manager will check that the data has been tabulated correctly.

3.6 Assessment Oversight and Tier 2 Data Review

The Quality Assurance Manager (QA Manager) will work with the Project Manager to assure that the above data management and data validation process is implemented correctly. This will be accomplished by conducting a Tier 2 Data Review, as well as performing the additional tasks outlined below.

The QA Manager will review the laboratory analytical data for the following:

1. Potential identification of significant and noticeable data quality issues/deficiencies; and
2. Review of the data for detected constituents of concern. This evaluation will not involve an in-depth review of all raw data. Constituents of concern in excess of the ESL as enumerated in Table 1 will be evaluated for use in delineating the extent of impact of the constituents. The goal of this evaluation would be to assess how remediation will be accomplished or if further assessment will be necessary. Particular attention will be paid to any constituents of concern detected in the soil samples above the regulatory standards presented in Table 1.

3.6.1 Additional Tasks

Field surveillance leading to the preparation of Field Reports and detailed assessments of laboratory data packages is the responsibility of the project QA Manager. The QA Manager will follow up with the Project Manager within 24 hours of sample collection and will be available to support the Project Manager if any discrepancies with the SAP are noted.

The QA Manager also will follow up with the Project Manager within 24 hours of receipt and review of the analytical data, and will be available to support the Project Manager with any discrepancies if found. The QA Manager will provide a final data/document review once the data has been tabulated and the report has been written.

4.0 SAMPLING LOCATION RATIONALE

This SAP presents the soil sampling planned to address the question of potential impacts from current and past uses of the Site. Prior to excavation at the Site, pre-excavation soil characterization will be conducted in the trench locations shown on Figure 4. These locations were chosen for additional characterization because past analytical results indicate the potential presence of constituents of concern in and around the backfilled tank excavations, under the station office area, and in the north yard at concentrations exceeding Remediation Goals. Each trench will be approximately 10-feet long and 5-feet deep. Three discrete samples will be collected from the floor of each trench; one in the middle and one at each end. The samples from the north yard and from in and around the former tanks will be analyzed for TPHg BTEX, MTBE (T1, T4, T5, and T6). The samples from the station office area will be analyzed for TPHg, TPHd, and TPHmo (T2 and T3). If there are locations at which soil is detected exceeding the Remediation Goals, these locations will be over-excavated during the excavation phase. New DUs will be designated for these excavations and added to the sampling plan.

During the excavation phase of work, as soil is excavated to the maximum depth of the planned excavation, screening will be conducted using visual observation and with a photoionization detector (PID) to evaluate the presence and relative concentration of organic vapors. When these screening methods indicate that the maximum extent of contaminated soil may have been reached, screening samples will be collected and analyzed in the field by a mobile laboratory operated by Analytical Sciences laboratory of Petaluma, California. The mobile laboratory screening will be particularly useful in the areas contaminated by the heavier hydrocarbons, which are not as easy to detect using hand-held field screening tools such as a PID.

This method will be used to guide and direct the excavation in real time. Field screening will be followed by confirmation sampling using ISM, discussed below.

The criterion for successful soil remediation is achieving average contaminant concentrations in soil below Remediation Goals. West Yost will evaluate remaining contaminant concentrations by conducting confirmation sampling using the Interstate Technology Regulatory Council's (ITRC) ISM Technical and Regulatory Guidance Document, (February 2012) Incremental Sampling Methodology (ISM) Because the ultimate objective is to make the site suitable for residential development and justify the removal of land use restrictions, the confirmation sampling plan is also designed to collect data that will be useful for human health risk assessment.

ISM results provide estimates of the mean contaminant concentrations in a defined volume or area of soil known as a decision unit (DU). In this case, ITRC confirmation sampling will be based on area DUs designed for the floor and sidewalls of the excavations. The sidewalls will be divided into two layers; 0 to 0.5 feet (surface), and 0.5 feet to the base of the excavation (subsurface soil). The sidewalls will be divided into DUs of 175 linear feet or less and the excavation floors will be divided into DUs with areas of 4,000 square feet or less.

The health risk assessment will focus on soil which future residents could potentially encounter which, by agreement with DTSC, is soil from the surface down to 0.5 feet below surface. DUs in this zone (DUs 1-6) are classed as Assessment DUs. There are 6 Assessment DUs; four around the perimeter of the large excavation (DUs 1-4) and two around the small excavation (DUs 5 & 6) (Figure 5). Four sidewall samples and three floor samples are also classified as Assessment DUs

(DUs 7, 8, 11, 12, 14, 15, and 17). The primary objective of ISM sampling of Assessment DUs will be to calculate the mean and 95 percent UCL of contaminant concentrations.

The residual concentrations of contaminants from the former fuel release mostly affect soil below 0.5 feet. The DUs below 0.5 feet are classified as Remediation DUs. There are 12 Remediation DUs. (DUs 7-18). The primary objective of ISM sampling in the Remediation DUs is to demonstrate that the mean concentrations are less than Remediation Goals. Some of these DUs (DUs 7, 8, 11, 12, 14, 15, and 17) are also considered Assessment DUs and will, therefore, received the same sampling strategy as the other Assessment DUs.

An ISM sample consist of many small increments. The number of increments is based on studies sited in the ISM guidance document. These studies show that increasing the number of increments improves the ability to predict the true mean of the parameters under study. However; the improvement begins to drop-off after 30 increments. A sample size of 32 was selected for this project because it is the first number greater than 30 that can be practically laid out in the field with divisions of halves, quarters, and eighths. The Remediation DUs will be divided into a grid of 8 columns and 4 rows. The Assessment DUs will be divided into a single row of 32, side-by-side, cells.

A sample increment will be collected from each of the 32 cells in each DU by systematic random sampling. Replicate samples will also be collected using different strategies for each DU class. Three replicate sample sets will be collected from every Assessment DU to provide the data necessary for calculation of the 95% UCL of each contaminant of concern. Fewer replicate samples are needed for the Remediation DUs. Confirmation of remediation requires an understanding of mean concentrations which can be done with one ISM sample per DU. Replicate samples are needed to evaluate how well the ISM samples predict the mean but are not needed for every DU.

The increment and replicate samples will be combined in the field, labeled, placed in a cooler with ice, transported to a freezer under chain of custody, and frozen overnight. They will then be transported under chain of custody to Eurofins laboratory in Garden Grove, California and processed in accordance with Section 6 of the ISM guidance document. Eurofins is a California-certified laboratory with experience in processing ISM samples. The DU samples will be analyzed by the following methods:

- TPHg/d/mo: EPA Method 8015B;
- Benzene, toluene, ethylbenzene, xylenes and Methyl tert-butyl ether (BTEX & MtBE) compounds: EPA Method 8620B; and LUFT 5 Metals: EPA Test Method 6010B;
- LUFT 5 Metals: EPA Test Method 6010B;
- Tetraethyl lead: EPA Method 8270C;
- PCBs - EPA Method 8082; and
- PAHs – EPA Method 8270C – SIM.

Proposed DU locations are shown on Figure 5. Specific rationale for DU locations are discussed below and listed on Table 4. Analytes are also listed on Table 4, and discussed in Section 5. Quality control samples are listed on Table 4, and discussed in Section 10.

Table 4. Sampling Rationale – Soil Samples

DU Number	Sample Replicates	Sample Numbers	Sample Depth	Analyses	Rationale
DU1	3	1, 2, 3	0-0.5 fbgs	TPHg/d/mo, BTEX, MTBE,LUFT-5 metals, tetraethyl lead	Potential surface exposure to future residents
DU2	3	4, 5, 6	0-0.5 fbgs		
DU3	3	7, 8, 9	0-0.5 fbgs		
DU4	3	10, 11, 12	0-0.5 fbgs		
DU5	3	13, 14, 15	0-0.5 fbgs	TPHg/d/mo, BTEX, MTBE,LUFT-5 metals, tetraethyl lead, PCBs	Potential surface exposure to future residents
DU6	3	16, 17, 18	0-0.5 fbgs		
DU7	3	19, 20, 21	0-0.5 fbgs - depth	TPHg/d/mo, BTEX, MTBE, LUFT-5 metals, tetraethyl lead, [PAHs (including Napthalene) in DUs 8 & 12]	Downgradient of former USTs and former pump islands
DU8	3	22, 23, 24	0-0.5 fbgs - depth		
DU9	1	25	0-0.5 fbgs - depth		
DU10	1	26	0-0.5 fbgs - depth		
DU11 (floor)	3	27, 28, 29,	at depth		
DU12 (floor)	3	30, 31, 32	at depth		
DU13	1	33	0-0.5 fbgs - depth	TPHg/d/mo, BTEX, MTBE, LUFT-5 metals, tetraethyl lead, PCBs, [PAHs (including Napthalene) in DUs 14 & 17]	Beneath station building in location of previously detected heavy hydrocarbons
DU14	3	34, 35, 36	0-0.5 fbgs - depth		
DU15	3	37, 38, 39	0-0.5 fbgs - depth		
DU16	1	40	0-0.5 fbgs - depth		
DU17 (floor)	3	41, 42, 43	at depth		
DU18	1	44	0-0.5 fbgs - depth		Beneath former hydraulic lift

DU = Decision unit
fbgs = foot below ground surface
TPHg/d/mo = Total petroleum hydrocarbons as gasoline, diesel, and motor oil
BTEX = Benzene, Toluene, Ethylbenzene, Xylenes
MTBE = Methyl Tert-Butyl Ether
PCBs = Polychlorinated biphenyls
PAHs = Polynuclear aromatic hydrocarbons

4.1 Soil Sampling Locations

As discussed in Section 2.3 above, confirmation sampling of the excavations will be conducted in accordance with the ITRC's ISM. This method involves sampling in designated increments over widespread areas; therefore, the sampling locations will essentially be spread throughout the entire excavated area of the Site, including excavation sidewalls. This section describes the rationale behind the placement and depths of the DUs for sampling, as well as the analytes for each DU. A DU is described as the smallest volume of soil about which a decision is to be made (ITRC, 2012). DUs are Site-specific and investigation specific, and can be used to make decisions for risk assessment or for remediation. For the Site, the DUs are intended to be used for both remediation confirmation sampling and for risk assessment. Each DU is primarily designated as a remediation unit, but each DU will also be used as an exposure area in the preparation of a future risk assessment for the Site.

The rationale for the designation of each DU is as follows:

- DUs 1-4, & 7-12: These DUs are downgradient of the former gasoline USTs or in the vicinity of the pump islands. Because this is a large excavation area it was divided in half for the purpose of designating DUs. The COCs for this area are those that are known to have been released from the USTs, the pumps, or related piping.
- DUs 5-6 & 14-18: These DUs are underneath the station building. COCs have been detected underneath the building in this area during removal of the hydraulic lifts, oil water separators, and associated piping and lines underneath the building.

5.0 REQUEST FOR ANALYSIS

This section discusses analytical support for the project, which depends on several factors including rationale for the analyses requested, analytes of concern, and laboratory information. QC sampling rationale is discussed in Section 10.0.

5.1 Analysis Narrative

As discussed in Section 4.1, analytes for each DU are based on past detections near each DU.

- DUs 1-4, & 7-12: These DUs are downgradient of the former gasoline USTs or in the vicinity of the pump islands. The analytes for this area are those that are known to have been released from the USTs, the pumps, or related piping, or are those required for health risk assessment. These analytes include TPHg BTEX, MTBE, and LUFT 5 metals;
- DUs 5-6 & 14-18: These DUs are underneath the station building. COCs that have been detected underneath the building in this area are: hydraulic oil; TPHd, PAHs in one sample (NMSB23). In addition, PCBs may have been contained in the hydraulic oil and tetraethyl lead in the gasoline. Therefore, the analytes are TPHmo, TPHd, TPHg BTEX, MTBE, PCBs, PAHs, and LUFT 5 metals; and

- The pre-excavation characterization samples will also be analyzed for the constituents detected in past samples collected in their vicinity. As such, Samples from the trenches in and around the former tanks and from the north yard (T1, T4, T5, T6 and T7) will be analyzed for TPHg BTEX, MTBE, and samples from the station office area (T2 and T3) will be analyzed for TPHg, BTEX, MTBE, TPHd, and TPHmo.

Table 2 summarizes the requested analytical methods.

5.2 Analytical Laboratories

On-site pre-confirmation sample screening laboratory services will be provided by Analytical Sciences laboratory of Petaluma, California. Analytical Sciences is certified by the State of California to perform the requested analyses.

All ISM samples will be submitted to Eurofins Calscience, Inc. laboratory (Eurofins) in Garden Grove, California. Eurofins is certified by the State of California to perform the requested analyses and has experience processing and analyzing ISM samples.

6.0 FIELD METHODS AND PROCEDURES

6.1 Field Equipment

6.1.1 List of Equipment Needed

Equipment needed to implement this SAP includes:

- Organic Vapor Meter (OVM) to determine the presence or absence of VOCs in soil;
- Hand sampler (hammer-type);
- Brass sample sleeves for hand sampler;
- Encore™-type samplers;
- Small coring-type samplers for ISM;
- Sample containers, labels, cooler(s), ice; and
- Plastic sheeting for temporarily stockpiling soil, if necessary.

6.1.2 Calibration of Field Equipment

The OVM must be calibrated prior to use in the field. The OVM uses a PID and is calibrated prior to field work to 100 parts per million of 1-liter of isobutylene. The instrument should be calibrated at the beginning of each work day. The flammable gas meter will calibrated according to the manufacturer's recommendation for the model being used.

6.2 Field Screening

Field personnel will use an OVM to assess the presence or absence of VOCs in soil samples chosen for field screening. The OVM, which measures in parts per million by volume (ppmv), is used for qualitative, not quantitative, assessment because the correlation between the volume measurements of the OVM and the weight measurements of the laboratory instruments is not well defined.

A field screen sample will be obtained with a sampler immediately adjacent to the marked sample location. A clod of the soil (approximately 50 grams) to be screened will be removed from the sampler and placed in a zipper-type freezer bag and sealed.

The field screen sample will then be separated into several pieces in the bag and allowed to temperature-equilibrate for approximately 15 to 30 minutes in the sun, allowing any VOCs which might be present in the soil to volatize out into the bag's headspace. The OVM nozzle will then be placed inside the sealed bag, by puncturing a small hole in the side of the bag, in order to measure the VOCs present, if any, in the headspace. The nozzle will remain inside the bag for approximately 15 to 30 seconds or until the maximum reading has been recorded on the OVM readout panel. The depth from which the sample came and the corresponding OVM reading will be recorded on the original field log sheet.

When OVM readings do not detect organic vapors or are equal concentrations in ambient air indicating, that the maximum extent of contaminated soil has likely been reached, screening samples will be collected by hand in containers provided by Analytical Sciences laboratory and analyzed in the field their mobile laboratory for total petroleum hydrocarbons. The mobile laboratory screening will be particularly useful in the areas contaminated by the heavier hydrocarbons, which are not as easy to detect using hand-held field screening tools such as a PID.

This method will be used to guide and direct the excavation in real time. Field screening the soil before confirmation sampling is intended to prevent re-mobilization of excavation equipment and repeat confirmation sampling with the goal of saving both time and money.

6.3 Soil Sampling

6.3.1 Soil Sampling

The following describes soil sampling procedures that will be used by field personnel to collect and handle soil samples:

Before samples are collected, careful consideration will be given to the type of analysis to be performed so that precautions are taken to prevent loss of volatile components or contamination of the sample, and to preserve the sample for subsequent analysis. All sampling equipment will be washed with an Environmental Protection Agency (EPA) approved detergent (such as liquinox or trisodium phosphate) between DUs to prevent cross-contamination.

6.3.1.1 ISM Sampling of DUs

The pre-defined DUs will first be gridded-off into 32 roughly uniform cells. Using the systematic random design, a random position for sample collection will be established for a given cell, and then the same sample collection position will be used in all of the remaining cells in the DU.

ISM samples of exposed soils will be collected and combined as follows: Increments will be collected from directly below the surface of each DU (excavation wall or floor) with small coring devices such as the CMIST, Core N' One™ tool, Terra Core Sampler, or Easy Draw Syringe® and PowerStop Handle®. Due to practical limitations, increments of similar volume rather than of similar mass will be collected. Each sample increment will be approximately 5 grams by volume. Individual increments will not be weighed in the field during collection. Similar mass per increment is assumed with similar volume collected. All of the increments from a DU will be combined in a sample container provided by the laboratory.

6.3.1.2 Discrete Sampling in Pre-excavation Characterization Trenches

Discrete soil samples will be collected for pre-excavation characterization by trenching in select locations. Samples will be collected from trench floors using a slide hammer with a hand sampler lined with 2-inch I.D. x 6-inch long steamed-cleaned or new brass or stainless steel sample sleeves. The sampler will be lowered into the trench and driven 6 inches into the trench floor using the slide hammer.

The sampler will then be extracted from the soil and the sample sleeve carefully removed for analysis. The sleeve will be sealed with Teflon tape beneath polyethylene end caps. The caps will be hermetically sealed to the brass tube with duct tape. The tube will then be labeled and handled as described in Section 9.0.

6.3.2 Decontamination Procedures

Re-usable sampling equipment will be decontaminated between each sample collected using the following procedure:

- Non-phosphate detergent and tap water wash, using a brush if necessary;
- Tap water rinse; and
- De-ionized/distilled water rinse (twice).

Equipment will be decontaminated in a pre-designated area on pallets or plastic sheeting, and clean bulky equipment will be stored on plastic sheeting in uncontaminated areas. Small equipment that has been cleaned will be stored in plastic bags. Materials to be stored more than a few hours will also be covered.

7.0 SAMPLE CONTAINERS, PRESERVATION AND STORAGE

7.1 Soil Samples

Soil samples will be chilled in an iced cooler immediately upon collection and stored at 4°C during transport to the laboratory.

Table 3 in Section 3.3.3 above summarizes the required containers and holding times for the various analyses for soil samples.

8.0 DISPOSAL OF RESIDUAL MATERIALS

In the process of collecting environmental samples during the Site investigation, the West Yost sampling team will generate different types of potentially contaminated investigation derived waste (IDW) that include the following:

- Used personal protective equipment (PPE);
- Used, disposable sampling equipment; and
- Decontamination fluids.

The EPA's National Contingency Plan (NCP) requires that management of IDW generated during sampling comply with all applicable or relevant and appropriate requirements (ARARs) to the extent practicable. The sampling plan will follow the Office of Emergency and Remedial Response (OERR) Directive 9345.3 02 (May 1991), which provides the guidance for the management of IDW. In addition, other legal and practical considerations that may affect the handling of IDW will be considered.

Used PPE and disposable equipment will be double bagged and placed in a municipal refuse dumpster. These wastes are not considered hazardous and can be sent to a municipal landfill. Any PPE and disposable equipment that is to be disposed of which can still be reused will be rendered inoperable before disposal in the refuse dumpster.

Decontamination fluids that will be generated in the sampling event will consist of deionized water, residual contaminants, and water with non-phosphate detergent. The fluids will be placed directly into 55-gallon drums that will be temporarily stored on-site pending receipt of analytical results. Based on the laboratory data derived from the investigation, West Yost will prepare a disposal package and coordinate the disposal of the drums.

9.0 SAMPLE DOCUMENTATION AND SHIPMENT

9.1 Field Notes

Field operations will be documented on preprinted daily field report forms and calibration sheets. Photographs also may be taken to document Site conditions during sampling. Information to be maintained is listed below.

9.1.1 Daily Field Reports

The Daily Field Reports will be used to document where, when, how, and from whom any vital project information was obtained. Report entries will be complete and accurate in order to permit reconstruction of field activities. A separate report will be maintained for each sampling event. Reports will have consecutively numbered pages. All entries will be legible, written in black ink, and signed by the individual making the entries.

At a minimum, the following information will be recorded during the collection of each sample:

- Sample location and description;
- Site or sampling area sketch showing sample location and measured distances;
- Sampler's name(s);
- Date and time of sample collection;
- Type of sample (soil, or water);
- Type of sampling equipment used;
- Field instrument readings and calibration;
- Field observations and details related to analysis or integrity of samples (e.g., weather conditions, noticeable odors, colors, etc.);
- Preliminary sample descriptions (e.g., for soils: clay loam, very wet; for water: clear water with strong ammonia like odor);
- Sample preservation methods ;
- Sample identification numbers and any explanatory codes, and chain of custody form numbers;
- Shipping arrangements (overnight airbill number); and
- Name(s) of recipient laboratory (ies).

In addition to the sampling information, the following specific information will also be recorded on the Daily Field Report for each day of sampling:

- Team members and their responsibilities;
- Time of arrival/entry on-site and time of Site departure;
- Other personnel on-site;
- Summary of any meetings or discussions with tribal, contractor, or federal agency personnel;
- Deviations from sampling plans, Site Safety Plans, and SAP procedures;
- Changes in personnel and responsibilities with reasons for the changes;

- Levels of safety protection; and
- Calibration readings for any equipment used and equipment model and serial number.

9.1.2 Photographs

Photographs may be taken at the sampling locations and at other areas of interest on-site or sampling area. They will serve to verify information entered in the field logbook. For each photograph taken, the following information will be written in the logbook or recorded in a separate field photography log:

- Time, date, location, and weather conditions;
- Description of the subject photographed; and
- Name of person taking the photograph.

9.2 Labeling

All samples collected will be labeled in a clear, precise, and permanent way for proper identification in the field and for tracking in the laboratory. A copy of the sample label is included in Appendix B. The samples will have pre-assigned, identifiable, and unique numbers. At a minimum, the sample labels will contain the following information: station location, date of collection, analytical parameter(s), and method of preservation. Every sample, including samples collected from a single location but going to separate laboratories, will be assigned a unique sample number.

9.3 Sampling Chain of Custody Forms and Custody Seals

Chain of custody records are used to document sample collection and shipment to laboratories for analysis. The sample numbers for all samples, including equipment rinseate samples, reference samples, laboratory QC samples, and duplicates will be documented on this form (see Section 10.0). All sample shipments for analysis will be accompanied by a chain of custody record. A copy of this form is included in Appendix B. Record(s) will be completed and sent with the samples for each laboratory and each shipment (i.e., each day). If multiple coolers are sent to a single laboratory on a single day, separate record(s) will be completed and sent with the samples for each cooler.

The chain of custody record will identify the contents of each shipment and maintain the custodial integrity of the samples. Generally, a sample is considered to be in someone's custody if it is either in someone's physical possession, in someone's view, locked up, or kept in a secured area that is restricted to authorized personnel. Until the samples are shipped, the custody of the samples will be the responsibility of West Yost. The Field Representative will sign the chain of custody record in the "relinquished by" box and note date, time, and airbill number. A photocopy will be made for West Yost's master files.

A self-adhesive custody seal will be placed across the lid of each sample. A copy of the seal is found in Appendix B. The shipping containers in which samples are stored (usually a sturdy picnic

cooler or ice chest) will be sealed with self-adhesive custody seals any time they are not in someone's possession or view before shipping. All custody seals will be signed and dated.

9.4 Packaging and Shipment

All sample containers will be placed in a sturdy picnic cooler. The following outlines the packaging procedures that will be followed for low concentration samples.

1. When ice is used, pack it in zip locked, double plastic bags. Seal the drain plug of the cooler with fiberglass tape to prevent melting ice from leaking out of the cooler.
2. The bottom of the cooler should be lined with bubble wrap to prevent breakage during shipment.
3. Check screw caps for tightness and, if not full, mark the sample volume level of liquid samples on the outside of the sample bottles with indelible ink.
4. Custody seal all container tops.
5. Affix sample labels onto the containers.
6. Wrap all glass sample containers in bubble wrap to prevent breakage.
7. Seal all sample containers in heavy duty plastic zip-lock bags.
8. Place samples in a sturdy cooler(s).
9. Fill empty space in the cooler with bubble wrap or Styrofoam peanuts to prevent movement and breakage during shipment.
10. Ice used to cool samples will be double sealed in two zip lock plastic bags and placed on top and around the samples to chill them to the correct temperature.
11. Each ice chest will be securely taped shut with fiberglass strapping tape, and custody seals will be affixed to the front, right and back of each cooler.

Records of the following information will be maintained by West Yost's field representative:

- Name and location of the Site or sampling area;
- Total number(s) by estimated concentration and matrix of samples shipped to each laboratory;
- If not carried by courier, carrier, air bill number(s), method of shipment (priority next day);
- Shipment date and date it should be received by lab;
- Irregularities or anticipated problems associated with the samples; and
- Whether additional samples will be shipped or if this is the last shipment.

10.0 QUALITY CONTROL

10.1 Field Quality Control Samples

Field quality control samples are intended to help evaluate conditions resulting from field activities and are intended to accomplish two primary goals; assessment of field contamination and assessment of sampling variability. The assessment of field contaminants looks for substances introduced in the field due to environmental factors or sampling equipment, and is done by using blanks of different types. The assessment of sampling variability includes variability due to sampling technique and instrument performance as well as variability possibly caused by the heterogeneity of the matrix being sampled. The following sections cover field QC.

10.1.1 Assessment of Field Variability (Field Duplicate or Co-located Samples)

Replicate samples from the DUs will also act as field duplicates. Duplicate samples will be preserved, packaged, and sealed in the same manner as other samples of the same matrix. The duplicates will be "blind" so that they will not be recognized by the laboratory as duplicates; therefore, they will be labeled with sample numbers similar to those of the primary sample from each DU.

Field duplicates of the discrete soil samples will be collected from the trench on the west side of the gas UST excavation. The samples will be collected at this location because it is the location of previous releases.

The analytical laboratory will provide a temperature blank, and a trip blank which will accompany the sample containers from the laboratory to the field and back again. The trip blank will be analyzed for the complete schedule of analyses requested.

10.2 Laboratory Quality Control Samples

Laboratory quality control samples are intended to assess the precision of the laboratory subsampling process. The laboratory will employ QA/QC procedures including analysis of a method blank, a matrix spike, sample replicates, and a laboratory control sample in accordance with Section 6.5 of the ITRC ISM Guidance document. Copies of the laboratories SOPs are included in Appendix A.

11.0 FIELD VARIANCES

As conditions in the field may vary, it may become necessary to implement minor modifications to sampling as presented in this plan. When appropriate, the Project Manager will be notified and verbal approval will be obtained before implementing the changes. Modifications to the approved plan will be documented in the sampling project report.

12.0 FIELD HEALTH AND SAFETY PROCEDURES

A Site specific Health and Safety Plan has been prepared for this investigation. A copy of that plan is included in Appendix C.

LEGEND

Approximate Site Boundary

N

0 1,000 2,000

Scale in Feet

FIGURE 1

Remedial Action Plan
Hamilton Square
970 C Street, Novato, CA
(T0609592161)

Site Location

THOMPSON DEVELOPMENT INC.
AN AFFILIATE OF WEST BAY BUILDERS INC.

WEST YOST ASSOCIATES

LEGEND

- Gas Station
- Canopy
- Approximate Site Boundary

N

0 100 200

Scale in Feet

FIGURE 2

Remedial Action Plan
Hamilton Square
970 C Street, Novato, CA
(T0609592161)

Site Vicinity

THOMPSON DEVELOPMENT INC.
AN AFFILIATE OF WEST BAY BUILDERS INC.

WEST YOST ASSOCIATES

LEGEND

- Former UST Location
- Estimated Extent of Tank Excavation
- Gas Station
- Canopy
- Approximate Site Boundary
- Storm Drain Inlet
- Hydaulic Lifts

N

0 40 80

Scale in Feet

FIGURE 3

Remedial Action Plan
Hamilton Square
970 C Street, Novato, CA
(T0609592161)

Site Plan

THOMPSON DEVELOPMENT INC.
AN AFFILIATE OF WEST BAY BUILDERS INC.

WEST YOST ASSOCIATES

LEGEND

- Estimated Extent of Former Tank Excavation
- Approximate Site Boundary
- Pre-excavation Test Pit

Proposed Excavations

- 6' bgs (TPHd/mo)
- 7' bgs
- 10' bgs

N

0 30 60

Scale in Feet

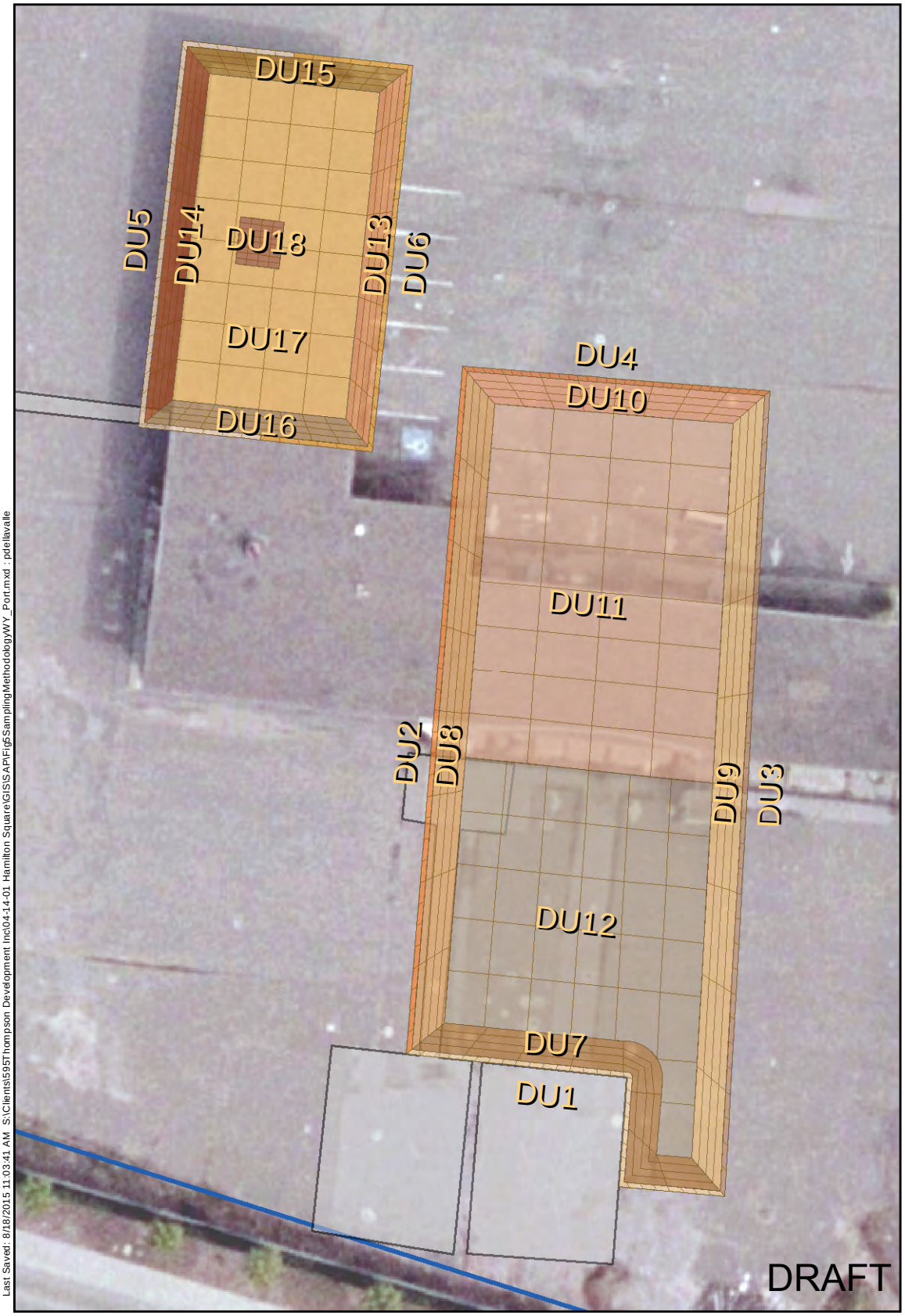
FIGURE 4

Sampling and Analysis Plan
Hamilton Square
970 C Street, Novato, CA
(T0609592161)

Proposed Excavations

THOMPSON DEVELOPMENT INC.
AN AFFILIATE OF WEST BAY BUILDERS INC.

WEST YOST ASSOCIATES



Symbology

DU Sample Grid

Estimated Extent of Tank Excavation

N

0 15 30

Scale in Feet

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FIGURE 5

Sampling and Analysis Plan
Hamilton Square
970 C St, Novato, CA
(T0609592161)

Incremental Sampling Methodology Plan

THOMPSON DEVELOPMENT INC.
AN AFFILIATE OF WEST BAY BUILDERS INC.

WEST YOST ASSOCIATES

APPENDIX A

Standard Operating Procedures

OVM READINGS PROCEDURE

The following describes the procedure used for monitoring volatile organic compounds during field work.

Field personnel will use an organic vapor meter (OVM) to determine the presence or absence of volatile organic compounds (VOCs) in soil samples chosen for field screening. The OVM uses a photoionizaton detector (PID) and is calibrated prior to field work to 100 parts per million of 1-liter of isobutylene. The OVM, which measures in parts per million by volume (ppmv), is used for qualitative, not quantitative, assessment because the correlation between the volume measurements of the OVM and the weight measurements of the laboratory instruments is not well defined.

A field screen sample is obtained from the brass tube immediately above or below the brass tube containing the sample selected for possible analysis. A clod of the soil (approximately 50 grams) to be screened is removed from the brass tube, and is placed in a Zip-Lock freezer bag and sealed.

The field screen sample is separated into several pieces in the bag and allowed to temperature equilibrate for approximately 15 to 30 minutes in the sun, allowing any VOCs which might be present in the soil to volatize out into the bag's headspace. The OVM nozzle is then placed inside the sealed bag, by puncturing a small hole in the side of the bag, in order to measure the VOCs present, if any, in the headspace. The nozzle remains inside the bag for approximately 15 to 30 seconds or until the maximum reading has been recorded on the OVM readout panel.

The depth from which the sample came and the corresponding OVM reading is recorded on the original field log sheet. Field observations, OVM and (odor and staining) readings are used in determining which soil samples are to be analyzed in the laboratory.

Title : **MULTI-INCREMENTAL SAMPLING (MIS)**

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PROPRIETARY INFORMATION STATEMENT

Revision 2.1 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 05/21/14
MANAGEMENT **DATE**

_____ 05-21-14
QA DEPARTMENT **DATE**

1. METHOD IDENTIFICATION

1.1. Multi-Incremental Sampling of Solid Matrices.

2. APPLICABLE MATRICES

2.1. Solid, soil, sludge and sediment samples.

3. ►DETECTION / QUANTITATION LIMITS

3.1. Not Applicable to this preparation procedure. Please refer to the determinative procedures that are specific to the target analytes being analyzed for.

4. SCOPE AND APPLICATION

4.1. Multi-Incremental Sampling is the process of taking multiple soil increments, across a defined decision unit in the field, and then again in the laboratory to produce a fully representative sample for preparation and analysis.

4.2. The procedure outlined in this SOP is not to be used for the preparation of VOC samples nor for samples requiring analysis for Explosives via EPA 8330B.

4.2.1. The procedures presented in this SOP are limited to samples that require nonvolatile analysis only. Volatile analyses (8260, 8015 GRO and DRO, Mercury and certain PAH's) are adversely impacted by the drying and sieving procedure due to volatilization of target analytes and is therefore not recommended.

4.2.1.1. Samples for 8260 or 8015 GRO should be collected using method 5035 (encore or terracore) kits.

4.2.1.1.1. Additionally, MIS aliquotting in the field, following the HEER guidance is preferred: use a collection device such as an easy-draw syringe and 500ml or 1 liter amber containers with methanol in a 1:1 ratio.

4.2.1.2. Samples for percent moisture, 8015 DRO/TPHD, mercury and the volatile PAH's should be taken immediately from the field sample, prior to drying and sieving.

4.2.2. Refer to Appendix A and Appendix B, for a listing of analytes and preferred treatment processes.

4.2.3. Samples for Explosives by EPA 8330B must undergo a grinding procedure prior to analysis. The grinding procedure is not outlined in this SOP.

4.3. Sub-sampling, homogenization, drying and sieving practices have an important effect on the reported results. Improper incremental sampling procedures can lead to results that have significant biases and large imprecision.

4.4. This is a time intensive procedure and great care must be taken to assure the samples are handled properly throughout all steps of this process. EPA recommended holding times start when the sample is initially collected. As the MIS procedure takes 1 to 5 days, monitoring holding times is critical.

5. METHOD SUMMARY

5.1. A solid/soil sample (50g to 2000g) is received directly from the field, often in large resealable bags. The sample is 'homogenized', large 'clumps' broken down to a consistent size, spread out on a tray and allowed to air dry for a minimum of one to five days.

5.2. Once dry, the entire sample is passed through a #10 sieve to reduce the particle size of the sample to less than 2mm. The sample is then incrementally sampled to produce an aliquot for preparation and analysis for any one of many nonvolatile analyses.

5.3. Comments

5.3.1. Collect samples to be tested for VOCs (including TPHg) separately from samples to be tested for SVOCs and non-volatile chemicals;

5.3.2. MI samples to be tested for VOCs:

5.3.2.1. Consider field preservation of increments in methanol using the procedure outlined in the HEER document. A summary is included below:

5.3.2.1.1. Please note that the 150 mL methanol composite should not be shipped to the lab, but instead should be allowed to equilibrate (sit) for 24 to 48 hours, under proper conditions (0−6°C).

5.3.2.1.2. Following this period of rest, a 20−40 mL aliquot of the methanol should be subsampled and that aliquot should be sent to the lab for analysis. This helps with any potential shipping issues.

5.3.2.1.3. We will need the tare weights of the methanol and container both pre and post sample collection in order to determine exact sample weight.

5.3.2.2. Hazardous materials shipping regulations restrict the volume of methanol to no more than 30 milliliters per container and a maximum of one liter per cooler;

5.3.2.2.1. If shipping methanol-preserved samples is not practical then consider freezing individual 5035 increments for shipment and having the increments combined in methanol at the lab;

5.3.2.3. Include naphthalene as a VOC;

5.3.3. MI samples to be tested for semi-volatile chemicals (see Appendix A, Table 1):

5.3.3.1. Collect samples to be tested for SVOCs separately from samples to be tested for VOCs;

5.3.3.2. Samples do not have to be field-preserved, but should be cooled and immediately subsampled for testing upon receipt at the laboratory;

5.3.4. At the lab:

5.3.4.1. Subsample bulk MI samples to be tested for SVOCs (see Table 1; including % Moisture, TPHd, some PAHs and mercury), immediately after the sample is homogenized and spread out and prior to drying and sieving.

5.3.4.1.1. Collect a separate sample from the wet material and test for percent moisture in order to convert analytical results to dry-weight basis;

5.3.4.1.2. All other analyses are already in a dry weight form and will not be further corrected for moisture.

5.3.4.2. Follow standard drying and sieving methods if additional tests are required for non-volatile chemicals using a different lab analysis.

5.3.5. If both SVOC and non-volatile PAHs are targeted as contaminants of potential concern then include testing for both in laboratory subsamples collected from the MI sample prior to drying and sieving.

6. DEFINITIONS

6.1. Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage, preparation or analysis. The blank is subjected to the usual analytical and measurement process to establish a background value.

6.2. Composite: A sample that is an aggregate of separate discrete samples.

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

6.4. Holding Times: The maximum times that samples may be held prior to analysis and still be considered valid or not compromised. The holding time for SVOC analyses is 14 days from collection.

6.5. Homogenize: To make uniform in consistency.

6.6. Increment: One of a series of regular additions or contributions:

6.7. Multi-Increment®: a comprehensive sampling methodology used to represent a specific population (decision unit) and provide a foundation for defensible decision making.

6.8. Multi-layered Sample: A sample consisting of two or more clearly differentiated components (visually distinct layers of material). The layers may be a result of density difference such as liquid/liquid layers, liquid/solid layers, solid/solid layers (small rocks and large rocks), or a combination of these layers.

6.9. Particle Size: The controlling lineal dimension of individual particles, or, the physical dimension of an object's pieces or parts.

6.10. Sieve: A tool to separate materials of one characteristic or size from another.

6.11. Sieving: A simple technique of separating particles of different sizes by passing the material through a sieve of predetermined mesh size.

6.12. Sub-sample: A portion of a sample taken for the purpose of estimating properties or composition of the whole sample.

6.13. VOC: Volatile Organic Compounds - have a low boiling point, and a high vapor pressure at room temperature which causes large numbers of molecules to evaporate or sublimate from the liquid or solid form of the compound and enter the surrounding air.

7. INTERFERENCES

7.1. The equipment used in this procedure will be used for multiple samples. Proper cleaning of all related equipment between samples is essential for the success of this preparation procedure. The use of a preparation blank for organic analyses will help to track the cleanliness of the equipment during processing.

7.2. Multi-incremental sampling must be conducted in an area free from contamination that is easily decontaminated and is vented to control dust and fumes.

7.3. All materials, benches, racks, etc. must be kept clean and free from dust and particulates that can contaminate the samples while being dried. Ensure that all preparation areas are wiped clean of dust and debris prior to beginning this procedure.

8. SAFETY

8.1. Solids, soils and sediments may contain chemically or biologically active toxicants. Exposure to these agents and associated reagent chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current Eurofins Calscience Health & Safety Manual.

8.1.1. At a minimum, Personal Protective Equipment (PPE) includes safety glasses, nitrile or latex gloves and lab coats. Additional safety equipment should be used as needed.

8.2. Cracked or broken glassware should be immediately discarded into a broken glassware receptacle. Broken glassware shall never be used.

8.3. Material Safety Data Sheets (MSDSs) are available for each laboratory reagent and 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. To ensure the safety of the technician, this procedure should not be performed alone. Another technician or chemist should be in the vicinity and must check in on the technician.

9. EQUIPMENT AND SUPPLIES

9.1. 2-mm Sieves (#10).

9.2. Aluminum foils and paper liners, large width.

9.3. Bakers racks, various sizes.

9.4. Certified clean sampling jars, 2oz, 4oz, 8oz and 16oz.

9.5. Cookie sheets/baking pans (3/4"-1" deep), plastic and stainless steel, various sizes.

9.6. Dispensers, plastic squeezable, for solvent, 1/2 liter.

9.7. Sample labels and indelible pens/markers.

9.8. Stainless steel spatulas, wooden tongue depressors, Teflon-coated or other plastic spatulas or spoons.

9.9. Stainless steel, Teflon-coated, or other plastic forceps and/or tweezers, large.

9.10. Stainless steel, square-bottomed scoops for IS aliquotting.

9.11. Stainless steel, Teflon coated and plastic bowls, medium and large.

9.12. Top–loading balance, capable of weighing to 0.1 grams.

9.13. Washing brushes, various types and sizes.

10. REAGENTS AND STANDARDS

10.1. Reagents are used only for the cleaning and drying of related incremental sampling equipment used in this procedure.

10.1.1. Reagent grade chemicals are used. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

10.1.2. Alconox detergent solution or equivalent.

10.1.3. Nitric Acid Solution 0.5 Normal, employed as a decontamination / cleaning solution.

10.1.4. Acetone or Methanol, reagent grade, used as a cleaning/drying solvent.

11. ►SAMPLE COLLECTION, PRESERVATION, CONTAINERS AND HOLDING TIMES

11.1. Please refer to the specific determinative extractive/digestive and analytical procedures for the target analytes of concern.

12. QUALITY CONTROL

12.1. For non-metals, non-VOC analyses (SVOC, wet chemistry), a blank must be prepared during this procedure.

12.1.1. The blank aliquot (clean Ottawa Sand) will go through all of the drying and sieving procedures and can then be used as a preparation blank for the organic analyses, separate from the method QC, to track any potential contamination from the process. Refer to the appropriate analytical method for additional QC procedures.

13. CALIBRATION AND STANDARDIZATION

13.1. Calibration and standardization protocols are defined by the determinative extractive and analytical procedures that are specific to the target analytes.

14. PROCEDURE

14.1. Drying Tray and Equipment Preparation:

14.1.1. The baking sheets used for drying the samples will be stainless steel or plastic. There are medium (13" x 18") and large (18" x 26") sheets. Choose the appropriate size based upon the volume of sample received. Too big is better than too small.

14.1.2. Prior to use, and between samples, the trays, sieves bowls and other sample related equipment must be washed thoroughly with Alconox detergent solution, rinsed and thoroughly dried. Use a brush for cleaning as needed.

14.1.3. After cleaning with Alconox, rinse the equipment with copious amounts of tap water until the detergent residue is removed and then do a final rinse with DI water.

14.1.3.1. After rinsing, stainless steel and Teflon coated equipment may be further rinsed with a dilute (0.5N) solution of Nitric Acid using a dispenser bottle.

14.1.4. Dry the equipment with clean paper towels, Kimwipe® type tissues and/or allow it to air dry on racks.

14.1.4.1. Stainless steel or Teflon coated equipment may be dried with the use of a solvent such as methanol or acetone. If solvent is used the equipment must be allowed to "dry" under the hood until the solvent has fully evaporated from the surface. And, the

solvent rinses must be collected in an appropriate satellite waste container for flammable solvents.

14.1.5. Once dried, the equipment is now ready for use.

14.1.5.1. This cleaning process must be followed between each sample. Multiple sets of sieves and bowls are suggested to expedite the process.

14.1.6. Prior to use for sample drying, the working surface of the trays are to be covered with aluminum foil or a clean paper liner.

14.1.7. It is suggested that two opposite sides of the baker's rack be covered with paper or aluminum foil, leaving the two ends open to air, to limit the amount of sample disturbance while still allowing air to access and pass over the samples.

14.2. ►Sample Preparation for Drying:

14.2.1. Preparation Blank

14.2.1.1. Each time a set of samples is prepared (one or more prepared at the same time using the same equipment) using the following procedure, a 'blank' must also be prepared.

14.2.1.2. The blank (sand) will go through the exact same drying, sieving and incremental sampling procedure as the field samples. This sand can then be used for preparation blanks for the associated organic methods.

14.2.2. Take a single aluminum foil or paper covered medium or large tray (depending on the sample volume received), and label it by writing the Work Order number, sample number and container ID ***on a corner of the paper, or on a label which is then affixed to the tray***.

14.2.2.1. If the tray is being used for the blank, label it as the Lot # of the sand and the date the samples are first being dried.

14.2.3. Apply the label to the edge of the tray so it is visible when the tray is placed in the baker's rack.

14.2.4. Samples will be received in bulk form and contained in one of many sample collection devices: brass, stainless or acetate sleeves, glass jars, resealable bags.

14.2.4.1. The entire sample (anywhere from 100g to 2000g) will be used in the procedure and care must be taken to ensure that the entire sample is removed from the collection device.

14.2.5. Decant water or Homogenize as follows:

14.2.5.1. Decantable water (a separate distinct water layer on top of the soil) will be poured off of the sample prior to drying unless otherwise dictated by the client or project-specific requirements.

14.2.5.1.1. Collect the decanted fluid in an appropriate waste collection device. Do not pour down the drain. If the project requires the aqueous aliquot be maintained, pour off into a clean sample jar and label.

14.2.5.2. Moisture, or water that is a part of the sample such as sludge, will be fully incorporated into the sample by stirring or mixing prior to drying.

14.2.5.2.1. If there is sufficient space in the sample container to homogenize the sample directly within it, use a clean, Teflon spoon or stainless spatula to mix thoroughly.

14.2.5.2.2. If there is not sufficient room to homogenize without the risk of losing material from the container, transfer the entire sample to a clean stainless steel bowl and mix thoroughly using a clean Teflon spoon or stainless steel spatula.

14.2.6. Once the tray is labeled, empty the entire contents of the sample container onto the tray. Break up any large sample clumps using the spatula and/or Teflon spoon but do not grind the sample. (A clean mortar and pestle may be used if absolutely needed, but do not grind the sample to a fine dust, only break up the clumps to a size consistent with the rest of the sample.)

14.2.6.1. Samples received in sleeves may be difficult to remove. Use a clean stainless steel spatula or Teflon spoon to help loosen the contents to ensure complete transfer.

14.2.7. Using a stainless steel spatula or Teflon spoon, spread out the sample evenly over the entire aluminum foil covered tray. The material should be approximately ¼ to ½ of an inch thick.

14.2.7.1. Extraneous material such as leaves, twigs, rocks or stones, etc. may be removed from the sample at this time, although this is not always necessary as they will be removed via the sieving process. Only remove if their presence may prevent proper drying (a layer of leaves, etc) of the sample. If removed, the extraneous objects are to be returned to the original sample container.

14.2.7.1.1. Use forceps or tweezers to remove these objects, and not fingers.

14.2.8. If mercury, volatile PAH's and/or TPH D is required, remove sufficient sample volume from the tray with a Teflon spatula or square bottom scoop and transfer into a jar of suitable size. Be sure to include enough sample volume for percent moisture determination and try to limit the amount of headspace present.

14.2.8.1. As much as possible, remove aliquots with small particle size (~2mm) from the tray.

14.2.9. Label the jar with the work order number, sample number and the next container ID from that of the original sample container (usually an "A", so this container would be a "B"). In addition, it is highly recommended that the required analyses are also written on the label.

14.2.9.1. Once completed, the sample jars are returned to sample control. Be sure to notify the PM so they can initiate log-in for the required analyses.

14.2.10. Following this, place the sample tray in the baker's rack with the label showing.

14.2.10.1. Follow the same procedure (14.2.2 – 14.2.7) for the blank and all other samples.

14.2.10.2. Record all pertinent information in the MIS logbook.

14.2.11. After the blank and all field samples have been properly spread out on the trays, and the trays have been placed in the racks, roll the racks over to the hood and place in front to facilitate air flow over the samples. Be sure that one of the open ends of the rack faces the hood (is perpendicular to the hood sash).

14.2.12. Pull the hood sash down to a level no more than 4 inches above the hood counter to maintain a constant flow of air in the lab without creating pockets of air that swirl and potentially disrupt the samples.

14.2.13. The samples must undergo a minimum of 24 hours of drying time and may be dried for up to five (5) days.

14.2.13.1. During the drying process, check each of the samples and if needed, gently "stir" the samples using a steel or Teflon spatula to expedite the release of moisture. Once you have stirred the samples about on the tray, re-spread out the soil to a standard depth of ¼ to ½ of an inch and continue the drying process.

14.2.13.2. If sample stirring is needed, remove the trays from the rack so as not to knock sample from one tray onto another and be careful not to lose any of the sample during the process.

14.2.14. When the samples appear to be dry, a minimum of 24 hours has passed and there are no obvious signs of moisture, the samples are now ready for sieving. ('Dry' samples should display a fairly consistent color, texture and appearance.)

14.2.14.1. It is advised that a small, representative aliquot (~10g) of each sample be weighed when assumed to have reached the point of 'dryness', and then again in a sequential manner to confirm that the change in mass has not varied by more than 0.5g. Sequential weighings should be at least one hour apart.

14.3. Sample Sieving Protocol:

14.3.1. The entire dried sample will be sieved prior to continuing with the incremental sampling procedure.

14.3.2. Retrieve a clean tray of suitable size and place on the bench, cover with a layer of paper or foil.

14.3.3. Retrieve a #10 (2mm) sieve and a dried-sample tray from the rack. Do not remove the sample label from the tray.

14.3.4. Hold the sieve over tray and begin adding sample to the sieve with a Teflon or other stainless steel spatula or spoon. (The soil can be formed into a mound on the tray to assist with the transfer process.)

14.3.4.1. At the start of the transfer process, do not attempt to lift the foil/paper off of the tray to pour the sample into the sieve as the foil may tear and subsequent loss of sample will occur. This can be done when there is a little sample left to aid in complete transfer of the sample to the sieve.

14.3.5. Shake the sieve gently from side to side allowing the sample to pass through the sieve onto the tray. (Move the sieve all over the tray; don't just allow the sample to form a mound in the middle of the tray.) Continue the process until the entire sample has passed through the sieve. Set the sieve aside for cleaning prior to further use.

14.3.5.1. Any large items left in the sieve should be returned to the original sample container.

14.3.5.2. During the sieving process the sample should have been allowed to deposit over all areas of the tray, if there are larger mounds, distribute the sample to a fairly even level, ¼ to ½ of an inch, using a clean Teflon or stainless steel spatula. Gently 'shaking' the tray from side to side may also help to evenly distribute the sample across the tray.

14.3.6. The sample is now ready for incremental sub-sampling.

14.4. Incremental Sub-Sampling Protocol:

14.4.1. Now that the sample has been spread out on the tray, it can be sub-sampled using an incremental approach. To do this, visually divide up the sample into 30 approximately equal 'sampling areas' – 6 rows and 5 columns.

14.4.1.1. It is suggested that you use a ruler to approximate the sampling areas. (Do not touch the sample with the ruler.) Instead, mark the outside of the tray with colored tape to designate the boundaries and then use the stem end of a clean Teflon or steel spatula to 'score' the sample into 30 sections.

14.4.1.2. Another approach is to use a template suitable for the size tray being used to demarcate the areas for sampling (if this is done, the template shall be made of suitable material such as Teflon).

14.4.2. To collect the samples for each analysis, use a square bottom stainless steel scoop to remove the soil from each of the sampling areas and transfer the aliquots to a clean jar. Remove equal aliquots from each increment.

14.4.2.1. Depending on the number of analyses and related QC required, the aliquots that will be removed from each sampling area will vary in weight from about 0.33 grams to as much as 1 or 2 grams of sample.

14.4.2.2. The aliquots for each analysis shall be collected separate from other analyses.

14.4.2.2.1. As an example: the testing needed involves metals and TPH Diesel, collect the first thirty aliquots for the metals analysis and place in a 2-oz jar or a metals digestion tube. Each aliquot collected is approximately 0.33 grams for a total of ~10 grams.

14.4.2.2.2. When taking an aliquot place the scoop all the way into the sample in order to capture any of the 'fines' that have settled to the bottom.

14.4.2.3. Label the container with the associated Sample and Container ID. Each container will have a separate container ID (A, B, C, etc.) Also include the analysis required.

14.4.2.4. Place the labeled container (jar or digestion tube) on a calibrated balance and tare. Place each of the thirty aliquots into the container. Once all thirty are combined, remove the container from the balance and record the weight to the nearest decimal place on the sample label.

14.4.2.5. Each aliquot will be combined together with the others and placed in a 2oz, 4oz, or other size jar, as needed. Be sure to use equivalent gram aliquots for the blank sample, where the blank is applicable – organics.

14.4.2.6. Record the applicable information in the MIS logbook:

14.4.2.6.1. Date, Workorder and Sample ID, Container ID

14.4.2.6.2. Circle the container type (jar, sleeve, bag, etc)

14.4.2.6.3. Enter date and time drying started

14.4.2.6.4. When complete, enter date and time drying finished

14.4.2.6.5. Include any needed comments

14.4.2.7. Make a copy of the logbook page(s) and provide to the PM.

14.4.2.8. The following table lists the minimum sample mass needed for samples and QC for the standard analyses.

Minimum Sample Mass Required for Analysis			
Analytical Method	**Environmental Sample Mass (g)**	**Prep Blank Mass (g)**	**MS/MSD Mass (g)**
EPA 8015 - ext	10	10	10/10
EPA 8081A	20	20	20/20
EPA 8082	20	20	20/20
EPA 8141A	10	10	10/10
EPA 8270C	20	20	20/20
EPA 8270C - PAH	10	10	10/10
EPA 8270C - PAH SIM	20	20	20/20
EPA 8310	20	20	20/20
EPA 6010 / 6020	1.0	N/A	1.0/1.0
6010 or 6020, Low Level*	10	N/A	10/10
EPA 7471	0.6	N/A	0.6/0.6
7471, Low Level*	5.0	N/A	5.0/5.0
% Moisture	10	N/A	Dup - 10

*Specifically required for Hawaii projects, may also be performed by client or project requirement. Clients may also request an increase of the sample size for the organic analyses.

14.4.3. The sub-sample is now ready for further preparation and/or digestion.

14.4.4. Return any sample that would not pass through the sieve to the original sample container.

14.4.5. Return any additional MIS sample (after sieving) to a clean jar and label as "extra" MIS sample with the workorder and sample ID included. Provide the last in the series of container ID's to this aliquot. (If last ID was an "E", label this as "F".)

14.4.6. Return all containers to sample control.

14.5. Clean all utensils and equipment. After cleaning place in clean plastic bags or wrap with fresh aluminum foil and place in a secure area.

15. CALCULATIONS

15.1. Calculation protocols are defined by the determinative extractive and analytical procedures that are specific to the target analytes.

16. METHOD PERFORMANCE

16.1. Method Performance is defined by the determinative extractive and analytical procedures that are specific to the target analytes.

17. ▶POLLUTION PREVENTION

17.1. ***None.***

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Data acceptance and acceptance criteria are defined by the determinative extractive and analytical procedures that are specific to the target analytes.

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, QA 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, 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.

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 / Preventive Action Record.

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

20.1. Out-of-Control and unacceptable data protocols are defined by the determinative extractive and analytical procedures that are specific to the target analytes.

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, the samples and wastes are identified, segregated, and either returned to the client (preferable) or placed into the proper laboratory waste stream.

21.2. Each specific laboratory area shall maintain clearly labeled waste containers for small quantity waste collection. These satellite 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.

21.3. 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.

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

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 Eurofins 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. The toxicity, carcinogenicity and other health hazards associated with the use of biological specimens and most laboratory chemicals have not been precisely defined. Each specimen and chemical should be handled assuming it is a potential health hazard. Exposure to these specimens and chemicals should be minimized through the use of proper protective equipment and safe laboratory practices as referenced in the current revision of Eurofins Calscience's Health, Safety, and Respiratory Protection Manual.

21.8. 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.

22. REFERENCES

22.1. Technical Guidance Manual Notes: Decision Unit and Multi-Increment* Sample Investigations. Roger Brewer and John Peard, Hazard Evaluation and Emergency Response (HEER), March 2011.

22.2. Technical Guidance Manual for the Implementation of the Hawaii State Contingency Plan, Interim Final, November 12, 2008.

22.3. ASTM D 6323-98 Standard Guide for Laboratory Subsampling of Media related to Waste Management Activities (Reapproved 2003).

22.4. United States EPA, "Guidance for Obtaining Representative Laboratory Analytical Sub-samples form Particulate Laboratory Samples", R. Gerlach and J. Nocerino, EPA/600/R-03/027, November 2003.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Recommendations for MIS field preservation or laboratory subsampling based on overall chemical stability (e.g., volatility and half life).

- 23.1.1. Table 1: Volatile Chemicals: Preserve Samples in Methanol in the Field)
- 23.1.2. Table 2: Semi-Volatile or Otherwise Semi-Stable Chemicals: Subsample MI Bulk Sample at Laboratory Upon Receipt Without Drying
- 23.1.3. Table 3: Metals (presumed stable but depends on target species): Dry and Sieve MI Samples for Laboratory Subsampling
- 23.1.4. Table 4: Non-Volatile or Otherwise Stable Chemicals: Dry and Sieve MI Samples for Laboratory Subsampling

23.2. Appendix B: Recommendations for MIS field preservation or laboratory subsampling of samples to be tested for PAHs.

- 23.2.1. Table 1: Semi-Volatile PAHs (H >0.00001 AND MW <200): Subsample MI Bulk Sample at Laboratory Upon Receipt Without Drying

23.2.2. Table 2: Non-Volatile PAHs (H <0.00001 OR MW >200): Dry and Sieve MI Samples for Laboratory Subsampling

24. MODIFICATIONS

24.1. Not Applicable, SOP references multiple independent sources.

25. REVISION HISTORY

Revision	Description	Author	Effective Date
0.0	SOP Promulgated	L. Scharpenberg	04/27/2010
1.0	SOP Revised	L. Scharpenberg	08/01/2010
2.0	SOP Revised	L. Scharpenberg	11/26/2012
2.1	SOP Revised	L. Scharpenberg	06/02/2014

APPENDIX A

Recommendations for MIS field preservation or laboratory subsampling based on overall chemical stability (e.g., volatility and half life)

Table 1: CHEMICAL PARAMETER	[1]PhysicalState		Molecular Weight	[2]Vapor Pressure mm Hg (25C)	Henry's Law Constant (H) (atm-m3/mol)
[3]Volatile Chemicals **Preserve** Samples in Methanol **in the Field** (or approved alternative, see text)					
ACETONE	V	L	58	2.3E+02	3.9E-05
BENZENE	V	L	78	9.5E+01	5.61E-03
BIS(2-CHLOROETHYL)ETHER	V	L	143	1.6E+00	1.7E-05
BROMODICHLOROMETHANE	V	L	164	5.0E+01	2.1E-03
BROMOFORM	V	S	253	5.4E+00	5.4E-04
BROMOMETHANE	V	G	95	1.6E+03	6.3E-03
CARBON TETRACHLORIDE	V	L	154	1.2E+02	2.7E-02
CHLOROBENZENE	V	L	113	1.2E+01	3.2E-03
CHLOROETHANE	V	G	65	1.0E+03	1.1E-02
CHLOROFORM	V	L	119	2.0E+02	3.7E-03
CHLOROMETHANE	V	G	50	4.3E+03	8.8E-03
2-CHLOROPHENOL	V	L	129	2.5E+00	1.1E-05
DIBROMOCHLOROMETHANE	V	S	208	5.5E+00	7.8E-04
1, 2-DIBROMOETHANE	V	S	188	1.1E+01	6.6E-04
1, 2-DICHLOROBENZENE	V	L	147	1.4E+00	1.9E-03
1, 3-DICHLOROBENZENE	V	L	147	2.2E+00	1.9E-03
1, 4-DICHLOROBENZENE	V	S	147	1.7E+00	2.4E-03
1, 1-DICHLOROETHANE	V	L	99	2.3E+02	5.6E-03
1, 2-DICHLOROETHANE	V	L	99	7.9E+01	1.2E-03
1, 1-DICHLOROETHYLENE	V	L	97	6.0E+02	2.7E-02
Cis 1,2-DICHLOROETHYLENE	V	L	97	2.0E+02	4.1E-03
Trans 1,2-DICHLOROETHYLENE	V	L	97	3.3E+02	9.3E-03
1, 2-DICHLOROPROPANE	V	L	113	5.3E+01	2.9E-03
1, 3-DICHLOROPROPENE	V	L	111	3.4E+01	3.7E-03
1, 4-DIOXANE	V	L	88	3.8E+01	4.9E-06
ETHANOL	V	L	46	5.9E+01	6.3E-06
ETHYLBENZENE	V	L	106	9.6E+00	7.8E-03
METHYL ETHYL KETONE	V	L	72	9.1E+01	5.6E-05
METHYL ISOBUTYL KETONE	V	L	100	2.0E+01	1.4E-04
METHYL TERT BUTYL ETHER	V	L	88	2.5E+02	5.9E-04
METHYLENE CHLORIDE	V	L	85	4.4E+02	3.2E-03
STYRENE	V	L	104	6.4E+00	2.7E-03
tert-BUTYL ALCOHOL	V	L	74	4.1E+01	1.2E-05
1,1,1,2- TETRACHLOROETHANE	V	L	168	4.6E+00	2.4E-03
1,1,2,2- TETRACHLOROETHANE	V	L	168	4.6E+00	3.7E-04
TETRACHLOROETHYLENE	V	L	166	1.9E+01	1.8E-02
TOLUENE	V	L	92	2.8E+01	6.6E-03
TPH (gasolines)	V	L	108	6.8E+02	7.2E-04
1,1,1- TRICHLOROETHANE	V	L	133	1.2E+02	1.7E-02
1,1,2- TRICHLOROETHANE	V	L	133	2.3E+01	8.3E-04
TRICHLOROETHYLENE	V	L	131	6.9E+01	9.8E-03
1,2,3-TRICHLOROPROPANE	V	L	147	3.7E+00	3.4E-04
1,2,3-TRICHLOROPROPENE	V	L	145	3.7E+00	2.8E-02
VINYL CHLORIDE	V	G	63	3.0E+03	2.7E-02
XYLENES	V	L	106	8.0E+00	7.1E-03

APPENDIX A, Cont'd

Table 2: CHEMICAL PARAMETER	[1]PhysicalState		Molecular Weight	[2]Vapor Pressure mm Hg (25C)	Henry's Law Constant (H) (atm-m3/mol)
[4]Semi-Volatile or Otherwise Semi-Stable Chemicals [6,7]**Subsample** MI Bulk Sample at Laboratory Upon Receipt **Without Drying**					
1, 1-BIPHENYL	*SV	S	154	8.9E-03	3.2E-04
BIS(2-CHLOROISOPROPYL)ETHER	*SV	L	171	8.5E-01	1.1E-04
CYANIDE (sodium)	*SV	S	27	1.0E+00	-
DALAPON	SV	L	143	1.9E-01	9.0E-08
1,2-DIBROMO-3-CHLOROPROPANE	*SV	L	236	5.8E-01	1.5E-04
[8]2,4-EDICHLOROPHENOL	NV	S	163	9.0E-02	2.2E-06
2, 4-DIMETHYLPHENOL	SV	S	122	1.0E-01	9.5E-07
[8]GLYPHOSATE	NV	S	169	9.8E-08	4.1E-19
HEXACHLOROBUTADIENE	SV	S	261	2.2E-01	1.0E-02
HEXACHLOROETHANE	SV	S	237	4.0E-01	3.9E-03
ISOPHORONE	SV	L	138	4.4E-01	6.6E-06
[9]MERCURY	*SV	L	201	2.0E-03	-
METHYL MERCURY	SV	S	216	-	-
NITROBENZENE	*SV	L	123	2.5E-01	2.4E-05
NITROGLYCERIN	SV	L	227	2.0E-04	9.8E-08
4-NITROTOLUENE	SV	S	137	1.6E-01	5.6E-06
3-NITROTOLUENE	*SV	S	137	1.9E-01	1.2E-05
2-NITROTOLUENE	*SV	S	137	2.1E-01	2.4E-05
[10]PAHs (varies, see Table 2)	*SV	S	---	---	---
PHENOL	SV	S	94	3.5E-01	3.4E-07
PROPICONAZOLE	SV	L	342	1.0E-06	4.1E-09
[11]TPH (middle distillates)	*SV	L	170	2 to 26	7.2E-04
1,2,4-TRICHLOROBENZENE	*SV	S	181	4.6E-01	1.4E-03

Table 3: CHEMICAL PARAMETER	[1]PhysicalState		Molecular Weight	[2]Vapor Pressure mm Hg (25C)	Henry's Law Constant (H) (atm-m3/mol)
[12]Metals (presumed stable but depends on target species) **Dry and Sieve** MI Samples for Laboratory Subsampling					
ANTIMONY	NV	S	122	-	-
ARSENIC	NV	S	75	-	-
BARIUM	NV	S	137	-	-
BERYLLIUM	NV	S	9	-	-
BORON	NV	S	14	-	-
CADMIUM	NV	S	112	-	-
CHROMIUM (Total)	NV	S	52	-	-
CHROMIUM III	NV	S	52	-	-
CHROMIUM VI	NV	S	52	-	-
COBALT	NV	S	59	-	-
COPPER	NV	S	64	-	-
LEAD	NV	S	207	-	-
MOLYBDENUM	NV	S	96	-	-
NICKEL	NV	S	59	-	-
SELENIUM	NV	S	81	-	-
SILVER	NV	S	108	-	-
THALLIUM	NV	S	204	-	-
VANADIUM	NV	S	51	-	-
ZINC	NV	S	67	-	-

APPENDIX A, Cont'd

Table 4: CHEMICAL PARAMETER	[1]Physical State		Molecular Weight	[2]Vapor Pressure mm Hg (25C)	Henry's Law Constant (H) (atm-m3/mol)
[5]Non-Volatile or Otherwise Stable Chemicals **Dry and Sieve** MI Samples for Laboratory Subsampling					
ALDRIN	NV	S	365	1.2E-04	4.4E-05
AMETRYN	NV	S	227	2.7E-06	2.4E-09
4,6- AMINO,2- DINITROTOLUENE	NV	S	197	-	1.6E-10
2,6-AMINO,4- DINITROTOLUENE	NV	S	197	-	1.6E-10
ATRAZINE	NV	S	216	2.9E-07	2.34E-09
BIS(2-ETHYLHEXYL)PHTHALATE	NV	S	391	1.4E-07	2.7E-07
CHLORDANE (TECHNICAL)	NV	S	410	9.8E-06	4.9E-05
CHLOROANILINE, p-	NV	S	128	7.1E-02	1.1E-06
CYCLO-1,3,5-TRIMETHYLENE-2,4,6-TRINITRAMINE (RDX)	NV	S	222	4.1E-09	6.3E-08
3,3-DICHLOROBENZIDINE	NV	S	253	2.6E-07	5.1E-11
DICHLORODIPHENYLDICHLOROETHANE (DDD)	NV	S	320	1.4E-06	6.6E-06
DICHLORODIPHENYLDICHLOROETHYLENE (DDE)	NV	S	318	6.0E-06	4.1E-05
DICHLORODIPHENYLTRICHLOROETHANE (DDT)	NV	S	354	1.6E-07	8.3E-06
DICHLOROPHENOXYACETIC ACID (2,4-D)	NV	S	221	8.3E-08	3.4E-08
DIELDRIN	NV	S	381	5.9E-06	1.0E-05
DIETHYLPHTHALATE	NV	S	222	2.1E-03	6.1E-07
DIMETHYLPHTHALATE	NV	S	194	3.1E-03	1.1E-07
1,3-DINITROBENZENE	NV	S	168	2.0E-04	4.9E-08
2,4-DINITROPHENOL	NV	S	184	3.9E-04	8.5E-08
2,4-DINITROTOLUENE (2,4-DNT)	NV	S	182	1.5E-04	5.4E-08
2,6-DINITROTOLUENE (2,6-DNT)	NV	S	182	5.7E-04	7.6E-07
DIOXINS (2,3,7,8 TCDD)	NV	S	356	1.5E-09	2.2E-06
DIURON	NV	S	233	6.9E-08	5.1E-10
ENDOSULFAN	NV	S	407	1.7E-07	6.6E-05
ENDRIN	NV	S	381	3.0E-06	6.3E-06
HEPTACHLOR	NV	S	373	4.0E-04	2.9E-04
HEPTACHLOR EPOXIDE	NV	S	389	2.0E-05	2.1E-05
HEXACHLOROBENZENE	NV	S	285	4.9E-05	1.7E-03
HEXACHLOROCYCLOHEXANE (gamma) LINDANE	NV	S	291	4.2E-05	5.1E-06
HEXAZINONE	NV	S	252	2.3E-07	2.2E-12
METHOXYCHLOR	NV	S	346	4.2E-05	2.0E-07
PENTACHLOROPHENOL	NV	S	266	1.1E-04	2.4E-08
PENTAERYTHRITOLTETRANITRATE (PETN)	NV	S	316	1.4E-07	1.2E-11
PERCHLORATE	NV	S	117	---	---
POLYCHLORINATED BIPHENYLS (PCBs, e.g. Aroclor 1254)	NV	S	326	7.7E-05	2.9E-04
SIMAZINE	NV	S	202	2.2E-08	9.5E-10
TERBACIL	NV	S	217	4.7E-07	1.2E-10
2,3,4,6- TETRACHLOROPHENOL	NV	S	232	4.2E-03	8.8E-06
TETRANITRO-1,3,5,7-TETRAAZOCYCLOOCTANE (HMX)	NV	S	296	2.4E-08	8.5E-10
TOXAPHENE	NV	S	414	6.7E-06	6.1E-06
TPH (residual fuels)	NV	L/S	200+	---	---
2,4,5- TRICHLOROPHENOL	NV	S	198	---	1.6E-06
2,4,6- TRICHLOROPHENOL	NV	S	198	---	2.7E-06
2,4,5-TRICHLOROPHENOXYACETIC ACID (2,4,5-T)	NV	S	255	<7.5E-5	4.6E-08
2,4,5-TRICHLOROPHENOXYPROPIONIC ACID (2,4,5-TP)	NV	S	270	9.7E-07	9.0E-09
TRIFLURALIN	NV	S	335	4.6E-05	1.0E-04
1,3,5- TRINITROBENZENE	NV	S	213	6.4E-06	3.2E-09
2,4,6-TRINITROPHENYLMETHYLNITRAMINE (TETRYL)	NV	S	287	1.2E-07	2.7E-09
2,4,6-TRINITROTOLUENE (TNT)	NV	S	227	8.0E-06	4.6E-07

APPENDIX A, Cont'd

Reference: Appendix 1, Table H in HEER office Environmental Hazard Evaluation guidance (HDOH 2008).

1. Physical state of chemical at ambient conditions (V - volatile, SV - Semi-Volatile, NV - nonvolatile, S - solid, L - liquid, G - gas). *SV: Meets criteria for potential consideration as a "volatile" chemical and inclusion in soil gas investigations for evaluation of potential vapor intrusion hazards (H >0.00001 and MW <200, see Footnote 3).

2. Vapor Pressures from National Library of Medicine TOXNET or ChemID databases.

3. Volatile Chemicals defined by vapor pressure >1 mm Hg at 25C. Collect soil gas samples in additional to soil samples at sites with significant releases of volatile chemicals for evaluation of vapor intrusion hazards.

4. Semi-Volatile and Semi-Stable Chemicals defined as: VP 0.1 to <1.0 OR (H >0.00001 and MW <200) OR Liquid at 25C OR Low Persistence OR Otherwise Semi-Stable. See also Footnote 1 (*SV). TPHd overlaps volatile and semi-volatile categories.

5. Non-Volatile Stable Chemicals defined as: VP <0.1 AND H <0.00001 (or H >0.00001 but MW >200) AND Solid at 25C OR Otherwise Stable.

6. Check with lab to determine feasibility of wet sieving sample to remove >2mm particles prior to subsampling.

7. Soil or sediment samples that consist entirely of <2mm material *do not* require drying and sieving to address fundamental error concerns, although some degree of drying and sieving may be desirable by the laboratory for testing purposes.

8. Nonvolatile and published half-life less than thirty days or less. Refer to Table 9-A in Section 9 of the HEER TGM.

9. Mercury stability depends on targeted species. Assumed liquid and semi-stable as default.

10. PAHS - See Table 2.

11. TPH diesel may not be adequately extractable from soil or sediment when placed in methanol, subsamples should be collected and extracted at the laboratory (e.g., using methylene chloride).

12. The stability of a targeted metal depends in part on the species present and can be highly variable. Testing for a specific species of a metal may require alternate collection and preservation methods and should be evaluated on a site-by-site basis with respect to the site investigation objectives.

APPENDIX B:

Recommendations for MIS field preservation or laboratory subsampling of samples to be tested for PAHs.

Table 1: [1]**CHEMICAL PARAMETER**	[2]**PhysicalState**		**Molecular Weight**	[3]**Vapor Pressure mm Hg (25C)**	**Henry's Law Constant (H) (atm-m3/mol)**
Semi-Volatile PAHs (H >0.00001 AND MW <200) [4]**Subsample** MI Bulk Sample at Laboratory Upon Receipt **Without Drying**					
ACENAPHTHENE	SV	S	154	2.2E-03	1.8E-04
ACENAPHTHYLENE	SV	S	152	6.7E-03	1.5E-03
ANTHRACENE	SV	S	178	6.6E-06	5.6E-05
FLUORENE	SV	S	166	3.2E-04	9.5E-05
METHYLNAPHTHALENE, 1-	SV	S	142	6.7E-02	5.1E-04
METHYLNAPHTHALENE, 2-	SV	S	142	5.5E-02	5.1E-04
[5]NAPHTHALENE	SV	S	128	8.5E-02	4.4E-04
PHENANTHRENE	SV	S	178	1.2E-04	3.9E-05
PYRENE	SV	S	202	4.5E-06	1.2E-05

Table 2: [1]**CHEMICAL PARAMETER**	[2]**PhysicalState**		**Molecular Weight**	[3]**Vapor Pressure mm Hg (25C)**	**Henry's Law Constant (H) (atm-m3/mol)**
Non-Volatile PAHs (H <0.00001 OR MW >200) [4]**Dry and Sieve** MI Samples for Laboratory Subsampling					
BENZO(a)ANTHRACENE	NV	S	228	5.0E-09	1.2E-05
BENZO(a)PYRENE	NV	S	252	5.5E-09	4.6E-07
BENZO(b)FLUORANTHENE	NV	S	252	5.0E-07	6.6E-07
BENZO(g,h,i)PERYLENE	NV	S	276	-	1.4E-07
BENZO(k)FLUORANTHENE	NV	S	252	9.7E-10	5.9E-07
CHRYSENE	NV	S	228	6.2E-09	5.1E-06
DIBENZO(a,h)ANTHTRACENE	NV	S	278	9.6E-10	1.2E-07
FLUORANTHENE	NV	S	202	9.2E-06	8.8E-06
INDENO(1,2,3-cd)PYRENE	NV	S	276	1.2E-10	3.4E-07

Reference: Appendix 1, Table H in HEER office Environmental Hazard Evaluation guidance (HDOH 2008).

1. PAHS - Eighteen targeted PAHs listed in Section 9 of the HEER TGM (HDOH 2009), Pyrene considered semi-volatile due to Henry's Law Constant >0.00001 even though MW marginally exceeds 200.

2. Physical state of chemical at ambient conditions (V - volatile, SV - Semi-Volatile, NV - nonvolatile, S - solid, L - liquid, G - gas).

3. Vapor Pressures from National Library of Medicine TOXNET or ChemID databases.

4. If target PAHs include both semi-volatile *and* non-volatile PAHs then subsample upon receipt at lab without drying and test for full suite of PAHs. If only non-volatile PAHs are targeted then sieve and dry samples before testing

5. Include naphthalene as a "volatile" chemical of concern in soil gas investigations at sites with significant releases of petroleum fuels (see TGM Section 9). Other petroleum-related SVOCs do not need to be included in soil gas investigations due to minimal presence in fuels and focus on TPH (and/or specific carbon ranges), BTEX and naphthalene as the main risk drivers for vapor intrusion hazards. Inclusion of additional SVOCs may be required for former manufactured gas plants, however, on a case-by-case basis.

Title : **EPA METHOD 8015B (M), TOTAL PETROLEUM HYDROCARBONS BY GC/FID**

Document No. : SOP-M507
Revision No. : 1.2
Supersedes : 1.1

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Revision 1.2 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 03/05/15
MANAGEMENT DATE

_____ 03-05-15
QA DEPARTMENT DATE

Reviewer Signature	Review Date	Comments	QA Signature

1. METHOD IDENTIFICATION

1.1. EPA 8015B (M), Total Petroleum Hydrocarbons by GC/FID.

2. APPLICABLE MATRICES

2.1. Aqueous, soil, solids, and sludges.

3. DETECTION / QUANTITATION LIMITS

3.1. Reporting Limits for TPH as Gasoline based on total purgeable hydrocarbons quantitation is 50−100 µg/L for aqueous matrices and 0.5 mg/kg for solid matrices.

3.1.1. Alternate purgeable volatile hydrocarbon types include: Aviation Fuel, Crude Oil.

3.2. Reporting Limits for TPH as Diesel based upon total extractable hydrocarbons quantitation is 50−500 µg/L for aqueous matrices and 5 mg/kg for solid matrices.

3.2.1. Alternate extractable semi-volatile hydrocarbon types include: Crude Oil, Jet A, Jet B, JP4, JP5, Fuel Oil, Generic Fuel Product, Hydraulic Oil, Kerosene, Mineral Oil, Motor Oil, Stoddard Solvent.

3.3. Reporting Limits for Carbon Range analysis based upon total carbon range C7−C36 or C7−C44 quantitation is 50−500 µg/L for aqueous matrices and 5 mg/kg for solid matrices.

3.4. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. This method is used to determine the total concentration of gas chromatographable petroleum-based hydrocarbons in three predominant ranges:

4.1.1. TPH as Gasoline (or other purgeable volatile hydrocarbon) corresponding to a range of hydrocarbons from approximately C4 to C12 and covering a boiling point range of < 50−200°C.

4.1.2. TPH as Diesel (or other extractable semi-volatile hydrocarbon) corresponding to a range of hydrocarbons from approximately C7 to C28 and covering a boiling point range of about 150−430°C.

4.1.3. Carbon Range corresponding to a range of hydrocarbons from approximately C7 to C44 and covering a boiling point range of < 150−430°C.

4.2. Approximate Analytical Time:

4.2.1. Preparation: < 5 minutes/sample for purge & trap.
30 minutes/sample for extraction.

4.2.2. Analysis: 45 minutes/sample.

5. METHOD SUMMARY

5.1. Samples to be analyzed for Gasoline or other purgeable volatile hydrocarbons are introduced into a gas chromatograph via a purge and trap sample concentrator. Samples to be analyzed for Diesel or other extractable semi-volatile hydrocarbons are solvent extracted and portion of the extract injected directly into a gas chromatograph. The gas chromatograph is temperature programmed to separate the hydrocarbons. Detection is achieved by the use of a flame ionization detector (FID). The samples analyzed for Gasoline are reported based on comparison to a gasoline standard or the specified reference hydrocarbon and samples analyzed for Diesel are reported based on comparison to a diesel standard or the specified reference hydrocarbon.

5.2. Samples analyzed for Carbon Range analysis are analyzed similar to Diesel, use Diesel as the calibration and quantitation standard but have additional straight chain alkane marker standards that serve to provide specific retention ranges that allow quantitation within that range.

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.

6.3.1. 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, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours***..

6.3.2. 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. Limit of Detection (LOD): ***The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.12. Limit of Quantitation (LOQ): ***The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

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, dated 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. 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. Performance of this method is restricted to analysts experienced in the use of the instruments and apparatus required to execute this method and interpretation of the outputs thereof. 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.

7.2. Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing equipment that lead to artifacts and/or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferants under the conditions of the analysis by running laboratory method blanks.

7.3. The use of high purity solvents and reagents and pre-conditioning of disposables (i.e., filter paper, boiling stones, extraction thimbles) that come in contact with the sample or extract help to minimize interference problems.

7.4. Contamination by carryover can occur whenever high and low level samples are analyzed sequentially. Suspected high level samples should be analyzed diluted and at the end of the sequence to prevent carryover contamination. In addition, sample syringes, purging devices, and labware should be thoroughly rinsed with solvent between samples.

7.5. Autosampler positional contamination can also occur and can easily go undetected. For an autosampler position that is suspected to contained sample of unusually high concentration, a blank should be analyzed on that position (and the following position) prior to analyzing other samples.

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 ***Eurofins*** Calscience Health & Safety Manual. In general, safety glasses and lab coats are required to be worn in all designated laboratory areas. Protective gloves shall be worn when handling chemicals.

8.3. Processes that promote vaporization of volatile chemicals into the work area (e.g., separatory shakeout or sonication) should be performed inside an exhaust hood vented to the exterior of the laboratory.

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

9. EQUIPMENT AND SUPPLIES

9.1. Purge/Trap Gas Chromatograph: Hewlett Packard 5890 Gas Chromatograph, Hewlett Packard 5890 Series II Gas Chromatograph, Agilent 6890N Network Gas Chromatograph, Agilent 7890A Gas Chromatograph, or equivalent configured with a

Tekmar LSC 2000 concentrator and an ALS 2016/2032 autosampler or equivalent instrumentation. The system is configured to allow for on-column injections.

9.2. Purge/Trap Gas Chromatographic Column: J&W Scientific DB-5, 30-m × 0.53-mm ID, 1.5-µm film thickness or equivalent.

9.2.1. Use the following operating parameters as guidance for TPH as gasoline analysis.

- Carrier Gas (Nitrogen) flow rate: 8–10 mL/minute
- Makeup Gas (Nitrogen) flow rate: 30 mL/minute
- Injector Temperature: No Injector
- Detector Temperature: 220°C (Manufacturer recommended)
- Temperature Program:
  1. Initial Temperature: 45°C, hold 6 minutes
  2. Program: 45°C to 150°C @ 5°C/minute
  3. Final Temperature/hold: 150°C, hold 2 minutes

9.3. Extractable/Direct Injection Gas Chromatograph: Hewlett Packard 6890 Series Gas Chromatograph, Agilent 6890N Network Gas Chromatograph, Agilent 7890A Gas Chromatograph, or equivalent configured with Agilent 7683B Series Autosampler or equivalent instrumentation. The system is configured, specifically, for on-column injections.

9.4. Extractable/Direct Injection Gas Chromatographic Column: J&W Scientific DB-5, 10-m × 0.25-mm ID, 0.5- µm film thickness or equivalent.

9.4.1. Use the following operating parameters as guidance for TPH as diesel analysis.

- Carrier Gas (Nitrogen) flow rate: 2–5 mL/minute
- Makeup Gas (Nitrogen) flow rate: 20–25 mL/minute
- Injector Temperature: 280–320°C
- Detector Temperature: 280–320°C
- Temperature Program:
  1. Initial Temperature: 40°C, hold 0.3 minutes
  2. Program: 40°C to 320°C @ 60°C/minute
  3. Final Temperature/hold: 320°C, hold 3–6 minute

9.5. Instrument Software

9.5.1. Requires a PC-based data system or equivalent.

9.5.2. Agilent GC ChemStation Version A.08.03[847], Agilent GC ChemStation Version A.09.01[1206], Agilent GC ChemStation Version B.03.02[341], or equivalent.

9.6. Instrument Maintenance and Troubleshooting

9.6.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.6.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.7. Gases

9.7.1. High purity helium (as carrier).

9.7.2. Dry grade air.

9.7.3. Purified hydrogen.

9.7.4. High purity nitrogen (for concentration of extract).

9.8. Kuderna-Danish (KD) apparatus.

9.8.1. Concentrator tubes, 10-mL, ground glass joints.

9.8.2. Snyder columns, three ball macro.

9.8.3. Evaporative flasks, 250-mL.

9.8.4. Concentrator tube holder with nitrogen injectors.

9.9. Shakers

9.9.1. Lab-Line Orbit Shaker or equivalent (aqueous).

9.9.2. Lab-Line Dual Action Shaker or equivalent (solids).

9.10. Analytical balance capable of weighing to the nearest 0.1 g.

9.11. Lab-Line Multi-Unit (Six Station) Extraction Heater.

9.12. Boiling chips, pre-rinsed with solvent.

9.13. Syringes, 10-µL capacity, 5-mL glass gastight, additional volumes as necessary.

9.14. Purging vessels, as specified for purge and trap unit, cleaned.

9.15. 2000-mL glass beakers.

9.16. Vials, 40-mL capacity, equipped with a Teflon-lined screw cap, pre-cleaned.

9.17. Separatory funnels, 1-L and 2-L with Teflon stopcock.

9.18. Fume Hood, exhaust vented from building.

9.19. Ring stands or fume hood hardware to hold separatory funnels.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Methylene Chloride, pesticide grade.

10.1.2. Methanol, purge and trap grade.

10.1.3. Sodium Sulfate, anhydrous, granular.

10.1.4. Silica Gel, 6-12 Mesh (Nominal).

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 following tables for standard concentrations, alternate spiking levels will be noted where appropriate.

SPIKE CONCENTRATION TABLE

Analyte	Matrix	Stock Conc (ppm)	Volume Added (mL)	Initial Sample Amount	Unit	Final Volume (mL)	On Column (µg)	Final Conc (ppm) In Extract	Final Conc (ppm) In Sample
TPH as Gas	Aqueous	2000	0.005	5.00	mL	5.00	10.0	2.00	2.00
In Methanol (P/T)	Solid	2000	0.005	1.00	g	5.00	10.0	2.00	10.0
TPH as Diesel	Aqueous	20000	0.500	500	mL	25.0	1.20	400	20.0
Extractable in	Solid	20000	0.200	10.0	g	10.0	1.20	400	400
Methylene Chloride	Aqueous	20000	0.100	500	mL	5.00	1.20	400	4.00

SURROGATE CONCENTRATION TABLE

Analyte	Matrix	Stock Conc (ppm)	Volume Added (mL)	Initial Sample Amount	Unit	Final Volume (mL)	On Column (µg)	Final Conc (ppm) In Extract	Final Conc (ppm) In Sample
BFB	Aqueous	500	0.001	5	mL	5.0	0.50	0.1	0.10
In Methanol (P/T)	Solid	500	0.001	1.0	g	5.0	0.50	0.1	0.50
C28	Aqueous	1000	1.25	500.00	mL	25.00	0.15	50.00	2.50
In Methylene Chloride	Solid	1000	0.5	10.00	g	10.00	0.15	50.00	50.0

Note: BFB = 1,4-Bromofluorobenzene; C28 = n-Octacosane

10.2.2. For the previous tables, the following equations apply.

$$\text{Spike Concentration}_{\text{SAMPLE}}\ (\text{ppm}) = \frac{\text{Stock Conc (ppm)} \times \text{Spike Vol (mL)}}{\text{Initial Sample Amount (mL or g)}}$$

$$\text{Spike Concentration}_{\text{EXTRACT}}\ (\text{ppm}) = \frac{\text{Stock Conc (ppm)} \times \text{Spike Vol (mL)}}{\text{Final Extract Volume (mL)}}$$

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, SHIPMENT AND STORAGE

11.1. Holding times are based on generic guidance in EPA SW-846, Chapter 4, Table 4.1, Update III.

11.2. Samples should be collected in Teflon-lined glass containers with minimal headspace.

Analysis	Sample Matrix	Volume	Preservation	Holding Time
Gasoline or other Volatile Fuel	Soil/solid	2 oz	Cool, ≤ 6°C	Analyzed within 14 days.

Analysis	Sample Matrix	Volume	Preservation	Holding Time
Gasoline or other Volatile Fuel	Soil/solid	3 × EnCore®	Cool, ≤ 6°C	Extract within 48 hours, Analyzed within 14 days.
	Water	2 × 40 mL	Cool, ≤ 6°C	Analyzed within 14 days, with HCl to pH < 2.

Analysis	Sample Matrix	Volume	Preservation	Holding Time
Diesel or other Semi-Volatile Fuel	Soil/solid	2 oz	Cool, ≤ 6°C	Extract within 14 days, Analyzed within 40 days.
	Water	500−1000* mL	Cool, ≤ 6°C	Extract within 7 days, Analyzed within 40 days.

* Standard aqueous volume is 500 mL; special projects may require 1000 mL.

11.3. Samples submitted with acid preservation should be designated as such on the chain of custody and containers.

11.4. All samples must be iced or refrigerated from the time of collection until extraction or analysis.

11.5. All samples must be extracted and analyzed prior to expiration of the holding time.

11.6. Additional sample quantities may be required for analysis of matrix-specific QC.

11.7. Additional sample handling information can be found in the Sample Control SOPs.

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. Surrogates shall be added to the QC samples.

12.3. The low concentration standard of the initial multipoint calibration should be at or below the applicable reporting limit. When the low concentration standard is above the reporting limit, a spike at the reporting limit shall be analyzed as part of the initial multipoint calibration and documented. The purpose is to verify that detection and quantitation at the reporting limit is achievable.

12.4. Matrix-Based Quality Control (Surrogates and MS/MSDs)

12.4.1. Matrix-based Quality Control consists of QC samples prepared and processed using actual environmental samples. This consists of a matrix spike and matrix spike duplicates (MS/MSD) and surrogates added to each sample.

12.4.2. 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 the historical average recovery ±3S.

12.4.2.1. If the surrogate compound recoveries are acceptable, report the surrogates and sample data without qualification.

12.4.2.2. 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 measure 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.

12.4.2.3. By itself, unacceptable surrogate recovery does not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

12.4.2.3.1. Check the surrogate spiking solutions for degradation and contamination.

12.4.2.3.2. 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-analyzed or, if insufficient sample remains, reference made to the associated MB surrogate recoveries and the sample data reported with qualification.

12.4.2.3.2.1. 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.

12.4.2.3.2.2. If the MB surrogates are unacceptable, all associated sample data must invalidated and all associated samples re-analyzed.

12.4.3. The acceptance criteria for MS/MSDs are as follows:

12.4.3.1. 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.

12.4.3.2. 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.

12.4.3.2.1. 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.

12.4.3.2.2. If the %REC or RPD of the MS/MSD and LCS/LCSD are unacceptable, all associated sample data must invalidated and all associated samples re-analyzed.

12.5. Event-Based Quality Control (LCSs and MBs)

12.5.1. Event-based quality control consists of QC samples prepared and processed with each batch. This consists of a laboratory control sample and laboratory control sample duplicate (LCS) and a method blank (MB).

12.5.2. The acceptance criteria for LCS compounds vary depending upon historical data. The upper and lower acceptance limits for %REC of each LCS compound are the historical average recovery ±3S. All LCS compounds must be within acceptance limits. If one or more LCS compounds are not acceptable, the problem must be identified and corrected. The LCS and all associated samples must then be re-analyzed.

12.5.2.1. If the %REC is ***above*** the acceptance limit and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

12.5.2.2. ***An LCS/LCSD shall be prepared whenever there is insufficient sample volume to perform the needed matrix QC (MS/MSD) or as required by project QAPP. In all other instances a single LCS shall be prepared.***

12.5.3. Ideally, the concentration of target analytes in a method blank (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:

12.5.3.1. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB 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. Additional information regarding internal quality control checks is provided in SOP-T020.

13. ►CALIBRATION AND STANDARDIZATION

13.1. EXTRACTABLE/ DIRECT INJECTION CALIBRATION

13.1.1. Prior to the analysis of any samples, the following analytical parameters must be established:

13.1.1.1. A valid five-point initial calibration curve where the %RSD is less than or equal to 20%. The recommended calibration levels are 5, 200, 400, 800, and 1600 ppm, but may vary depending upon the analytical criteria specific to the project at hand.

13.1.1.2. A ***continuing*** calibration (midpoint) verification (CCV) standard with a %D (between the CCV and initial calibration RFs) being less than or equal to 15%. The RF from the CCV shall be used for quantitation.

13.1.2. When a new five-point initial calibration curve is generated, it must be confirmed acceptable by the analysis of ***the initial calibration verification (ICV)***, an external midpoint standard of a separate source. For the initial calibration to be acceptable, the %D between the initial calibration RF and external midpoint standard must be less than or equal to 15%.

13.1.3. If CCV does not pass (%D > 15%), it should be reanalyzed. If upon reanalysis, it passes, then the system shall be deemed "in-control" and the analyst may proceed with analysis of samples. If upon reanalysis, it does not pass, the cause should be investigated and a new five-point initial calibration curve must be generated and verified prior to analysis of samples.

13.2. PURGE AND TRAP CALIBRATION

13.2.1. Prior to the analysis of any samples, the following analytical parameters must be established:

13.2.1.1. A valid five-point initial calibration curve where the %RSD is less than or equal to 20%. The recommended calibration levels are 0.05, 1.0, 2.0, 5.0, and 10.0 ppm, but may vary depending upon the analytical criteria specific to the project at hand.

13.2.1.2. A ***continuing*** calibration (midpoint) verification (CCV) standard with a %D (between the CCV and initial calibration RFs) being less than or equal to 15%. The average RF from the initial calibration curve shall be used for quantitation.

13.2.1.2.1. When a new five-point initial calibration curve is generated, it must be confirmed acceptable by the analysis of ***the initial calibration verification (ICV)***, an external midpoint standard of a separate source. For the initial calibration to be acceptable, the %D between the initial calibration RF and external midpoint standard must be less than or equal to 15%.

13.2.1.2.2. If a CCV does not pass (%D > 15%), it should be reanalyzed.

13.2.1.2.3. If upon reanalysis, it passes, then the system shall be deemed "in-control" and the analyst may proceed with analysis of samples. If upon reanalysis, it does not pass, the cause should be investigated and a new five-point initial calibration curve must be generated and verified prior to analysis of samples.

13.3. RETENTION TIME WINDOWS

13.3.1. Total Petroleum Hydrocarbons (TPH) are distinguished on the basis of the retention time ranges for the characteristic components in each fuel type.

13.3.2. The retention time range for TPH Gasoline and Diesel is equivalent to the range of the reference standard. Typically there will be an overlap of the upper range of Gasoline with the lower range of Diesel. The EPA 8015B (M) method is modeled on the defunct California DHS LUFT method without the established retention time range markers of the EPA 8015B Method.

13.3.3. Other fuel types will use the characteristic retention time range of the reference standard.

13.3.4. Carbon Chain analysis uses a Diesel standard for Calibration and QC samples with additional Alkane range markers, reference Section 13.3.5.

13.3.5. The retention time for each Carbon-Chain Analysis range is defined during initial calibration and is used to quantitate the hydrocarbons found during analysis. Each range is established from the retention times of the following alkane hydrocarbon markers:

- C5 Pentane
- C6 n-Hexane
- C7 n-Heptane
- C8 n-Octane
- C9 n-Nonane
- C10 n-Decane
- C11 n-Undecane
- C12 n-Dodecane
- C13 n-Tridecane
- C14 n-Tetradecane
- C16 n-Hexadecane
- C18 n-Octadecane
- C20 n-Eicodecane
- C22 n-Docosane

- C23 n-Tricosane
- C24 n-Tetracosane
- C28 n-Octacosane
- C32 n-Dotriacontane
- C36 n-Hexatriacontane
- C40 n-Tetracontane
- C44 n-Tetratetracontane

14. ▶PROCEDURE

14.1. EXTRACTION/DIRECT INJECTION METHOD

14.1.1. SOLID SAMPLE PREPARATION

14.1.1.1. Take a clean 40-mL vial and label it with aqua tape (aqua tape for methylene chloride) and the appropriate sample identification.

14.1.1.2. Place the vial on a top loading balance and tare the balance to zero.

14.1.1.3. Take the appropriate sample, remove the top layer of sample (about ¼ inch) and weigh out 10-g sample into the vial.

14.1.1.4. Add approximately 2-g sodium sulfate and mix with a clean spatula until the sample is "free-flowing". If additional sodium sulfate is required, repeat with additional 2-g portions (not to exceed 10-g. total) of sodium sulfate until sample becomes "free flowing."

14.1.1.5. **OPTIONAL**: Add 1−2-g Silica Gel to remove polar, non-hydrocarbon oil and greases if required by project requirements.

14.1.1.6. Add 0.5-mL surrogate solution.

14.1.1.7. Add 10-mL of pesticide grade methylene chloride to the vial and tightly cap the vial.

14.1.1.8. Place the vial on shaker machine for 4 minutes. Transfer the methylene chloride layer into clean 40-mL holding vial labeled with the appropriate sample identification.

14.1.1.9. Transfer sufficient concentrated extract into 2-mL autosampler vial for analysis.

14.1.1.10. Store all extracts at 4°C until analysis.

14.1.2. WATER SAMPLE PREPARATION

14.1.2.1. 500-mL Extraction with Partial Concentration

14.1.2.1.1. Take a clean 1-L separatory funnel and label it with aqua tape and the appropriate sample identification.

14.1.2.1.2. Mark sample container to measure amount of sample provided.

14.1.2.1.3. Shake the sample to homogenize and transfer approximately 500 mL into the separatory funnel.

14.1.2.1.4. Add 25 mL of pesticide grade methylene chloride to sample container, cap, shake and pour into separatory funnel.

14.1.2.1.5. Using water, measure volume of sample provided by pouring water into sample container to mark and then pouring water into a graduated cylinder to measure total volume. Record volume in logbook.

14.1.2.1.6. Add 1.25-mL surrogate solution to sample in separatory funnel.

14.1.2.1.7. Cap the separatory funnel and place on shaker machine for 2 minutes, venting periodically into a fume hood.

14.1.2.1.8. Place in ring stand and allow phases to separation.

14.1.2.1.9. Transfer the lower methylene chloride layer into a 250-mL Erlenmeyer flask labeled with aqua tape and the sample identification. Repeat extraction two additional times with 25-mL portions of methylene chloride and collect all extract in the flask.

14.1.2.1.10. Add 5−10-g sodium sulfate to the flask to remove water entrained in the extract. Sodium Sulfate will "clump" when attached to water. Sufficient water is removed when the sodium sulfate added remains dispersed along bottom of flask without clumping.

14.1.2.1.11. **OPTIONAL**: Add 1−2-g silica gel to remove polar, non-hydrocarbon oil and greases if required by project requirements.

14.1.2.1.12. Extract is ready for partial concentration.

14.1.2.1.13. Take entire volume of Methylene Chloride extract and concentrate to 25 mL using a 40-mL glass VOA vial and nitrogen gas injector until level matches reference 25-mL level in second vial used for this purpose.

14.1.2.1.14. Transfer extract into 2-mL autosampler vials labeled with the appropriate sample identification.

14.1.2.1.15. Lower reporting levels will require concentration of extract as follows:

14.1.2.1.15.1. For 100-ppb RL = 2.5-mL extract, concentrate to 0.5 mL with 0.25 mL

of surrogate solution, LCS with 0.1-mL solution.

14.1.2.1.15.2. For 50-ppb RL = 5.0-mL extract, concentrate to 0.5 mL with 0.125 mL of surrogate solution, LCS with 0.05-mL solution.

14.1.2.1.15.3. Transfer appropriate amount of extract into a 10-mL K-D concentrator tube labeled with aqua tape and the sample identification.

14.1.2.1.15.4. Place K-D concentrator in nitrogen evaporator apparatus and bubble nitrogen until the proper concentrate volume is achieved. Transfer final extract concentrate in 2-mL autosampler vials labeled with the appropriate sample identification.

14.1.2.2. 1000-mL Extraction with Full Concentration

14.1.2.2.1. Take a clean 2-L separatory funnel and label it with aqua tape and the appropriate sample identification.

14.1.2.2.2. Mark sample container to measure amount of sample provided.

14.1.2.2.3. Shake the sample to homogenize and transfer all the sample (assuming 1000-mL sample container) into the separatory funnel.

14.1.2.2.4. Add 60 mL of pesticide grade methylene chloride to sample container, cap, shake and pour into separatory funnel.

14.1.2.2.5. Using water, measure volume of sample provided by pouring water into sample container to mark and then pouring water into a graduated cylinder to measure total volume Record volume on log book.

14.1.2.2.6. Add 0.2-mL surrogate solution to sample in separatory funnel, LCS add 0.05-mL solution.

14.1.2.2.7. Cap the separatory funnel and place on shaker machine for 2 minutes, venting periodically into a fume hood.

14.1.2.2.8. Place in ring stand and allow phases to separation.

14.1.2.2.9. Transfer the lower methylene chloride layer into a 250-mL Erlenmeyer flask labeled with aqua tape and the sample identification. Repeat extraction

two additional times with 60-mL portions of methylene chloride and collect all extract in the flask.

14.1.2.2.10. Add 5−10-g sodium sulfate to the flask to remove water entrained in the extract. Sodium Sulfate will "clump" when attached to water. Sufficient water is removed when the sodium sulfate added remains dispersed along bottom of flask without clumping.

14.1.2.2.11. **OPTIONAL**: Add 1−2-g silica gel to remove polar, non-hydrocarbon oil and greases if required by project requirements.

14.1.2.2.12. Extract is ready for full concentration.

14.1.2.2.13. Take entire volume of Methylene Chloride extract and concentrate using 250-mL KD Evaporator Flask, 10-mL Concentrator Tube and 3-Bubble Snyder Column.

14.1.2.2.14. Place in hot bath using 2000-mL beakers filled with water on heating unit.

14.1.2.2.15. Concentrate to 2 mL.

14.1.2.2.16. Transfer extract into 2-mL autosampler vials labeled with the appropriate sample identification.

14.1.2.3. Store all extracts and concentrates at 4°C until analysis.

14.1.2.4. For projects that have raised reporting limits, difficult matrices, or suspected to contain high analyte levels, the sample amounts and volumes may be modified as appropriate.

14.1.3. SAMPLE ANALYSIS

14.1.3.1. Program the analytical sequence into the data system.

14.1.3.2. Load one of the extract vials for each sample into the autosampler tray according to the sequence entered into the data system and store duplicate vials at 4°C as backup for potential reanalysis.

14.1.3.3. The extracts are analyzed by direct injection into the E/DI gas chromatograph via the autoinjector.

14.1.3.4. For high level samples where detector saturation is of concern, extract should be diluted to achieve a signal within the quantitation range, preferably near mid calibration range.

14.1.3.5. For samples that have been overdiluted (detector response below the low standard), the sample should be reprepared with less of a dilution to achieve a signal within the quantitation range, preferably near mid calibration range.

14.2. PURGE AND TRAP METHOD

14.2.1. SAMPLE PREPARATION

14.2.1.1. The purge and trap procedure involves minimal sample preparation. A portion of the sample is transferred directly to the purge and trap sample concentrator.

14.2.2. SOIL/SOLID SAMPLE ANALYSIS

14.2.2.1. Place a clean purging vessel on a top loading analytical balance and tare the balance to zero.

14.2.2.2. Take the appropriate sample, remove top layer of sample (about ¼ inch), weigh out 1 g into the clean purging vessel, add 5 mL of reagent water, and add surrogate or spiking compounds when required for the project.

14.2.2.3. Attach the vessel to the P/T autosampler minimizing time vessel is open to the environment.

14.2.2.4. Repeat above steps for all samples in batch.

14.2.2.5. Initiate the analytical sequence.

14.2.2.6. For suspected high level samples where detector saturation is of concern, appropriate dilutions should be made by purging a smaller aliquot of sample.

14.2.2.7. For high level samples where further dilution could result in non-representative aliquots, methanolic extraction followed by P/T of the extract should be performed by the following procedure.

14.2.2.7.1. Take the appropriate sample, remove top layer of sample (about ¼ inch), and weigh out 4 g into a clean 40-mL vial.

14.2.2.8. Add 10 mL of purge and trap grade methanol to the vial and tightly cap.

14.2.2.9. Shake the sample for 2 minutes.

14.2.2.9.1. High Level Samples: Transfer the methanol layer into a small vial minimizing headspace. Label with the appropriate sample identification.

14.2.2.9.2. Dispose 40-mL vial and store extract vial at 4°C until analysis.

14.2.2.10. Using a microsyringe, transfer an aliquot of the extract into a cleaned purging vessel containing 5 mL of water containing surrogate, internal, and, if applicable, matrix spiking standards.

14.2.2.11. Attach the vessel to the P/T autosampler minimizing time vessel is open to the environment.

14.2.2.12. Initiate the analytical sequence.

14.2.3. WATER SAMPLE ANALYSIS

14.2.3.1. Using a 5-mL gastight syringe, transfer 5 mL of the sample into a clean purging vessel and add surrogate or spiking compounds.

14.2.3.2. Attach the vessel to the P/T autosampler minimizing time vessel is open to the environment.

14.2.3.3. Repeat above steps for all samples in batch.

14.2.3.4. Initiate the analytical sequence.

14.2.3.5. For medium and high level water samples where detector saturation is of concern, appropriate dilutions should be made by purging a smaller aliquot of sample.

14.3. At the time of sample loading, the pH of each aqueous sample shall be measured with narrow range pH paper to determine if the pH of the sample is < 2 (refer to SOP-T301). The pH range (< 2 or ≥ 2) of each sample shall be documented on the log book.

14.4. The samples are loaded in the following order or in any other acceptable order:

1) Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Method Blank (MB)
4) Samples (up to 10 per first portion of batch)
5) ***Continuing*** Calibration Verification (CCV)
6) Samples (up to 10 per second portion of batch)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

14.4.1. Item 1: A CCV is used to verify the acceptance of the initial five point calibration on a continuing basis. An acceptable CCV is required at least every 12 hours and at the end of the sequence.

14.4.1.1. 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.

14.4.1.2. In establishing the CCV frequency, all samples and dilutions are counted as sample runs.

14.4.2. Item 2: A LCS is a known matrix that has been spiked with a known concentration of all 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.

14.4.2.1. For aqueous samples, the LCS consists of the compounds spiked into clean water. For solid samples, the LCS consists of the compounds spiked into washed sea sand.

14.4.2.2. A LCS is required for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.2.3. The LCSD, ***if required***, is handled identically to the LCS. In addition to assessing the accuracy of the analytical measurement, the LCSD, in combination with the LCS, can be used to assess the precision of the analytical process expressed as relative percent difference (RPD).

14.4.3. Item ***3***: The MB is a known matrix similar to the samples being analyzed that 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, etc.).

14.4.3.1. For aqueous samples, the MB consists of organic free water. For solid samples, the MB consists of washed sea sand.

14.4.3.2. A MB is required with every batch of 20 samples per matrix or portion thereof, whichever is more frequent. It should be noted, however, that as necessary (e.g., after high level samples), additional MBs and instrument blanks may be placed in the sequence.

14.4.4. Items ***4 and 6***: Up to 20 samples per batch. High concentration samples should be sufficiently diluted to ensure that instrumentation is not contaminated. Dilution of samples will result in increased reporting limits.

14.4.5. Item ***7***: The MS is the actual matrix spiked with known concentrations of all target analytes. The sample that 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.

14.4.5.1. The purpose of a 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) of the spiked compounds.

14.4.5.2. 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".

14.4.6. 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 MSD, in combination with the MS, can be used to assess the precision of the analytical measurements. The measurement is expressed as relative percent difference (RPD).

14.4.7. Item ***9***: An acceptable CCV is required at the completion of every 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 pertinent information in the run logbook.

14.6. Initiate the sequence.

15. CALCULATIONS

15.1. Analyte quantitation is accomplished by comparison of chromatographic profile and relative retention times between the sample and retention time range previously established in section 13.3.

15.2. For this method, the data system shall be programmed to integrate the total resolved and unresolved peak area within the retention time range for use in the calculations below. The analyst shall verify and ensure proper baseline integration of all chromatographic output.

15.3. The analyst must identify and record the surrogate area peak. This value is subtracted out of the total chromatographic peak area for each output as detailed in calculations below. In addition, this value is used during data entry so that automated calculations can be performed.

15.4. Standards are prepared using the following formula:

$$\text{Standard Concentration (ppm)} = \frac{\text{Standard Material (µg)}}{\text{Solvent (mL)}}$$

15.5. The response factor (RF) of the reference standard is calculated using the following formula:

$$\text{Response Factor} = \frac{\text{Area Count}_{(\text{STANDARD})} - \text{Area Count}_{(\text{SURROGATE})}}{\text{Standard Concentration (ppm)}}$$

15.6. The sample concentration shall be calculated against the standard reference material for the analyte requested using the following formula:

$$\text{Sample Concentration (ppm)} = \frac{\text{Area Count}_{(\text{SAMPLE})} - \text{Area Count}_{(\text{SURROGATE})}}{RF} \times \frac{V_F}{S} \times DF$$

where: RF = Response factor (AC/ppm)
V_F = Final volume of extract.
S = Amount of sample in mL for liquid (g for solid).
DF = Dilution factor

15.7. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{CF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the average CFs for the target analyte.
CF_{ave} = mean of the 5 initial CFs for the target analyte.

15.8. The percent difference of each analyte is calculated as follows:

$$\%D = \frac{|CF_{ave} - CF|}{CF_{ave}} \times 100$$

where: %D = percent difference of target analyte.
CF = target analyte's daily CF.
CF_{ave} = mean of the 5 initial CFs for the target analyte.

15.9. 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.

15.10. The recovery of the MS compounds is calculated as follows:

$$\%REC_{MS} = \left(\frac{C_{recovered} - C_{sample}}{C_{added}}\right) \times 100$$

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.

15.11. 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 recovered in measurement 1.
C_2 = concentration of target analyte recovered in measurement 2.

15.12. Where the chromatographic pattern significantly differs from that of the target standard, the total peak area should be quantitated using the target standard and result qualified to indicate that chromatographic pattern does not match that of the calibration standard.

15.13. Unless specified otherwise by the client, all TPH concentrations will be reported in µg/L (ppb) for aqueous samples and mg/kg (ppm) for solid samples.

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

18. ▶DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS compounds vary depending upon historical data. The upper and lower acceptance limits for %REC of each LCS compound are based upon the historical average recovery ±3S. All LCS compounds must be within acceptance limits. If one or more LCS compounds are not acceptable, the problem must be identified and corrected.

18.1.1. If the LCS %REC is ***above*** of the 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 ***prepared and analyzed*** when the LCS/LCSD is used in place of MS/MSD due to insufficient sample quantity ***or when required by project QAPP***.

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.

18.3. 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 ***mg/kg (ppm)*** 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 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 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 recoveries, to determine acceptance of the sample results.

20.1.2. LCS: 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 group leader 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 ***Eurofins*** 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. REFERENCES

22.1. EPA Method 8000B, Determinative Organic Separations, Revision 2, "Test Methods for Evaluating Solid Waste, Volume 1B, Laboratory Manual", Third Edition, US Environmental Protection Agency, September, 1996.

22.2. EPA Method 8015B, Non-Halogenated Organics using GC/FID, Revision 2, "Test Methods for Evaluating Solid Waste, Volume 1B, Laboratory Manual", Third Edition, US Environmental Protection Agency, September, 1996.

23. TABLES, DIAGRAMS, FLOWCHARTS AND DATA VALIDATION

23.1. Appendix A: Additional Quality Control Criteria for Department of Defense Project.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 8015B Revision 2 are noted.

Calscience SOP M507 Section	Reference Document EPA Method 8015B Section	Summary of Modification
All	All	Revise criteria for various fuel types.

25. ▶REVISION HISTORY

Revision	Description	Author(s)	Effective Date
1.0	Section 3: Revise reporting limits and add reference to detection limits. Section 6: Add LOD/LOQ definitions. Section 9: Update the list of equipment and supplies. Section 10: Revise standard preparation procedure. Section 13: Insert additional hydrocarbon markers. Section 14: Revise solid sample preparation procedure for extraction/direct injection method, and revise CV to CCV. Section 23: Add Appendix A. Section 24: Add modifications. Section 25: Add revision history. Appendix A: Add DoD requirements.	K. Chang	03/30/12
1.1	Section 9: Update instrument parameters and gas supplies. Section 10: Revise standard preparation procedure. Section 14: Revise solid sample preparation procedure for extraction/direct injection method. Section 25: Add revision history.	I. Kwak / S. Tseng	02/01/13
1.2	Entire document: Update company name. Section 6: Update definitions. Sections 8 and 17: Add SDS. Sections 12, 14, and 20: Update LCSD requirement. Section 13: Update CCV criteria. Section 18: Update LCSD requirement and unit. Appendix A: Update LCSD procedure.	L. Hunt	03/16/15

Appendix A

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA 8015B (M), Total Petroleum Hydrocarbons by GC/FID – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. ▶DETECTION / QUANTITATION LIMITS

2.1. The ***reporting limits*** 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. Limit of Detection (LOD)

5.1.1. LOD determination 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. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

5.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

5.1.2.2. LOD 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., second column confirmation, pattern recognition, etc.).

5.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.1.3. No samples shall be analyzed without a valid LOD.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.3. Continuing Calibration Verification (CCV)

5.3.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

5.3.2. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.4. Retention Time Window

5.4.1. 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.

5.4.1.1. When initial calibration is performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S.

5.4.1.2. When initial calibration is not performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the low-to-midpoint CCV standard ± 3S.

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

5.5.1. Method Blanks (MBs)

5.5.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.5.1.1.1. 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).

5.5.1.1.2. 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).

5.5.1.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

5.5.1.2. 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 LOD.

5.5.1.2.1. 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.

5.5.2. Laboratory Control Samples (LCS/LCSDs)

5.5.2.1. 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.

5.5.2.1.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.5.2.2. All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.6. Matrix Based Quality Control (Surrogates and MS/MSDs)

5.6.1. Surrogates

5.6.1.1. 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.

5.6.2. Matrix Spikes (MS/MSDs)

5.6.2.1. The RPD is ≤ 30%.

5.6.2.2. 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.

5.6.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

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 field 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) Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Method Blank (MB)
4) Samples (up to 10 per batch, excluding QC check samples and MBs)
5) ***Continuing Calibration Verification (CCV)***
6) ***Samples (up to 10 per batch, excluding QC check samples and MBs)***
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

6.2.1. Items 1, ***5, and 9***: 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 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

6.2.2. Items ***4*** and ***6***: Up to 10 sample (excluding QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

6.2.3. 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.

6.2.3.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.2.4. 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 Manual for Environmental Laboratories, Version 4.2, October 25, 2010.

Title : **EPA METHOD 8260B, VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY / MASS SPECTROMETRY (GC/MS)**

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PROPRIETARY INFORMATION STATEMENT

Revision 0.4 changes are noted in bold italicized typeface and preceded by a "►" marker.

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QA DEPARTMENT DATE

Reviewer Signature	Review Date	Comments	QA Signature

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 / QUANTITATION LIMITS

3.1. The reporting limits (RLs) for this method are as follows:

	Water	Soil	Oil
VOCs	0.5~100 µg/L	5.0~250 µg/kg (wet-weight)	500~25000 µg/kg
Lower-QL VOCs	0.5~50.0 µg/L		

3.2. The RLs will be proportionally higher for samples which require dilution or reduced sample size.

3.3. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

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*	chlorobenzene	1,2-dichloroethane
t-amyl methyl ether (TAME)	chloroethane	1,1-dichloroethene
benzene	chloroform	c-1,2-dichloroethene
bromobenzene	chloromethane*	t-1,2-dichloroethene
bromochloromethane	2-chlorotoluene	1,2-dichloropropane
bromodichloromethane	4-chlorotoluene	1,3-dichloropropane
bromoform	dibromochloromethane	2,2-dichloropropane
bromomethane*	1,2-dibromo-3-chloropropane*	1,1-dichloropropene
2-butanone*	1,2-dibromoethane (EDB)	c-1,3-dichloropropene
t-butyl alcohol (TBA)*	dibromomethane	t-1,3-dichloropropene
n-butylbenzene	1,2-dichlorobenzene	diisopropyl ether (DIPE)
s-butylbenzene	1,3-dichlorobenzene	ethanol*
t-butylbenzene	1,4-dichlorobenzene	ethylbenzene
carbon disulfide*	dichlorodifluoromethane*	ethyl t-butyl ether (ETBE)
carbon tetrachloride	1,1-dichloroethane	hexachloro-1,3-butadiene

2-hexanone*	1,1,1,2-tetrachloroethane	trichloroethene
isopropylbenzene	1,1,2,2-tetrachloroethane	trichlorofluoromethane
p-isopropyltoluene	tetrachloroethene	1,2,3-trichloropropane
methyl t-butyl ether (MTBE)	tetrahydrofuran	1,2,4-trimethylbenzene
methylene chloride	toluene	1,3,5-trimethylbenzene
4-methyl-2-pentanone (MIBK)*	1,2,3-trichlorobenzene	vinyl acetate
naphthalene	1,2,4-trichlorobenzene	vinyl chloride
n-propylbenzene	1,1,1-trichloroethane	o-xylene
styrene	1,1,2-trichloroethane	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	2-methyl-2-butanone (TAA)
2-chloropropane	methylcyclohexane
cyclohexane	propanedinitrile
cyclohexanone	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 5030) and closed system purge-and-trap method (EPA Method 5035).

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 Samples	5030	SOP-M212
Closed System Purge-and-Trap for Soil/Waste Samples	5035	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.

6.3.1. 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, unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours.

6.3.2. 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. Limit of Detection (LOD): ***The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.13. Limit of Quantitation (LOQ): ***The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

6.14. 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.

6.15. 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.

6.16. 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.

6.17. 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.

6.18. 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.

6.19. 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.

6.20. 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.

6.21. 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.

6.22. 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.

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

6.24. 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, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. 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.

6.26. 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.

6.27. 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.

6.28. Term Specific to GC/MS Analysis

6.28.1. 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).

6.29. ***Refer to the current revision of the Eurofins Calscience Quality Systems Manual for additional terms and definitions.***

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. If elevated baselines are observed during the analysis of blanks and standards, the chromatographic system should be considered contaminated. This contamination may be the result of impure carrier gas, inadequate gas conditioning, septum bleed, column oxidation, and/or pyrolysis products in the injector or column. Such contamination is unacceptable and should be addressed through a program of preventive maintenance and corrective action.

7.7. 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.

7.8. Use of sensitive mass spectrometers to achieve lower quantitation levels will increase the potential to detect laboratory contaminants as interferences.

7.9. Co-elution of the p- and m-xylene isomers may occur.

7.10. 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 Eurofins 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) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** 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 6890 Series Gas Chromatograph, Agilent 6890N Gas Chromatograph, Agilent 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 5973Network Mass Selective Detector (MSD), Agilent 5975B MSD, Agilent 5975C 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 (EM) detector.

9.3. Instrument Software

9.3.1. Requires a PC-based data system or equivalent.

9.3.2. Agilent MSD ChemStation Version E.02.00.493, Agilent MSD ChemStation Version E.02.01.1177, or equivalent equipped with NIST mass spectral library.

9.4. Instrument Maintenance and Troubleshooting

9.4.1. Refer to the current revision of SOP-T066 and instrument manuals for maintenance and troubleshooting.

9.4.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.5. Analytical Column: 25-m × 0.2-mm ID, 1.12-µm film thickness, mid-polar, low bleed, narrow-bore, capillary, fused silica, J&W Scientific DB-624 or equivalent.

9.6. Purge Gas: Helium, He, or nitrogen, N_2, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.7. Carrier Gas: Helium, He, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.8. VOA vials, 28-mm × 95-mm (40 mL capacity) and 28-mm × 57-mm (20-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.

9.8.1. Bake VOA vials in an oven at 90°C for 24 hours prior to use.

9.9. Storage vials, 15-mm × 45-mm (4 mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.

9.10. Volumetric flasks, 25-mL, 50-mL, or other capacity, glass, Class A.

9.11. 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 Certificate or equivalent documentation.

9.12. 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.

9.13. 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. 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 bisulfate, $NaHSO_4$, monohydrate, colorless crystals, reagent grade or equivalent.

10.1.8. Methanol, CH_3OH, clear colorless liquid, purge and trap grade or equivalent.

10.1.9. Refer to the specific SOPs of the preparatory methods for additional reagents.

10.1.10. 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.

10.2.2. ***Pre-certified stock standard solutions, each in sealed glass ampules, containing 2000–20000 ppm of various (custom and catalogued mixes) of non-gaseous volatile organic target analytes are used to prepare calibration and check standards.***

10.2.2.1. ***Use following table as guidance to prepare the primary source working standard in methanol.***

VENDOR	CAT #	Description	Conc. PPM	uls	MLs	PPM
ACCU	S-21698-R7	CUSTOM VOC STANDARD	2000-20000	1000	40	50-500
CHEMSERV.	From NEAT	ACROLEIN	10000	400	40	50-500
RESTEK	30216	VINYL ACETATE	2000	1000	40	50-500
RESTEK	30265	2-CHLOROETHYL VINYL ETHER	2000	1000	40	50-500
RESTEK	30465	CALIFORNIA OXYGENATES MIX # 1	2000-10000	1000	40	50-500
RESTEK	30633	8260B CALIBRATION MIX # 1	2000	1000	40	50-500
RESTEK	30006	VOA CALIBRATION MIX # 1	5000	400	40	50-500

10.2.2.2. ***Prepare the 0.5–5.0 ppm gaseous and non-gaseous volatile organic working standard solution by diluting the appropriate volume of 50-500 ppm gaseous and non-gaseous volatile organic stock standard to 1.0 mL with methanol.***

10.2.2.3. ***The 0.5-5.0 ppm 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 ***12500*** ppm of each surrogate, ***12500*** ppm of each internal standard (except TBA-d_9), and ***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), dibromofluoromethane, 1,2-dichloroethane-d_4, and toluene-d_8.

10.2.3.2. The internal standards are t-butyl alcohol-d_9 (TBA-d_9), chlorobenzene-d_5, 1,4-dichlorobenzene-d_4, 1,4-difluorobenzene, and pentafluorobenzene.

10.2.3.2.1. The internal standards selected should permit most analytes of interest in a chromatogram to have relative retention times of 0.80–1.20.

10.2.3.3. 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.

10.2.3.4. 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	

10.2.3.5. 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	

10.2.3.6. Prepare the first calibration standard or CCV solution, and purge and trap for hardware turning.

10.2.4. Calibration standard solutions contain various concentrations of target analytes, surrogates, and internal standards in methanol.

10.2.4.1. Add the appropriate volumes of the working and stock standards and the appropriate volume of the ***50/***250 ***or 250/1250*** ppm ***(as per autosampler)*** surrogate and internal standard working standard to 5.0 mL of reagent water, and purge and trap for initial calibration.

10.2.4.1.1. For lower limit of quantitation, add the appropriate volumes of the working and stock standards and the appropriate volume of the 50***/250*** ppm surrogate and internal standard working standard to 20 mL of reagent water.

10.2.4.1.2. 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.

10.2.4.2. 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, *Acetonitrile, Iodomethane or Isobutyl alcohol;* 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

10.2.4.3. 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, *Acetonitrile, Iodomethane, or Isobutyl alcohol;* 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

10.2.4.4. The midpoint standards are also used as the continuing calibration verification solutions.

10.2.4.5. The calibration levels for the initial calibration of a non-routine target analyte may be established differently per client request or project specific DQOs.

10.2.5. Initial calibration verification (ICV) solutions contain 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.

10.2.5.1. 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.

10.2.5.1.1. 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.

10.2.5.1.2. 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 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, *Acetonitrile, Iodomethane, or Isobutyl alcohol;* 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 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, *Acetonitrile, Iodomethane, or Isobutyl alcohol;* 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 calibration level for the initial calibration verification of a non-routine target analyte may be established differently per client request or project specific DQOs.

10.2.6. Continuing calibration verification (CCV) solutions contain 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.

10.2.6.1. 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.

10.2.6.1.1. 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.

10.2.6.1.2. 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 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, *Acetonitrile, Iodomethane, or Isobutyl alcohol*; 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 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, *Acetonitrile, Iodomethane, or Isobutyl alcohol;* 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

10.2.6.4. The calibration level for the continuing calibration verification of a non-routine target analyte may be established differently per client request or project specific DQOs.

10.2.7. Surrogate and internal standard working standard solutions contain 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.

10.2.7.1. 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 sample including each calibration standard, calibration verification standard, quality control (QC) check sample, and method blank prior to purge-and-trap extraction via 5.0 mL purge volume.

10.2.7.1.1. For lower limit of quantitation, manually add 4.0 µL of the 50 ppm surrogate and internal standard working standard to each sample including each calibration standard, calibration verification standard, QC check sample, and method blank prior to purge-and-trap extraction via 20 mL purge volume.

10.2.7.1.2. For samples processed via mobility or methanol extraction, manually add 5.0 µL of the 50 ppm

surrogate and internal standard working standard to each mobility-procedure or methanol extract including each mobility-procedure or methanol extract designated as QC check sample and method blank prior to purge-and-trap extraction via 5.0 mL purge volume.

10.2.7.2. 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 sample including each calibration standard, calibration verification standard, QC check sample, and method blank prior to purge-and-trap extraction via 5.0 mL purge volume.

10.2.7.2.1. 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 sample including each calibration standard, calibration verification standard, QC check sample, and method blank prior to purge-and-trap extraction via 20 mL purge volume.

10.2.7.2.2. For samples processed via mobility or methanol extraction, configure the autosampler to inject 1.0 µL of the 250 ppm surrogate and internal standard working standard into each mobility-procedure or methanol extract including each mobility-procedure or methanol extract designated as QC check sample and method blank prior to purge-and-trap extraction via 5.0 mL purge volume.

10.2.8. Spike working standard solutions contain 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.

10.2.8.1. Use the second source 50 ppm gaseous volatile organic working standard solution as the gaseous spike working standard solution. Use the second source non-gaseous volatile organic stock standard solution as the non-gaseous spike working standard solution.

10.2.8.2. The spike standards are used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCSs).

10.2.8.3. Add 5.0 µL of the gaseous spike working standard and 5.0 µL of the non-gaseous spike working standard to each MS/MSD and LCS sample prior to purge-and-trap extraction via 5.0 mL purge volume.

10.2.8.3.1. For lower limit of quantitation, add 4.0 µL of the gaseous spike working standard and 4.0 µL of the non-gaseous spike working standard to each MS/MSD and LCS sample prior to purge-and-trap extraction via 20 mL purge volume.

10.2.8.4. Add 5.0 µL of the gaseous spike working standard and 5.0 µL of the non-gaseous spike working standard to each mobility-procedure or methanol extract designated as MS/MSD and LCS prior to purge-and-trap extraction via 5.0 mL purge volume.

10.2.9. All working standards must be replaced after three months (unless specified otherwise) or sooner if routine QC or comparison with check standards indicates a problem.

10.2.9.1. Store all working standards with minimal headspace under dark and refrigerated condition.

10.2.9.2. Return the working standards to the refrigerator or freezer as soon as possible after use to prevent the loss of volatile organic compounds.

10.2.9.3. Check all working standards frequently for signs of degradation or evaporation.

10.2.10. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2.10.1. Return the stock standards to the refrigerator or freezer as soon as possible after use to prevent the loss of volatile organic compounds.

10.2.10.2. 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 is known or suspected to contain 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 5030 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 5035 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 20 mL pre-cleaned clear glass VOA 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. In the event that the headspace greater than 6 mm is evident, and the vial is used for analysis, the data should be qualified.

11.6. Aqueous and oil samples should be maintained in a chilled state (0–6°C), not frozen, post sample collection until received at the laboratory. If shipped on same day as collection, sediment samples should be maintained in a chilled state, 0–6°C, post sample collection. Otherwise freeze sediment samples as soon as possible after collection and maintain them at ≤ -10°C until shipment. Solid samples may be frozen 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 aqueous, oil, and unfrozen solid samples are stored in a 0–6°C cooler. Sediment samples are stored in a ≤ -10°C freezer. Solid samples may be stored in a ≤ -10°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. Per client request or project specific data quality objectives (DQOs), apply the specified minimum contact time 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. Per client request or project specific DQOs, apply the specified minimum contact time 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. Per client request or project specific DQOs, apply the specified minimum contact time between the solid 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. The grand mean approach cannot be used for Department of Defense projects.

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 (such as Department of Defense project criteria), 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 RSD or correlation of any analyte is unacceptable, review the results (e.g., proper identification, area count, response factor, etc.) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards.

12.2.7.2. 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 to rule out problems due to random chance.

12.2.7.2.1. In some cases, replace the calibration standard may be necessary.

12.2.7.3. If a calibration standard is replaced and/or reanalyzed, recalculate the RSD or correlation, and document the rationale for re-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, re-prepare, and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective actions, which may include replacement 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.

12.4.2.3. For EPA Region 9 requirement, the initial calibration is deemed valid if the %D for each analyte is ≤ 15%.

12.4.3. The %D of each non-CCC is evaluated only per client request or project specific DQOs.

12.4.3.1. 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%.

12.4.4. The internal standard response and retention time for the CCV must be evaluated during or immediately after data acquisition.

12.4.4.1. 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.

12.4.4.2. 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.

12.4.4.3. Following corrective action, reanalysis of samples analyzed while the system was malfunctioning is required.

12.4.5. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result, re-prepare, 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 (MBs and LCSs)

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

12.5.1.1. An LCS shall be prepared whenever there is insufficient sample volume to perform the needed matrix QC (duplicate or MS/MSD) or as required by project QAPP. In all other instances a single LCS shall be prepared.

12.5.2. The acceptance criteria for MBs are as follows:

12.5.2.1. 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.

12.5.2.2. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

12.5.2.3. 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.

12.5.3. ►The acceptance criteria for LCS compounds are as follows:

12.5.3.1. The lower and upper acceptance limits for %REC and RPD ***(if applicable)*** of each LCS/LCSD compound are based upon the historical average recovery ± 3S that is updated at least annually.

12.5.3.1.1. If historical data is unavailable, the lower and upper acceptance limits for %REC of each LCS compound are 80% and 120%, respectively. The RPD ***(between LCS and LCSD)*** is ≤ 20%.

12.5.3.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each LCS compound in a water sample are 70% and 130%, respectively. The RPD is ≤ 30%.

12.5.3.1.3. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each LCS compound in a soil sample are 65% and 135%, respectively. The RPD is ≤ 50%.

12.5.3.2. All LCS 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.

12.5.3.3. 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.

12.5.3.4. 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.

12.5.3.5. 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

12.5.3.6. 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.

12.6. 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 each 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 each surrogate compound in a soil sample are 70% and 125%, respectively.

12.6.2.2. If the surrogate compound recoveries are acceptable, report the surrogate 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. Unacceptable surrogate recoveries do not automatically 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 recoveries, 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. If insufficient sample remains, reference the associated MB surrogate recoveries and report the sample data with qualification.

12.6.2.4.3.1. If, upon re-processing 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/MSD 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. Specifically, an acceptable LCS usually supports matrix interference.

12.7. If the %REC or RPD of the MS/MSD and LCS 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. Mass Spectrometer Tuning

13.1.1. 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 5−50 ng of BFB meets the tuning criteria. The acceptance criteria for the tune are listed in Section 12.1.

13.1.2. Obtain the mass spectrum of BFB as follows:

13.1.2.1. 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 acquired within 20 scans of the elution of BFB.

13.1.2.1.1. The background subtraction should be designed only to eliminate column bleed or instrument background ions.

13.1.2.1.2. Do not subtract part of the BFB peak or any other discrete peak that does not coelute with BFB.

13.1.3. All subsequent standards, samples, and blanks associated with a specific tune must use identical mass spectrometer operating conditions.

13.1.4. Whenever invasive maintenance of the hardware is performed, the system must be re-tuned.

13.2. Mass Spectrometer 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.

14.1.4. Once established, the same operating conditions must be applied to all subsequent standard, sample, and blank analyses.

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 / Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Laboratory Control Sample Duplicate (LCSD)–***Optional***
4) Method Blank (MB)
5) Samples (up to 20 per batch, excluding QC check samples and MBs)
6) Matrix Spike (MS)
7) Matrix Spike Duplicate (MSD)

14.4.1. Item 1: An acceptable tune demonstrates satisfactory hardware performance, and a CCV is used to verify the acceptance of the initial multi-point calibration on a continuing basis. A tune meeting the acceptance criteria and an acceptable CCV are required daily prior to sample analysis and every 12 hours thereafter at the beginning of an analytical batch.

14.4.1.1. The tuning standard is also the CCV solution.

14.4.2. Item 2: 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.

14.4.2.1. 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.

14.4.2.2. 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.

14.4.3. 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 15.8. The LCSD is required if MS/MSD are not prepared and analyzed along with field samples.

14.4.4. 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 (e.g., surrogates, internal standards, etc.).

14.4.4.1. 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.

14.4.4.2. 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.

14.4.5. ►Item 5: 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.

14.4.5.1. ***NOTE: For prescreening water samples of unknown concentration using portable PID detector, use the following precautions:***

14.4.5.1.1. First take a 5 mL aliquot of water sample from the vial using syringe and set aside.

14.4.5.1.2. Use rest of the vial for PID screening so that sample aliquot is uncompromised and sustains no loss of analytes.

14.4.5.1.3. Use the 5 mL aliquot for necessary dilution or run without dilution as determined by PID reading.

14.4.5.2. All dilutions should keep the responses of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

14.4.6. Item 6: 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.

14.4.6.1. 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.

14.4.6.2. 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."

14.4.7. Item 7: 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.

14.4.8. Solvent blanks consisting of reagent water 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 without 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 with 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 Eurofins 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 and 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) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

18. ▶DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. 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.

18.1.1. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

18.1.2. 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.

18.2. The acceptance criteria for LCS compounds vary depending upon historical data. The lower and upper acceptance limits for %REC and RPD of each LCS compound are based upon the historical average recovery ± 3S that is updated at least annually. All LCS compounds must be within acceptance limits (see Section 12.5.3. for additional information).

18.2.1. For EPA Region 9 requirement, refer to Section 12.5.3.1.2. and Section 12.5.3.1.3. for acceptance criteria.

18.2.2. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD ***(when applicable)*** is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.3. ***If the LCS/LCSD is used in place of the MS/MSD due to insufficient sample amount, or if LCS/LCSD is required per client or project specific DQO, both the LCS and LCSD data must be reported.***

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. For EPA Region 9 requirement, refer to Section 12.6.2.1.2. and Section 12.6.2.1.3. for acceptance criteria.

18.3.2. If the surrogate compound recoveries are acceptable, report the surrogate and sample data without qualification.

18.3.3. 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. 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.

18.3.4. Unacceptable surrogate recoveries do not necessarily invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.4.1. Check the surrogate and internal standard solutions for degradation and contamination.

18.3.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate recoveries, the same sample should be re-processed and re-analyzed.

18.3.4.3. 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. If insufficient sample remains, reference the associated MB surrogate recoveries and report the sample data with qualification.

18.3.4.3.1. If upon re-processing 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.

18.3.4.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

18.3.5. 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.

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. For EPA Region 9 requirement, refer to Section 12.6.4.1.2. and Section 12.6.4.1.3. for acceptance criteria.

18.4.2. 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.

18.4.3. 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.

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.

18.6. Additional information regarding internal quality control checks is provided in ***the current revision of*** 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 ***Director***, 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.

20.1.2. LCS: 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 ***group leader*** 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, ***refer to the current revision of SOP-T020 for procedures on data reporting and corrective action***.

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 Eurofins 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: Requirements for Low Level 1,2,3,-Trichloropropane (TCP) and 1,4-Dioxane Determined by EPA 8260B Using Selected Ion Monitoring (SIM) Mode.***

24. MODIFICATIONS

24.1. The following modifications from EPA Method 8260B Revision 2 are noted.

Calscience SOP M311 Section	Reference Document EPA Method 8260B Section	Summary of Modification
12.2.	7.3	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 is modified.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
0.1	Section 3: Update terminology for RL and add reference to the determinations of DL and RL. Section 4: Revise the scope to include additional analytes, and update EPA method numbers. Section 5: Update EPA method numbers. Section 6: Add LOD and LOQ definitions. Section 7: Update interferences.	K. Chang	08/17/12

Revision	Description	Author(s)	Effective Date
0.1	Section 9: Update the list of equipment and supplies. Section 10: Revise standard preparation. Section 11: Revise the requirements on preservation, headspace, and container. Section 12: Revise quality control criteria. Section 13: Revise subtitles. Section 14: Revise tuning and data reporting procedures. Section 18: Update section references, and add EPA Region 9 requirements. Section 24: Revise modifications. Section 25: Add revision history. Appendix A: Update the ion list for additional analytes. Appendix B: Update DoD quality control requirements and criteria.	K. Chang	08/17/12
0.2	Correct minor typos/grammar throughout. Section 4: Delete unused prep methods. Section 6: Update "batch" definition. Section 9: Revise equipment. Section:10: Update calibration tables Section 11: Revise sample preservation and storage. Section 12: Revise quality control criteria. Section 14: Revise LCSD requirement. Section 18: Revise LCSD requirement. Section 25: Update Revision History. Appendix A: Update the ion table.	I. Kwak / L. Hunt	08/12/13
0.3	Entire document: Update company name.	L. Hunt	03/09/15
0.4	Section 6: Update definitions. Sections 8 and 17: Add SDS. Section 10: Update calibration standards. Sections 12 and 14: Update LCSD requirement. Section 14: Add prescreening procedure. Appendix A: Update ions. Appendix D: Delete BP criteria appendix and replace with requirements for low level 1,2,3,-TCP and 1,4-dioxane by 8260B SIM.	Y. Patel / L. Hunt	03/18/15

►Appendix A

LIST OF PRIMARY AND SECONDARY IONS OF TARGET ANALYTES, SURROGATES, AND INTERNAL STANDARDS

Eurofins Calscience, Inc.

►Appendix A

Primary and Secondary Ions

Compound Name	Characteristic Ion(s)	
	Primary	Secondary
acetone	58	43
acetonitrile	41	40
acrolein	56	55
acrylonitrile	53	52 , 51
allyl chloride	76	41 , 40 , 78
tert-amyl methyl ether (TAME)	73	87 , 55
benzene	78	51
bromobenzene	156	77 , 158
bromochloromethane	***130***	***128***
bromodichloromethane	83	85 , 127
1,4-bromofluorobenzene (surrogate)	95	174
bromoform	173	175 , 254
bromomethane	94	96
1,3-butadiene	54	53 , 39
2-butanone	***43***	***72***
tert-butyl alcohol (TBA)	59	57 , 41
tert-butyl alcohol-d_9 (internal standard)	65	66
n-butylbenzene	91	92 , 134
sec-butylbenzene	105	134
tert-butylbenzene	134	119 , 91
carbon disulfide	76	78
carbon tetrachloride	117	119
chlorobenzene	112	77 , 114
chlorobenzene-d_5 (internal standard)	117	82
chloroethane	64	66
2-chloroethyl vinyl ether	63	65 , 106
chloroform	83	85
chloromethane	50	52
chloroprene	53	88 , 90 , 51
1-chloropropane	42	41 , 39
2-chloropropane	43	41 , 39 , 63
2-chlorotoluene	91	126
4-chlorotoluene	91	126
cyclohexane	84	56 , 41 , 55
cyclohexanone	55	69 , 98 , 42
dibromochloromethane	129	127

Appendix A

Primary and Secondary Ions (Cont.)

Compound Name	Characteristic Ion(s)	
	Primary	Secondary
1,2-dibromo-3-chloropropane	75	155
1,2-dibromoethane	107	109 , 188
dibromofluoromethane (surrogate)	113	111
dibromomethane	93	95 , 174
1,2-dichlorobenzene	146	111 , 148
1,3-dichlorobenzene	146	111 , 148
1,4-dichlorobenzene	146	111 , 148
1,4-dichlorobenzene-d_4 (internal standard)	152	150
trans-1,4-dichloro-2-butene	53	88 , 75
dichlorodifluoromethane	85	87
1,1-dichloroethane	63	65 , 83
1,2-dichloroethane	62	98 , 64 , 49
1,2-dichloroethane-d_4 (surrogate)	65	102 , 67
1,1-dichloroethene	***61***	***96*** , ***95***
cis-1,2-dichloroethene	96	61 , 98
trans-1,2-dichloroethene	96	61 , 98
1,2-dichloropropane	63	112
1,3-dichloropropane	76	78
2,2-dichloropropane	77	97
1,1-dichloropropene	75	110 , 77
cis-1,3-dichloropropene	75	77 , 39
trans-1,3-dichloropropene	75	77 , 39
diethyl ether	***59***	***74*** , ***45***
1,4-difluorobenzene (internal standard)	114	88
diisopropyl ether (DIPE)	45	87
1,4-dioxane	88	58 , 43 , 57
ethanol	45	46 , 43
ethylbenzene	91	106
ethyl tert-butyl ether (ETBE)	59	87
ethyl methacrylate	69	41 , 99
hexachloro-1,3-butadiene	225	223 , 227
hexane	57	56 , 43 , 41
2-hexanone	43	58
iodomethane	142	127 141
isobutyl alcohol (iso-butanol)	43	41 , 42 , 74
isopropanol (2-propanol)	45	59

Appendix A

Primary and Secondary Ions (Cont.)

Compound Name	Characteristic Ion(s)	
	Primary	Secondary
isopropylbenzene	105	120
p-isopropyltoluene	119	91 , 134
methacrylonitrile	41	67
methyl acetate	43	74 , 59
methyl tert-butyl ether (MTBE)	73	57
methyl methacrylate	69	41 , 100 , 39
2-methyl-2-butanone (TAA)	59	55 , 73
methylcyclohexane	83	55 , 98 , 41
methylene chloride	84	86
4-methyl-2-pentanone (MIBK)	***58***	***85***
naphthalene	128	127
pentafluorobenzene (internal standard)	168	137
propanedinitrile	66	38 , 39 , 65
propionitrile	54	52 , 55 , 40
n-propylbenzene	91	120
styrene	104	78
1,1,1,2-tetrachloroethane	131	133 , 119
1,1,2,2-tetrachloroethane	83	131 , 85
tetrachloroethene	***166***	***164*** , 131
tetrahydrofuran	42	41 , 71 , 72
thiophene	84	58 , 45
toluene	***91***	***92***
toluene-d_8 (surrogate)	98	100
1,2,3-trichlorobenzene	180	182 , 145
1,2,4-trichlorobenzene	180	182 , 145
1,1,1-trichloroethane	97	99 , 61
1,1,2-trichloroethane	83	97 , 85
trichloroethene	95	97 , 130 , 132
trichlorofluoromethane	101	103
1,2,3-trichloropropane	***75***	***112*** , ***77***
1,1,2-trichloro-1,2,2-trifluoroethane	101	151 , 153
2,2,4-trimethyl pentane	57	56 , 41
1,2,4-trimethylbenzene	105	120
1,3,5-trimethylbenzene	105	120
vinyl acetate	***86***	***43***
vinyl chloride	62	64

Appendix A

Primary and Secondary Ions (Cont.)

o-xylene	*91*	*106*
p/m-xylenes	*91*	*106*

Appendix B

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, 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. Limit of Detection (LOD)

5.1.1. LOD determination 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. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

5.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

5.1.2.2. LOD 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.).

5.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.1.3. No samples shall be analyzed without a valid LOD.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.3. Initial Calibration (IC)

5.3.1. 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

5.3.2. If the %RSD criterion for an analyte is not met, employ one of the following calibration options.

5.3.2.1. 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.

5.3.2.1.1. Calibration may not be forced through the origin.

5.3.2.2. 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.

5.3.2.2.1. This option requires at least six calibration levels.

5.4. Initial Calibration Verification (ICV)

5.4.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

5.4.2. If any project-specific analyte does not meet the %D, internal standard response and/or retention time criteria, the initial calibration is deemed unacceptable for sample analysis to begin. Document the unacceptable result, re-prepare, and reanalyze the ICV within 2 hours after the failed ICV. If the ICV criteria remain unacceptable, investigate, effect corrective actions, which may include replacement of standard solutions or instrument maintenance, and recalibrate.

5.5. Continuing Calibration Verification (CCV)

5.5.1. 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

5.5.2. If any project-specific analyte does not meet the %D, internal standard response and/or retention time criteria, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result, re-prepare, and reanalyze the CCV within 2 hours after the failed CCV. If the CCV criteria remain unacceptable, effect corrective actions and recalibrate.

5.5.3. The concentration of the CCV standard shall be between the low point and the midpoint of the calibration range.

5.6. Retention Time Window

5.6.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration.

5.6.1.1. Absolute retention time window for each analyte/surrogate is determined from the elution time of the analyte/surrogate in the midpoint calibration standard.

5.6.1.2. Document the serial number of the analytical column associated with the retention time window.

5.6.1.3. Record the retention time in minutes for each analyte/surrogate to three decimal places.

5.7. Event Based Quality Control (MBs and LCSs)

5.7.1. Method Blanks (MBs)

5.7.1.1. The MB is considered to be contaminated if one of the following conditions is met.

5.7.1.1.1. 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).

5.7.1.1.2. 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).

5.7.1.1.3. The MB result otherwise affects the sample results as per the test method requirements or the project specific data quality objectives (DQOs).

5.7.1.2. 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 LOD.

5.7.1.2.1. 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.

5.7.2. Laboratory Control Samples (LCSs)

5.7.2.1. The lower and upper acceptance limits for %REC of each LCS compound in aqueous and solid matrices are listed in Appendix C.

5.7.2.2. 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.

5.7.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.7.2.3. 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.

5.8. Matrix Based Quality Control (Surrogates, Internal Standards, and MS/MSDs)

5.8.1. Surrogates

5.8.1.1. The lower and upper acceptance limits for %REC of each surrogate compound in aqueous and solid matrices are listed in Appendix C.

5.8.1.2. 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.

5.8.2. Internal Standards

5.8.2.1. If the EICP area of any internal standard in each standard, sample, and blank 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.

5.8.2.2. If the retention time of any internal standard in each standard, sample, and blank 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.

5.8.2.3. Following corrective action, reanalysis of samples analyzed while the system was malfunctioning is required.

5.8.2.4. 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.

5.8.3. Matrix Spikes (MS/MSDs)

5.8.3.1. 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%.

5.8.3.2. 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.

5.8.3.2.1. 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 / Continuing Calibration Verification (CCV)
2) Laboratory Control Sample (LCS)
3) Method Blank (MB)
4) Samples (up to 20 per batch, excluding QC check samples and MBs)
5) Matrix Spike (MS)

6) Matrix Spike Duplicate (MSD)

6.1.1. Item 6: 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 7: 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

Eurofins Calscience, 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

REQUIREMENTS FOR LOW LEVEL 1,2,3-TRICHLOROPROPANE (TCP) AND 1,4-DIOXANE DETERMINED BY EPA 8260B USING SELECTED ION MONITORING (SIM) MODE

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. ***EPA Method 8260B, Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) – Determination of Low Level 1,2,3-TCP and 1,4-Dioxane in Selected Ion Monitoring (SIM) Mode.***

2. APPLICABLE MATRICES

2.1. ***This method is applicable to soil/solid and aqueous matrices.***

3. DETECTION / QUANTITATION LIMITS

3.1. ***The reporting limits (RLs) for this method are as follows:***

	Water	Soil
1,2,3-TCP	0.005 µg/L	0.02 µg/kg
1,4-Dioxane	1.000 µg/L	5.00 µg/kg

3.2. ***The RLs will be proportionally higher for samples which require dilution or reduced sample size.***

3.3. ***Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.***

4. METHOD SUMMARY

4.1. ***This analysis is performed using purge and trap and GC/MS.***

4.2. ***1,2,3-TCP and 1,4-dioxane are identified by matching the retention time and fragment ions from the sample with those of the reference standard. Quantitation is performed by the isotopic dilution procedure. 1,2,3-trichloropropane-d_5 (1,2,3-TCP-d_5) and 1,4-dioxane-d_8 are used as the internal standards, which are added at the same concentration to the samples and standards.***

5. REAGENTS AND STANDARDS

5.1. ***The working calibration standard solution containing 50 ppm of 1,4-dioxane and 0.05 ppm of 1,2,3-TCP in methanol is used to prepare calibration standards.***

5.2. ***Inject the appropriate volume of the 0.05–50 ppm working calibration standard into 25 mL of reagent water for a water matrix analysis and into 5 mL water for a soil matrix analysis for initial calibration.***

	Initial		Final	
Analyte	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
1,4-Dioxane	500	500	50.0	5.00
1,2,3-Trichloropropane	0.5		0.05	

5.3. ***Use the following calibration levels as guidance to prepare the calibration standards for water matrix calibration using 25 mL purge.***

Analyte	Standard Compound Concentration (ug/L)						
123-TCP			0.005	0.01	0.02	0.05	0.10
1,4 - Dioxane	1.0	2.0	5.0	10.0	20.0	50.0	100.0
123-TCP-d5(IS)	0.04	0.04	0.04	0.04	0.04	0.04	0.04
1,4-Diox-d8(IS)	20	20	20	20	20	20	20
1,4-Dichlorobutane(S)	8	8	8	8	8	8	8

5.4. ***Use the following calibration levels as guidance to prepare the calibration standards for soil matrix calibration using 5.0 mL purge.***

Analyte	Standard Compound Concentration (ug/Kg)						
123-TCP		0.01	0.020	0.05	0.10	0.20	0.40
1,4 - Dioxane	5.0	10.0	20.0	50.0	100.0	200.0	400.0
123-TCP-d5(IS)	0.04	0.04	0.04	0.04	0.04	0.04	0.04
1,4-Diox-d8(IS)	20	20	20	20	20	20	20
1,4-Dichlorobutane(S)	8	8	8	8	8	8	8

5.4.1. ***The mid-range standards are also used as the continuing calibration verification solutions.***

5.5. ***The internal standards 1,2,3-trichloropropane-d_5 and 1,4-dioxane-d_8 and surrogate standard 1,4-dichlorobutane at concentrations of 10, 5000, and 2000 µg/mL concentration, respectively, is used to make working IS+SS mix in methanol for spiking all samples and QC samples including MB before analysis. The internal standard concentration in the working standard is 0.040 ppb for 123-TCP-d_5 and 20 ppb for 1,4-dioxane-d_8 and 8 ppb concentration for surrogate 1,4-dichlorobutane.***

5.5.1. ***Use the first run instrument blank with BFB from working 8260 internal/surrogate standard solution as the tuning standard solution.***

5.5.2. ***This procedure is possible due to split ratio configured for GC that allows the purge or injection of 5–50 ng of BFB as specified by the test methods.***

5.5.3. ***The initial calibration verification (ICV) solution contains the appropriate concentration of each target analyte, 8 ppb of the***

surrogate, 20 ppb of internal standard 1,4-dioxane-d_8, and 0.040 ppb of 1,2,3-TCP-d_5 in reagent water. The ICV solution must be of a source differing from that used for the initial multi-point calibration.

5.5.4. ***Use the following calibration level as guidance to prepare the ICV solution for water matrix.***

Analyte	ICV Concentration in ppb (µg/L)
1,2,3-TCP	0.02
1,4-Dioxane	20.0
123-TCP-d5 (IS)	0.04
1,4-Dioxane-d8 (IS)	20.0
1,4-Dichlorobutane (S)	8.0

5.5.5. ***Use the following calibration level as guidance to prepare the ICV solution for soil matrix.***

Analyte	ICV Concentration in ppb (µg/kg)
1,2,3-TCP	0.10
1,4-Dioxane	100.0
123-TCP-d5 (IS)	0.04
1,4-Dioxane-d8 (IS)	20.0
1,4-Dichlorobutane (S)	8.0

5.5.6. ***The continuing calibration verification (CCV) solution contains the appropriate concentration of each target analyte, 8 ppb of the surrogate, 20 ppb of internal standard 1,4-dioxane-d_8 and 0.040 ppb of 1,2,3-TCP-d_5 in reagent water. The CCV solution must be of the same source as that used for the initial multi-point calibration.***

5.5.7. ***Add the appropriate volumes of the working standards and the appropriate volume of the surrogate and internal standard working standard to 25 mL of reagent water, and purge and trap for continuing calibration verification.***

5.5.8. ***Use the following calibration level as guidance to prepare the CCV solutions for water matrix.***

Analyte	CCV Concentration in ppb (µg/L)
1,2,3-TCP	0.02
1,4-Dioxane	20.0
123-TCP-d5 (IS)	0.04
1,4-Dioxane-d8 (IS)	20.0
1,4-Dichlorobutane (S)	8.0

5.5.9. ***Use the following calibration level as guidance to prepare the CCV solution for soil matrix.***

Analyte	CCV Concentration in ppb (µg/kg)
1,2,3-TCP	0.10
1,4-Dioxane	100.0
123-TCP-d5 (IS)	0.04
1,4-Dioxane-d8 (IS)	20.0
1,4-Dichlorobutane (S)	8.0

5.5.9.1. ***One CCV solution is used daily for every tune batch of 12 hrs.***

5.5.10. ***For Water: The surrogate and internal standard working standard solution containing 1 ppm of 123-TCP-d_5 (IS), 500 ppm of 1,4-dioxane-d_8 (IS) and 200 ppm 1,4-dichlorobutane (S) are prepared in methanol for water matrix.***

5.5.11. ***For Soil: The surrogate and internal standard working standard solution containing 0.2 ppm of 123-TCP-d_5 (IS), 100 ppm of 1,4-dioxane-d_8 (IS) and 40 ppm 1,4-dichlorobutane (S) are prepared in methanol for soil matrix.***

5.6. ***If autosampler is capable of injecting standard solution automatically, configure the autosampler to inject 1.0 µL of the either water or soil surrogate and internal standard working standard into each aliquot for water or soil matrix sample including each calibration standard, calibration verification standard, QC check sample, and method blank prior to purge-and-trap extraction.***

6. QUALITY CONTROL

6.1. ***Hardware Tuning***

6.1.1. ***Prior to running the calibration standards, the tuning standard solution must be analyzed and meet the BFB tune acceptance criteria as described earlier for 8260B method, and criteria must be demonstrated every 12 hours.***

6.2. ***Initial Calibration (IC)***

6.2.1. ***The initial multi-point calibration must be established prior to the processing of samples.***

6.2.1.1. ***The calibration curve is established with five, six, or seven calibration standards.***

6.2.2. ***The IC is deemed valid if the %RSD for each analyte is ≤ 15%.***

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

6.3. ***Initial Calibration Verification (ICV)***

6.3.1. ***The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.***

6.4. ***Continuing Calibration Verification (CCV)***

6.4.1. ***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.***

6.4.2. ***The initial calibration is deemed valid if the following condition is met.***

6.4.2.1. ***The %D for each analyte is ≤ 20%.***

6.4.2.1.1. ***If the calibration option is average relative response, the %D is the percent difference.***

6.5. ***The internal standard response and retention time for the ICV and CCV must be evaluated during or immediately after data acquisition.***

6.5.1. ***If the EICP area of any internal standard in an ICV or 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.***

6.5.2. ***If the retention time of any internal standard in an ICV or 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.***

7. PROCEDURE

7.1. ***Instrument Setup***

7.1.1. ***Refer to the current revision of SOP-M212 or SOP-M213 for purge-and-trap system setup.***

7.1.2. ***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	Splitless
Initial temp	200 ° C
Initial flow	0.8 mL/min
Purge flow	8.0 mL / min
Inlet pressure	13.53 psi
Split ratio	10:01
Split flow	8.0 mL/min
Total flow rate	11.6 mL/min
Initial temperature	40°C, hold 4.00 min
Temperature program	40°C to130°C at 9.00°C/min 130°C to 230°C at 40.00°C/min
Run time	16.5 min
Transfer line temperature	260°C
SIM parameters	
Group ID	1
Resolution	Low
Group start time	2
Ions/Dwell	46/70
Ions/Dwell	58/70
Ions/Dwell	64/70
Ions/Dwell	88/70
Ions/Dwell	96/70
Group 2	2
Resolution	Low
Group start time	11
Ions/Dwell	55/30
Ions/Dwell	62/30

7.1.3. ***Use the following P & T operating conditions as guidance for running this method.***

Valve Oven Temp.:	150°C	Sample Preheat Time:	1.00 min.
Dry Purge Temp.:	20.0°C	Bake Time:	8.00 min.
Transfer Line Temp.:	150°C	Sample Temp.:	40.0°C
Dry Purge Flow:	150 mL/min.	Bake Temp.:	280°C
Sample Mount Temp.:	90.0 °C	Purge Time:	11.0 min.
GC Start:	Start of Desorb	Bake Flow:	40.0 mL/min.
Purge Ready Temp.:	40.0 °C	Purge Temp.:	0.0°C
Desorb Preheat Temp.:	245° C	Condenser Bake Temp.:	230°C
Standby Flow:	0.0 mL/min.	Purge Flow:	40 mL/min.
Desorb Drain:	On	Focus Temp.:	-150°C
Pre-Purge Time:	0.50 min.	Condenser Ready Temp.:	40.0°C
Desorb Time:	4.00 min.	Inject Time:	1.00 min.
Pre-Purge Flow:	40 mL/min.	Condenser Purge Temp.:	20.0°C
Desorb Temp.:	250°C	Inject Temp.:	180°C
Sample Heater:	Off	Dry Purge Time:	1.00 min.
Desorb Flow:	30 mL/min.	Standby Temp.:	100°C

7.1.3.1. ***123-TCP and 1,4-dioxane are identified by matching the retention time and fragment ions and ion abundances from the sample with those of the reference standard. Identification requires expert judgment, especially when sample components are not completely resolved, or if 123-TCP and/or 1,4-dioxane is present at very low concentration (near the detection limit). Background ions or interfering ions from coeluting compounds may make identification (and quantitation) difficult to achieve.***

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

Document No. : SOP-M601
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Supersedes : 6.0

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PROPRIETARY INFORMATION STATEMENT

Revision 6.1 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 03/18/15
MANAGEMENT **DATE**

_____ 03-18-15
QA DEPARTMENT **DATE**

Reviewer Signature	Review Date	Comments	QA Signature

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, mobility-procedure extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes.

3. DETECTION / QUANTITATION LIMITS

3.1. The RLs will be proportionally higher for samples which require dilution or reduced sample size.

3.2. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

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

3.2.2. 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. All matrices, excluding filtered groundwater samples but including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require acid digestion prior to analysis.

4.1.1. Groundwater samples that have been prefiltered and acidified will not need acid digestion.

4.1.2. 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:

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

6.3.1. 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, unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours.

6.3.2. 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. Limit of Detection (LOD): The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.

6.13. Limit of Quantitation (LOQ): The smallest concentration that produces a quantitative result with known and recorded precision and bias.

6.14. 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.

6.15. 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.

6.16. 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.

6.17. 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.

6.18. 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.

6.19. 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.

6.20. 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.

6.21. 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.

6.22. 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.

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

6.24. 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, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. 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.

6.26. 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.

6.27. Terms Specific to ICP-AES Analysis

6.27.1. Dissolved Metals: The concentration of metals determined in an aqueous sample after the sample is filtered through a 0.45-µm filter.

6.27.2. Instrument Detection Limit (IDL): A tool for evaluating the instrument noise level and response changes over time for analytes of interest. IDLs can be estimated by calculating the average of the standard deviations of three analytical runs performed on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples).

6.27.3. Interference Check Sample (ICS): A solution containing both interfering and analyte elements of known concentration that can be used to verify background and inter-element correction factors.

6.27.4. Linear Dynamic Range: The concentration range above the highest calibration point over which the functional relationship between analyte signal and analyte concentration remains linear based on a one-point calibration. A sample result that falls within the linear dynamic range is considered valid and may be reported, thus avoiding the need to dilute and re-analyze the sample.

6.27.5. Method of Standard Addition (MSA): An alternative calibration procedure employed when the signal response of the analyte of interest is different in a particular matrix than when it is in reagent water. The procedure is generally reserved for analyzing complex matrices. The standard addition technique involves the addition of known amounts of the target analyte to each of a series of replicate sample aliquots. The final concentrations of the sample replicates should span the calibration range of the method. The analytical response versus the standard addition concentration for each of

the replicates is plotted. After performing a linear regression, the curve is extrapolated to the x-axis. The analyte concentration in the original unspiked sample is equal to the inverse of the x-intercept.

6.27.6. Optimum Concentration Range: A concentration range, 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.

6.27.7. 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.

6.27.8. Sensitivity: The average of the standard deviations of three runs of a reagent blank solution on three non-consecutive days with seven consecutive measurements per day.

6.27.9. Suspended Metals: The concentration of metals determined in the portion of an aqueous sample that is retained by a 0.45-µm filter.

6.27.10. Total Recoverable Metals (Total Acid Soluble Metals): The concentration of metals determined in an unfiltered sample following digestion using hot mineral acid. "Total recoverable metals" is referred to herein as "total metals."

6.28. ***Refer to the current revision of the Eurofins Calscience Quality Systems Manual for additional terms and definitions.***

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 not 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 12.13.) 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 buildup 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 re-analyzed 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. Clean chemistry methods and procedures are necessary in reducing the magnitude and variability of the calibration blank.

8. ►SAFETY

8.1. Concentrated nitric and hydrochloric acids are moderately toxic and extremely irritating to skin and mucus membranes. 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 and standard 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. 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 ***Eurofins*** 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) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** for all chemicals to be used prior to handling.

9. EQUIPMENT AND SUPPLIES

9.1. Inductively Coupled Argon Plasma Emission Spectrometer, PerkinElmer Optical Emission Spectrometer Optima 5300 DV, PerkinElmer Optical Emission Spectrometer Optima 7300 DV, 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 93plus Autosampler, PerkinElmer ESI SC-4 Autosampler, or equivalent.

9.2. Instrument Software

9.2.1. Require a PC based data system or equivalent.

9.2.2. PerkinElmer WinLab32 for ICP Version 3.4.0.0253, PerkinElmer WinLab 32 for ICP Version 4.0.0.0305, or equivalent.

9.3. Instrument Maintenance and Troubleshooting

9.3.1. Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.

9.3.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.4. ICP Torch and Nebulizer Gas: Argon, Ar, 99.998%, cryogenic liquid, Praxair Argon Cryogenic Liquid or equivalent.

9.5. Purge Gas: Nitrogen, N_2, 99.998%, cryogenic liquid, Praxair Nitrogen Cryogenic Liquid or equivalent.

9.6. Volumetric flasks, 100 mL, 500 mL, 1000 mL, or other capacity, glass, Class A.

9.7. Bottles, various sizes, PTFE fluoropolymers, polyethylene, or polypropylene, with screw caps.

9.7.1. Acid clean previously unused bottles with 1% HNO_3 solution prior to use.

9.8. Autosampler vessels, 16-mm OD (15 mL capacity), translucent polypropylene, disposal.

9.9. Autosampler vessels, 30-mm OD (50 mL capacity), with screw caps, translucent polypropylene, disposal.

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

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.

10.1.2. Chips, Teflon.

10.1.3. Beads, glass.

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

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

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

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

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

10.1.7.1. Prepare the 1:1 HNO_3 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.

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

10.1.8.1. 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.

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

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

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. 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. Dilute the appropriate volumes of the stock standards, concentrated HCl, and concentrated HNO_3 to the specified volumes with reagent water for initial calibration.

10.2.2.1.1. If the addition of silver to the recommended acid combination initially results in a precipitate, then add the appropriate volume of reagent water and warm the flask until the solution clears. Cool and

dilute to the appropriate final volume with reagent water. Higher concentrations of silver require additional HCl. Determine the stability the silver in the solution if necessary.

10.2.2.2. Use the analyte and acid concentrations outlined in Appendix C as guidance to prepare the calibration standards.

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 sample digestates prepared via EPA Method 3010.

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 3040.

10.2.4. Initial Calibration Verification (ICV) Solutions

10.2.4.1. Dilute the appropriate volumes of the stock standards, concentrated HCl, and concentrated HNO_3 to the specified volumes with reagent water for initial calibration.

10.2.4.1.1. Each target analyte in the ICV solution must be at a concentration within the established linear dynamic range.

10.2.4.2. Use the analyte and acid concentrations outlined in Appendix C as guidance to prepare the ICV solutions.

10.2.4.3. The ICV solution must be of a source differing from that used for the initial one-point calibration. If it is of the same source, then it must be of different lot.

10.2.5. Continuing Calibration Verification (CCV) Solutions

10.2.5.1. Dilute the appropriate volumes of the initial calibration standards with equal volume of calibration blank.

10.2.5.1.1. Each target analyte in the CCV solution is at a concentration near the midpoint of the calibration curve.

10.2.5.2. Use the analyte and acid concentrations outlined in Appendix C as guidance to prepare the CCV solutions.

10.2.5.3. Prepare the CCV solution fresh daily.

10.2.5.4. The CCV solution is of a source same as that used for the initial one-point calibration.

10.2.6. Internal Standard Solution

10.2.6.1. Prepare the internal standard solution by diluting the appropriate volumes of the stock standards, concentrated HCl, and concentrated HNO_3 to 2000 mL with reagent water.

10.2.6.2. Use the analyte and acid concentrations outlined in Appendix C as guidance to prepare the internal standard solution.

10.2.6.3. The internal standard solution 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. Dilute the appropriate volumes of the stock standards, concentrated HCl, and concentrated HNO_3 to the desired volumes with reagent water for potential interference check.

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. Dilute the appropriate volumes of the stock standards, concentrated HCl, and concentrated HNO_3 to the specified volumes with reagent water for daily spectral interference check.

10.2.8.2. Use the analyte and acid concentrations outlined in Appendix C as guidance to prepare the ICS-AB and ICS-A solutions.

10.2.8.3. 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 working standard solutions by diluting the appropriate volumes of the second source stock standards, concentrated HCl, and concentrated HNO_3 to the specified volumes with reagent water.

10.2.9.2. Use the analyte and acid concentrations outlined in Appendix C as guidance to prepare the spike working standard solutions.

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

10.2.9.4. The spike standard must be of a source differing from that used for the initial one-point calibration. If it is of the same source, then it must be of different lot.

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

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

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

10.2.9.8. Add 250 µL of the spike standard to each 5 mL aliquot of mobility-procedure extract designated as LCS/LCSD and MS/MSD prior to dilution and acidification.

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 12.6.).

10.2.11. All working standards must be replaced after the stock standard expiration dates (unless specified otherwise) or sooner if routine QC or comparison with check standards indicates a problem.

10.2.11.1. Add the appropriate types and volumes of acids such that the mixed standard solutions are matrix matched with the sample digestates.

10.2.11.1.1. If internal standards are utilized, then the types and volumes of acids added to a mixed standard solution do not need to be matrix matched with the sample digestates.

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

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

10.2.11.4. Demonstrate the stability of a low-level working standard (i.e., concentration < 1 ppm) prior to use.

10.2.12. 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 250 mL pre-cleaned high density polyethylene (HDPE) containers with Teflon-lined closures.

11.1.1. Aqueous samples for dissolved metals determination shall be field filtered within 15 minutes of sample collection and preserved with 1:1 HNO_3 solution to pH < 2.

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

11.2. Solid samples should be collected in 4 oz or 8 oz pre-cleaned clear glass wide-mouth jars with Teflon-lined closures, or 6 in decontaminated brass or stainless steel sleeves with Teflon-lined closures.

11.3. Mobility-procedure extracts should be collected in 3 oz pre-cleaned polypropylene digestion tubes with polypropylene lids, or 250 mL pre-cleaned HDPE containers with Teflon-lined closures.

11.3.1. Mobility-procedure extracts shall be preserved with 1:1 HNO_3 solution to pH < 2.

11.3.2. If precipitate is observed upon the addition of 1:1 HNO_3 solution to a small aliquot of the mobility-procedure extract, do not acid preserve the mobility-procedure extract. Digest the mobility-procedure extract within 24 hours.

11.4. Aqueous and Solid samples shall be maintained in a chilled state (0–6°C), not frozen, post sample collection until received at the laboratory.

11.5. Upon receipt, the aqueous and solid samples are stored in a 0–6°C cooler.

11.5.1. Unfiltered aqueous samples for dissolved metals determination must be filtered as soon as possible, immediately preserved with 1:1 HNO_3 solution to pH < 2, and digested and/or analyzed within 6 months of sample collection.

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

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

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

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

11.5.6. Solid samples must be digested and analyzed within 6 months of sample collection.

11.5.7. Mobility-procedure extracts with acid preservation (pH < 2) must be digested and analyzed within 180 days post mobility extraction.

11.5.7.1. Mobility-procedure extracts shall be stored at ambient temperature prior to digestion and analysis.

11.5.8. Mobility-procedure extracts without acid preservation (pH ≥ 2) must be preserved with 1:1 HNO_3 solution to pH < 2 for at least 24 hours prior to digestion, and digested and analyzed within 180 days post mobility extraction.

11.5.8.1. Mobility-procedure extracts shall be stored at ambient temperature prior to digestion and analysis.

11.6. Refer to the specific SOPs of the preparatory methods and Appendix D for additional information on sample collection, preservation, and holding time.

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 every six months, when the daily spectral interference check is deemed unacceptable, or when an instrumentation change occurs.

12.2. Instrument Detection Limit (IDL)

12.2.1. The instrument detection limit for each analyte shall be performed at initial instrument setup.

12.2.1.1. The IDL in mg/L is determined by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a method blank with seven consecutive measurements per day.

12.2.2. The data and calculations should be kept on file.

12.3. Initial Calibration (IC)

12.3.1. The initial one-point calibration must be established daily prior to the processing of sample digestates.

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

12.3.1.2. The concentration level of each analyte in the high-level calibration standard shall not exceed its anticipated linear dynamic range.

12.3.2. The IC is deemed valid if the replicate %RSD for each analyte is ≤ 5%.

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

12.4. Initial Calibration Verification (ICV)

12.4.1. Immediately following the establishment of a valid initial calibration, an ICV standard must be analyzed prior to sample analysis.

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

12.4.3. 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 re-analyze the ICV within 2 hours after the failed ICV. If the ICV remains unacceptable, investigate, effect corrective action, which may include re-preparation of standard solutions or instrument maintenance, and recalibrate.

12.5. Initial Calibration Blank (ICB)

12.5.1. Immediately following the analysis of an ICV standard, an ICB must be analyzed prior to sample analysis.

12.5.2. 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).

12.5.3. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Re-prepare and re-analyze the ICB.

12.6. Linear Dynamic Range

12.6.1. 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.

12.6.1.1. 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.

12.6.1.1.1. The concentration level of each analyte in the lowest concentration standard shall be at or below the RL.

12.6.1.2. 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.

12.6.2. 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.

12.6.2.1. 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.

12.6.3. 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%.

12.6.4. 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.

12.6.4.1. The effective range must be checked, and the correlation coefficient of the second order curve fit should be ≥ 0.995.

12.6.4.2. 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.

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

12.7.1. Following the establishment of a valid initial calibration, an ICS-AB and ICS-A solutions must be analyzed daily prior to sample analysis. Per client request or project specific DQOs, an ICS-AB solution must be analyzed at the end of sequence.

12.7.1.1. 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.

12.7.2. The ICS-AB is deemed acceptable if the %D for each analyte is ≤ 20%.

12.7.3. The ICS-A is deemed acceptable if the absolute value of the concentration for each non-spiked analyte is < RL (unless it is a verified trace impurity from one of the spiked analytes).

12.7.4. If these criteria are not met, no sample analysis shall begin. Determine the source of problem, effect corrective action, and re-analyze the ICS-AB and/or ICS-A.

12.7.4.1. If an ICS-AB and/or ICS-A at the start of sequence are unacceptable, effect corrective action prior to analyzing any samples.

12.7.4.2. Per client request or project specific DQOs, if an ICS-AB at the end of sequence is unacceptable, effect corrective action and re-analyze all samples since the last acceptable ICS-AB.

12.7.5. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months, when the daily spectral interference check is deemed unacceptable, or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions, occurs.

12.8. Continuing Calibration Verification (CCV)

12.8.1. 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 24-hour shift, and at the end of sequence.

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

12.8.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and re-analyze the CCV within 2 hours after the failed CCV. If the CCV remains unacceptable, effect corrective action and recalibrate.

12.8.3.1. If a failed CCV is the first of the day, effect corrective action and recalibrate prior to analyzing any samples.

12.8.3.2. If a failed CCV is not the first of the day, effect corrective action, recalibrate, and re-analyze all samples since the last acceptable CCV.

12.9. Continuing Calibration Blank (CCB)

12.9.1. Immediately following the analysis of a CCV standard, a CCB must be analyzed prior to sample analysis.

12.9.2. 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).

12.9.3. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Re-prepare and re-analyze the CCB.

12.9.3.1. If a failed CCB is the first of the day, effect corrective action prior to analyzing any samples.

12.9.3.2. If a failed CCB is not the first of the day, effect corrective action and re-analyze all samples since the last acceptable CCB.

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

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

12.10.1.1. LCSD shall be prepared and processed if there is insufficient sample amount to perform matrix based QC (i.e., MS/MSD), or if it is mandatory per client request or project specific DQOs.

12.10.2. The acceptance criteria for MBs are as follows:

12.10.2.1. Ideally, the concentrations of target analytes in an MB should be less than the respective limits specified in the project specific DQO. In the absence of project specific DQO, the concentrations of target analytes in an MB should be less than or equal to the respective RLs. If regulatory limits are available, the concentrations of target analytes in an MB should be less than 10% of the respective regulatory limits. If the concentration of any target analyte exceeds its specified limit, the source of contamination must be investigated and, if possible, eliminated.

12.10.2.2. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.10.2.3. 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.

12.10.3. The acceptance criteria for LCS/LCSD elements are as follows:

12.10.3.1. The lower and upper acceptance limits for %REC of each LCS/LCSD element are 80% and 120%, respectively. The RPD is ≤ 20% (between LCS and LCSD).

12.10.3.1.1. If historical data is available, the lower and upper acceptance limits for %REC and RPD of each LCS/LCSD element are based upon the historical average recovery ± 3S that is updated at least annually.

12.10.3.2. All LCS (including LCSD if required) 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.

12.10.3.3. 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.

12.10.3.4. 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.

12.10.3.5. 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

12.10.3.6. 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.

12.10.3.7. 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.

12.11. Matrix Based Quality Control (MS/MSDs)

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

12.11.2. The acceptance criteria for MS/MSD elements are as follows:

12.11.2.1. The lower and upper acceptance limits for %REC of each MS/MSD element are 75% and 125%, respectively. The RPD is ≤ 20% (between MS and MSD).

12.11.2.1.1. 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.

12.11.2.2. 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.

12.11.2.3. 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.

12.11.3. 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.

12.12. If the %REC or RPD of the LCS/LCSD and MS/MSD are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

12.13. Dilution Test

12.13.1. If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrument detection limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination.

12.13.2. If this criterion is not met, a physical or chemical interference effect shall be suspect. Perform post digestion spike addition.

12.14. Post Digestion Spike (PDS) Addition

12.14.1. A PDS sample is prepared by adding the spike standard to a portion of a digested sample, or its dilution. The spike addition should produce a concentration of 10−100 times the RL.

12.14.2. The lower and upper acceptance limits for %REC of each PDS element are 75% and 125%, respectively.

12.14.3. If the %REC of the PDS element is not within the established acceptance limits, a matrix effect shall be suspect. Perform MSA (see Section 14.15.) on all samples in the same preparation batch per client request or project specific DQOs.

12.15. 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 current revision of SOP-T043.

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 12.3.

13.3.2. After obtaining an acceptable one-point calibration curve and prior to processing field or QC sample 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 12.4. and Section 12.5.

13.3.3. The initial one-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. 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.

Description	Operating Condition
RF Power	1100~1450 watts
Viewing Height	
Axial Plasma	14~18 mm
Radial Plasma	-1~5 mm
Argon Coolant Flow	15~19 L/min
Argon Nebulizer Flow	0.5~1.5 L/min
Sampler	
Pump rate	0.6~1.0 mL/min
Wash time	15 sec
Preflush Time	1 min
Read Time	2~10 sec
Read Delay Time	15 sec
Number of readings/replicate	2

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. Follow the instrument manufacturer's instructions 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. Follow the instrument manufacturer's instructions for optimization in the axial and radial modes.

14.1.4. Align the torch viewing position weekly.

14.1.4.1. Aspirate a standard solution containing 10 mg/L of Mn for radial viewing and 1 mg/L of Mn for axial viewing.

14.1.4.2. Allow the instrument software to set the torch viewing position with the highest signal intensity.

14.1.4.3. For radial viewing, the intensity of Mn at 257.610 nm should be greater than 10000 counts. For axial viewing, the intensity of Mn at 257.610 nm should be greater than 700000 counts.

14.1.4.4. If these criteria are not met, effect corrective action and re-align the torch viewing position.

14.1.5. Check the sensitivity daily.

14.1.5.1. Aspirate a standard solution containing 7.5 mg/L of As and 7.5 mg/L of Pb.

14.1.5.2. For axial viewing, the standard emission count of As at 193.696 nm should be greater than 10000, and the standard emission count of Pb at 220.353 nm should be greater than 40000.

14.1.5.3. If these criteria are not met, perform instrument maintenance, re-align the torch viewing position, and check the sensitivity prior to initial calibration.

14.1.6. The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits (IDLs).

14.1.7. 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.

14.1.8. 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.

14.1.8.1. A general description of spectral interferences and the analytical requirements for background correction are discussed in Section 7.

14.1.8.2. 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.

14.1.8.3. 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.

14.1.9. 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.

14.1.10. 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.

14.1.11. Program the system to average a minimum of two integrations (i.e., replicate readings) on each blank, standard, and sample. Report the average.

14.1.11.1. 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.

14.1.11.2. 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 12.6.).

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 solutions must be analyzed daily prior to sample analysis. Per client request or project specific DQOs, an ICS-AB solution must be analyzed at the end of sequence. The acceptance criteria are listed in Section 12.7.

14.4.1. If an ICS-AB and/or ICS-A at the start of sequence are unacceptable, effect corrective action prior to analyzing any samples.

14.4.2. Per client request or project specific DQOs, if an ICS-AB at the end of sequence is unacceptable, effect corrective action and re-analyze 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 within a 24-hour shift, 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 12.8. and Section 12.9.

14.5.1. If a failed CCV/CCB is the first of the day, effect corrective action and recalibrate prior to analyzing any samples.

14.5.2. If a failed CCV/CCB is not the first of the day, effect corrective action, recalibrate, and re-analyze 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 digestion tubes. After transferring aliquots of the digestates to autosampler vessels, the autosampler vessels 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. Acid digestion is not necessary if groundwater samples for dissolved metals determination are prefiltered and acidified prior to analysis.

14.6.2.1. All associated QC samples (i.e., MB, LCS/LCSD, MS/MSD, and PDS) in the same preparation batch must undergo the same filtration and acidification procedures.

14.6.2.2. Samples which are not digested must either use an internal standard or be matrix-matched with the standards.

14.7. Blank, standard, and sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standard
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 per batch, including QC check samples and MBs)
13) Matrix Spike (MS)
14) Matrix Spike Duplicate (MSD)
15) Dilution Test Sample (per client request or project specific DQOs)
16) Post Digestion Spike (PDS) (per client request or project specific DQOs)
17) Ending ICS-AB (per client request or project specific DQOs)
18) Ending CCV
19) Ending CCB

14.7.1. Item 1: The CB is an aliquot of acidified reagent water used to establish the zero point of the initial calibration curve.

14.7.2. Item 2: The initial calibration standard is a high-level calibration standard 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 immediately following initial calibration.

14.7.4. Item 4: The ICB is an aliquot of acidified reagent water used to monitor contamination. An acceptable ICB is required immediately following ICV.

14.7.5. Items 5, 6, and 17: The ICS-AB and ICS-A are used to verify the accuracy of the interelement correction factors. An acceptable ICS-AB and ICS-A are required daily prior to sample analysis. Per client request or project specific DQOs, an acceptable ICS-AB is required at the end of sequence.

14.7.6. Items 7 and 18: A CCV is a standard 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 within a 24-hour shift, and at the end of sequence.

14.7.7. Items 8 and 19: A CCB is an aliquot of acidified reagent water used to monitor contamination. An acceptable CCB is required immediately following CCV.

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). For mobility-procedure extracts, the MB consists of the mobility-procedure extract designated as MB.

14.7.8.2. One MB is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) 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 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 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). For mobility-procedure extracts, the LCS consists of the specified elements spiked into the mobility-procedure extract designated as LCS.

14.7.9.2. One LCS is required every day preparatory methods (i.e., leachings, filtrations, digestions, etc.) 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.

14.7.10.1. LCSD is processed and analyzed if there is insufficient sample amount to perform matrix based QC (i.e., MS/MSD), or if it is mandatory per client request or project specific data quality objectives (DQOs).

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.

14.7.11.1. All dilutions should keep the responses in the upper half of the linear range of the curve.

14.7.11.2. Digestates with concentrations exceeding the calibration range but within the linear dynamic range may be reported without dilution per client request or project specific DQOs.

14.7.12. Item 13: 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.

14.7.12.1. 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 processed 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 dilution test sample is prepared from the five-fold dilution of a high concentration sample post digestion. The high concentration sample is diluted to one-fifth of the original concentration post digestion to confirm that no interference is observed in the original sample.

14.7.14.1. The purpose of the dilution test sample is to assess matrix effects.

14.7.14.2. To comply with client request or project specific DQOs, one dilution test sample is required for every batch of 20 samples per matrix or portion thereof processed concurrently.

14.7.15. Item 16: The PDS is the same sample matrix from which the MS/MSD samples were prepared or from another sample in the same preparation batch, 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.

14.7.15.1. The purpose of the PDS is to confirm matrix effects. The measurement is expressed as percent recovery (%REC). The formula for calculating %REC is listed in Section 15.4.

14.7.15.2. The number of PDS required is based upon client request or project specific DQOs.

14.7.16. Rinse blanks or solvent blanks consisting of acidified reagent water may be added elsewhere in the sequence, as necessary (i.e., after suspected high concentration sample digestates), to rinse the analytical system or check for potential carryover or cross-contamination.

14.7.16.1. The rinse time is set to one minute. Rinse time may be reduced through a suitable demonstration.

14.8. Ensure that a sufficient amount of internal standard solution is present in the standard vessel at the beginning of the sequence.

14.9. 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.

14.10. 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.

14.10.1. Record the reagent and standard identification numbers on the sequence table printout.

14.11. Initiate the sequence.

14.12. Dilution test and post digestion spike addition (see Section 12.13. and Section 12.14.) are recommended prior to reporting concentration data for the elements.

14.12.1. 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.

14.13. If spectral overlap is suspected, then the use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

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.

14.14.1.1. Proper quantitation requires the appropriate selection of a wavelength from which the intensity 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 re-analyze.

14.15. Method of Standard Additions (MSA)

14.15.1. The standard addition technique involves adding known amounts of a standard solution to one or more aliquots of a processed 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.

14.15.1.1. The MSA may be appropriate for analyses of digestates, on analyses submitted as part of a delisting petition, whenever a new sample matrix is being analyzed, and on every batch that fails the post digestion spike addition per client request or project specific DQOs.

14.15.2. The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample, 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 acidified reagent water. The analytical signals of A and B, S_A and S_B, are measured and corrected for non-analyte signals. The unknown sample concentration C_x is calculated using the formula listed in Section 15.12. 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.

14.15.3. Improved results can be obtained by employing a series of standard additions. A series of standard solutions containing different known quantities of the analyte are added to equal volumes of the sample, 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.

14.15.4. For the results of the MSA technique to be valid, the following limitations must be taken into consideration:

14.15.4.1. 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.

14.15.4.2. 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.

14.15.4.3. The determination must be free of spectral interference and corrected for nonspecific background interference.

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:

$$\%D = \frac{\left|C_{expected} - C_{measured}\right|}{C_{expected}} \times 100$$

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 digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.10. The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:

$$C_S = \frac{C_x \times V_x \times D}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

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.
C_{ss} = solids content in %.
D = dilution factor, if the digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.11. The target analyte concentration for a mobility-procedure extract is calculated as follows:

$$C_{MP} = \frac{C_x \times V_x \times D}{V_{MP}}$$

where: C_{MP} = concentration of target analyte in mobility-procedure extract in mg/L.
C_x = concentration of target analyte in digestate in mg/L.
V_x = volume of digestate in mL.
V_{MP} = volume of mobility-procedure extract digested in mL. Unless specified otherwise, V_{MP} = 5.
D = dilution factor, if the digestate was diluted prior to analysis. If no dilution was made, D = 1.

15.12. 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 sample aliquot A.
S_B = analytical signal (corrected for the blank) of sample aliquot 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.

15.13. Refer to the preparatory method(s) for additional calculations.

15.14. All concentrations shall be reported in mg/L (ppm) for aqueous samples, and mg/kg (ppm) for soil and solid waste samples.

15.14.1. Per client request or project specific DQOs, report all concentrations in mg/kg (ppm) on a dry-weight basis for soil and solid waste samples.

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

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. Ideally, the concentrations of target analytes in an MB should be less than the respective limits specified in the project specific DQO. In the absence of project specific DQO, the concentrations of target analytes in an MB should be less than or equal to the respective RLs. If regulatory limits are available, the concentrations of target analytes in an MB should be less than 10% of the respective regulatory limits. If the concentration of any target analyte exceeds its specified limit, the source of contamination must be investigated and, if possible, eliminated.

18.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. 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.

18.2. 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% (between LCS and LCSD). All LCS (including

LCSD if required) elements must be within acceptance limits (see Section 12.10.3. for additional information).

18.2.1. Refer to Section 12.10.3.1.1. for acceptance criteria if historical data is available.

18.2.2. If the LCS and/or LCSD %REC is outside of the acceptance limits high, the RPD (when applicable) is within acceptance limits, and all target analytes in the associated samples are not detected, the sample data can be reported without qualification.

18.2.2.1. If the LCS/LCSD is used in place of the MS/MSD due to insufficient sample amount, or if LCS/LCSD is required per client or project specific DQO, both the LCS and LCSD data must be reported.

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% (between MS and MSD).

18.3.1. Refer to Section 12.11.2.1.1. 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. If the %REC of the PDS element and the %REC of the MS/MSD elements are not within the established acceptance limits, matrix effects are confirmed. Perform MSA (see Section 14.15.) on all samples in the same preparation batch per client request or project specific DQOs.

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.

18.7.1. Per client request or project specific DQOs, report all concentrations in mg/kg (ppm) on a dry-weight basis 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 ***Director***, Project Manager, ***Quality Control Director***, 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/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 acceptance 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 re-analyzed 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 ***Eurofins*** 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. *Flame Atomic Absorption Spectrophotometry,* Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1A, Method 7000B, USEPA, Revision 2, February 2007.

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

23. APPENDICES, 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 Department of Defense Projects.

23.7. Appendix G: Control Limits for Department of Defense Projects.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 6010B Revision 2 are noted.

Calscience SOP M601 Section	Reference Document EPA Method 6010B Section	Summary of Modification
12.4. and 12.8.	7.4	The control limits of replicate %RSD are modified from < 5% to ≤ 5%.
12.5. and 12.9.	8.6.1.3	The acceptance criteria of ICB and CCB are modified.
12.14.	8.5.2	The spike concentration of PDS is modified from 10–100 times the IDL to 10–100 times the RL.
14.2.	7.2.5	Procedure on the determination of detection limit was modified to conform to the requirements specified in 40 CFR Part 136 Appendix B and 2009 TNI Standard.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
5.3	Added LOD/LOQ definitions, Software and Maintenance sections.	L. Lem	03/11/13
6.0	All (Except Sections 1, 16, 17, 19, 20, and 21): Update method information, quality control requirements, and procedures. Appendix C: Update the tables for standard solution preparation. Appendix F: Update DoD quality control requirements and criteria. Appendix G: Relocate DoD QC sample control limit tables from Appendix F.	K. Chang	12/12/13
6.1	Entire document: Update company name. Section 6: Update definitions. Sections 8 and 17: Add SDS. Sections 19 and 20: Update responsibilities.	L. Hunt	03/23/15

Appendix A

RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Eurofins Calscience, 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)

Eurofins Calscience, 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

Eurofins Calscience, Inc.

Appendix C

Initial Calibration Standard Solution Preparation

Initial Calibration Standard						
Element		Initial Conc (ppm)	Initial Vol (mL)	Final Conc (ppm)	Final Vol (mL)	Solvent Acid Conc [a]
Aluminum	Al	200 + 2000	60 + 7.5	27	1000	5% (v/v) HCl + 6% (v/v) HNO_3
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	
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	0.2	2	100	5% (v/v) HCl + 5% (v/v) HNO_3
Lithium [b]	Li	1000	0.2	2	100	
Sulfur [b]	S	1000	0.2	2	100	

[a] HCl and HNO_3 are concentrated trace metals grade acids.

[b] Bi, *Li*, and S standards are prepared separately.

Appendix C

Initial Calibration Verification (ICV) Standard Solution Preparation

Initial Calibration Verification (ICV) Standard						
Element		Initial Conc (ppm)	Initial Vol (mL)	Final Conc (ppm)	Final Vol (mL)	Solvent Acid Conc [a]
Aluminum	Al	200	4	4	200	5% (v/v) HCl + 6% (v/v) HNO_3
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	
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	0.1	1	100	5% (v/v) HCl + 5% (v/v) HNO_3
Lithium [b]	Li	1000	0.1	1	100	
Sulfur [b]	S	1000	0.1	1	100	

[a] HCl and HNO_3 are concentrated trace metals grade acids.

[b] Bi, *Li*, and S standards are prepared separately.

Appendix C

Low-Level Initial Calibration Verification (LLICV) Standard Solution Preparation

Low-Level Initial Calibration Verification (LLICV) Standard						
Element		Initial Conc (ppm)	Initial Vol (mL)	Final Conc (ppm)	Final Vol (mL)	Solvent Acid Conc [a]
Aluminum	Al	10000	0.5	5	1000	10% (v/v) HNO_3
Antimony	Sb	10000	0.15	1.5	1000	
Arsenic	As	10000	0.1	1	1000	
Barium	Ba	10000	0.1	1	1000	
Beryllium	Be	10000	0.1	1	1000	
Boron	B	10000	0.2	2	1000	
Cadmium	Cd	10000	0.1	1	1000	
Calcium	Ca	10000	1	10	1000	
Chromium	Cr	10000	0.1	1	1000	
Cobalt	Co	10000	0.1	1	1000	
Copper	Cu	10000	0.1	1	1000	
Iron	Fe	10000	1	10	1000	
Lead	Pb	5000 [b]	0.2	1	1000	
Magnesium	Mg	10000	1	10	1000	
Manganese	Mn	10000	0.05	0.5	1000	
Molybdenum	Mo	10000	0.1	1	1000	
Nickel	Ni	10000	0.1	1	1000	
Phosphorus	P	10000	1	10	1000	
Potassium	K	10000	5	50	1000	
Selenium	Se	10000	0.15	1.5	1000	
Silicon	Si	10000	0.5	5	1000	
Silver	Ag	10000	0.05	0.5	1000	
Sodium	Na	10000	5	50	1000	
Strontium	Sr	10000	0.3	3	1000	
Thallium	Tl	10000	0.15	1.5	1000	
Tin	Sn	10000	0.5	5	1000	
Titanium	Ti	10000	0.3	3	1000	
Vanadium	V	10000	0.1	1	1000	
Zinc	Zn	10000	0.1	1	1000	
Bismuth [b]	Bi	1000	1	10	100	5% (v/v) HNO_3
Lithium [b]	Li	1000	0.5	5	100	
Sulfur [b]	S	1000	1	10	100	
Lead	Pb	10000	100	5000	200	H_2O

[a] HNO_3 is concentrated trace metals grade acid.

[b] Bi, Li, and S standards are prepared separately; 5000-ppm Pb standard is prepared separately.

Appendix C

Continuing Calibration Verification (CCV) Standard Solution Preparation

Continuing Calibration Verification (CCV) Standard						
Element		Initial Conc (ppm)	Initial Vol (mL)	Final Conc (ppm)	Final Vol (mL)	Solvent Acid Conc [a]
Aluminum	Al	27	50	13.5	100	5% (v/v) HCl + 6% (v/v) HNO_3
Antimony	Sb	9	50	4.5	100	
Arsenic	As	7.5	50	3.75	100	
Barium	Ba	15	50	7.5	100	
Beryllium	Be	1.125	50	0.5625	100	
Boron	B	7.5	50	3.75	100	
Cadmium	Cd	1.5	50	0.75	100	
Calcium	Ca	60	50	30	100	
Chromium	Cr	1.2	50	0.6	100	
Cobalt	Co	3.75	50	1.875	100	
Copper	Cu	1.875	50	0.9375	100	
Iron	Fe	7.5	50	3.75	100	
Lead	Pb	7.5	50	3.75	100	
Magnesium	Mg	15	50	7.5	100	
Manganese	Mn	1.5	50	0.75	100	
Molybdenum	Mo	1.2	50	0.6	100	
Nickel	Ni	1.2	50	0.6	100	
Phosphorus	P	12	50	6	100	
Potassium	K	54	50	27	100	
Selenium	Se	3	50	1.5	100	
Silicon	Si	12	50	6	100	
Silver	Ag	0.75	50	0.375	100	
Sodium	Na	72	50	36	100	
Strontium	Sr	0.6	50	0.3	100	
Thallium	Tl	3	50	1.5	100	
Tin	Sn	6	50	3	100	
Titanium	Ti	1.2	50	0.6	100	
Vanadium	V	3.75	50	1.875	100	
Zinc	Zn	5	50	2.5	100	
Bismuth [b]	Bi	2	50	1	100	5% (v/v) HCl + 5% (v/v) HNO_3
Lithium [b]	Li	2	50	1	100	
Sulfur [b]	S	2	50	1	100	

[a] HCl and HNO_3 are concentrated trace metals grade acids.

[b] Bi, Li, and S standards are prepared separately.

Appendix C

Interference Check Standard AB (ICS-AB) Solution Preparation

Interference Check Standard AB (ICS AB)						
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)	Solvent Acid Conc [a]
Aluminum	Al	1200	10	24	500	5% (v/v) HCl + 6% (v/v) HNO_3
Antimony	Sb	500	1	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	
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	
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	200	0.5	0.2	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	
Bismuth	Bi					
Lithium	Li					
Sulfur	S					

[a] HCl and HNO_3 are concentrated trace metals grade acids.

Appendix C

Interference Check Standard A (ICS-A) Solution Preparation

Interference Check Standard A (ICS A)						
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)	Solvent Acid Conc [a]
Aluminum	Al	1200	10	24	500	5% (v/v) HCl + 6% (v/v) HNO_3
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] HCl and HNO_3 are concentrated trace metals grade acids.

Internal Standard Solution Preparation

Internal Standard						
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)	Solvent Acid Conc [a]
Holmium	Ho	10000	1	5	2000	5% (v/v) HCl + 6% (v/v) HNO_3
Terbium	Tb	10000	1	5	2000	
Yttrium	Y	10000	1	5	2000	

[a] HCl and HNO_3 are concentrated trace metals grade acids.

Appendix C

Spike Standard Solution Preparation

Spike Standards 1 & 2						
Element		Initial Conc. (ppm)	Initial Volume (mL)	Final Conc. (ppm)	Final Volume [a] (mL)	Solvent Acid Conc [a]
Aluminum	Al	10000	10	100	1000	10% (v/v) HNO_3
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 [b]	Bi	1000	20	200	100	5% (v/v) HNO_3
Lithium [b]	Li	1000	20	200	100	
Sulfur [b]	S	1000	20	200	100	
Lead	Pb	10000	100	5000	200	H_2O

[a] HNO_3 is concentrated trace metals grade acid.

[b] Bi, Li, and S standards are prepared separately; 5000-ppm Pb standard is prepared separately.

Appendix D

SAMPLE HOLDING TIMES, REQUIRED DIGESTION VOLUMES AND RECOMMENDED COLLECTION VOLUMES FOR METAL DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES

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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)

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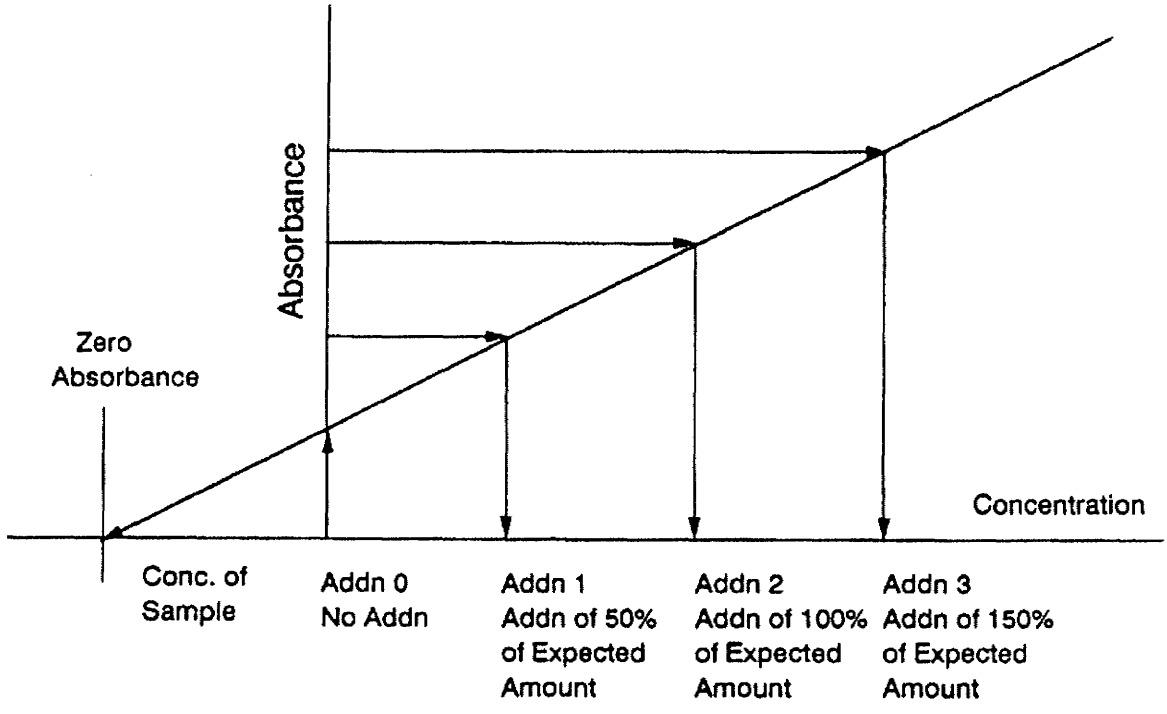
Appendix E

Standard Addition Plot (Example)



Appendix F

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECTS

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1. METHOD IDENTIFICATION

1.1. EPA Method 6010B, Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) – Additional Quality Control Criteria for Department of Defense (DoD) Projects.

2. DETECTION / QUANTITATION 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. Initial Calibration Verification (ICV)

4.1.1. The concentration of the ICV standard shall be at or near the midpoint of the calibration range.

4.2. Low-Level Initial Calibration Verification (LLICV) Solution

4.2.1. Prepare the LLICV working standard solutions by diluting the appropriate volumes of the stock standards and concentrated HNO_3 to the specified volumes with reagent water.

4.2.2. Use the analyte and acid concentrations outlined in Appendix C as guidance to prepare the LLICV working standard solutions.

4.2.3. Dilute the appropriate volumes of the LLICV working standard solution with reagent water for low-level initial calibration verification.

4.2.3.1. Each target analyte in the LLICV solution is at a concentration expected to be the LOQ.

4.2.4. Prepare the LLICV solution fresh daily.

4.2.5. The LLICV solution is of a source same as that used for the initial one-point calibration.

4.2.6. The concentration of the LLICV standard shall be less than or equal to the LOQ.

4.3. Continuing Calibration Verification (CCV)

4.3.1. The concentration of the CCV standard shall be greater than the low calibration standard and less than or equal to the midpoint of the calibration range.

4.4. The use of a standard from a second lot obtained from the same manufacturer (independently prepared from different source materials) is acceptable for use as a second source standard.

5. QUALITY CONTROL

5.1. Limit of Detection (LOD)

5.1.1. Detection limit (DL) determination shall be performed for each analyte 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. LOD verification must be performed immediately following each DL determination and quarterly thereafter.

5.1.2.1. LOD verification sample shall be prepared by spiking a quality system matrix at a concentration of at least 2 times but no greater than 4 times the DL for each analyte.

5.1.2.2. LOD verification is deemed valid if the apparent signal-to-noise (S/N) ratio of each analyte is at least 3 and the results must meet all method requirements for analyte identification.

5.1.2.2.1. For a data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations. This is initially estimated based on a minimum of 4 method blank analyses and later established with a minimum of 20 method blank results.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the DL determination and LOD verification.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.1.2.4. In situation where the test method is set up and used on an infrequent basis, LOD verification may be performed on a one per batch basis.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the calibration range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ for each analyte.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking a quality system matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.2.2.3. In situation where the test method is set up and used on an infrequent basis, LOQ verification may be performed on a one per batch basis.

5.3. Initial Calibration (IC)

5.3.1. The LOQ and the calibration standard establish the quantitation range which must lie within the linear dynamic range.

5.3.1.1. When sample results exceed the quantitation range, dilute and re-analyze the sample (when sufficient sample volume and holding time permit) to bring results within the quantitation range. Results outside the quantitation range shall be reported as estimated values and qualified using appropriate data qualifiers that are explained in the case narrative.

5.4. Low-Level Initial Calibration Verification (LLICV)

5.4.1. Immediately following the analysis of an ICV standard, an LLICV standard must be analyzed prior to sample analysis.

5.4.2. The LOQ is deemed valid if the replicate %RSD for each analyte is ≤ 5%, and the %D for each analyte is ≤ 20%.

5.4.3. If these criteria are not met, effect corrective action and recalibrate.

5.5. Initial Calibration Blank (ICB)

5.5.1. Immediately following the analysis of an LLICV standard, an ICB must be analyzed prior to sample analysis.

5.5.2. The instrument operating condition is deemed satisfactory for sample analysis to begin if no analytes are detected at a concentration > LOD.

5.5.3. If these criteria are not met, no sample analysis shall begin. Determine the source of contamination. Re-prepare and re-analyze the ICB.

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

5.6.1. Following the establishment of a valid initial calibration, an ICS-AB and ICS-A solutions must be analyzed daily prior to sample analysis.

5.6.2. The ICS-AB is deemed acceptable if the %D for each analyte is ≤ 20%.

5.6.3. The ICS-A is deemed acceptable if the absolute value of the concentration for each non-spiked analyte is < LOD (unless it is a verified trace impurity from one of the spiked analytes).

5.6.4. If these criteria are not met, no sample analysis shall begin. Determine the source of problem, effect corrective action, and re-analyze the ICS-AB and/or ICS-A.

5.7. Continuing Calibration Verification (CCV)

5.7.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily after every batch of 10 field samples or portion thereof within a 24-hour shift, and at the end of sequence.

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

5.7.3. If these criteria are not met, the initial calibration is deemed unacceptable for sample analysis to resume. Document the unacceptable result and re-analyze two consecutive CCVs within 1 hour after the failed CCV.

5.7.3.1. If these two CCVs pass, report both CCVs and the sample data without re-analysis.

5.7.3.2. If either of these two CCVs fails, or if the two CCVs cannot be analyzed within 1 hour, effective corrective action, recalibrate, and re-analyze all samples since the last acceptable CCV.

5.8. Continuing Calibration Blank (CCB)

5.8.1. Immediately following the analysis of a CCV standard, a CCB must be analyzed prior to sample analysis.

5.8.2. The instrument operating condition is deemed satisfactory for sample analysis to resume if no analytes are detected at a concentration > LOD.

5.8.3. If these criteria are not met, no sample analysis shall resume. Determine the source of contamination. Re-prepare and re-analyze the CCB. Re-analyze all samples since the last acceptable CCB.

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

5.9.1. Method Blanks (MBs)

5.9.1.1. The MB shall be considered to be contaminated if one of the following conditions is met.

5.9.1.1.1. The concentration of any target analyte in the MB exceeds 1/2 the LOQ, and is greater than 1/10 the amount measured in any associated sample or 1/10 the regulatory limit (whichever is greater).

5.9.1.1.2. The concentration of any common laboratory contaminant in the MB exceeds LOQ.

5.9.1.2. If the MB is contaminated, re-process the affected samples associated with the failed MB in a subsequent preparation batch, except when the sample results are below the LOD.

5.9.1.2.1. If insufficient sample volume remains for re-processing, 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.

5.9.2. Laboratory Control Samples (LCS/LCSDs)

5.9.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD element in aqueous and solid matrices are listed in Appendix G.

5.9.2.2. All reported analytes must be spiked. The concentration of each spike compound shall be at or below the midpoint of the calibration if project specific concentration is not specified.

5.9.2.3. 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.

5.9.2.3.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery if the control limits are statistically-derived based on historical data with at least 30 data points generated under the same analytical process.

5.9.2.4. 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.

5.10. Matrix Based Quality Control (MS/MSDs)

5.10.1. Matrix Spikes (MS/MSDs)

5.10.1.1. The lower and upper acceptance limits for %REC of each MS/MSD element in aqueous and solid matrices are listed in Appendix G. The RPD is ≤ 20%.

5.10.1.2. All reported analytes must be spiked. The sample selected for spiking must be one of the samples collected for the specific DoD project.

5.10.1.3. 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.

5.10.1.3.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery if the control limits are statistically-derived based on historical data with at least 30 data points generated under the same analytical process.

5.11. Dilution Test

5.11.1. If MS/MSD fails, and the analyte concentration prior to dilution is > 50 × LOQ, prepare a dilution test sample per preparation batch per matrix with a 1:5 dilution.

5.11.2. The analyte concentration in the dilution test sample must be within ± 10% of the original determination.

5.11.3. If this criterion is not met, effect corrective action (e.g., perform MSA) if required by the project, or report the results with the appropriate data qualifier (J-flag) for the specific analyte(s) in the parent sample, and explain in the case narrative.

5.12. Post Digestion Spike (PDS) Addition

5.12.1. If MS/MSD fails, and the analyte concentration prior to dilution is < 50 × LOQ, prepare a PDS sample per preparation batch per matrix.

5.12.2. A PDS sample is prepared by adding the spike standard to a portion of a digested sample, or its dilution. The spike addition should produce a concentration of 10–100 times the LOQ.

5.12.3. The acceptance criteria for PDS elements are as follows:

5.12.3.1. The lower and upper acceptance limits for %REC of each PDS element are 80% and 120%, respectively.

5.12.3.2. If these criteria are not met, effect corrective action (e.g., perform MSA) if required by the project, or report the results with the appropriate data qualifier (J-flag) for the specific analyte(s) in the parent sample, and explain in the case narrative.

6. PROCEDURE

6.1. Following the establishment of a valid initial calibration, an LLICV standard must be analyzed daily immediately following ICV.

6.1.1. If LLICV fails, effect corrective action prior to analyzing any samples.

6.2. Blank, standard, and sample vessels are loaded in the following or other logical order:

1) Calibration Blank (CB)
2) Initial Calibration Standard
3) Initial Calibration Verification (ICV)
4) Low-Level Initial Calibration Verification (LLICV)
5) Initial Calibration Blank (ICB)

6) Interference Check Solution AB (ICS-AB)
7) Interference Check Solution A (ICS-A)
8) Continuing Calibration Verification (CCV)
9) Continuing Calibration Blank (CCB)
10) Method Blank (MB)
11) Laboratory Control Samples (LCS)
12) Laboratory Control Sample Duplicates (LCSD)
13) Samples (up to 10 per batch, including QC check samples and MBs)
14) Matrix Spike (MS)
15) Matrix Spike Duplicate (MSD)
16) Dilution Test Sample
17) Post Digestion Spike (PDS)
18) Ending CCV
19) Ending CCB

6.2.1. Item 4: An LLICV is a standard used to confirm the accuracy of measurement at or near the LOQ. An acceptable LLICV is required daily immediately following ICV.

6.2.2. Item 5: The ICB is an aliquot of acidified reagent water used to monitor contamination. An acceptable ICB is required immediately following LLICV.

6.2.3. Item 16: The dilution test sample is prepared from the five-fold dilution of a high concentration sample post digestion. The high concentration sample is diluted to one-fifth of the original concentration post digestion to confirm that no interference is observed in the original sample.

6.2.3.1. The purpose of the dilution test sample is to assess matrix effects.

6.2.3.2. If MS/MSD fails, one dilution test sample is required for every batch of 20 samples per matrix or portion thereof processed concurrently.

6.2.4. Item 17: The PDS is the same sample matrix from which the MS/MSD samples were prepared or from another sample in the same preparation batch, 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.

7. REFERENCES

7.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 5.0, July 2013.

Appendix G

CONTROL LIMITS FOR DEPARTMENT OF DEFENSE PROJECTS

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Appendix G

DoD Control Limits of LCS/LCSD/MS/MSD Elements in Aqueous Matrix

Analyte		Mean	Standard Deviation	Control Limit		ME Limit	
				Lower	Upper	Lower	Upper
Aluminum	Al	100.0	4.8	86	115	81	119
Antimony	Sb	100.2	4.2	88	113	83	117
Arsenic	As	99.9	4.3	87	113	83	117
Barium	Ba	100.3	4.1	88	113	84	117
Beryllium	Be	100.4	4.0	89	112	84	116
Bismuth	Bi	95.8	3.2	86	105	83	109
Boron	B	98.8	4.8	85	113	80	118
Cadmium	Cd	100.8	4.1	88	113	84	117
Calcium	Ca	100.0	4.2	87	113	83	117
Chromium	Cr	101.1	3.9	90	113	86	117
Cobalt	Co	101.2	4.2	89	114	84	118
Copper	Cu	100.2	4.6	86	114	82	119
Iron	Fe	100.7	4.7	87	115	82	120
Lead	Pb	99.3	4.4	86	113	82	117
Lithium	Li	100.7	5.3	85	117	80	122
Magnesium	Mg	98.8	4.8	85	113	80	118
Manganese	Mn	101.9	4.1	90	114	86	118
Molybdenum	Mo	101.1	4.0	89	113	85	117
Nickel	Ni	100.5	4.1	88	113	84	117
Phosphorus	P	100.5	4.2	88	113	84	117
Potassium	K	99.9	4.7	86	114	81	119
Selenium	Se	98.5	5.2	83	114	78	119
Silicon	Si	100.6	6.1	82	119	76	125
Silver	Ag	99.1	5.1	84	115	79	120
Sodium	Na	100.9	4.7	87	115	82	120
Strontium	Sr	101.3	3.8	90	113	86	117
Sulfur	S	100.7	3.9	89	112	85	116
Thallium	Tl	99.5	4.7	85	114	81	118
Tin	Sn	101.3	4.4	88	115	84	119
Titanium	Ti	101.1	3.4	91	111	88	115
Vanadium	V	100.2	3.6	90	111	86	115
Zinc	Zn	100.6	4.6	87	115	82	119

Note: ME limits are applicable to LCS/LCSD elements only.

Appendix G

DoD Control Limits of LCS/LCSD/MS/MSD Elements in Solid Matrix

Analyte		Mean	Standard Deviation	Control Limit		ME Limit	
				Lower	Upper	Lower	Upper
Aluminum	Al	96.7	7.5	74	119	67	127
Antimony	Sb	96.4	5.7	79	114	74	119
Arsenic	As	96.2	4.9	82	111	77	116
Barium	Ba	98.3	5.0	83	113	78	118
Beryllium	Be	97.8	5.1	83	113	77	118
Boron	B	93.0	7.1	72	114	65	121
Cadmium	Cd	97.5	5.3	82	113	76	119
Calcium	Ca	98.1	5.8	81	116	75	121
Chromium	Cr	98.9	4.6	85	113	81	117
Cobalt	Co	98.7	4.5	85	112	81	117
Copper	Cu	99.1	6.0	81	117	75	123
Iron	Fe	99.7	6.1	81	118	75	124
Lead	Pb	96.8	5.1	81	112	76	117
Lithium	Li	98.8	4.5	85	112	81	117
Magnesium	Mg	96.1	6.1	78	115	72	121
Manganese	Mn	99.1	4.9	84	114	80	119
Molybdenum	Mo	98.7	5.7	82	116	76	122
Nickel	Ni	98.1	4.9	83	113	79	118
Phosphorus	P	103.1	3.8	92	114	88	118
Potassium	K	98.3	5.8	81	116	75	122
Selenium	Se	94.5	5.6	78	111	72	117
Silver	Ag	97.3	5.0	82	112	77	117
Sodium	Na	100.1	5.8	83	118	77	123
Strontium	Sr	98.5	5.0	83	114	79	119
Thallium	Tl	96.8	4.6	83	111	78	115
Tin	Sn	100.1	6.6	80	120	74	127
Titanium	Ti	98.2	5.2	83	114	77	119
Vanadium	V	98.3	5.4	82	114	77	120
Zinc	Zn	97.4	5.0	82	113	77	117

Note: ME limits are applicable to LCS/LCSD elements only.

Title : **EPA METHOD 8082, POLYCHLORINATED BIPHENYLS (PCBs) AS AROCLORS BY GAS CHROMATOGRAPHY**

Document No. : SOP-M407
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PROPRIETARY INFORMATION STATEMENT

Revision 4.1 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 04/03/15
MANAGEMENT **DATE**

_____ 04-03-15
QA DEPARTMENT **DATE**

Reviewer Signature	Review Date	Comments	QA Signature

1. METHOD IDENTIFICATION

1.1. EPA Method 8082, Polychlorinated Biphenyls (PCBs) as Aroclors by Gas Chromatography.

2. APPLICABLE MATRICES

2.1. This method is applicable to water, oil, soil, and solid wastes.

3. DETECTION / QUANTITATION LIMITS

3.1. The reporting limits (RLs) for this method are as follows:

	Water	Soil	Sediment
PCBs as Aroclors	1.0 µg/L	50 µg/kg (wet-weight)	10 µg/kg (wet-weight)

	Oil	Wipe/Filter
PCBs as Aroclors Aroclor 1221	1000 µg/kg	1.0 µg/sample

3.2. The RLs will be proportionally higher for sample extracts which require dilution or cleanups.

3.3. Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedure on establishing detection and reporting limits.

4. SCOPE AND APPLICATION

4.1. EPA Method 8082 is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors in extracts from various matrices, using a gas chromatographic system configured with a fused-silica capillary column coated with a slightly polar silicone.

4.1.1. Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns compared to those of Aroclor standards.

4.2. The following compounds are routinely determined by this method.

Aroclor-1016	Aroclor-1242	Aroclor-1260
Aroclor-1221	Aroclor-1248	Aroclor-1262
Aroclor-1232	Aroclor-1254	Aroclor-1268

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. EPA Method 8082 describes chromatographic procedures that will allow for the identification of Aroclors in the extract and their qualitative and quantitative analysis by gas chromatography. Detection is achieved using an electron capture detector (ECD).

5.2. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample.

5.2.1. Aqueous samples are extracted via EPA Methods 3510 or 3520 at neutral pH using methylene chloride exchanged into hexane.

5.2.2. Solid samples are extracted via EPA Methods 3540 or 3550 using methylene chloride-acetone (1:1) exchanged into hexane, or via EPA Method 3545 using ***acetone-hexane (1:1)*** exchanged into hexane.

5.2.3. Solid samples for TCLP, SPLP, or STLC analysis are prepared using the appropriate mobility extraction method, and the resulting mobility-procedure extracts (leachates) are extracted via EPA Methods 3510 or 3520 at neutral pH using methylene chloride exchanged into hexane.

5.2.4. Oil samples are prepared in accordance with EPA Method 3580 using hexane as the diluent.

5.2.5. A variety of cleanup procedures may be applied to the extracts, depending on the nature of the target analytes and the matrix interferences.

5.3. Acceptable preparatory methods include, but are not limited to, the following:

Type of Sample Preparation	Method	SOP No.
Separatory Funnel Liquid-Liquid Extraction	EPA 3510	SOP-M200
Continuous Liquid-Liquid Extraction	EPA 3520	SOP-M201
Soxhlet Extraction	EPA 3540	SOP-M203
Pressurized Fluid Extraction	EPA 3545	SOP-M204
Ultrasonic Extraction	EPA 3550	SOP-M202
Waste Dilution	EPA 3580	SOP-M205
Cleanup	EPA 3600(M)	SOP-M234
Gel-Permeation Cleanup	EPA 3640	SOP-M233
TCLP	EPA 1311	SOP-M226
SPLP	EPA 1312	SOP-M227
STLC (California Code of Regulations)	CCR T22.11.5.A-II	SOP-M228

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.

6.3.1. 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, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours***.

6.3.2. 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. ***Limit of Detection (LOD): The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.12. ***Limit of Quantitation (LOQ): The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

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, dated 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. 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. ***Refer to the current revision of the Eurofins Calscience Quality Systems Manual for additional terms and definitions.***

7. INTERFERENCES

7.1. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

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

7.2.1. Sample syringes should be thoroughly rinsed with solvent between sample injections.

7.2.2. Analysis of a suspected high level sample should be followed by an analysis of solvent blank to check for cross-contamination. In addition, suspected high level samples may be diluted and then analyzed at the end of the sequence to prevent carryover contamination.

7.3. Interference can also occur when "dirty" samples leave residue in the analytical column. To minimize this effect, a guard column should be used and cut frequently or replaced. In addition, the analytical column can be "baked" after such samples. Other maintenance procedures include cleaning the inlet or replacing injection liner and seal.

7.4. Phthalate esters introduced during sample preparation can pose a major problem in PCB determinations.

7.4.1. Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination.

7.4.2. Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

7.4.3. Phthalate ester interferences may be removed using EPA Method 3665 (Sulfuric Acid/Permanganate Cleanup) prior to analysis.

7.5. Sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur can be removed through the use of EPA Method 3660 (Sulfur Cleanup).

8. ►SAFETY

8.1. Compounds covered by this method have been tentatively classified as known or suspected human carcinogens. Primary standards of these 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 ***Eurofins*** 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) ***or Safety Data Sheets (SDSs)*** are available for each laboratory standard and reagent chemical. Employees should review and be familiar with the hazards and precautions outlined in the MSDS ***or SDS*** 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 6890 Series Gas Chromatograph, Agilent 7890A Gas Chromatograph, or equivalent configured with the following components.

9.1.1. Autoinjector, Agilent 7680 Series, Agilent 7683 Series, or equivalent.

9.2. Instrument Software

9.2.1. Agilent GC ChemStation Version A.09.01[1206], Agilent GC ChemStation Version B.04.02[98], or equivalent.

9.2.2. ***PC-based data system or equivalent.***

9.3. Instrument Maintenance and Troubleshooting

9.3.1. Refer to the current revision of SOP-T066 and instrument hardware and software manuals for instrument maintenance and troubleshooting.

9.4. Primary Detection Channel

9.4.1. Detector: Electron capture detector (ECD).

9.4.2. Analytical Column: 30-m × 0.32-mm ID, 0.50-µm film thickness, narrow-bore, capillary, silicone coated fused-silica, Restek Rtx®-CLPesticides2 or equivalent.

9.5. Confirmation Detection Channel

9.5.1. Detector: Electron capture detector (ECD).

9.5.2. Analytical Column: 15-m × 0.32-mm ID, 0.50-µm film thickness, narrow-bore, capillary, silicone coated fused-silica, Restek Rtx®-CLPesticides or equivalent.

9.6. Guard Column: 5-m × 0.32-mm ID, intermediate-polarity deactivated, uncoated fused silica, Restek IP Deactivated Guard Column or equivalent.

9.7. Carrier Gas: Nitrogen, N_2, high purity (99.998%), compressed, Praxair 4.8 grade or equivalent.

9.8. Carrier Gas: Hydrogen, H_2, high purity (99.995%), compressed, Praxair 4.5 grade or equivalent.

9.9. Makeup Gas: Nitrogen, N_2, high purity (99.998%), compressed, Praxair 4.8 grade or equivalent.

9.10. Makeup Gas: Methane, CH_4, 5%, and argon, Ar, 95%, compressed, Praxair P-5 Mixture or equivalent.

9.11. 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 Certificate or equivalent documentation.

9.12. Storage vials, 15-mm × 45-mm (4-mL capacity), screw top, clear glass, with Teflon-lined screw caps and septa, disposable.

9.13. Autoinjector vials, 12-mm × 32-mm (2-mL capacity), crimp top, clear glass, with aluminum crimp caps and Teflon-lined septa, disposable.

9.14. Vial inserts, 300 µL, clear glass, with conical bottom and spring.

9.15. Balance, analytical, calibrated, capable of weighing to the nearest 0.1 mg.

9.16. 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.

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 200 g of anhydrous $Na_2S_2O_3$ in reagent water and dilute to 2 L with additional reagent water.

10.1.5. Methylene chloride (or dichloromethane), CH_2Cl_2, clear colorless liquid, pesticide grade or equivalent.

10.1.6. Hexane, C_6H_{14}, clear colorless liquid, pesticide grade or equivalent.

10.1.7. Acetone, CH_3COCH_3, clear colorless liquid, pesticide grade or equivalent.

10.1.8. ***1:1 Acetone / Hexane solvent mixture.***

10.1.9. Refer to the specific SOPs of the preparatory methods for additional reagents.

10.1.10. 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 100/1000 ppm of each target analyte, and 200 ppm of each surrogate are used to prepare calibration and check standards.

10.2.1.1. Prepare each working standard solution by diluting the appropriate volumes of the stock standards to the specified volumes with hexane.

10.2.1.2. The 20-ppm working standards are prepared as follows:

	Initial		Final	
Analyte	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
Aroclor 1016	100	800	20	4.0
Aroclor 1260	100	800		
surrogates	200	80	4.0	

	Initial		Final	
Analyte	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
Aroclor 1016	1000	80	20	4.0
Aroclor 1260	1000	80		
surrogates	200	80	4.0	

Analyte	Initial		Final	
	Conc. (ppm)	Volume (µL)	Conc. (ppm)	Volume (mL)
Aroclor 1221	100	800	20	4.0
Aroclor 1254	100	800	20	4.0
Aroclor 1232	100	800	20	4.0
Aroclor 1262	100	800	20	4.0
Aroclor 1248	100	800	20	4.0
Aroclor 1268	100	800	20	4.0
Aroclor 1242	100	800	20	4.0
surrogates	200	80	4.0	4.0

10.2.1.3. The 500-ppb working standard is prepared as follows:

Analyte	Initial		Final	
	Conc. (ppm)	Volume (µL)	Conc. (ppb)	Volume (mL)
Aroclor 1221	100	20	500	4.0
Aroclor 1254	100	20		
Aroclor 1232	100	20	500	4.0
Aroclor 1262	100	20		
Aroclor 1248	100	20	500	4.0
Aroclor 1268	100	20		
Aroclor 1242	100	20	500	4.0

10.2.2. Pre-certified stock standard solution, in sealed glass ampule, containing 200 ppm each of decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TMX) is used to prepare surrogate working standard.

10.2.2.1. Prepare the 2.0-ppm surrogate working standard solution by diluting 10 mL of the 200-ppm surrogate stock standard to 1.0 L with acetone or other acetone miscible solvent.

10.2.3. Pre-certified stock standard solutions, each in sealed glass ampules, containing 100/1000 ppm of each target analyte are used to prepare spike working standards.

10.2.3.1. Prepare each 10-ppm spike working standard solution by diluting the appropriate volumes of the stock standards to the specified volumes with acetone or other acetone miscible solvent.

10.2.3.2. The 10-ppm spike working standards are prepared as follows:

Analyte	Initial		Final	
	Conc. (ppm)	Volume (mL)	Conc. (ppm)	Volume (mL)
Aroclor 1016	1000	2.0	10	200
Aroclor 1260	1000	2.0		
Aroclor 1221	100	1.0	10	10
Aroclor 1254	100	1.0	10	10
Aroclor 1232	100	1.0	10	10
Aroclor 1262	100	1.0	10	10
Aroclor 1248	100	1.0	10	10
Aroclor 1268	100	1.0	10	10
Aroclor 1242	100	1.0	10	10

10.2.4. The calibration standard solution contains various concentrations of target analytes and surrogates in hexane.

10.2.4.1. Dilute the appropriate volumes of the 20-ppm working standards to the specified volumes with hexane for initial calibration.

10.2.4.2. Use the following calibration levels as guidance to prepare the calibration standards.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A	S	A + S	A + S	A + S
100	20	20 + 4.0	20	4.0
250	50	20 + 4.0	50	4.0
500	100	20 + 4.0	1000	40
750	150	20 + 4.0	150	4.0
2000	400	20 + 4.0	400	4.0

Note: A = Aroclor; S = Surrogate

10.2.4.3. The midpoint standard is also used as the continuing calibration verification solution.

10.2.5. The initial calibration verification (ICV) solutions contain 500 ppb of each target analyte and 100 ppb of each surrogate in hexane. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

10.2.5.1. Dilute 100 µL of the second source 20-ppm working standard to 4.0 mL with hexane for initial calibration verification.

10.2.5.2. Use the following calibration level as guidance to prepare the ICV solution.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A	S	A + S	A + S	A + S
500	100	20 + 4.0	100	4.0

Note: A = Aroclor; S = Surrogate

10.2.6. The continuing calibration verification (CCV) solution contains 500 ppb of each target analyte and 100 ppb of each surrogate in hexane. The CCV solution is of a source same as that used for the initial five-point calibration.

10.2.6.1. Dilute 1000 µL of the 20-ppm working standard to 40 mL with hexane for continuing calibration verification.

10.2.6.2. Use the following calibration level as guidance to prepare the CCV solution.

Calibration Level (ppb)		Initial		Final
		Concentration (ppm)	Volume (µL)	Volume (mL)
A	S	A + S	A + S	A + S
500	100	20 + 4.0	1000	40

Note: A = Aroclor; S = Surrogate

10.2.7. The surrogate working standard solution contains 2.0 ppm each of decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TMX) in acetone or other acetone miscible solvent.

10.2.7.1. Add 500 µL of the 2.0-ppm surrogate working standard to each sample including each quality control (QC) check sample and method blank prior to solvent extraction.

10.2.7.2. Add 500 µL of the 2.0-ppm surrogate working standard to each mobility-procedure extract including each mobility-procedure extract designated as QC check sample and method blank prior to solvent extraction.

10.2.8. The spike working standard solution contains 10 ppm of each target analyte in acetone or other acetone miscible solvent. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

10.2.8.1. Use the 10-ppm spike working standard solution containing only Aroclor 1016 and Aroclor 1260 if samples are not expected to contain any Aroclor. Use the 10-ppm spike working standard solution containing the specific Aroclor(s) if samples are expected to contain these Aroclor(s).

10.2.8.2. The spike standards are used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

10.2.8.3. Add 200 µL of the spike working standard containing only Aroclor 1016 and Aroclor 1260 to each MS/MSD and LCS/LCSD sample prior to solvent extraction.

10.2.8.4. Per client request or project-specific data quality objectives (DQOs), add 200 µL of the spike working standard containing the specific Aroclor(s) to each MS/MSD and LCS/LCSD sample prior to solvent extraction.

10.2.8.5. Add 200 µL of the spike working standard containing only Aroclor 1016 and Aroclor 1260 to each mobility-procedure extract designated as MS/MSD and LCS/LCSD prior to solvent extraction.

10.2.8.6. Per client request or project-specific DQOs, add 200 µL of the spike working standard containing the specific Aroclor(s) to each mobility-procedure extract designated as MS/MSD and LCS/LCSD prior to solvent extraction.

10.2.9. All working standards must be replaced after six months (unless specified otherwise) or sooner if routine QC or comparison with check standards indicates a problem.

10.2.9.1. Store all working standards under dark and refrigerated condition.

10.2.10. All stock standards must be inspected and documented in the Chemicals and Supplies Verification Logbook prior to use.

10.2.10.1. 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 1-L pre-cleaned amber glass containers with Teflon-lined closures. Collect all samples in duplicate.

11.1.1. If the aqueous sample is known or suspected to contain residual chlorine, add 4 mL of the 10% $Na_2S_2O_3$ solution per 1 L of sample. The 10% $Na_2S_2O_3$ solution may be added to the sample container prior to sample collection.

11.1.2. If MS/MSD analyses are required, collect one sample in quadruplicate.

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, wipe, or filter samples should be collected in 40-mL pre-cleaned amber glass or clear glass VOA vials with Teflon-lined closures.

11.4. Mobility-procedure extracts should be collected in 500-mL pre-cleaned amber glass containers with Teflon-lined closures.

11.4.1. If the mobility-procedure extract is known or suspected to contain residual chlorine, add 2 mL of the 10% $Na_2S_2O_3$ solution per 500 mL of mobility-procedure extract.

11.4.2. Completely fill and hermetically seal the sample container with minimum headspace.

11.5. Aqueous and non-aqueous samples shall be maintained in a chilled state post sample collection until received at the laboratory. Aqueous and non-aqueous samples should not be frozen (e.g., do not use dry ice as the refrigerant).

11.5.1. For additional information on aqueous and non-aqueous sample collection and preservation, refer to Code of Federal Regulations (CFR), Title 40, Part 136 (§136.3).

11.5.2. For additional information on sample collection and preservation, refer to SOP-M229 and EPA Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Third Edition, Volume 1, Section 6.3.

11.6. Upon receipt, the aqueous and non-aqueous samples are stored in a 0–6°C cooler.

11.6.1. Aqueous samples must be solvent extracted within 7 days of sample collection.

11.6.2. Non-aqueous samples must be solvent extracted within 14 days of sample collection.

11.6.3. Mobility-procedure extracts must be solvent extracted within 7 days post mobility extraction.

11.6.3.1. Mobility-procedure extracts shall be stored in a 0–6°C cooler post mobility extraction if solvent extraction is not to be performed within 24 hours.

11.6.4. All solvent extracts are then stored under dark and refrigerated (0–6°C) conditions and must be analyzed within 40 days post solvent extraction.

12. ►QUALITY CONTROL

12.1. Initial Calibration (IC)

12.1.1. The initial five-point calibration must be established prior to the processing of sample extracts.

12.1.1.1. The calibration curve is established with a minimum of five calibration standards.

12.1.1.1.1. A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other Aroclor mixtures. Hence, it is not necessary to establish the initial five-point calibration for each of the other Aroclors.

12.1.1.1.2. In situations where only a few Aroclors are of interest for a specific project, it will be necessary to

establish the initial five-point calibration for each Aroclor of interest.

12.1.1.2. If the calibration curve is not established for each Aroclor other than Aroclor 1016 and Aroclor 1260, analyze the 500-ppb working standards for pattern recognition.

12.1.1.2.1. The 500-ppb working standards may also be used to determine the single-point calibration factor for each Aroclor if both of the following conditions are met.

12.1.1.2.1.1. The linearity of the detector response is demonstrated using the calibration standards containing only Aroclor 1016 and Aroclor 1260.

12.1.1.2.1.2. The calibration option is linear least squares regression and the regression is forced through zero.

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 RSD of any analyte is unacceptable, review the results (e.g., proper identification, area count, response factor, etc.) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards.

12.1.3.2. 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 to rule out problems due to random chance.

12.1.3.2.1. In some cases, replace the calibration standard may be necessary.

12.1.3.3. If a calibration standard is replaced and/or reanalyzed, recalculate the RSD, and document the rationale for re-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 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. 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 12-hour shift, and at the end of sequence.

12.3.1.1. For EPA Region 9 requirement, 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.

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 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.

12.4.1.1. Retention time window width is ± 3S (where S is the standard deviation of the three retention times for that analyte/surrogate) or ± 0.030 minute, whichever is greater.

12.4.1.1.1. For each multi-component analyte (i.e., Aroclor), calculate the standard deviation for each one of the five major characteristic peaks.

12.4.2. 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.

12.4.2.1. When initial calibration is performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S or ± 0.030 minute, whichever is greater.

12.4.2.2. When initial calibration is <u>not</u> performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the CCV standard ± 3S or ± 0.030 minute, whichever is greater.

12.4.3. Retention time for each analyte/surrogate in the calibration verification standard is verified as follows:

12.4.4. Retention time window for each analyte/surrogate is verified as follows:

12.4.4.1. When initial calibration is performed, the ICV standard and all CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the midpoint calibration standard.

12.4.4.2. When initial calibration is not performed, all succeeding CCV standards throughout the course of an analytical sequence within a 12-hour shift must fall within the daily retention time window established by the first CCV standard.

12.4.4.3. 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.

12.5. Event Based Quality Control (MBs and LCSs)

12.5.1. Event based quality control consists of QC samples prepared and processed with each preparatory event. This consists of a method blank (MB), a laboratory control sample ***(LCS)***, and, ***in some cases, a*** laboratory control sample duplicate (LCS).

12.5.1.1. ***An LCSD shall be prepared and processed if there is insufficient sample amount to perform matrix based QC (i.e., MS/MSD), or if it is mandatory per client request or project-specific DQOs.***

12.5.2. The acceptance criteria for MBs are as follows:

12.5.2.1. 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.

12.5.2.2. If a target analyte is found in the MB, but not in the associated samples, report the sample and MB data without qualification.

12.5.2.3. 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.

12.5.3. The acceptance criteria for ***LCS or*** LCS/LCSD compounds are as follows:

12.5.3.1. The lower and upper acceptance limits for %REC of each LCS compound are 50% and 135%, respectively. The RPD is ≤ 25%.

12.5.3.1.1. If historical data is available, 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.

12.5.3.2. All LCS/LCSD compounds must be within acceptance limits. If one or more LCS/LCSD compounds are not acceptable, determine the cause of the problem and effect corrective action.

12.6. Matrix Based Quality Control (Surrogates 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 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 in an aqueous sample are 50% and 135%, respectively. The lower and upper acceptance limits for %REC of each surrogate compound in a non-aqueous sample are 50% and 130%, respectively.

12.6.2.1.1. If historical data is available, 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.

12.6.2.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each surrogate compound are 60% and 150%, respectively.

12.6.2.2. If the surrogate compound recoveries are acceptable, report the surrogate 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 or cleanup. 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 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

recoveries, the same extract should be 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-processing 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 be 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 MS/MSD compounds are as follows:

12.6.3.1. The lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 25%.

12.6.3.1.1. If historical data is available, 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.

12.6.3.1.2. For EPA Region 9 requirement, the lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 30%.

12.6.3.2. 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.

12.6.3.3. 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.

12.6.4. 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.

12.7. 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. Analytical Balance

13.1.1. Calibrate the analytical balance at 2 mg, 1 g, and 100 g using Class 2 weights as outlined in the current revision of SOP-T043.

13.1.2. If control limits are not specified, calibration shall be within ± 0.1% or ± 0.5 mg, whichever is greater. If control limits are specified, calibration shall be within the specified limits. If the values are not within these limits, recalibrate the balance.

13.2. Chromatograph Initial Calibration

13.2.1. Establish an acceptable five-point calibration curve. The acceptance criteria for the initial calibration are listed in Section 12.1.

13.2.1.1. Because of the sensitivity of the electron capture detector, always clean the injection port and column prior to performing the initial calibration.

13.2.1.2. Recalibration is required for the following maintenance procedures.

13.2.1.2.1. Change, replace, or reverse the analytical column.

13.2.2. After obtaining an acceptable five-point calibration curve and prior to processing field or QC sample extracts, an ICV standard must be analyzed to verify the initial calibration. The acceptance criteria for the ICV are listed in Section 12.2.

13.2.3. The initial five-point calibration and ICV shall include all anticipated target analytes for the duration of the use of the initial calibration.

13.3. Retention Time Window

13.3.1. Retention time window width for each analyte/surrogate 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.

13.3.2. Document the serial number of the analytical column associated with the retention time window study.

13.3.3. Record the retention time in minutes for each analyte/surrogate to three decimal places.

14. ►PROCEDURE

14.1. Instrument Setup

14.1.1. Use the following GC operating conditions as guidance to establish the GC temperature program and flow rate necessary to separate the analytes of interest.

Description	GC Operating Condition
Inlet mode	splitless
Inlet temperature	220°C
Inlet pressure	6.2041 psi
Total flow rate	87.6 mL/min
Carrier gas flow rate	1.7 mL/min
Makeup gas flow rate	30 mL/min
Detector temperature	300°C
Initial temperature	120°C
Temperature program	120°C to 300°C at 15°C/min
Final temperature	300°C, hold 15 min

14.1.2. Autoinjector is set to inject 2 µL of field or QC sample extract.

14.1.3. Once established, the same operating conditions must be applied for all subsequent standard, sample, and blank analyses.

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 12-hour shift, and at the end of sequence. If the QC and retention time 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 12.4.3.

14.2.1. For EPA Region 9 requirement, refer to Section 12.3.1.1. for CCV frequency.

14.2.2. If a failed CCV is the first of the day, effect corrective action prior to analyzing any samples.

14.2.3. If a failed CCV is not the first of the day, effect corrective action and reanalyze all samples since the last acceptable CCV.

14.3. Following extraction by one of the methods specified in Section 5.2., the extracts for the QC and actual environmental samples are received in autoinjector vials. The autoinjector vials are then loaded onto the GC sample tray.

14.4. Standard and sample vials are loaded in the following or other logical order:

1) Instrument Blank (IB)
2) Continuing Calibration Verification (CCV)
3) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD), ***when required***
5) Method Blank (MB)
6) Samples (up to 20 per batch, including QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

14.4.1. Item 1: The IB is a vial of hexane used to determine whether the GC 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). IB is optional.

14.4.2. Items 2 and 9: 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, after every batch of 20 samples or portion thereof within a 12-hour shift, and at the end of sequence.

14.4.2.1. For EPA Region 9 requirement, refer to Section 12.3.1.1. for CCV frequency.

14.4.2.2. More frequent (e.g., every 10 samples) calibration verification may be useful to minimize the number of sample extract re-analyses that would be required in the event of an unacceptable CCV.

14.4.3. Item 3: 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.

14.4.3.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid and oil samples, the LCS consists of the specified compounds spiked into washed sea sand. For wipe samples, the LCS consists of the specified compounds spiked into unused gauze pad. For filter samples, the LCS consists of the specified compounds spiked into unused filter paper. For mobility-procedure extracts,

the LCS consists of the specified compounds spiked into the mobility-procedure extract designated as LCS.

14.4.3.2. One LCS is required every day preparatory methods (i.e., extractions, cleanups, 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***, if required,*** 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 15.6.

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 (i.e., surrogates, etc.).

14.4.5.1. For aqueous samples, the MB consists of clean reagent water. For solid and oil samples, the MB consists of washed sea sand. For wipe samples, the MB consists of unused gauze pad. For filter samples, the MB consists of unused filter paper. For mobility-procedure extracts, the MB consists of the mobility-procedure extract designated as MB.

14.4.5.2. One MB is required every day preparatory methods (i.e., extractions, cleanups, etc.) are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent.

14.4.5.3. 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 hexane 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.

14.4.6. Item 6: Up to 20 sample (including QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not contaminated. Dilution or cleanup of extracts 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 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.

14.4.7.1. 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 15.5.

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 15.6.

14.4.9. 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.

14.5. Ensure that a sufficient amount of hexane is present in the autoinjector solvent rinse bottles and that a sufficient unused volume exists in the autoinjector waste bottles 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. Establish the daily retention time window for each analyte/surrogate (see Section 12.4.2.1. and Section 12.4.2.2.).

14.8.1.1. Tentative identification of an analyte/surrogate occurs when a peak from a sample extract falls within the daily retention time window.

14.8.1.1.1. For each multi-component analyte (i.e., Aroclor), choose a minimum of 5 characteristic peaks that are at least 25% of the height of the largest characteristic peak for the analyte, and determine the retention time window of each characteristic peak.

14.8.1.1.2. The set of peaks for each Aroclor should include at least one peak that is unique to that Aroclor.

14.8.1.1.2.1. For Aroclor 1016 and Aroclor 1260, none of the peaks chosen should be found in both of these Aroclors.

14.8.1.2. Use the succeeding CCV standards analyzed throughout the course of an analytical sequence within a 12-hour shift to evaluate retention time stability (see Section 12.4.3.). If any analyte(s)/surrogate(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.

14.8.1.2.1. If any major characteristic peak(s)/surrogate(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.

14.8.1.3. For Aroclors other than Aroclor 1016 and Aroclor 1260, identification shall rely primarily on pattern recognition. However, retention times should be utilized as a guide.

14.8.2. 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 extract and the calibration standards.

14.8.2.1. PCBs as Aroclor may be quantitated from the total area of the PCB pattern and on the basis of the Aroclor standard that is most similar to the sample (total area approach), or the area of 5 or more major characteristic peaks (subset peak approach).

14.8.2.1.1. If total area approach is employed, any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area.

14.8.2.1.2. Total area approach is recommended if weathering of PCBs in the environment and changes resulting from waste treatment processes alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable, or if samples contain more than one Aroclor.

14.8.2.1.3. The reasons for applying total area approach on sample quantitation and the problems associated with sample matrix should be fully documented.

14.8.2.2. Proper quantitation requires the appropriate selection of a baseline from which the area of the characteristic peak(s) can be determined.

14.8.2.2.1. For multi-component analyte quantitation, a forced baseline or baseline-to-baseline integration across the entire target range is required to ensure the appropriate integration of analyte response.

14.8.2.3. Determine the concentration based on the initial calibration curve.

14.8.2.3.1. Calculate the concentration of each target analyte in a sample extract using the average of the initial RFs and the total area of the five predetermined peaks. The formula for calculating concentration is listed in Section 15.7.

14.8.2.3.2. Refer to Appendix A for examples of the predetermined peaks of each multi-component analyte.

14.8.2.3.3. The data system is programmed to perform the calculation of concentration.

14.8.2.4. If the instrument response exceeds the calibration range, dilute the extract and reanalyze.

14.8.3. Tentative identification of a target analyte occurs when a peak from a sample extract falls within the analyte's retention time window. Confirmation is necessary when the composition of samples is not well characterized. Qualitative confirmation techniques are by second column with dissimilar stationary phase, GC/MS with Selected Ion Monitoring (SIM) or Full Scan mode, or GC data from two different detectors.

14.8.4. Second column confirmation is made on a "confirmation" channel configured with a column of dissimilar stationery phase and a second detector. The principle is that the retention time of the target analyte will differ between the primary and confirmation column and, unless the detected compound is the particular target analyte, it will not be observed within both retention time windows.

14.8.4.1. Report the higher result between the primary and confirmation column. The RPD between results must be ≤ 40%.

14.8.4.1.1. If one result is significantly higher (e.g., > 40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are observed, examine the baseline parameters established by the instrument data system (or operator) during peak integration. A rising baseline may cause the mis-integration of the peak for the lower result.

14.8.4.1.2. If no anomalies are observed, review the chromatographic conditions. If there is no evidence

of chromatographic problems, then it may be appropriate to report the lower result.

14.8.4.1.3. The data user must be advised of the disparity between the results on the two columns. Under some circumstances, including those involving in monitoring compliance with an action level or regulatory limit, further cleanup of the sample or additional analyses may be required when the two results in question span the action level or regulatory limit.

14.8.4.2. In cases where a peak is not observed in the confirmation column's retention time window, the analyte is reported as "ND."

14.8.4.3. A calibration curve and retention time window for each analyte/surrogate are also established and maintained for the confirmation channel. The calibration and quality control requirements for the confirmation channel are identical to those of the primary channel.

14.8.5. GC/MS confirmation is more reliable than second column confirmation. In this case, where confirmation is required by project requirements, the sample is re-analyzed on GC/MS. When GC/MS results indicate that a target analyte is not present, the GC result is reported as "ND."

14.8.6. Confirmation is required for all positive results unless the samples meet all of the following requirements:

14.8.6.1. All samples (aqueous, solid, ***or*** oil) come from the same source (e.g., same monitoring well). However, samples of the same matrix from the same site but from differing sources (e.g., different monitoring wells) are not exempted.

14.8.6.2. All chemical parameters have been previously analyzed, identified, and confirmed by a second column with dissimilar stationary phase, GC/MS with Selected Ion Monitoring (SIM) or Full Scan mode, or GC data from two different detectors. Documentation of such must be maintained.

14.8.6.3. The resulting chromatograms are relatively simple and do not contain complex or overlapping peaks.

14.8.6.4. Chromatograms are largely unchanged from those for which confirmation was carried out.

14.8.7. Manual integration of peaks shall adhere to the procedures and documentation policies outlined in the current revision of SOP-T023.

14.8.7.1. When the instrument software produces proper integrations, it is highly recommended to use the integrations produced by the instrument software for consistency.

14.8.7.2. 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.

14.8.7.3. Manual integration should be minimized by properly maintaining the instrument, updating the retention times, and configuring the peak integration parameters.

14.9. Recommended Instrument Maintenance

14.9.1. Perform the following tasks to remedy the column adsorption problem.

14.9.1.1. Inject an 800-ppb single-component pesticide standard solution to prime (or deactivate) the column.

14.9.1.2. Run one or more solvent blanks consisting of hexane until no carryover is observed prior to analyzing any standards or samples.

14.9.2. Perform the following tasks to eliminate the degradation problem.

14.9.2.1. For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter.

14.9.2.2. Break off the first few centimeters (up to 30 cm) of the injection port side of the column.

14.9.2.3. Check the injector temperature and lower it to 205°C, if necessary.

14.9.2.4. Remove the columns and solvent backflush according to the manufacturer's instructions.

14.9.2.5. If all else fail, it may be necessary to deactivate the metal injector body and/or replace the columns.

14.9.3. Perform the following tasks to rinse the analytical column.

14.9.3.1. Depending on the nature of the residues expected, the first rinse might be reagent water, followed by methanol and acetone, with methylene chloride as the final rinse. In some cases, methylene chloride may be the only solvent necessary.

14.9.3.2. After the final rinse, the analytical column should be filled with methylene chloride and remained flooded overnight to allow materials within the stationary phase to migrate into the solvent.

14.9.3.3. The analytical column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen passing through the column.

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 peaks for target analyte being measured.
C_x = concentration of target analyte being measured in µg/L.

15.2. The percent relative standard deviation is calculated as follows:

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where: %RSD = percent relative standard deviation.
SD = standard deviation of the RFs for the target analyte.
RF_{ave} = mean of the 5 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 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.
$C_{recovered}$ = concentration of target analyte recovered.
C_{added} = concentration of target analyte added.
Note: Concentrations must be in equivalent units.

15.5. 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.

15.6. 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.

15.7. The target analyte concentration for a sample extract is calculated as follows:

$$C_{ex} = \frac{A_x}{RF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in µg/L.
A_x = area of the characteristic peaks for target analyte.
RF_{ave} = mean of the 5 initial RFs for the target analyte.

15.8. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_{ex} \times D}{V_A}$$

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_{ex} = volume of extract in mL.
V_A = volume of aqueous sample solvent extracted in mL.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.9. ►The target analyte concentration for a solid (***or*** oil) sample is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S}$$

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_{ex} = volume of extract in mL.
W_S = mass of solid (***or*** oil) sample solvent extracted in g.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.10. The target analyte concentration for a solid sample on a dry-weight basis is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S \times \left(\frac{C_{ss}}{100}\right)}$$

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_{ex} = volume of extract in mL.
W_S = mass of solid sample solvent extracted in g.
C_{ss} = solids content in %.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.11. The target analyte concentration for a wipe (or filter) sample is calculated as follows:

$$C_W = C_{ex} \times V_{ex} \times D$$

where: C_W = concentration of target analyte in wipe (or filter) sample in µg/sample.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in L.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.12. The target analyte concentration for a mobility-procedure extract is calculated as follows:

$$C_{MP} = \frac{C_{ex} \times V_{ex} \times D}{V_{MP}}$$

where: C_{MP} = concentration of target analyte in mobility-procedure extract in µg/L.
C_{ex} = concentration of target analyte in extract in µg/L.
V_{ex} = volume of extract in mL.
V_{MP} = volume of mobility-procedure extract solvent extracted in mL. Unless specified otherwise, V_{MP} = 100.
D = dilution factor, if the extract was diluted prior to analysis. If no dilution was made, D = 1.

15.13. Refer to the preparatory method(s) for additional calculations.

15.14. All concentrations shall be reported in µg/L (ppb) for aqueous samples, µg/kg (ppb) for oil, soil and solid waste samples, and µg/sample for wipe and filter samples.

15.14.1. 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.

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

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. 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:

18.1.1. If a target analyte is found in the MB but not in the associated samples, report the sample and MB data without qualification.

18.1.2. 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.

18.2. The acceptance criteria for LCS/LCSD compounds are predetermined. The lower and upper acceptance limits for %REC of each LCS/LCSD compound are 50% and 135%, respectively. The RPD is ≤ 25%. All LCS/LCSD compounds must be within acceptance limits (see Section 12.5.3. for additional information).

18.2.1. 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.

18.2.2. ***If an LCS/LCSD pair was analyzed, both the LCS and the LCSD must be reported.***

18.3. The acceptance criteria for surrogate compound recoveries are predetermined. The lower and upper acceptance limits for %REC of each surrogate compound in an aqueous sample are 50% and 135%, respectively. The lower and upper acceptance limits for %REC of each surrogate compound in a non-aqueous sample are 50% and 130%, respectively.

18.3.1. For EPA Region 9 requirement, refer to Section 12.6.2.1.2. for acceptance criteria.

18.3.2. If the surrogate compound recoveries are acceptable, report the surrogate and sample data without qualification.

18.3.3. 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. 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.

18.3.4. By itself, unacceptable surrogate recoveries do not invalidate sample data. The following must be accomplished if surrogate recoveries are not acceptable.

18.3.4.1. Check the surrogate standard solutions for degradation and contamination.

18.3.4.2. If the nonconformance is due to poor instrument performance or if the above actions fail to reveal the cause of the unacceptable surrogate recoveries, the same extract should be re-analyzed.

18.3.4.3. 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.

18.3.4.3.1. If, upon re-processing 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.

18.3.4.3.2. If the MB surrogates are unacceptable, all associated sample data must be invalidated and all associated samples re-processed and re-analyzed.

18.3.5. 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.

18.4. The acceptance criteria for MS/MSD compounds are predetermined. The lower and upper acceptance limits for %REC of each MS/MSD compound are 50% and 135%, respectively. The RPD is ≤ 25%.

18.4.1. For EPA Region 9 requirement, refer to Section 12.6.3.1.2. for acceptance criteria.

18.4.2. 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.

18.4.3. 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.

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, µg/kg (ppb) for oil, soil, and solid waste samples, and µg/sample for wipe and filter 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 ***Director***, Project Manager, ***Quality Control Director,*** 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 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 ***Eurofins*** 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. *Polychlorinated Biphenyls (PCBs) by Gas Chromatography*, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8082, USEPA, Revision 0, 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. *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.

22.7. *Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs)*, SW-846 Method 8081 or 8080, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, December 1999.

23. ►TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Quantitation Peaks for Multiple-Component Target Compounds.

23.2. Appendix B: Additional Quality Control Criteria for Department of Defense Project.

24. MODIFICATIONS

24.1. The following modifications from EPA Method 8082 Revision 0 are noted.

Calscience SOP M407 Section	Reference Document EPA Method 8082 Section	Summary of Modification
All	All	None.

25. ►REVISION HISTORY

Revision	Description	Author(s)	Effective Date
4.0	Section 2: Add tissue matrix. Section 3: Update terminology for RL, and add reference to the determinations of DL and RL. Section 4: Revise the scope to indicate routine analytes. Section 5: Update method summary and EPA method numbers. Section 6: Delete internal standard definition. Add LOD and LOQ definitions. Section 7: Update interferences. Section 8: Update safety information. Section 9: Update the list of equipment and supplies. Section 10: Revise reagent and standard preparations. Section 11: Revise the requirements on collection and preservation. Section 12: Revise quality control criteria. Section 13: Add calibration procedures. Section 14: Update procedures. Section 15: Add references to solvent extraction, mobility extraction, and tissue matrix. Section 18: Update section references, and add EPA Region 9 requirements.	J. Kang / K. Chang	01/28/13

Revision	Description	Author(s)	Effective Date
4.0	Section 22: Update references. Section 23: Update appendices. Section 24: Add modifications. Section 25: Add revision history. Appendix A: Update Aroclor patterns. Appendix B: Update DoD quality control requirements and criteria.	J. Kang / K. Chang	01/28/13
5.1	Entire document: Update company name. Entire document: Remove tissue matrix. Section 5: Update method 3545 extraction solvent. Section 6: Update definitions. Sections 8 and 17: Add SDS. Section 9: Update equipment. Section 10: Add acetone/hexane. Sections 10, 12, 14, 18, and Appendix B: Update LCSD requirement. Sections 19 and 20: Update responsibilities.	L. Hunt	04/13/15

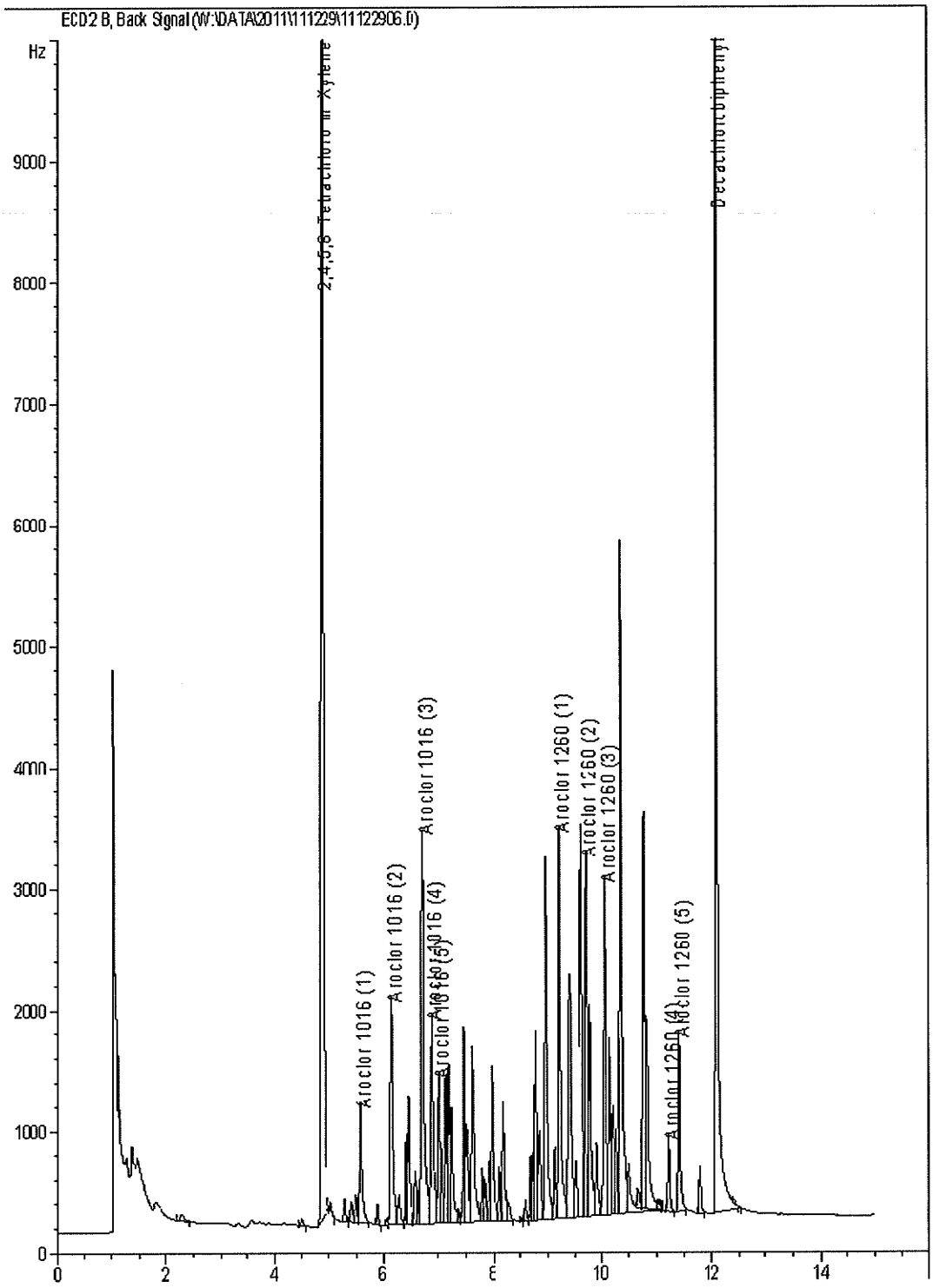
Appendix A

QUANTITATION PEAKS FOR MULTIPLE-COMPONENT TARGET COMPOUNDS

Eurofins Calscience, Inc.

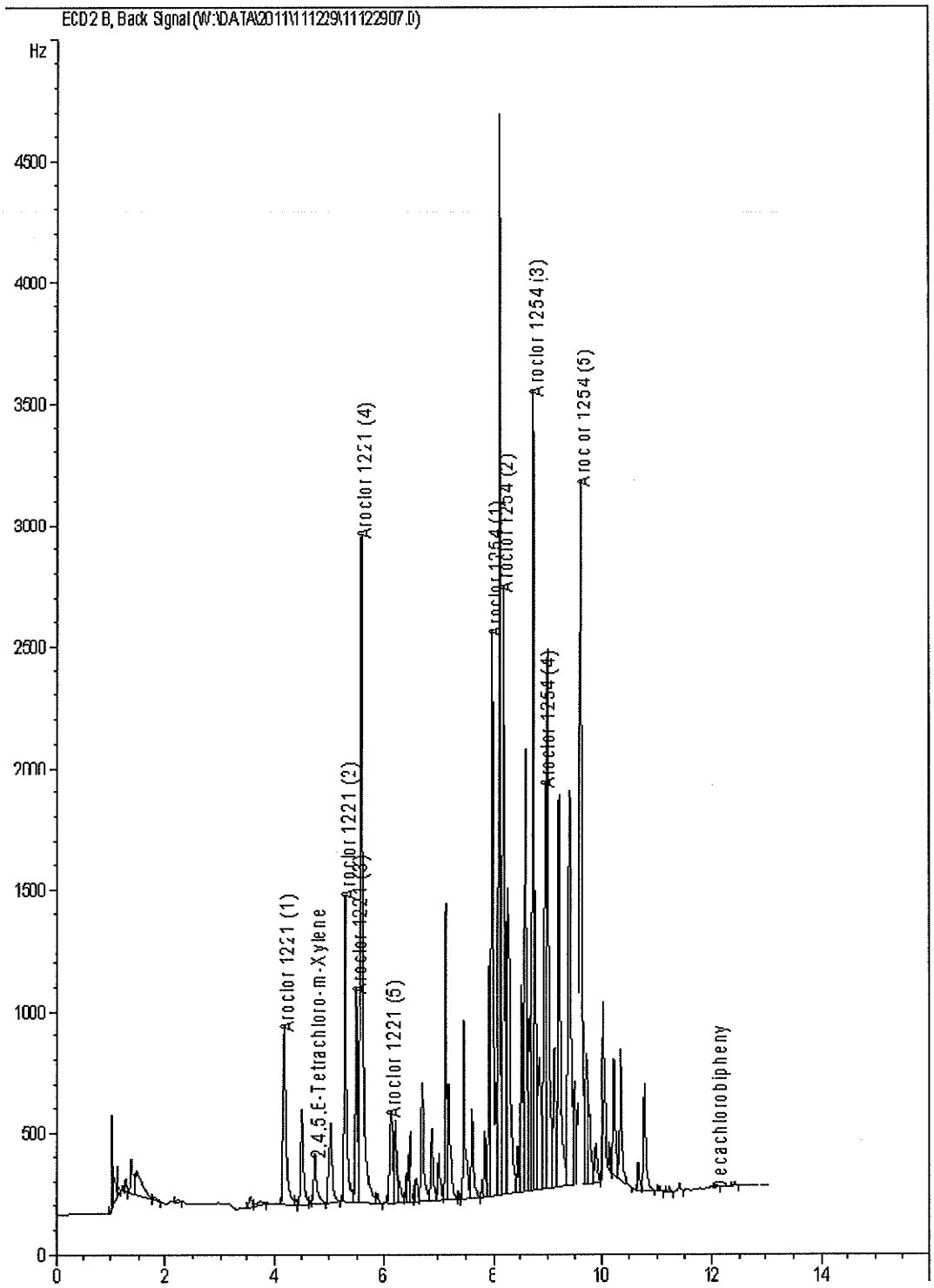
Appendix A

Quantitation Peaks for Aroclor 1016 and Aroclor 1260



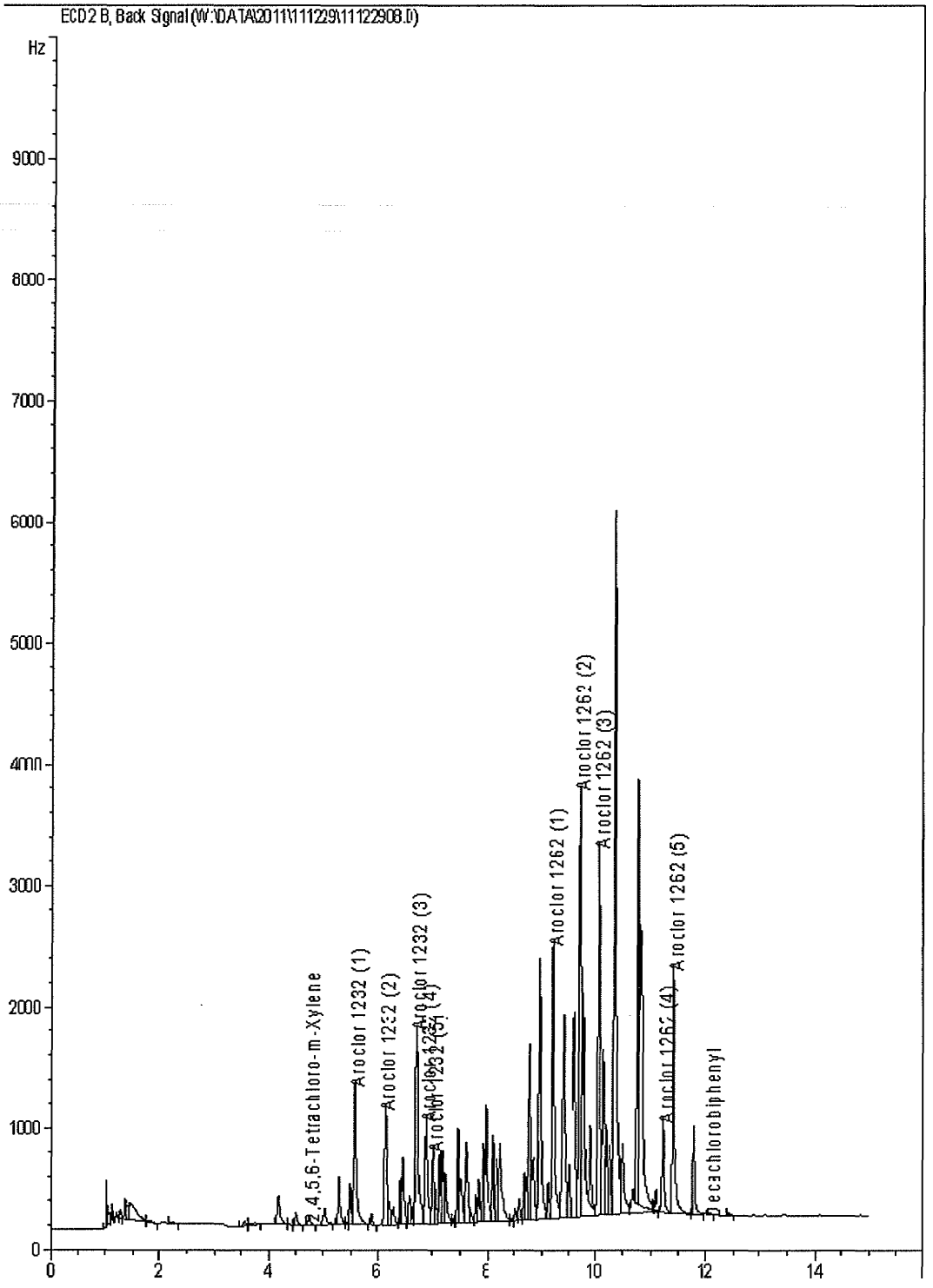
Appendix A

Quantitation Peaks for Aroclor 1221 and Aroclor 1254



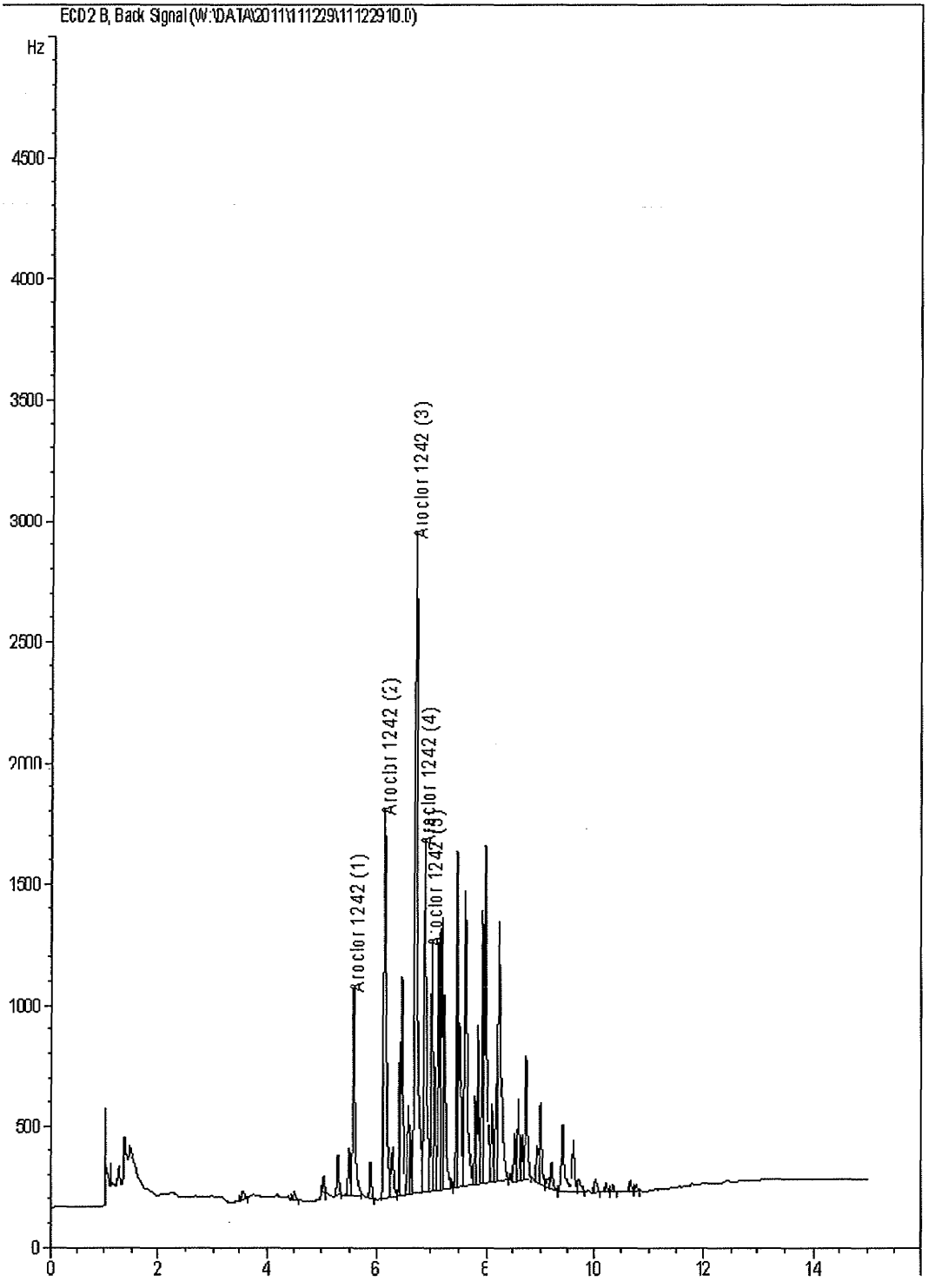
Appendix A

Quantitation Peaks for Aroclor 1232 and Aroclor 1262



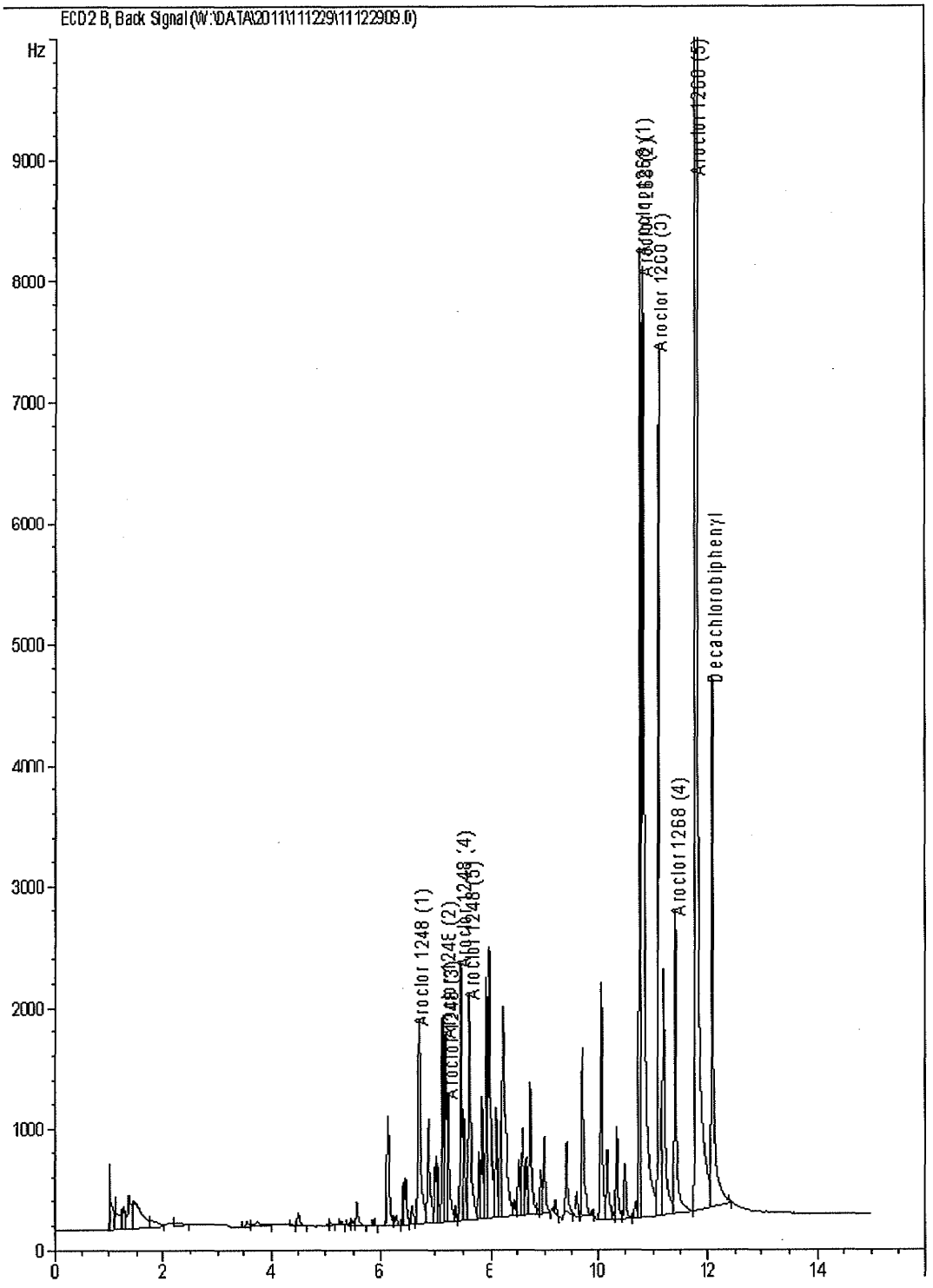
Appendix A

Quantitation Peaks for Aroclor 1242



Appendix A

Quantitation Peaks for Aroclor 1248 and Aroclor 1268



Appendix B

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8082, Polychlorinated Biphenyls (PCBs) as Aroclors by Gas Chromatography – Additional Quality Control Criteria for Department of Defense (DoD) Project.

2. DETECTION / QUANTITATION 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 solution 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. Limit of Detection (LOD)

5.1.1. LOD determination 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. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

5.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

5.1.2.2. LOD 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., second column confirmation, pattern recognition, etc.).

5.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

5.1.2.3. If these criteria are not met, perform either one of the following tasks.

5.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

5.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

5.1.3. No samples shall be analyzed without a valid LOD.

5.2. Limit of Quantitation (LOQ)

5.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

5.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

5.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

5.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

5.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

5.2.2.2. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

5.3. Initial Calibration (IC)

5.3.1. The initial five-point calibration must be established for each Aroclor prior to the processing of sample extracts.

5.3.1.1. Results may not be quantitated using a single point.

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, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

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 the retention time of the analyte/surrogate in the midpoint calibration standard ± 3S.

5.5.1.2. When initial calibration is not performed, daily retention time window for each analyte/surrogate is the retention time of the analyte/surrogate in the low-to-midpoint CCV standard ± 3S.

5.6. Event Based Quality Control (MBs and LCSs)

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, and 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, and 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 LOD.

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.

5.6.2. Laboratory Control Samples (LCSs)

5.6.2.1. The lower and upper acceptance limits for %REC of each LCS/LCSD compound in aqueous and solid matrices are listed below.

Analyte	Aqueous Matrix Control Limit		Solid Matrix Control Limit	
	Lower	Upper	Lower	Upper
Aroclor 1016	25	145	40	140
Aroclor 1260	30	145	60	130

5.6.2.2. 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.

5.6.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

5.6.2.3. All project-specific analytes of concern must be within control limits. If a project-specific analyte of concern exceeds its control limit, determine the cause of the problem and effect corrective action.

5.7. Matrix Based Quality Control (Surrogates and MS/MSDs)

5.7.1. Surrogate

5.7.1.1. The lower and upper acceptance limits for %REC of each surrogate compound in aqueous and solid matrices are listed below.

Analyte	Aqueous Matrix Control Limit		Solid Matrix Control Limit	
	Lower	Upper	Lower	Upper
Decachlorobiphenyl	40	135	60	125

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. Matrix Spikes (MS/MSDs) and Surrogate

5.7.2.1. The lower and upper acceptance limits for %REC of each MS/MSD compound in aqueous and solid matrices are listed below. The RPD is ≤ 30%.

Analyte	Aqueous Matrix Control Limit		Solid Matrix Control Limit	
	Lower	Upper	Lower	Upper
Aroclor 1016	25	145	40	140
Aroclor 1260	30	145	60	130

5.7.2.2. 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.

5.7.2.2.1. Laboratory's in-house control limits may not be greater than ± 3S of the average recovery.

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 field 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) Laboratory Control Sample (LCS)
4) Laboratory Control Sample Duplicate (LCSD), ***when required***
5) Method Blank (MB)
6) Samples (up to 10 per batch, excluding QC check samples and MBs)
7) Matrix Spike (MS)
8) Matrix Spike Duplicate (MSD)
9) Ending CCV

6.2.1. Items 2 and 9: 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, after every batch of 10 field samples or portion thereof within a 12-hour shift, and at the end of sequence.

6.2.2. Item 6: Up to 10 sample (excluding QC check sample and method blank) extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrument is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

6.2.3. 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.

6.2.3.1. The sample selected for spiking must be one of the samples collected for the specific DoD project.

6.2.4. 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).

6.3. Data Interpretation

6.3.1. The flagging criteria and data reporting procedure for second column confirmation are as follows:

6.3.1.1. If RPD is > 40%, apply the appropriate data qualifier (J-flag) and document in the case narrative.

6.3.1.2. Follow project-specific reporting requirements when reporting data.

6.3.1.2.1. If project-specific reporting requirements are unavailable, apply method-specific reporting requirements.

6.3.1.2.2. If method-specific reporting requirements are unavailable, report the results from the primary column or detector, unless there is a scientifically valid and documented reason for not doing so.

6.3.2. Identify unconfirmed results with the appropriate data qualifiers and document in the case narrative.

7. REFERENCES

7.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 25, 2010.

Title : **EPA METHOD 8270C, SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY / MASS SPECTROMETRY (GC/MS)**

Document No. : SOP-M404
Revision No. : 4.9
Supersedes : 4.8

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PROPRIETARY INFORMATION STATEMENT

Revision 4.9 changes are noted in bold italicized typeface and preceded by a "►" marker.

APPROVED FOR RELEASE BY: _____ 03/05/15
MANAGEMENT **DATE**

_____ 03-05-15
QA DEPARTMENT **DATE**

Reviewer Signature	Review Date	Comments	QA Signature

1. METHOD IDENTIFICATION

1.1. EPA Method 8270C, Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS).

2. APPLICABLE MATRICES

2.1. This method is applicable to water/aqueous matrices, soil/solids, oil, sludges and hazardous waste.

3. ►DETECTION / QUANTITATION LIMITS

3.1. The ***reporting limits (RLs)*** for this method are as follows:

Soil/Solid	Water	Oil
0.5 mg/kg (wet-weight)	10 µg/L	50 mg/kg

3.2. The ***RLs*** will be proportionally higher for sample extracts which require dilution or cleanup.

3.3. Operation of the instrument in Selected Ion Monitoring (SIM) mode will allow a lower ***RL*** to be achieved for a specific analyte or suite of analytes. Optimization for a specific analyte or suite of analytes may be accompanied by other extractive or analytical modifications. Reference the appendices for available options and ***RLs***.

3.4. ***Refer to the current revision of SOP-T006, Determination of Detection Limits, for procedures on establishing detection and reporting limits.***

4. SCOPE AND APPLICATION

4.1. EPA Method 8270C is used to determine the concentration of a large number of semi-volatile organic compounds in various matrices. The method can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivitization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. The following compounds may be determined by this method:

Base/Neutral Extractables

acenaphthene	2-chloronaphthalene	fluorene
acenaphthylene	4-chlorophenyl phenyl ether	hexachlorobenzene
anthracene	chrysene	hexachloro-1,3-butadiene
azobenzene	dibenz(a,h)anthracene	hexachlorocyclopentadiene
benzidine	1,2-dichlorobenzene	hexachloroethane
benzo(a)anthracene	1,3-dichlorobenzene	indeno(1,2,3-cd)pyrene
benzo(b)fluoranthene	1,4-dichlorobenzene	isophorone
benzo(k)fluoranthene	3,3'-dichlorobenzidine	naphthalene
benzo(a)pyrene	diethyl phthalate	nitrobenzene
benzo(g,h,i)perylene	dimethyl phthalate	n-nitrosodimethylamine
benzyl butyl phthalate	di-n-butyl phthalate	n-nitrosodiphenylamine
bis(2-chloroethyl)ether	di-n-octyl phthalate	n-nitrosodi-n-propylamine

bis(2-chloroethoxy)methane	2,4-dinitrotoluene	phenanthrene
bis(2-ethylhexyl)phthalate	2,6-dinitrotoluene	pyrene
bis(2-chloroisopropyl)ether	1,2-diphenylhydrazine	1,2,4-trichlorobenzene
4-bromophenyl phenyl ether	fluoranthene	
2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)		

Acid Extractables

4-chloro-3-methylphenol	4,6-dinitro-2-methylphenol	pentachlorophenol
2-chlorophenol	2,4-dinitrophenol	phenol
2,4-dichlorophenol	2-nitrophenol	2,4,6-trichlorophenol
2,4-dimethylphenol	4-nitrophenol	

Hazardous Substances

aniline	dibenzofuran	2-nitroaniline
benzoic acid	2-methylnaphthalene	3-nitroaniline
benzyl alcohol	2-methylphenol	4-nitroaniline
4-chloroaniline	4-methylphenol	2,4,5-trichlorophenol

Others

pyridine	1-methylnaphthalene

Pesticides

aldrin	4,4'-DDE	endrin
α-BHC	4,4'-DDT	endrin aldehyde
β-BHC	4,4'-DDD	heptachlor
γ-BHC (lindane)	dieldrin	heptachlor epoxide
δ-BHC	endosulfan I	methoxychlor
α-chlordane	endosulfan II	toxaphene
γ-chlordane	endosulfan sulfate	

PCBs

aroclor-1016	aroclor-1242	aroclor-1260
aroclor-1221	aroclor-1248	aroclor-1262
aroclor-1232	aroclor-1254	

4.2. 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 8270C determination, either by regulatory reference or validation studies.

4.3. 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 8270C describes chromatographic procedures that will allow for the separation of the semi-volatile organic compounds in the extract and their qualitative and quantitative analysis by mass spectrometry. Detection is achieved using a mass selective detector either in Total Ion Scan (TIC) mode for full list reporting or Selected Ion Monitoring (SIM) mode for lower ***RL*** reporting for selected analytes.

5.2. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory methods include the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Separatory Funnel Liquid-Liquid Extraction	3510C	SOP-M200
Continuous Liquid-Liquid Extraction	3520C	SOP-M201
Soxhlet Extraction	3540C	SOP-M203
Pressurized Fluid Extraction	3545A	SOP-M204
Ultrasonic Extraction	***3550C***	SOP-M202
Waste Dilution	3580A	SOP-M205
TCLP	1311	SOP-M226
SPLP	1312	SOP-M227
STLC (California)	T22.11.5.AII	SOP-M228

5.3. Solid samples are extracted via EPA Methods 3540C or ***3550C*** using methylene chloride, or via EPA Method 3545A using methylene chloride. Liquid samples are extracted via EPA Methods 3510C or 3520C at a neutral pH using methylene chloride. Oil samples are prepared in accordance with EPA Method 3580A using methylene chloride as the diluent. Solid samples for TCLP, SPLP, or STLC analysis are extracted using the appropriate extractant with the leachate then prepared by either separatory funnel or liquid-liquid extraction.

5.4. The extracts that are dirty and dark in color are subjected to Florisil cleanup.

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.

6.3.1. 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, ***unless client-specific QAPP guidance overrides this directive to a lesser time period or the method-specific SOP provides a different time period, but in no case to exceed 24 hours.***

6.3.2. 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. ***Limit of Detection (LOD): The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%.***

6.13. ***Limit of Quantitation (LOQ): The smallest concentration that produces a quantitative result with known and recorded precision and bias.***

6.14. 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.

6.15. 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.

6.16. 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.

6.17. 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.

6.18. 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.

6.19. 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.

6.20. 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.

6.21. 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.

6.22. 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.

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

6.24. 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, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.

6.25. 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.

6.26. 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.

6.27. 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. 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. In addition, sample syringes should be thoroughly rinsed with solvent between sample injections.

7.2. Interference can also occur when "dirty" samples leave residue in the injector or analytical column. To minimize this effect, a guard columns should be used and cut frequently or replaced. Also, the analytical column can be "baked" after such samples.

7.3. Solvents, reagents, glassware, and other sample processing equipment may yield discrete contaminants. This can lead to spurious peaks and/or an elevated baseline, resulting in possible misinterpretation of chromatograms.

7.4. Plastics contain significant amounts of leachable phthalate esters and must not be used during any stage of analytic processing.

7.5. The following provides information regarding possible target analyte losses/interferences during analytic processing:

7.5.1. The base-neutral extraction may cause significantly reduced recoveries of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

7.5.2. Benzidine is subject to oxidative losses during extract concentration and poor chromatographic behavior.

7.5.3. Under the alkaline condition step of sample preparation, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected.

7.5.4. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

7.5.5. Depending upon chromatographic conditions and instrument setup, n-nitrosodimethylamine may be difficult to separate from the solvent.

7.5.6. N-nitrosodiphenylamine decomposes in the GC inlet and cannot be separated from diphenylamine.

7.5.7. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 4-chloroaniline, all nitroanilines, and benzyl alcohol are subject to erratic chromatographic

behavior. This effect is especially pronounced where the system contains high-boiling residue.

7.5.8. Pyridine may perform poorly (degrade) at normal injection port temperatures.

7.6. As a matter of routine prior to injection, all dirty or dark colored sample extracts for GC/MS determination are subjected to column Florisil cleanup. In this procedure, a glass column is packed with Florisil and topped with a water adsorbent. The methylene chloride solvent separates the target analytes from interferants by allowing the target analytes to elute through the column. Meanwhile, the Florisil retains the interferants.

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

8.3. The following compounds covered by this method have been tentatively classified as known or suspected human carcinogens: benzo(a) anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a) pyrene, dibenz(a,h) anthracene, and n-nitroso-dimethylamine. 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.

9. EQUIPMENT AND SUPPLIES

9.1. Gas Chromatograph: Agilent 6890N Gas Chromatograph or equivalent configured with splitless injection port and Agilent 7673/7683 Series Autoinjector and PC based data system.

9.2. Mass Spectrometer: Agilent 5973/5973N Mass Selective Detector (MSD) or equivalent capable of scanning from 35 to 500 amu every one second or less, utilizing a 70-V nominal electron energy in the electron-impact ionization (EI) mode. The MS is directly coupled (capillary direct) to the column via a heated interface.

9.2.1. The MSD must be capable of producing a mass spectrum for DFTPP which meets all of the criteria in Section 12.1.1. when 1 µL of the tuning standard (50 ng of DFTPP) is injected.

9.3. Instrument Software

9.3.1. Requires a PC based data system or equivalent.

9.3.2. Agilent Environmental MSD ChemStation Version E.02 or equivalent.

9.4. Instrument Maintenance and Troubleshooting

9.4.1. Refer to the current revision of SOP-T066 for instrument maintenance and troubleshooting.

9.4.2. Additional information can be found in the user manual or operating guide for the specific instrument.

9.5. Analytical Column: 30-m × 0.25-mm ID, 0.5-µm (or 0.25-µm) film thickness, silicone coated fused-silica capillary column, HP-5 MS or equivalent.

9.6. Carrier Gas: High purity helium.

9.7. 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 N.I.S.T. Traceable Certification.

10. REAGENTS AND STANDARDS

10.1. Reagents

10.1.1. Methylene chloride, CH_2Cl_2, pesticide grade or equivalent.

10.1.2. Acetone, CH_3COCH_3, pesticide grade or equivalent.

10.1.3. Sodium thiosulfate, $Na_2S_2O_3$, 10% (w/v). Prepare the solution by dissolving granular $Na_2S_2O_3$ (reagent grade or equivalent) in reagent water.

10.1.4. Reagent water, interferant free.

10.1.5. Sand, washed, sea or standard Ottawa.

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

10.2. Standards

10.2.1. The tuning standard solution contains 50 ppm each of decafluorotriphenylphosphine (DFTPP), benzidine, pentachlorophenol, and 4,4'-DDT in methylene chloride.

10.2.1.1. Inject 1 µL of the tuning standard for hardware tuning.

10.2.2. Pre-certified stock standard solutions, each in sealed glass ampules, containing 200/2000 ppm of each target analyte, 5000 ppm of each base/neutral surrogate, 10000 ppm of each acid surrogate, and 2000 ppm of each internal standard are used to prepare calibration and check standards.

10.2.3. Calibration standard solutions containing various concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride are used to prepare calibration standards.

10.2.3.1. The calibration standards are prepared as follows:

Analyte		Standard Compound Concentration (ppm)						
base/neutrals		5	10	20	50	80	120	160
acids	2.5*	5/10*	10/20*	20/40*	50/100*	80/160*	120/240*	160/320*
internal standards	40	40	40	40	40	40	40	40
surrogates		5	10	20	50	80	120	160

* 3/4-Methylphenol only.

10.2.3.2. The 10-ppm calibration standard is considered part of the initial multi-point calibration if an analyte yields poor response from the 5-ppm calibration standard.

10.2.3.3. The system performance check compounds (SPCCs) are n-nitrosodi-n-propylamine, hexachlorocyclopentadiene, 2,4-dintrophenol, and 4-nitrophenol.

10.2.3.4. The calibration check compounds (CCCs) are phenol, 1,4-dichlorobenzene, 2-nitrophenol, 2,4-dichlorophenol, hexachlorobutadiene, 4-chloro-3-methylphenol, 2,4,6-trichlorophenol, acenaphthene, n-nitrosodiphenylamine, pentachlorophenol, fluoranthene, di-n-octylphthalate, and benzo(a)pyrene.

10.2.3.5. The 50-, 80-, and 120-ppm standards are also used as the continuing calibration verification solutions.

10.2.4. The initial calibration verification (ICV) solution contains the midpoint concentration of each target analyte, internal standard, check compound, and surrogate in methylene chloride. 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.

10.2.4.1. The ICV solution is prepared as follows:

Analyte	Standard Compound Concentration (ppm)
base/neutrals	80
acids	80/160*
internal standards	40
surrogates	80

* 3/4-Methylphenol only.

10.2.5. The continuing calibration verification (CCV) solutions contain mid-range concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial multi-point calibration.

10.2.5.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppm)
base/neutrals	80
acids	80/160*
internal standards	40
surrogates	80

* 3/4-Methylphenol only.

10.2.5.2. One CCV solution is used daily.

10.2.6. The surrogate standard solution contains 400 ppm each of 2-fluorophenol, phenol-d_6, nitrobenzene-d_5, 2-fluorobiphenyl, 2,4,6-tribromophenol, and p-terphenyl-d_{14} in acetone or methylene chloride.

10.2.6.1. Add 500 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.

10.2.7. The internal standard solution contains 2000 ppm each of 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} in methylene chloride.

10.2.7.1. Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.

10.2.8. The spike standard solution contains 1000 ppm each of phenol, 2-chlorophenol, 1,4-dichlorobenzene, n-nitrosodi-n-propylamine, 1,2,4-trichlorobenzene, naphthalene, 4-chloro-3-methylphenol, dimethyl phthalate, acenaphthylene, acenaphthene, 4-nitrophenol, 2,4-dinitrotoluene, fluorene, pentachlorophenol, pyrene, and benzyl butyl phthalate in acetone or methylene chloride. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

10.2.8.1. This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

10.2.8.2. Add 200 µL of the spike standard to each MS/MSD and LCS/LCSD sample prior to extraction.

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

10.2.10. 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 1-L pre-cleaned amber glass containers with Teflon-lined closures. Soil samples should be collected in 4-oz. pre-cleaned

clear glass wide-mouth jars with Teflon-lined closures. Oil samples should be collected in 40-mL VOA vials with Teflon-lined closures.

11.1.1. Aqueous samples shall be preserved with 4 mL of 10% $Na_2S_2O_3$ solution per 1 L of sample to remove residual chlorine.

11.2. Samples should be maintained in a chilled state (≤ 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 cooler at temperature ≤ 6°C. Aqueous samples must be extracted within seven (7) days of collection. An extraction holding time of 14 days applies to all non-aqueous samples.

11.4. All extracted samples are then stored in freezer at (≤ -10°C) conditions and must be analyzed within a 40-day period post extraction.

12. QUALITY CONTROL

12.1. Hardware Tuning

12.1.1. Prior to running the calibration standards, the GC/MS DFTPP tuning standard must be analyzed and meet the following acceptance criteria:

Mass	Ion Abundance Criteria
51	30 – 60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40 – 60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5 – 9% of mass 198
275	10 – 30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17 – 23% of mass 442

12.1.1.1. The degradation (or percent breakdown) for 4,4'-DDT is ≤ 20%. The formula for calculating %B is listed in Section 15.10.

12.1.1.2. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible.

12.1.2. These criteria must be demonstrated every 12 hours.

12.1.3. If a tune does not meet the acceptance criteria, correct the problem and re-tune the system.

12.1.4. Whenever invasive maintenance of the GC/MS hardware is performed, the system must be re-tuned.

12.2. Initial Calibration (IC)

12.2.1. The initial multi-point calibration must be established prior to the processing of sample extracts.

12.2.2. The IC is deemed valid if the %RSD for each CCC is ≤ 30%, the %RSD for each analyte (except CCC) is ≤ 15%, and the RF_{ave} value for each SPCC is ≥ 0.050.

12.2.3. Where the %RSD for each target analyte is ≤ 15%, the response factor is assumed to be invariant, and the average response factor 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 following conditions are met:

12.2.4.1. The mean of the %RSD values for all analytes in the calibration is ≤ 15%. The mean %RSD is calculated by summing the %RSD value for each analyte and dividing by the total number of analytes.

12.2.4.2. The mean %RSD criterion applies to all analytes in the 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.

12.2.4.3. 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.

12.2.4.4. 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.

12.2.4.4.1. 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.

12.2.8. The relative retention time (RRT) of each target analyte in each calibration standard should agree to within ± 0.06 RRT units.

12.2.8.1. The RRT criterion is not a requirement. However, non-compliance should be considered indicative of a problematic calibration for the affected target analytes.

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

12.2.9.1. 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 RF value for each SPCC is ≥ 0.050.

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 ≤ 50%.

12.3.3. 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). Investigate, effect corrective actions, which may include re-preparation of standard solutions, and recalibrate, if necessary.

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 during analysis.

12.4.2. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%, and the RF value for each SPCC is ≥ 0.050.

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. The %D of each non-CCC is evaluated only per client request or project specific DQOs.

12.4.3.1. 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 ≤ 50%.

12.4.4. The internal standard responses and retention times for the CCV must be evaluated immediately during or after data acquisition.

12.4.4.1. If the retention time for any internal standard changes by more than 30 seconds from the midpoint standard level of the most recent initial calibration, the chromatographic system must be inspected for malfunctions and corrective action must be effected.

12.4.4.2. If the EICP area for any internal standard changes by a factor of two (−50% to +100%) from the midpoint standard level of the most recent initial calibration, the system must be inspected for malfunctions and corrective action effected.

12.4.4.3. Following corrective action, re-analysis of samples analyzed while the system was malfunctioning is required.

12.4.5. 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 or demonstrate acceptable performance with two consecutive CCVs.

12.4.5.1. To demonstrate acceptable performance with two consecutive CCVs, the concentrations of the two CCV standards must be at two different levels within the calibration range. In addition, the concentration of one CCV standard shall be below the mid level.

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.

12.5.2.2. 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. Upper and lower 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
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-extracted and/or 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), surrogates added to each sample, and internal standards added to each sample.

12.6.2. The acceptance criteria for surrogate spike compound recoveries are as follows:

12.6.2.1. The lower and upper acceptance limits for %REC of each surrogate spike compound are based upon the historical average recovery ± 3S that is updated at least annually.

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 such factors as interferences and high analyte concentration or a problem may have occurred during extraction or cleanup. 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.

12.6.2.4. 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 internal standard and surrogate spiking 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 extract should be re-analyzed.

12.6.2.4.3. 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-extracted 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-extracted 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. The internal standard responses (area counts) for all samples including QC check samples and method blanks must be monitored.

12.6.3.2. If the area count of any internal standard in a sample or blank changes by a factor of two (−50% to +100%) from the area count of the corresponding internal standard determined in the daily CCV within the same 12-hour period, corrective action must be taken.

12.6.3.2.1. The samples including QC check samples and method blanks should be re-analyzed, the CCV solution should be checked for proper concentrations and re-analyzed, or the data should be qualified.

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.

12.6.4.2. 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-extracted 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 the analysis of sample or QC extracts, the GC/MS system must be hardware tuned and an acceptable multi-point calibration established. The acceptance criteria for the parameters are listed in Sections 12.1. and 12.2.

13.1.1. 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 no more than 20 scans prior to the elution of DFTPP.

13.1.2. The spectrometer must produce a mass spectrum that meets all criteria when 50 ng of DFTPP is introduced in GC/MS.

13.1.3. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not background-subtract part of the DFTPP peak.

13.1.4. Benzidine and pentachlorophenol should be present at their normal responses and no peak tailing should be present. If the benzidine and/or pentachlorophenol responses are low or peak tailing exists, effect corrective action and retune/recalibrate prior to analyzing any samples. Corrective action may include but not be limited to 1) replacing the injection port liner, 2) cleaning the injection port, or 3) clipping the analytical column.

13.1.5. 4,4'-DDT is included in the tune solution to check for degradation. The acceptance criteria for degradation of 4,4'-DDT to DDE and DDD is less than or equal to 20%. If 4,4'-DDT degradation exceeds 20%, effect corrective action and re-tune the system prior to analyzing any samples. Corrective action may include but not be limited to 1) replacing the injection port liner, 2) cleaning the injection port, or 3) clipping the guard column.

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.

13.2.2. After obtaining an acceptable multi-point calibration curve and prior to processing 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 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. 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
Carrier gas flow rate	1 mL/min at 7.15 psi
Initial temperature	40°C, hold 1.50 min
Temperature program	40°C to 280°C at 22.00°C/min 280°C to 310°C at 5.00°C/min
Final temperature	310°C, hold 6.00 min
Transfer line temperature	285°C
Scan range	35~500 amu

14.1.2. Autoinjector is set to inject 1 µL of sample or QC extract.

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 during analysis. 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 failed CCV is the first of the day, corrective action must be effected prior to analyzing any samples.

14.2.2. If not, effect corrective action and reanalyze all samples since the last acceptable CCV.

14.3. Following extraction by one of the methods specified in Section 5.2., the extracts for the QC and actual environmental samples are received in autoinjector vials. The autoinjector vials are then loaded onto the GC/MS sample tray.

14.4. Sample vials 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)

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. Only the CCCs and SPCCs are monitored for acceptance. An acceptable CCV is required daily prior to sample analysis and every 12 hours thereafter during analysis.

14.4.3. Item 3: 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.

14.4.3.1. For aqueous samples, the LCS consists of the specified compounds spiked into clean reagent water. For solid and oil samples, the LCS consists of the specified compounds spiked into washed sea sand.

14.4.3.2. One LCS is required every day extractions 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 15.6. ***The LCSD is required if MS/MSD are not prepared and analyzed along with field samples.***

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 (i.e., surrogates, internal standards, etc.).

14.4.5.1. For aqueous samples, the MB consists of clean reagent water. For solid and oil samples, the MB consists of washed sea sand.

14.4.5.2. An MB is required every day extractions are performed for every batch of 20 samples per matrix or portion thereof, whichever is more frequent. It should be noted, however, that as necessary (e.g., after high level samples), additional MBs may be placed in the sequence.

14.4.5.3. When samples that are extracted 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 methylene chloride 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.

14.4.6. Item 6: Up to 20 sample extracts per batch. Complex extracts should be sufficiently diluted or subjected to cleanup procedures to ensure that instrumentation is not contaminated. Dilution or cleanup of extracts will result in increased reporting limits.

14.4.7. Item 7: 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.

14.4.7.1. 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 15.5.

14.4.7.2. One MS is required for every batch of 20 samples per matrix or portion thereof extracted concurrently.

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 15.6.

14.5. Ensure that a sufficient amount of methylene chloride is present in the autoinjector solvent rinse bottles and that a sufficient unused volume exists in the autoinjector waste bottles. Specifically, ensure that the solvent rinse bottles are full and waste bottles are empty 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 run log book.

14.7. Initiate the sequence.

14.8. Data Interpretation

14.8.1. Evaluate the area count of each internal standard compound in all samples including QC check samples and method blanks.

14.8.1.1. If the area count of any internal standard in the sample or blank changes by a factor of two (−50% to +100%) from the area count of the corresponding internal standard determined in the daily CCV within the same 12-hour period, corrective action must be taken.

14.8.1.1.1. The samples including QC check samples and method blanks should be re-analyzed, the CCV solution should be checked for proper concentrations and re-analyzed, or the data should be qualified.

14.8.2. The qualitative identification of each analyte 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.

14.8.2.1. The reference mass spectrum should be obtained from the GC/MS within the same 12-hour period as the sample analysis.

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.

14.8.3. Analytes should be identified as present when the following criteria are met:

14.8.3.1. 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.

14.8.3.2. 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 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 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.

14.8.3.5. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component, appropriate selection of analyte spectra and background spectra is important.

14.8.3.6. 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 coelute, the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

14.8.4. 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 with the retention time nearest that of a given analyte.

14.8.4.1. If the %RSD of a target analyte's response factor is ≤ 15%, then the concentration in the extract may be determined using the average response factor (RF_{ave}) from the initial calibration. The formula for calculating %RSD is listed in Section 15.2.

14.8.4.2. 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 below are for the purpose of understanding.

14.8.4.2.1. The concentration of the analyte in an aqueous sample is calculated using the concentration of the analyte in the extract, the volume of the extract, and the volume of the aqueous sample extracted. The formula for calculating the concentration is listed in Section 15.8.

14.8.4.2.2. The concentration of the analyte in a solid or oil sample is calculated using the concentration of the analyte in the extract, the volume of the extract, and the mass of the solid or oil sample extracted. The formula for calculating the concentration is listed in Section 15.9.

14.8.5. Upon request, a library search may be made for the purpose of tentative identification of compounds not associated with the calibration standards. Refer to the reporting procedure outlined in the current revision of SOP-T025.

15. CALCULATIONS

15.1. The response factor is 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.
C_{is} = concentration of the applicable internal standard.
A_{is} = area of the characteristic ion for the applicable internal standard.
C_x = concentration of target analyte being measured.

Note: Concentrations must be in equivalent units.

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 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.

15.6. 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 recovered in measurement 1.
C_2 = concentration of target analyte recovered in measurement 2.

Note: Concentrations must be in equivalent units.

15.7. The target analyte concentration for a sample extract is calculated as follows:

$$C_{ex} = \frac{A_x \times C_{is}}{A_{is} \times RF_{ave}}$$

where: C_{ex} = concentration of target analyte in extract in mg/L.
A_x = area of the characteristic ion for target analyte.
C_{is} = concentration of the applicable internal standard in mg/L.
A_{is} = area of the characteristic ion for the applicable internal standard.
RF_{ave} = mean of the 5 or 6 initial RFs for the target analyte.

15.8. The target analyte concentration for an aqueous sample is calculated as follows:

$$C_A = \frac{C_{ex} \times V_{ex} \times D}{V_A}$$

where: C_A = concentration of target analyte in aqueous sample in µg/L.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = volume of extract in mL.
V_A = volume of aqueous sample extracted in L.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.9. The target analyte concentration for a solid (or oil) sample is calculated as follows:

$$C_S = \frac{C_{ex} \times V_{ex} \times D}{W_S}$$

where: C_S = concentration of target analyte in solid (or oil) sample in mg/kg.
C_{ex} = concentration of target analyte in extract in mg/L.
V_{ex} = volume of extract in mL.
W_S = mass of solid (or oil) sample extracted in g.
D = dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1.

15.10. The percent breakdown is calculated as follows:

$$\%B = \frac{A_{degradation}}{A_{total}} \times 100$$

where: %B = percent breakdown of DDT.
$A_{degradation}$ = total degradation peak areas (see Note 1).
A_{total} = total peak areas (see Note 2).

Note 1: The total degradation peak areas are the areas of DDE and DDD for DDT breakdown.

Note 2: The total peak areas are the areas of DDT, DDD, and DDE for DDT breakdown.

15.11. 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 the applicable internal standard.

15.12. All concentrations shall be reported in µg/L (ppb) for aqueous samples, and mg/kg (ppm) for oil, soil, and solid waste samples.

15.12.1. 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.

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

18. ►DATA ASSESSMENT AND ACCEPTANCE CRITERIA

18.1. The acceptance criteria for LCS compounds vary depending upon historical data. The lower and upper acceptance limits for %REC of each LCS compound are based upon the historical average recovery ± 3S. All LCS compounds must be within acceptance limits (see Section 12.5.2. for additional information).

18.1.1. If the LCS is above 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 ***prepared and analyzed when required by project QAPP or*** 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 surrogate spike compound recoveries vary depending upon historical data. The lower and upper acceptance limits for %REC of each surrogate spike compound are 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 factors such 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/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.

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 aqueous samples, and mg/kg (ppm) 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 ***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: 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 ***Eurofins*** 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. Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS), Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8270C, USEPA, Revision 3, December 1996.

22.2. Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS), Test Methods for Evaluating Solid Waste (SW-846), Pre-promulgation Version, Method 8270D, USEPA, Revision 4, February 2006.

22.3. Determinative Chromatographic Separations, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1B, Method 8000B, USEPA, Revision 2, December 1996.

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, November 2000.

22.7. Organic Analytes, Test Methods for Evaluating Solid Waste (SW-846), Third Edition, Volume 1, Chapter Four, USEPA, Revision 4, November 2000.

22.8. Semivolatile Organic Compounds (SVOCs), SW-846 Method 8270, Region 9 Quality Assurance Data Quality Indicator Tables, USEPA, December 1999.

23. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1. Appendix A: Requirements for Low Level N-Nitrosodimethylamine (NDMA) Determined by EPA 8270C in the Selected Ion Monitoring (SIM) Mode.

23.2. Appendix B: Requirements for Low Level Polynuclear Aromatic Hydrocarbons (PAHs) Determined by EPA 8270C in the Selected Ion Monitoring (SIM) Mode.

23.3. Appendix C: Requirements for Low Level Organochlorine Pesticides and Polychlorinated Biphenyl (PCB) Congeners Determined by EPA 8270C in the Selected Ion Monitoring (SIM) Mode.

23.4. Appendix D: Additional Quality Control Criteria for Department of Defense Project.

23.5. Appendix E: Requirements for Low Level Polynuclear Aromatic Hydrocarbons (PAHs) and Phthalates Determined by EPA 8270C in the Selected Ion Monitoring (SIM) Mode for solid matrices.

24. MODIFICATIONS

Calscience SOP M404 Section	Reference Document EPA Method 8270C Section	Summary of Modification
All	All	None.

25. REVISION HISTORY

Revision	Description	Author(s)	Effective Date
4.8	SOP Updated.	Y. Patel	11/12/12
	Sec.6: LOD / LOQ definations added. Sec.9 Instrument Software and maintenance reference added. Sec.10 Table of ICAL, ICV and CCV replaced. Sec.11 Samples and extract storage requirements corrected as per method. Sec. 12 Alternate calibration options added for ICAL, ICV and CCV Sec. 24 and 25 created. Appendix A, B, C, D & E updated.		
4.9	Entire document: Update company name and replace EQLs with RLs. Section 6: Update definitions. Sections 8 and 17: Add SDSs. Sections 14 and 18 and appendices: Update LCSD requirement.	L. Hunt	03/09/15

Appendix A

REQUIREMENTS FOR LOW LEVEL N-NITROSODIMETHYLAMINE (NDMA) DETERMINED BY EPA 8270C IN THE SELECTED ION MONITORING (SIM) MODE

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. Low level n-nitrosodimethylamine (NDMA) determined by EPA 8270C in the Selected Ion Monitoring (SIM) mode.

2. APPLICABLE MATRICES

2.1. This method is applicable to soil/solid matrices.

3. ►DETECTION / QUANTITATION LIMITS

3.1. The ***reporting limits (RLs)*** for this method are as follows:

Soil/Solid

3 µg/kg

3.2. The ***RLs*** will be proportionally higher for sample extracts which require dilution or cleanup.

4. SAMPLE PREPARATION

4.1. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory method is the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Pressurized Fluid Extraction	3545A	SOP-M204

4.2. The initial sample aliquot mass for soil/solid sample is 20 g.

4.2.1. The final extract volume at the completion of the concentration step is 2 mL.

4.2.2. The resulting preparation factor for soil/solid sample is 10:1.

5. STANDARDS

5.1. Pre-certified stock standard neat compound, in sealed glass ampule, containing 100 mg of NDMA, is used to prepare calibration standards.

5.2. Pre-certified stock standard solutions, each in sealed glass ampules, containing 2000 ppm of NDMA, 2000 ppm of surrogate, and 1000 ppm of internal standard are used to prepare calibration and check standards.

5.3. Calibration standard solutions containing 1000 ppb of NDMA, 5000 ppb of internal standard, and 1000 ppb of surrogate in methylene chloride are used to prepare calibration standards.

5.3.1. The calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppb)				
NDMA	2	10	20	50	100
internal standard	20	20	20	20	20
surrogate	2	10	20	50	100

5.4. The initial calibration verification (ICV) solution contains 20 ppb each of NDMA, internal standard, and surrogate in methylene chloride. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.5. The continuing calibration verification (CCV) solutions contain mid-range concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial multi-point calibration.

5.5.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppb)
NDMA	20
internal standard	20
surrogate	20

5.6. One CCV solution is used daily.

5.7. Surrogate standard solution containing 1000 ppb of 1,4-dichlorobenzene-d_4 in acetone or methylene chloride.

5.7.1. Add 40 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.

5.8. Spike standard solution containing 1000 ppb of NDMA in acetone or methylene chloride.

5.8.1. This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

5.8.2. Add 40 µL of the spike standard to each MS/MSD and LCS/LCSD sample prior to extraction.

5.9. Internal standard solution containing 1000 ppb of n-nitrosodimethylamine-d_6 in methylene chloride.

5.9.1. Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.

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

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

6. SELECTED ION MONITORING (SIM) PARAMETERS

6.1. The MSD will focus on the following selected ions of NDMA.

Analyte	Ions
n-nitrosodimethylamine-d_6	46, 80
n-nitrosodimethylamine	42, 74
1,4-dichlorobenzene-d_4	115, 150, 152

Appendix B

REQUIREMENTS FOR LOW LEVEL POLYNUCLEAR AROMATIC HYDROCARBONS (PAH) DETERMINED BY EPA 8270C IN THE SELECTED ION MONITORING (SIM) MODE

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. Low level polynuclear aromatic hydrocarbons (PAHs) determined by EPA 8270C in the Selected Ion Monitoring (SIM) mode.

2. APPLICABLE MATRICES

2.1. This method is applicable to aqueous and soil/solid matrices.

3. ►DETECTION / QUANTITATION LIMITS

3.1. The ***reporting limits (RLs)*** for this method are as follows:

Soil/Solid	Aqueous
100 µg/kg	1.0 µg/L

3.2. The ***RLs*** will be proportionally higher for sample extracts which require dilution or cleanup.

4. SAMPLE PREPARATION

4.1. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory method is the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Separatory Funnel Liquid-Liquid Extraction	3510C	SOP-M200
Continuous Liquid-Liquid Extraction	3520C	SOP-N201
Pressurized Fluid Extraction	3545A	SOP-M204

4.2. The initial sample aliquot volume for aqueous sample is 1000 mL, and the initial sample aliquot mass for soil/solid sample is 10 g.

4.2.1. The final extract volume at the completion of the concentration step is 2 mL.

4.2.2. The resulting preparation factor is for aqueous sample is 500:1, and for soil/solid sample is 5:1.

5. STANDARDS

5.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing 2000 ppm of each PAH target analyte, 5000 ppm of each base/neutral surrogate, and 2000 ppm of each internal standard are used to prepare calibration and check standards.

5.2. Calibration standard solutions containing 20 ppm of each PAH target analyte, 2000 ppm of each internal standard, 20 ppm of each check compound, and 20 ppm of each surrogate in methylene chloride are used to prepare calibration standards.

5.2.1. The calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppm)				
PAHs	0.1	0.5	1.0	2.0	5.0
internal standards	5.0	5.0	5.0	5.0	5.0
CCCs	0.1	0.5	1.0	2.0	5.0
surrogates	0.1	0.5	1.0	2.0	5.0

5.2.2. The calibration check compounds (CCCs) are acenaphthene, fluoranthene, and benzo(a)pyrene.

5.3. The initial calibration verification (ICV) solution contains 1.0 ppm of each PAH / target analyte, 5.0 ppm of each internal standard, 1.0 ppm of each check compound, and 1.0 ppm of each surrogate in methylene chloride. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.4. The continuing calibration verification (CCV) solutions contain mid-range concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial multi-point calibration.

5.4.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppm)
PAHs	1.0
internal standards	5.0
CCCs	1.0
surrogates	1.0

5.5. One CCV solution is used daily.

5.6. The surrogate standard solution contains 4.0 ppm each of nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14} in acetone or methylene chloride.

5.6.1. Add 500 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.

5.7. Spike standard solution containing 4.0 ppm each of acenaphthene and pyrene in acetone or methylene chloride. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.7.1. This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCS/LCSDs).

5.7.2. Add 500 µL of the spike standard to each MS/MSD and LCS/LCSD sample prior to extraction.

5.8. The internal standard solution contains 250 ppm each of naphthalene-d_8, acenaphthene-d_{10}, chrysene-d_{12}, and perylene-d_{12} in methylene chloride.

5.8.1. Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.

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

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

6. QUALITY CONTROL

6.1. Initial Calibration (IC)

6.1.1. The IC is deemed valid if the %RSD for each CCC is ≤ 30%, and the %RSD for each analyte (except CCC) is ≤ 15%.

6.2. Initial Calibration Verification (ICV)

6.2.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%.

6.3. Continuing Calibration Verification (CCV)

6.3.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%.

7. SELECTED ION MONITORING (SIM) PARAMETERS

7.1. The Mass Selective detector will focus on the following selected ions of the PAHs.

Analyte	Ions	Retention Time Range
1,4-dichlorobenzene-d_4	150, 152, 115	9.54 to 10.14 min
naphthalene-d_8	136, 68, 108	12.28 to 12.88 min
nitrobenzene-d_5	82, 54, 128	10.82 to 11.42 min
naphthalene	128, 129, 127	12.32 to 12.92 min
2-methylnaphthalene	142, 141, 115	13.98 to 14.58 min
1-methylnaphthalene	142, 141, 115	14.23 to 14.83 min
acenaphthene-d_{10}	164, 162, 80	16.71 to 17.31 min
2-fluorobiphenyl	172, 171, 85	15.02 to 15.62 min
acenaphthylene	152, 151, 76	16.28 to 16.88 min
acenaphthene	153, 154, 76	16.79 to 17.39 min
fluorene	166, 165, 82	18.20 to 18.80 min
phenanthrene-d_{10}	188, 94, 80	20.82 to 21.42 min
phenanthrene	178, 89, 76	20.88 to 21.48 min
anthracene	178, 76, 89	21.01 to 21.61 min

Analyte	Ions	Retention Time Range
fluoranthene	202, 203, 101	24.35 to 24.95 min
chrysene-d_{12}	240, 236, 120	28.59 to 29.19 min
pyrene	202, 200, 101	24.97 to 25.57 min
p-terphenyl-d_{14}	244, 122, 212	25.68 to 26.28 min
benzo(a) anthracene	228, 114, 226	28.54 to 29.14 min
chrysene	228, 114, 226	28.65 to 29.25 min
perylene-d_{12}	264, 132, 260	32.48 to 33.08 min
benzo(b) fluoranthene	252, 253, 126	31.53 to 32.13 min
benzo(k) fluoranthene	252, 253, 126	31.59 to 32.19 min
benzo(a) pyrene	252, 253, 126	32.32 to 32.92 min
indeno(1,2,3-c,d) pyrene	276, 138, 277	35.13 to 35.73 min
dibenz(a,h) anthracene	278, 279, 139	35.24 to 35.84 min
benzo(g,h,i) perylene	276, 138, 277	35.83 to 36.43 min

Appendix C

REQUIREMENTS FOR LOW LEVEL ORGANOCHLORINE PESTCIDIES AND POLYCHLORINATED BIPHENYL (PCB) CONGENERS DETERMINED BY EPA 8270C IN THE SELECTED ION MONITORING (SIM) MODE

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8270C, Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) – Determination of Low Level Organochlorine Pesticides and Polychlorinated Biphenyl (PCB) Congeners in Selected Ion Monitoring (SIM) Mode.

2. APPLICABLE MATRICES

2.1. This method is applicable to aqueous and soil/solid matrices.

3. DETECTION / QUANTITATION LIMITS

3.1. The ***reporting limits (RLs)*** for this method are as follows:

Soil/Solid	Aqueous
5 µg/kg	0.1 µg/L

3.2. The ***RLs*** will be proportionally higher for sample extracts which require dilution or cleanup.

4. SAMPLE PREPARATION

4.1. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory method is the following:

Type of Sample Preparation	EPA Method No.	SOP No.
Separatory Funnel Liquid-Liquid Extraction	3510C	SOP-M200
Continuous Liquid-Liquid Extraction	3520C	SOP-M201
Pressurized Fluid Extraction	3545A	SOP-M204

4.2. The initial sample aliquot volume for aqueous sample is 1000 mL, and the initial sample aliquot mass for soil/solid sample is 20 g.

4.2.1. The final extract volume at the completion of the concentration step is 2 mL.

4.2.2. The resulting preparation factor is for aqueous sample is 500:1, and for soil/solid sample is 10:1.

5. STANDARDS

5.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing 20 ppm of each pesticide target analyte, 20 ppm of each PCB congener target analyte, 5000 ppm of each base/neutral surrogate, and 2000 ppm of each internal standard are used to prepare calibration and check standards.

5.2. Calibration standard solutions containing 20 ppm of each pesticide target analyte (2,4'-DDD, 2,4'-DDE, 2,4'-DDT, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, DDMU, and DDNU),

20 ppm of each PCB congener target analyte, 2000 ppm of each internal standard, 20 ppm of each check compound, and 20 ppm of each surrogate in hexane are used to prepare calibration standards.

5.2.1. The calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppm)				
pesticides	0.05	0.5	1.0	2.0	5.0
PCB congeners	0.01	0.05	0.5	1.0	2.0
internal standards	5.0	5.0	5.0	5.0	5.0
surrogates	0.01	0.05	0.5	1.0	2.0

5.2.2. The 1.0-ppm standard is also used as the continuing calibration verification solution.

5.3. The initial calibration verification (ICV) solution contains 1.0 ppm of each pesticide or PCB congener target analyte, 5.0 ppm of each internal standard, and 1.0 ppm of each surrogate in hexane. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.4. The continuing calibration verification (CCV) solutions contain mid-range concentrations of target analytes, internal standards, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial five-point calibration.

5.4.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppm)
pesticides	1.0
PCB congeners	0.5
internal standards	5.0
surrogates	0.5

5.4.2. One CCV solution is used daily.

5.5. Surrogate standard solution containing 4.0 ppm of p-terphenyl-d_{14} in acetone or methylene chloride.

5.5.1. Add 500 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.

5.6. Spike standard solution containing 4.0 ppm of each pesticide or 100 ppm PCB congener in acetone or methylene chloride. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

5.6.1. This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCSs).

5.6.2. Add 10 µL of the spike standard to each MS/MSD and LCS/LCSD sample prior to extraction.

5.7. The internal standard solution for pesticide analysis contains 250 ppm of acenaphthene-d_{10} in methylene chloride. The internal standard solution for PCB congener analysis contains 250 ppm each of phenanthrene-d_{10} and chrysene-d_{12} in methylene chloride.

5.7.1. Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.

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

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

6. QUALITY CONTROL

6.1. Initial Calibration (IC)

6.1.1. The IC is deemed valid if the %RSD for each analyte is ≤ 30%.

6.2. Initial Calibration Verification (ICV)

6.2.1. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%.

6.3. Continuing Calibration Verification (CCV)

6.3.1. The initial calibration is deemed valid if the %D for each pesticide analyte is ≤ 50%, and the %D for each PCB congener analyte is ≤ 20%.

7. SELECTED ION MONITORING (SIM) PARAMETERS

7.1. The Mass Selective detector will focus on the following selected ions of the pesticides.

Analyte	Ions	Retention Time
acenaphthene-d_{10}	164, 162, 80	4.088 min
DDNU	178, 248, 213	6.868 min
2,4'-DDE	246, 318, 176	9.049 min
DDMU	212, 282, 176	9.086 min
4,4'-DDE	246, 318, 176	10.088 min
p-terphenyl-d_{14}	244, 122, 212	10.130 min
2,4'-DDD	235, 165, 199	10.629 min
2,4'-DDT	235, 237, 165	11.488 min
4,4'-DDD	235, 237, 165	12.146 min

7.2. The Mass Selective detector will focus on the following selected ions of the PCB congeners.

Analyte	Congener Number	Ions	Retention Time
phenanthrene-d_{10}		188, 94, 80	9.641 min
2,4'-dichlorobiphenyl	8	222, 152	10.021 min
2,2',5-trichlorobiphenyl	18	256, 186	10.268 min
2,4,4'-trichlorobiphenyl	28	256, 186	10.496 min
2,2',5,5'-tetrachlorobiphenyl	52	292, 220	10.792 min
2,2',4,5'-tetrachlorobiphenyl	49	292, 220	10.815 min
2,2',3,5'-tetrachlorobiphenyl	44	292, 220	11.000 min
3,4,4'-trichlorobiphenyl	37	256, 186	11.114 min
2,4,4',5-tetrachlorobiphenyl	74	292, 220	11.301 min
2,3',4',5-tetrachlorobiphenyl	70	292, 220	11.380 min
2,3',4,4'-tetrachlorobiphenyl	66	292, 220	11.406 min
2,2',4,5,5'-pentachlorobiphenyl	101	326, 254	11.564 min
2,2',4,4',5-pentachlorobiphenyl	99	326, 254	11.604 min
2,3',4,4',6-pentachlorobiphenyl	119	326, 254	11.681 min
2,2',3,4,5'-pentachlorobiphenyl	87	326, 254	11.810 min
p-terphenyl-d_{14}		244, 122, 212	11.819 min
3,4,4',5-tetrachlorobiphenyl	81	292, 220	11.877 min
2,3,3',4',6-pentachlorobiphenyl	110	326, 254	11.913 min
2,2',3,5,5',6-hexachlorobiphenyl	151	360, 290	11.948 min
3,3',4,4'-tetrachlorobiphenyl	77	292, 220	12.000 min
2,2',3,4',5',6-hexachlorobiphenyl	149	360, 290	12.066 min
2,3',4,4',5'-pentachlorobiphenyl	123	326, 254	12.115 min
2,3',4,4',5-pentachlorobiphenyl	118	326, 254	12.150 min
2,3,4,4',5-pentachlorobiphenyl	114	326, 254	12.200 min
2,2',3,4,4',6,6'-heptachlorobiphenyl	184	394, 324	12.206 min
2,2',4,4',5,5'-hexachlorobiphenyl	153	360, 290	12.296 min
2,3',4,4',5',6-hexachlorobiphenyl	168	360, 290	12.330 min
2,3,3',4,4'-pentachlorobiphenyl	105	326, 254	12.387 min
2,2',3,4,4',5'-hexachlorobiphenyl	138	360, 290	12.536 min
2,3,3',4,4',6-hexachlorobiphenyl	158	360, 290	12.558 min
2,2',3,4',5,5',6-heptachlorobiphenyl	187	394, 324	12.632 min
2,2',3,4,4',5',6-heptachlorobiphenyl	183	394, 324	12.672 min
3,3',4,4',5-pentachlorobiphenyl	126	326, 254	12.704 min
2,2',3,3',4,4'-hexachlorobiphenyl	128	360, 290	12.794 min

Analyte	Congener Number	Ions	Retention Time
2,3',4,4',5,5'-hexachlorobiphenyl	167	360, 290	12.824 min
2,2',3,3',4,5',6'-heptachlorobiphenyl	177	394, 324	12.892 min
2,3,3',4,4',5-hexachlorobiphenyl	156	360, 290	13.022 min
2,3,3',4,4',5'-hexachlorobiphenyl	157	360, 290	13.087 min
2,2',3,4,4',5,5'-heptachlorobiphenyl	180	394, 324	13.138 min
chrysene-d_{12}		240, 236, 120	13.253 min
2,2',3,3',4,4',5-heptachlorobiphenyl	170	394, 324	13.433 min
2,2',3,3',4,5',6,6'-octachlorobiphenyl	201	430, 358	13.463 min
3,3',4,4',5,5'-hexachlorobiphenyl	169	360, 290	13.464 min
2,3,3',4,4',5,5'-heptachlorobiphenyl	189	394, 324	13.790 min
2,2',3,3',4,4',5,6-octachlorobiphenyl	195	430, 358	13.828 min
2,2',3,3',4,4',5,5'-octachlorobiphenyl	194	430, 358	14.125 min
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206	464, 196	14.486 min
decachlorobiphenyl	209	428, 358	14.741 min

Appendix D

ADDITIONAL QUALITY CONTROL CRITERIA FOR DEPARTMENT OF DEFENSE PROJECT

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. EPA Method 8270C, Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) – Additional Quality Control Criteria for 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 spike standard solution contains 1000 ppm of each target analyte in acetone or methylene chloride. 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.

3.1.1. The standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCSs).

3.1.2. Add 200 µL of the spike standard to each MS/MSD and LCS sample prior to extraction.

3.1.3. The spike standard solution contains all anticipated target analytes.

3.2. 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.

4. QUALITY CONTROL

4.1. Limit of Detection (LOD)

4.1.1. LOD determination 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.

4.1.2. LOD verification must be performed immediately following an LOD determination and quarterly thereafter to verify method sensitivity.

4.1.2.1. LOD verification sample shall be prepared by spiking an appropriate matrix at approximately 2 to 3 times the detection limit for a single-analyte standard, or greater than 1 to 4 times the detection limit for a multi-analyte standard.

4.1.2.2. LOD 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., second column confirmation, pattern recognition, etc.).

4.1.2.2.1. For data system that does not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least 3 standard deviations greater than the mean method blank concentrations.

4.1.2.3. If these criteria are not met, perform either one of the following tasks.

4.1.2.3.1. Repeat the LOD determination and verification at a higher concentration. Set the LOD at the higher concentration.

4.1.2.3.2. Perform and pass 2 consecutive LOD verifications at a higher concentration. Set the LOD at the higher concentration.

4.1.3. No samples shall be analyzed without a valid LOD.

4.2. Limit of Quantitation (LOQ)

4.2.1. LOQ shall be set at or above the concentration of the lowest initial calibration standard and within the linear dynamic range.

4.2.1.1. The procedure for establishing the LOQ must empirically demonstrate precision and bias at the LOQ.

4.2.1.2. The LOQ and associated precision and bias must meet client requirements and must be reported. If the test method is modified, precision and bias at the new LOQ must be demonstrated and reported.

4.2.2. LOQ verification must be performed quarterly to verify precision and bias at the LOQ.

4.2.2.1. LOQ verification sample shall be prepared by spiking an appropriate matrix at approximately 1 to 2 times the claimed LOQ.

4.2.3. LOQ verification is deemed valid if the recovery of each analyte is within the established test method acceptance criteria or client data objectives for accuracy.

4.3. Tuning

4.3.1. The degradation (or percent breakdown) for 4,4'-DDT is ≤ 20%. The formula for calculating %B is listed in Section 15.10.

4.3.2. Benzidine and pentachlorophenol should be present at their normal responses and should not exceed a tailing factor of 2.

4.4. Initial Calibration

4.4.1. The initial multi-point calibration must be established prior to the processing of sample extracts.

4.4.2. The IC is deemed valid if the %RSD for each CCC is ≤ 30%, the %RSD for each analyte (except CCC) is ≤ 15%, and the RF_{ave} value for each SPCC is ≥ 0.050.

4.4.3. If these criteria are not met ,other calibration options are as follows:

4.4.3.1. 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.

4.4.3.2. The section calibration option is non-linear quadratic least squares regression with equal weighting factor. The IC is deemed valid if the coefficient of determination, r^2, is ≥ 0.99.

4.4.3.2.1. This option requires at least six calibration levels for second order and seven levels for third order.

4.4.4. The relative retention time (RRT) of each target analyte in each calibration standard must be within ± 0.06 RRT units.

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

4.5. Initial Calibration Verification (ICV)

4.5.1. The initial calibration is deemed valid if the %D for each project analyte is ≤ 20%.

4.5.1.1. If the calibration option is average relative response, the %D is the percent difference.

4.5.1.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

4.5.2. 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 actions, which may include re-preparation of standard solutions, and recalibrate, if necessary.

4.6. Continuing Calibration Verification (CCV)

4.6.1. Following the establishment of a valid initial calibration, a CCV standard must be analyzed daily prior to sample analysis and every 12 hours thereafter during analysis.

4.6.2. The initial calibration is deemed valid if the %D for each analyte is ≤ 20%, and the RF value for each SPCC is ≥ 0.050.

4.6.2.1. If the calibration option is average relative response, the %D is the percent difference.

4.6.2.2. If the calibration option is linear or quadratic least squares regression, the %D is the percent drift.

4.7. Retention Time Window

4.7.1. Establishment of retention time window position is accomplished by using the midpoint calibration standard once per initial calibration.

4.7.1.1. Absolute retention time window for each analyte, surrogate, or internal standard is the retention time of the respective analyte, surrogate, or internal standard in the midpoint calibration standard ± 30 seconds.

4.7.1.2. Document the serial number of the analytical column associated with the retention time window.

4.8. Internal Standard Verification

4.8.1. The internal standard responses and retention times for all standards and samples must be evaluated.

4.8.1.1. If the retention time for any internal standard changes by more than 30 seconds from the midpoint standard level of the most recent initial calibration, the chromatographic system must be inspected for malfunctions and corrective action must be effected.

4.8.1.2. If the EICP area for any internal standard changes by a factor of two (−50% to +100%) from the midpoint standard level of the most recent initial calibration, the system must be inspected for malfunctions and corrective action effected.

4.8.1.3. Following corrective action, re-analysis of samples analyzed while the system was malfunctioning is required.

4.8.1.4. If corrective action fails in a sample, the results shall be reported with the appropriate data qualifier (Q-flag) for the specific analyte(s) associated with the failed internal standard.

4.9. Event Based Quality Control (LCSs and MBs)

4.9.1. Laboratory Control Samples (LCSs)

4.9.1.1. The lower and upper acceptance limits for %REC of each LCS compound in aqueous matrix are as follows:

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Polynuclear Aromatics				
2-Methylnaphthalene	45	105	35	115
Acenaphthene	45	110	35	120
Acenaphthylene	50	105	40	115
Anthracene	55	110	45	120
Benzo(a)anthracene	55	110	45	120
Benzo(a)pyrene	55	110	45	120
Benzo(b)fluoranthene	45	120	35	130
Benzo(k)fluoranthene	45	125	30	135
Benzo(g,h,i)perylene	40	125	25	135
Chrysene	55	110	45	120
Dibenzo(a,h)anthracene	40	125	30	140
Fluoranthene	55	115	45	125
Fluorene	50	110	40	120
Indeno(1,2,3-c,d)pyrene	45	125	30	140
Naphthalene	40	100	30	115
Phenanthrene	50	115	40	130
Pyrene	50	130	35	140
Phenolic/Acidic				
2,4,5-Trichlorophenol	50	110	40	120
2,4,6-Trichlorophenol	50	115	40	125
2,4-Dichlorophenol	50	105	40	115
2,4-Dimethylphenol	30	110	15	125
2,4-Dinitrophenol	15	140	10	160
2-Chlorophenol	35	105	25	115
2-Methylphenol	40	110	25	120
2-Nitrophenol	40	115	25	125
3-Methylphenol / 4-Methylphenol	30	110	20	125
4,6-Dinitro-2-methylphenol	40	130	25	145
4-Chloro-3-methylphenol	45	110	35	120
4-Nitrophenol	0	125	0	145
Pentachlorophenol	40	115	25	130
Phenol	0	115	0	135
Benzoic acid	0	125	0	150
Basic				
3,3'-Dichlorobenzidine	20	110	10	125
4-Chloroaniline	15	110	10	125

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Phthalate Esters				
Bis(2-ethylhexyl)phthalate	40	125	30	140
Butyl benzyl phthalate	45	115	35	130
Di-n-butyl phthalate	55	115	45	125
Di-n-octyl phthalate	35	135	20	155
Diethyl phthalate	40	120	30	130
Dimethyl phthalate	25	125	10	145
Nitrosoamines				
N-Nitrosodi-n-propylamine	35	130	20	145
N-Nitrosodimethylamine	25	110	10	125
N-Nitrosodiphenylamine	50	110	35	120
Chlorinated Aliphatics				
Bis(2-chloroethoxy)methane	45	105	35	115
Bis(2-chloroethyl)ether	35	110	25	120
Bis(2-chloroisopropyl)ether	25	130	10	150
Hexachloro-1,3-butadiene	25	105	15	115
Hexachloroethane	30	95	15	105
Halogenated Aromatics				
1,2,4-Trichlorobenzene	35	105	25	120
1,2-Dichlorobenzene	35	100	20	115
1,3-Dichlorobenzene	30	100	20	110
1,4-Dichlorobenzene	30	100	20	110
2-Chloronaphthalene	50	105	40	115
4-Bromophenyl phenyl ether	50	115	40	125
4-Chlorophenyl phenyl ether	50	110	40	120
Hexachlorobenzene	50	110	40	120
Nitroaromatics				
2,4-Dinitrotoluene	50	120	40	130
2,6-Dinitrotoluene	50	115	35	130
2-Nitroaniline	50	115	35	125
3-Nitroaniline	20	125	10	145
4-Nitroaniline	35	120	20	130
Nitrobenzene	45	110	35	120
Neutral Aromatics				
Carbazole	50	115	35	130
Dibenzofuran	55	105	45	115
Others				
1,2-Diphenylhydrazine	55	115	45	120
Benzyl alcohol	30	110	15	125
Isophorone	50	110	40	125

4.9.1.2. The lower and upper acceptance limits for %REC of each LCS compound in solid matrix are as follows:

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Polynuclear Aromatics				
2-Methylnaphthalene	45	105	35	115
Acenaphthene	45	110	35	120
Acenaphthylene	45	105	35	115
Anthracene	55	105	45	115
Benzo(a)anthracene	50	110	40	120
Benzo(a)pyrene	50	110	40	120
Benzo(b)fluoranthene	45	115	35	125
Benzo(k)fluoranthene	45	125	30	135
Benzo(g,h,i)perylene	40	125	25	140
Chrysene	55	110	45	120
Dibenzo(a,h)anthracene	40	125	25	140
Fluoranthene	55	115	45	125
Fluorene	50	110	40	115
Indeno(1,2,3-c,d)pyrene	40	120	25	135
Naphthalene	40	105	30	120
Phenanthrene	50	110	40	120
Pyrene	45	125	35	135
Phenolic/Acidic				
2,4,5-Trichlorophenol	50	110	40	120
2,4,6-Trichlorophenol	45	110	30	120
2,4-Dichlorophenol	45	110	35	120
2,4-Dimethylphenol	30	105	20	115
2,4-Dinitrophenol	15	130	10	150
2-Chlorophenol	45	105	35	115
2-Methylphenol	40	105	30	115
2-Nitrophenol	40	110	30	120
3-Methylphenol / 4-Methylphenol	40	105	30	120
4,6-Dinitro-2-methylphenol	30	135	10	155
4-Chloro-3-methylphenol	45	115	35	125
4-Nitrophenol	15	140	10	160
Pentachlorophenol	25	120	10	135
Phenol	40	100	30	110
Benzoic acid	0	110	0	130
Basic				
3,3'-Dichlorobenzidine	10	130	0	145
4-Chloroaniline	10	95	0	110
Phthalate Esters				
Bis(2-ethylhexyl)phthalate	45	125	35	140
Butyl benzyl phthalate	50	125	35	135
Di-n-butyl phthalate	55	110	45	120
Di-n-octyl phthalate	40	130	25	145
Diethyl phthalate	50	115	40	125
Dimethyl phthalate	50	110	40	120
Nitrosoamines				
N-Nitrosodi-n-propylamine	40	115	30	125
N-Nitrosodimethylamine	20	115	10	130

Analyte	Control Limit		ME Limit	
	Lower	Upper	Lower	Upper
Nitrosoamines				
N-Nitrosodiphenylamine	50	115	40	125
Chlorinated Aliphatics				
Bis(2-chloroethoxy)methane	45	110	30	120
Bis(2-chloroethyl)ether	40	105	25	115
Bis(2-chloroisopropyl)ether	20	115	10	130
Hexachloro-1,3-butadiene	40	115	25	130
Hexachloroethane	35	110	20	120
Halogenated Aromatics				
1,2,4-Trichlorobenzene	45	110	30	120
1,2-Dichlorobenzene	45	95	35	105
1,3-Dichlorobenzene	40	100	30	110
1,4-Dichlorobenzene	35	105	25	115
2-Chloronaphthalene	45	105	35	115
4-Bromophenyl phenyl ether	45	115	35	130
4-Chlorophenyl phenyl ether	45	110	35	120
Hexachlorobenzene	45	120	35	130
Nitroaromatics				
2,4-Dinitrotoluene	50	115	35	130
2,6-Dinitrotoluene	50	110	35	125
2-Nitroaniline	45	120	30	130
3-Nitroaniline	25	110	15	125
4-Nitroaniline	35	115	20	125
Nitrobenzene	40	115	30	125
Neutral Aromatics				
Carbazole	45	115	30	130
Dibenzofuran	50	105	40	110
Others				
Benzyl alcohol	20	125	10	140
Isophorone	45	110	30	125

4.9.2. Method Blanks (MBs)

4.9.2.1. The concentration of a target analyte in an MB should be ≤ ½ RL. The concentrations of common laboratory contaminants should be < RL.

4.9.2.2. If these criteria are not met, investigate and eliminate the source of contamination.

4.9.2.3. Determine whether to reprocess the samples associated with the failed MB based on the following checks:

4.9.2.3.1. 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.

4.9.2.3.2. The blank contamination affects the sample results as per the test method requirements or the individual project data quality objectives.

4.9.2.4. Any sample that meets either one or both of the checks described in Section 4.6.2.3. shall be reprocessed in a subsequent preparatory batch, except when the sample analysis resulted in a non-detect.

4.9.2.4.1. 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.

4.10. Matrix Based Quality Control (Surrogates and MS/MSDs)

4.10.1. Surrogates

4.10.1.1. The lower and upper acceptance limits for %REC of each surrogate spike compound in aqueous matrix are as follows:

Analyte	Control Limit	
	Lower	Upper
2-Fluorobiphenyl	50	110
Terphenyl-d_{14}	50	135
2,4,6-Tribromophenol	40	125
2-Fluorophenol	20	110
Phenol-d_5 / Phenol-d_6	10	115
Nitrobenzene-d_5	40	110

4.10.1.2. The lower and upper acceptance limits for %REC of each surrogate spike compound in solid matrix are as follows:

Analyte	Control Limit	
	Lower	Upper
2-Fluorobiphenyl	45	105
Terphenyl-d_{14}	30	125
2,4,6-Tribromophenol	35	125
2-Fluorophenol	35	105
Phenol-d_5 / Phenol-d_6	40	100
Nitrobenzene-d_5	35	100

4.10.2. Matrix Spikes (MS/MSDs)

4.10.2.1. The lower and upper acceptance limits for %REC of each MS/MSD compound in aqueous matrix are as follows:

Analyte	Control Limit	
	Lower	Upper
Polynuclear Aromatics		
2-Methylnaphthalene	45	105
Acenaphthene	45	110
Acenaphthylene	50	105
Anthracene	55	110
Benzo(a)anthracene	55	110
Benzo(a)pyrene	55	110
Benzo(b)fluoranthene	45	120
Benzo(k)fluoranthene	45	125
Benzo(g,h,i)perylene	40	125
Chrysene	55	110
Dibenzo(a,h)anthracene	40	125
Fluoranthene	55	115
Fluorene	50	110
Indeno(1,2,3-c,d)pyrene	45	125
Naphthalene	40	100
Phenanthrene	50	115
Pyrene	50	130
Phenolic/Acidic		
2,4,5-Trichlorophenol	50	110
2,4,6-Trichlorophenol	50	115
2,4-Dichlorophenol	50	105
2,4-Dimethylphenol	30	110
2,4-Dinitrophenol	15	140
2-Chlorophenol	35	105
2-Methylphenol	40	110
2-Nitrophenol	40	115
3-Methylphenol / 4-Methylphenol	30	110
4,6-Dinitro-2-methylphenol	40	130
4-Chloro-3-methylphenol	45	110
4-Nitrophenol	0	125
Pentachlorophenol	40	115
Phenol	0	115
Benzoic acid	0	125
Basic		
3,3'-Dichlorobenzidine	20	110
4-Chloroaniline	15	110
Phthalate Esters		
Bis(2-ethylhexyl)phthalate	40	125
Butyl benzyl phthalate	45	115
Di-n-butyl phthalate	55	115
Di-n-octyl phthalate	35	135
Diethyl phthalate	40	120
Dimethyl phthalate	25	125
Nitrosoamines		
N-Nitrosodi-n-propylamine	35	130
N-Nitrosodimethylamine	25	110

Analyte	Control Limit	
	Lower	Upper
Nitrosoamines		
N-Nitrosodiphenylamine	50	110
Chlorinated Aliphatics		
Bis(2-chloroethoxy)methane	45	105
Bis(2-chloroethyl)ether	35	110
Bis(2-chloroisopropyl)ether	25	130
Hexachloro-1,3-butadiene	25	105
Hexachloroethane	30	95
Halogenated Aromatics		
1,2,4-Trichlorobenzene	35	105
1,2-Dichlorobenzene	35	100
1,3-Dichlorobenzene	30	100
1,4-Dichlorobenzene	30	100
2-Chloronaphthalene	50	105
4-Bromophenyl phenyl ether	50	115
4-Chlorophenyl phenyl ether	50	110
Hexachlorobenzene	50	110
Nitroaromatics		
2,4-Dinitrotoluene	50	120
2,6-Dinitrotoluene	50	115
2-Nitroaniline	50	115
3-Nitroaniline	20	125
4-Nitroaniline	35	120
Nitrobenzene	45	110
Neutral Aromatics		
Carbazole	50	115
Dibenzofuran	55	105
Others		
1,2-Diphenylhydrazine	55	115
Benzyl alcohol	30	110
Isophorone	50	110

4.10.2.2. The lower and upper acceptance limits for %REC of each MS/MSD compound in solid matrix are as follows:

Analyte	Control Limit	
	Lower	Upper
Polynuclear Aromatics		
2-Methylnaphthalene	45	105
Acenaphthene	45	110
Acenaphthylene	45	105
Anthracene	55	105
Benzo(a)anthracene	50	110
Benzo(a)pyrene	50	110
Benzo(b)fluoranthene	45	115
Benzo(k)fluoranthene	45	125
Benzo(g,h,i)perylene	40	125

Analyte	Control Limit	
	Lower	Upper
Polynuclear Aromatics		
Chrysene	55	110
Dibenzo(a,h)anthracene	40	125
Fluoranthene	55	115
Fluorene	50	110
Indeno(1,2,3-c,d)pyrene	40	120
Naphthalene	40	105
Phenanthrene	50	110
Pyrene	45	125
Phenolic/Acidic		
2,4,5-Trichlorophenol	50	110
2,4,6-Trichlorophenol	45	110
2,4-Dichlorophenol	45	110
2,4-Dimethylphenol	30	105
2,4-Dinitrophenol	15	130
2-Chlorophenol	45	105
2-Methylphenol	40	105
2-Nitrophenol	40	110
3-Methylphenol / 4-Methylphenol	40	105
4,6-Dinitro-2-methylphenol	30	135
4-Chloro-3-methylphenol	45	115
4-Nitrophenol	15	140
Pentachlorophenol	25	120
Phenol	40	100
Benzoic acid	0	110
Basic		
3,3'-Dichlorobenzidine	10	130
4-Chloroaniline	10	95
Phthalate Esters		
Bis(2-ethylhexyl)phthalate	45	125
Butyl benzyl phthalate	50	125
Di-n-butyl phthalate	55	110
Di-n-octyl phthalate	40	130
Diethyl phthalate	50	115
Dimethyl phthalate	50	110
Nitrosoamines		
N-Nitrosodi-n-propylamine	40	115
N-Nitrosodimethylamine	20	115
N-Nitrosodiphenylamine	50	115
Chlorinated Aliphatics		
Bis(2-chloroethoxy)methane	45	110
Bis(2-chloroethyl)ether	40	105
Bis(2-chloroisopropyl)ether	20	115
Hexachloro-1,3-butadiene	40	115
Hexachloroethane	35	110
Halogenated Aromatics		
1,2,4-Trichlorobenzene	45	110

Analyte	Control Limit	
	Lower	Upper
Halogenated Aromatics		
1,2-Dichlorobenzene	45	95
1,3-Dichlorobenzene	40	100
1,4-Dichlorobenzene	35	105
2-Chloronaphthalene	45	105
4-Bromophenyl phenyl ether	45	115
4-Chlorophenyl phenyl ether	45	110
Hexachlorobenzene	45	120
Nitroaromatics		
2,4-Dinitrotoluene	50	115
2,6-Dinitrotoluene	50	110
2-Nitroaniline	45	120
3-Nitroaniline	25	110
4-Nitroaniline	35	115
Nitrobenzene	40	115
Neutral Aromatics		
Carbazole	45	115
Dibenzofuran	50	105
Others		
Benzyl alcohol	20	125
Isophorone	45	110

4.10.2.3. The RPD between the MS/MSD compounds is ≤ 30%.

5. REFERENCES

5.1. Department of Defense Quality Systems Manuals for Environmental Laboratories, Version 4.2, October 25, 2010.

Appendix E

REQUIREMENTS FOR LOW LEVEL POLYNUCLEAR AROMATIC HYDROCARBONS (PAH) AND PTHTHALATES DETERMINED BY EPA 8270C IN THE SELECTED ION MONITORING (SIM) MODE FOR SOLID MATRICES

Eurofins Calscience, Inc.

1. METHOD IDENTIFICATION

1.1. Low level polynuclear aromatic hydrocarbons (PAHs) and Phthalates determined by EPA 8270C in the Selected Ion Monitoring (SIM) mode for solid matrices.

2. APPLICABLE MATRICES

2.1. This method is applicable to soil/solid matrices.

3. DETECTION / QUANTITATION LIMITS

3.1. The ***reporting limits (RLs)*** for this method are as follows:

Soil/Solids

2–10 µg/kg

3.2. The ***RLs*** will be proportionally higher for sample extracts which require dilution or cleanup.

4. SAMPLE PREPARATION

4.1. Prior to performing this procedure, the appropriate sample preparation technique must be performed on each sample. Acceptable preparatory method is the following:

4.2.

Type of Sample Preparation	EPA Method No.	SOP No.
Pressurized Fluid Extraction	3545A	SOP-M204

4.3. The initial sample aliquot mass for soil/solid sample is 100 g.

4.3.1. The final extract volume at the completion of the concentration step is 2 mL.

4.3.2. The resulting preparation factor for soil/solid sample is 50:1.

5. PROCEDURE MODIFICATIONS FOR LOW LEVEL REPORTING IN SOLID MATRICES

5.1. Sample Preparation

5.1.1. Utilizing SOP M204 "EPA Method 3545, Pressurized Fluid Extraction (PFE)" the sample weight and final extract volume are modified as follows:

5.1.2. Sample weight: Increased from 20 g to 100g

5.1.3. Final extract volume: No change, remains 2 mL.

6. STANDARDS

6.1. Pre-certified stock standard solutions, each in sealed glass ampules, containing 2000 ppm of each PAH / phthalate target analyte, 5000 ppm of each base/neutral surrogate, and 2000 ppm of each internal standard are used to prepare calibration and check standards.

6.2. Calibration standard solutions containing 200 ppm of each PAH / phthalate target analyte, 2000 ppm of each internal standard and 200 ppm of each surrogate in methylene chloride are used to prepare calibration standards.

6.2.1. The calibration standards are prepared as follows:

Analyte	Standard Compound Concentration (ppm)						
PAHs / Phthalates	0.1	0.5	5.0	8.0	10.0	15.0	20.0
internal standards	5.0	5.0	5.0	5.0	5.0	5.0	5.0
CCCs	0.1	0.5	5.0	8.0	10.0	15.0	20.0
surrogates	0.1	0.5	5.0	8.0	10.0	15.0	20.0

6.2.2. The calibration check compounds (CCCs) are acenaphthene, fluoranthene, benzo(a)pyrene, and di-n-octyl phthalate.

6.3. The initial calibration verification (ICV) solution contains 10 ppm of each PAH / phthalate target analyte, 5.0 ppm of each internal standard, 10 ppm of each check compound, and 10 ppm of each surrogate in methylene chloride. The ICV solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

6.4. The continuing calibration verification (CCV) solutions contain mid-range concentrations of target analytes, internal standards, check compounds, and surrogates in methylene chloride. The CCV solutions are of a source same as that used for the initial multi-point calibration.

6.4.1. The CCV solutions are prepared as follows:

Analyte	Standard Compound Concentration (ppm)
PAHs / Phthalates	10.0
internal standards	5.0
CCCs	10.0
surrogates	10.0

6.5. One CCV solution is used daily.

6.6. The surrogate standard solution contains 400 ppm each of nitrobenzene-d_5, 2-fluorobiphenyl and p-terphenyl-d_{14} in acetone or methylene chloride.

6.6.1. Add 50 µL of the surrogate standard to each sample including the quality control (QC) check samples and method blanks prior to extraction.

6.7. The spike standard solution contains 200 ppm each of PAHs and phthalates in acetone or methylene chloride. The spike standard solution must be of a source differing from that used for the initial five-point calibration. If it is of the same source, then it must be of different lot.

6.7.1. This standard is used to prepare QC check samples such as matrix spikes (MS/MSDs) and laboratory control samples (LCSs).

6.7.2. Add 100 µL of the spike standard to each MS/MSD and LCS sample prior to extraction.

6.8. The internal standard solution contains 250 ppm each of naphthalene-d_8, acenaphthene-d_{10}, chrysene-d_{12}, phenanthrene-d_{10} and perylene-d_{12} in methylene chloride.

6.8.1. Add 10 µL of internal standard solution per 0.5 mL of sample extract including the QC check sample and method blank extracts at the completion of the concentration step.

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

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

7. QUALITY CONTROL

7.1. Initial Calibration (IC)

7.1.1. The IC is deemed valid if the %RSD for each CCC is ≤ 30%, and the %RSD for each analyte (except CCC) is ≤ 15%.

7.2. Initial Calibration Verification (ICV)

7.2.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%.

7.3. Continuing Calibration Verification (CCV)

7.3.1. The initial calibration is deemed valid if the %D for each CCC is ≤ 20%.

8. SELECTED ION MONITORING (SIM) PARAMETERS

8.1. The Mass Selective detector will focus on the following selected ions of the PAHs and Phthalates.

Analyte	Ions	Retention Time Range (min)
naphthalene-d_8	136,68	6.11 to 6.45
nitrobenzene-d_5	82, 54,128	5.38 to 5.49
naphthalene	128, 129, 127	6.09 to 6.49
2-methylnaphthalene	142, 141	6.92 to 7.12
1-methylnaphthalene	142, 141	7.04 to 7.37
acenaphthene-d_{10}	164, 162, 160	8.01 to 8.39
2-fluorobiphenyl	172, 171	7.29 to 7.62
acenaphthylene	152, 151, 153	7.86 to 8.18
acenaphthene	153, 154, 152	8.12 to 8.35
fluorene	166, 165, 167	8.59 to 8.99
phenanthrene-d_{10}	188, 94, 80	9.69 to 9.95
phenanthrene	178, 176, 179	9.69 to9.91
anthracene	178, 176, 179	9.82 to 10.05
fluoranthene	202, 203, 101	11.01 to 11.34
chrysene-d_{12}	240, 236, 120	12.70 to 13.02
pyrene	202, 200, 203	11.25 to 11.60
p-terphenyl-d_{14}	244, 122, 212	11.95 to 11.76
benzo(a) anthracene	228, 229, 226	12.64 to 12.86
chrysene	228, 229, 226	12.79 to 13.11
perylene-d_{12}	264, 265, 260	14.78 to 15.38
benzo(b) fluoranthene	252, 253, 125	14.27 to 14.99
benzo(k) fluoranthene	252, 253, 125	14.41 to 14.61
benzo(a) pyrene	252, 253, 125	14.84 to 15.16
indeno(1,2,3-c,d) pyrene	276, 138, 277	17.02 to 17.19
dibenz(a,h) anthracene	278, 279, 139	16.99 to 17.35
benzo(g,h,i) perylene	276, 138, 277	17.50 to 17.84
Dimethyl phthalate	163, 164, 194	7.79 to 8.13
Diethy phthalate	149, 177, 150	8.60 to 8.85
di-n-butyl phthalate	149, 150, 104	10.34 to 10.71
Butyl benzyl phthalate	149, 91, 206	12.02 to 12.34
bis(2-Ethyl hexyl) phthalate	149, 279, 167	12.79 to 13.15
di-n-octyl phthalate	149, 279, 150	13.70 to 14.04

APPENDIX B

Field Activity Forms, Sample Forms, and Labels

Daily Field Report

Client Name

Job/Site Name

Location

Project number

Date

Notes:

CLIENT/SOURCE	☐GRAB ☐COMPOSITE OTHER:
SITE NAME	DATE
SAMPLE #	TIME
ANALYSIS	PRESERVATIVE
	COLL. BY

CLIENT/SOURCE	☐GRAB ☐COMPOSITE OTHER:
SITE NAME	DATE
SAMPLE #	TIME
ANALYSIS	PRESERVATIVE
	COLL. BY

CLIENT/SOURCE	☐GRAB ☐COMPOSITE OTHER:
SITE NAME	DATE
SAMPLE #	TIME
ANALYSIS	PRESERVATIVE
	COLL. BY

ENVIRONMENTAL SAMPLING SUPPLY

LOT#

SAMPLE ID

SAMPLED BY	DATE
	TIME
LOCATION	PRESERVATIVE
ANALYSIS	CLIENT

Oakland, CA • Houston, TX • Chicago, IL • Richmond, VA
(510) 562-4988 www.essvial.com (800) 233-8425

ENVIRONMENTAL SAMPLING SUPPLY

LOT#

SAMPLE ID

SAMPLED BY	DATE
	TIME
LOCATION	PRESERVATIVE
ANALYSIS	CLIENT

Oakland, CA • Houston, TX • Chicago, IL • Richmond, VA
(510) 562-4988 www.essvial.com (800) 233-8425

CUSTODY SEAL

ENVIRONMENTAL SAMPLING SUPPLY
9601 San Leandro St. Oakland, CA 800-233-8425

Date: _____

Signature: _____

PEEL HERE

Environmental Analysis Request/Chain of Custody

eurofins | Lancaster Laboratories Environmental

Acct. # _____ Group # _____ Sample # _____

Client:					Matrix				Analyses Requested										For Lab Use Only
Project Name/#:	Site ID #:				☐ Sediment	☐ Ground	☐ Surface		Preservation Codes										SF #: _____
Project Manager:	P.O. #:					☐ Potable	☐ NPDES												SCR #: _____
Sampler:	PWSID #:				☐ Soil	Water		Other:	Total # of Containers										Preservation Codes: H = HCl; T = Thiosulfate; N = HNO_3; B = NaOH; S = H_2SO_4; P = H_3PO_4; O = Other
Phone #:	Quote #:																		
State where sample(s) were collected:																			
Sample Identification	**Collection** Date	Time	Grab	Composite															**Remarks**

Turnaround Time Requested (TAT) (please check): Standard ☐ Rush ☐ (Rush TAT is subject to laboratory approval and surcharges.)	Relinquished by:	Date	Time	Received by:	Date	Time
Date results are needed:	Relinquished by:	Date	Time	Received by:	Date	Time
Rush results requested by (please check): E-Mail ☐ Phone ☐	Relinquished by:	Date	Time	Received by:	Date	Time
E-mail Address:						
Phone:	Relinquished by:	Date	Time	Received by:	Date	Time
Data Package Options (please check if required)	Relinquished by:	Date	Time	Received by:	Date	Time
Type I (Validation/non-CLP) ☐ MA MCP ☐						
Type III (Reduced non-CLP) ☐ CT RCP ☐	Relinquished by Commercial Carrier:			Temperature upon receipt _____ °C		
Type IV (CLP SOW) ☐ TX TRRP-13 ☐						
Type VI (Raw Data Only) ☐	UPS _____ FedEx _____ Other _____					
EDD Required? Yes ☐ No ☐ If yes, format: _____						

McCampbell Analytical, Inc.

1534 Willow Pass Rd. / Pittsburg, Ca. 94565-1701
www.mccampbell.com / main@mccampbell.com
Telephone: (877) 252-9262 / Fax: (925) 252-9269

CHAIN OF CUSTODY RECORD

TURN AROUND TIME: RUSH ☐ 1 DAY ☐ 2 DAY ☐ 3 DAY ☐ 5 DAY ☐

GeoTracker EDF ☐ PDF ☐ EDD ☐ Write On (DW) ☐ EQuIS ☐ 10 DAY ☐

Effluent Sample Requiring "J" flag ☐ **UST Clean Up Fund Project** ☐ **; Claim #**_____

Report To: **Bill To:**

Company:

Tele: ( ) **E-Mail:**

Project #: **Project Name:**

Project Location: **Purchase Order#**

Sampler Signature:

SAMPLE ID	Location/ Field Point Name	SAMPLING		# Containers	MATRIX								METHOD PRESERVED			Analysis Request																			
		Date	Time		Ground Water	Waste Water	Drinking Water	Sea Water	Soil	Air	Sludge	Other	HCL	HNO_3	Other	BTEX & TPH as Gas (8021/ 8015) MTBE	TPH as Diesel (8015)	Total Petroleum Oil & Grease (1664 / 5520 E/B&F)	Total Petroleum Hydrocarbons (418.1)	EPA 505/ 608 / 8081 (Cl Pesticides)	EPA 608 / 8082 PCB's ; Aroclors / Congeners	EPA 507 / 8141 (NP Pesticides)	EPA 515 / 8151 (Acidic Cl Herbicides)	EPA 524.2 / 624 / 8260 (VOCs)	EPA 525.2 / 625 / 8270 (SVOCs)	EPA 8270 SIM / 8310 (PAHs / PNAs)	CAM 17 Metals (200.8 / 6020)***	LUFT 5 Metals (200.8 / 6020)***	Metals (200.8 / 6020)***	Lab to Filter sample for Dissolved metals analysis					

****MAI clients MUST disclose any dangerous chemicals known to be present in their submitted samples in concentrations that may cause immediate harm or serious future health endangerment as a result of brief, gloved, open air, sample handling by MAI staff. Non-disclosure incurs an immediate $250 surcharge and the client is subject to full legal liability for harm suffered. Thank you for your understanding and for allowing us to work safely.**

***** If metals are requested for water samples and the water type is not specified on the chain of custody, then MAI will default to metals by E200.8.**

Relinquished By:	Date:	Time:	Received By:
Relinquished By:	Date:	Time:	Received By:
Relinquished By:	Date:	Time:	Received By:

ICE/t°_____
GOOD CONDITION_____
HEAD SPACE ABSENT_____
DECHLORINATED IN LAB_____
APPROPRIATE CONTAINERS_____
PRESERVED IN LAB_____

COMMENTS:

VOAS O&G METALS OTHER HAZARDOUS:
PRESERVATION_____**pH<2**_____

APPENDIX C

Health and Safety Plan

Excavation Work Plan
Health and Safety Plan

Prepared for

Thomson Development Inc.

April 2015

WEST YOST ASSOCIATES
Consulting Engineers

595-04-14-01

This report printed on 50% post-consumer paper

WEST YOST ASSOCIATES
consulting engineers

WATER WASTEWATER STORMWATER

Excavation Work Plan
Health and Safety Plan

Hamilton Square, 970 C Street
Novato, California

Prepared for

Thompson Development Inc.

April 2015

WEST YOST ASSOCIATES
Consulting Engineers

595-04-14-01

Andy Rodgers

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1.0 INTRODUCTION

This Health and Safety Plan has been prepared to minimize the threat of serious injury to workers during the excavation activities at 970 C Street, Novato, California (Site).

It is the responsibility of every person working on the project site to behave cautiously and avoid actions or situations that could jeopardize his or her own safety and well-being. This Site Safety Plan offers guidelines and precautions that the workers on this project should consider.

West Yost Associates (West Yost) is not responsible for *enforcing* the guidelines of this Health and Safety Plan. West Yost is not responsible or liable for the injuries of any person working on the project site with the exception of West Yost employees, to the extent that they are covered by Worker's Compensation Insurance.

2.0 EMERGENCY RESPONSE

Dialing **911** on the telephone will provide access to ambulance, fire and police services.

2.1 Emergency Information

Ambulance:	911
Hospital:	Novato Community Hospital
	180 Rowland Way Novato CA 94945
	911 Emergency or (415) 209-1300
Poison Control Center:	911
Police:	911
Fire Department:	911
Agency Contacts:	Scott Callow, County of Marin Environmental Health Department
	Office: (415) 499-6907
Emergency Contacts:	
On-Site Manager:	Andy Rodgers, West Yost
	Office: (707) 666-4812 or
	Mobile: (707) 480-1019
Project Manager:	Peter Dellavalle, West Yost
	Office: (707) 666-4814 or
	Mobile: (707) 490-5040

2.2 Hospital Route – Novato Community Hospital

Novato Community Hospital is the nearest hospital to the Site. The route (directions) to the hospital is described as follows (see Site Vicinity and Hospital Location Map in Appendix A):

- Head southwest on C St toward Main Gate Rd
- Turn right on to Main Gate Rd
- Turn right on to Nave Dr
- Take the ramp to US-101 N
- Turn right on to US-101 N
- Take the Rowland Blvd exit
- Turn right on to Rowland Blvd
- Turn left on to Rowland Way
- Novato Community Hospital is on the right side of the street at:
  180 Rowland Way, Novato, CA 94945

3.0 PURPOSE

This site safety plan is designed to protect the health and safety of personnel engaged in excavation activities from potential hazards associated with those activities. All such personnel will be briefed on the site safety plan and will have access to the plan at all times.

4.0 HAZARDS

This section assesses the chemical and physical hazards that are known to exist at the Site and those that may be created by the remediation effects.

The known hazards associated with this site are:

- Underground/overhead utilities,
- Chemical injury from contaminants potentially existing in soil,
- Physical injury from heavy equipment accident,
- Physical injury from sampling equipment and activities, and
- Trip/fall from site construction debris and/or equipment.

4.1 Utility Lines

Underground utilities were located for the drilling project. Underground Service Alert (USA) will be notified prior to drilling operations.

4.2 Chemical Hazards

The primary chemical of concern (COC) at this site is methyl tert-butyl ether (MTBE). Additional COCs include petroleum related hydrocarbons including benzene, ethylbenzene, toluene, and xylenes. Gasoline is flammable, explosive, and toxic through inhalation, ingestion, or dermal contact. Benzene – a constituent of gasoline – is considered carcinogenic to humans. Physical symptoms of exposure to these contaminants may include nausea, blurred vision, dizziness, or headaches. Work required in this project may expose personnel to materials that might contain any or all of these contaminants. Any personnel entering the Site shall be informed of all hazards associated with these contaminants.

The Occupational Health and Safety administration's (OSHA) Permissible Exposure Levels (PELs) for inhalation, in terms of the 8-hour time-weighted average (TWA) and the 15-minute short term exposure level (STEL), for these chemicals and gasoline are as described in Table 1 (29 CFR 1910.1000, 54 FR 2920, January 19, 1989, and California Department of Industrial Relations Permissible Exposure Limits for Chemical Contaminants).

Table 1. OSHA Permissible Exposure Levels

	TWA	STEL
Benzene	1 ppm	5ppm
Ethylbenzene	100 ppm	135 ppm
Toluene	100 ppm	150 ppm
Xylenes	100 ppm	150 ppm
Gasoline	300 ppm	500 ppm
MTBE	40 ppm	

4.3 Physical Hazards

The physical hazards expected to be present at the Site may include:

- Drilling Equipment
- Moving Equipment
- Heavy Equipment
- Power/hand tools
- Saw Cutting
- Snapping Cables, Slings and Rope
- Sharp Objects
- Loose Foundations
- Open Pits or Ditches
- Lifting Hazards
- General Debris
- Excessive Noise
- Fire/Explosions
- Weather Hazards
- Heat Stress

5.0 RISK CONTROL

This section describes the procedures to follow to ensure the avoidance of operational hazards.

5.1 Accident Prevention (General)

While work is in progress, only persons authorized by the site safety officer will be permitted entry.

Site-specific training in the use of equipment, as well as safety precautions, will be provided during the pre-field safety meeting. The training will be repeated for any worker not present for the initial training. The safety meeting will review the work scheduled for the Site, expected hazards, special conditions, equipment locations, Material Safety Data Sheets (MSDS) and generic hazardous substances information and required safety procedures and equipment. Daily, pre-shift "tailgate" meetings will summarize the health and safety plan and review any new revisions to the site safety plan. Written attendance and meeting records of all safety meetings will be maintained with the project file.

All personnel on site will receive the following instructions:

- Keep hands away from face while they might be contaminated.
- Do not eat, drink, or smoke while hands might be contaminated.
- Stay well clear of heavy machinery while in operation unless involved in its operation.

5.2 Mechanical Hazards

The following procedures shall be followed during all phases of the operation to reduce those risks associated with mechanical equipment:

- Stay well clear of drill rods and augers while they are rotating and being hoisted. Extreme care is to be exercised when steel cables are being used to lift the drilling apparatus from the ground.
- Stand clear of the operating circle of excavators, backhoes, etc.
- Equipment maintenance schedules are the responsibility of each individual contractor. Equipment is to be checked daily. Any equipment deemed to be in an unsafe state of repairs, or operated in an unsafe manner shall be shut down until corrective action is taken. Equipment safety features, such as back-up alarms, shall be checked daily.

5.3 Electrical Hazards

The following procedures shall be followed during all phases of operation, in order to reduce those risks associated with electrical hazards:

- USA will be contacted prior to site activities to locate the presence of underground cables, utility lines, pipes, and storage vessels.

- The local power company shall be contacted, in order to verify the minimum allowable clearance from high-voltage power lines. Under no circumstances will any person, piece of equipment, or phase of operation come within 10 feet of overhead power lines.
- If the work area is unavoidably close to buried or overhead power lines, the power shall be turned off, with the circuit breaker locked and tagged out.
- All electrical equipment is to be properly grounded, and under no circumstances are any modifications to be made to any piece of electrical equipment. All electrical equipment is to be inspected daily for damaged leads or plugs. Any piece of equipment that is damaged shall not be used on the Site, and shall be removed from the Site for disposal or repair.
- If splicing wires must connect electrical equipment, the source shall be de-energized first; the breaker box locked out and appropriately tagged by the person who is to perform the splicing operation. All connections are to be appropriately taped. Once the splicing operation is complete, the person who performed the splice shall bring the source back into operation.
- Each person that has cause or need to use a piece of electrical equipment shall ensure that he/she is fully familiar with the equipment's operation and features.

5.4 Chemical Hazards

To reduce the possibility of injury due to chemical hazards, personnel shall wear those pieces of Personal Protective equipment as specified by the task, in section 6.0 (Personal Protective Equipment).

The likelihood of exceeding the OSHA PELs (Table 1) during the performance of the work outlined in this plan is considered to be low due to the ventilated conditions and low concentrations of constituents previously documented at the Site. However, half-face air purifying respirators with organic vapor cartridges, fit-tested for each employee present, will be available on site. If warranted by OVM readings, periodic air monitoring will be conducted during the on-site work with Sensidyne- or Dreager-type detector tubes and pump, which will provide immediate information on airborne benzene concentrations. Should the testing methods indicate potentially hazardous concentrations of airborne contaminants, or if any of the symptoms are noted or observed in any of the on-site personnel, corrective action will be taken, including using respirators, if necessary.

ECON and Blankinship & Associates (2007) developed a flow chart that depicts complete exposure pathways for on-site trench workers (outdoor air) of the adjacent site to the north of the Site, which has similar subsurface conditions and is also impacted with hydrocarbons in subsurface soil and groundwater (Appendix B). The flow chart Exposure pathways and potential receptors discussed below are based on this flow chart, with the exclusion of exposure pathways for building occupants (indoor and outdoor air), of which there currently are none.

5.4.1 Pathways C1 and C2: Soil Ingestion

During excavation activities at the Site, it is possible that adult on-site workers could accidentally ingest soil or groundwater during their activities. Workers will be made aware of the potential hazard and will be advised to wear personal protective equipment and to wash hands before eating or drinking.

5.4.2 Pathways C3 and C4: Dermal Absorption

Site workers will be required to wear personal protective equipment (PPE) such as gloves, coveralls, Tyvek, or like material to limit or prevent contact with soil.

5.4.3 Pathways C6 and C7: Ingestion of Groundwater by On-site Worker

The water underlying the Site is not used for municipal, domestic, industrial process, industrial service or agricultural water supply or to replenish surface water. Water beneath the Site will not be used as a source of drinking water and therefore no receptors will be exposed by this route.

If groundwater is encountered during drilling or excavation activities, it is unlikely to appear potable as a result of mixing with silt and dirt created during excavation activities. As a result, it is highly unlikely that workers will be inclined to drink the water.

5.4.4 Outdoor Air Inhalation by On-site Worker

In accordance with the soil and groundwater management plan, dust control measures will be in place during excavation activities at the Site. The on-site worker is therefore not expected to be exposed to COCs in airborne dust at the Site.

5.5 Acoustical Hazards

In order to prevent hearing impairment, the use of earplugs or earmuffs shall be required for all personnel when heavy equipment is in use at the Site. However, should any personnel develop pain in the ear due to work-site noise, they shall immediately don a set of earplugs or muffs. Noise levels will also be controlled to conform to local ordinances.

5.6 Biological Hazards

In order to reduce the risk of biological contamination, PPE (Section 6.0) shall be worn for each specific task. This protective equipment shall be removed, and hands and face washed prior to contact with the mouth, by the hands, for such purposes as eating, drinking, or smoking. Smoking shall only be permitted in designated areas.

5.7 Heat Stress

If the ambient temperature exceeds 80◦F, workers will be observed for signs of heat stress. Breaks will be taken if any worker exhibits symptoms of heat stress. The breaks will last until symptoms are relieved and/or the pulse of the worker is less than 110 beats per minute. As a preventative measure, workers will be instructed to drink fluids to keep hydrated. For severe heat stress, a health-care professional will examine workers as soon as possible.

All personnel entering the work area should be familiar with the signs and symptoms of heat stress. These include:

- Heat Exhaustion—Dizziness, light-headedness, slurred speech, rapid pulse, confusion, fainting, fatigue, copious perspiration, cool skin that is sometimes pale and clammy, and nausea.
- Heat Stress—Hot, dry, flushed skin; delirium, and comma (in some cases).

5.8 Elevated Work

Some work tasks may require workers to access work areas above the ground. In these instances, a stairway, ladder, ramp, or personal hoist will be provided. Activities will use general safe access and fall protection safety in accordance with California Code of Regulations (CCR) Tile 8.

Ladders will be inspected before each use. Broken or damaged ladders will be tagged and not used. Ladders will be chosen as appropriate to the load, size and task requirements. Ladder inspection, use, and care will follow safe work practices identified by the manufacturer.

5.9 Excavation Hazards

Spoil piles and equipment will be placed at least 2 feet from the edges of open excavations. Utilities will be located before excavating begins. A Cal/OSHA Trench and Excavation Permit will be acquired and available on site for all excavations and trenches greater than 4 feet deep into which employees may enter to do work. Workers will not enter excavations containing groundwater unless a dewatering plan signed by a professional engineer is in effect. Any signs of previously disturbed soil, or vibrations from adjacent machinery or traffic, will be monitored as the excavation proceeds. Excavations and trenches deeper than 5 feet will require protective systems (e.g. sloping, shoring, trench boxes) to be in place. Whenever possible, situations involving entry into an excavation of any depth will be avoided.

5.10 Confined Space Hazards

When work is to be done in an area where the natural circulation of fresh air or the ability to readily escape the site is restricted, that site shall be considered a confined space, and the following guidelines shall be followed:

- Personnel shall monitor the levels of oxygen, combustible gasses, and organic vapors prior to entering. Under no circumstances shall the space be metered if the following levels are exceeded:
    1. Oxygen content is less than 19.5%
    2. Combustible gas level is greater than 3% of the LEL.
    3. Total hydrocarbons are greater than the action levels defined in Table 3 of this section, if all air contaminants have not been identified.
- Personnel shall monitor the levels of oxygen, combustible gasses, and organic vapors continuously while inside the confined space. If the values stated in the above are exceeded, the space shall be evacuated immediately.

At least one additional person, who shall be present for the express purpose of monitoring the personnel in the space, shall be within sight and call of those personnel within the space, while remaining outside of the space proper. This person shall have, readily available to him; all rescue equipment necessary to remove personnel who may require extraction from the space and the Site. This equipment shall include, but not be limited to, respiration equipment of the same level as those used by the personnel in the space, first aid equipment, including compresses, harness, and all the extraction equipment.

Portable fans or blowers shall be used to introduce fresh air into the confined space. These fans or blowers shall be located on the upwind side of the space. The space shall not be entered until values of oxygen, organic vapors, and combustible gasses are brought below and measured below their respective action levels.

- No personnel shall enter any unshored or unsupported excavation with a depth greater than 5 feet, or with unstable geological conditions.

5.11 Miscellaneous

The following miscellaneous safe working practices will be followed at all times:

- The site safety officer will account for all employees at the beginning and the end of each shift.
- Eating, drinking, chewing gum or tobacco, and smoking are prohibited during work operations, unless on break in a designated area.
- Contact with contaminated media will be minimized.
- Equipment and vehicles will not block roadways or exits from any building.
- Drummed material will be handled with equipment specifically designed for drums (drum slings and/or drum dollies).
- Workers will not stand near excavator bucket swing areas or earthmoving equipment, under elevated loads or ladders, or near the edges of excavations.

6.0 PERSONAL PROTECTIVE EQUIPMENT

The following modified **Level** D PPE will be used as necessary for site activities within work areas:

- Impervious clothing (gloves, Tyvek) shall be worn unless the Site Safety and Health Officer does not believe necessary. If hazardous materials (i.e. exposure to COCs) are encountered, employees will have the option, depending on the activity, to wear cotton/polyester, Nomex, or Tyvek coveralls large enough to fit over work clothing with sleeves and legs unrolled.
- Chemical-resistant, leather, electrical resistant or felt work gloves shall be worn depending upon the hazard.
- Safety glasses, goggles, or face shields, unless wearing a full-face respirator.

- Steel-toe/shank boots and boot covers if boots are not chemical resistant or materials cannot be adequately decontaminated (leather boots are typically appropriate when working with/on contaminated materials).
- Hard hat with high-voltage and impact resistance (Class B and/or E).
- High-visibility reflectorized safety vest when working with or near mobile equipment, vehicular traffic, locations with poor visibility (i.e. fog) and night operations.

Each worker will be responsible for maintaining his or her own PPE.

The level of protection can be increased by the site safety officer. Depending on the outcome of air monitoring readings, appropriate respiratory protection may be required if sufficient engineering controls cannot be established.

7.0 DECONTAMINATION

The type, level, and context of contamination at the Site do not warrant personal decontamination procedures beyond washing hands and removing disposable clothing on site. Disposable items and decontamination rinseate will be disposed of in the appropriate manner.

Air Monitoring Records

Date	Time	Sample Area – A Personal – P	Equipment Contaminants of Concern	Measurements

Site Safety Review Meeting

Date: _____ Time: _____ Project Number: _____

Site Location _____

Attendees

Site Safety Officer:

Name	Signature

APPENDIX A

Directions to Hospital

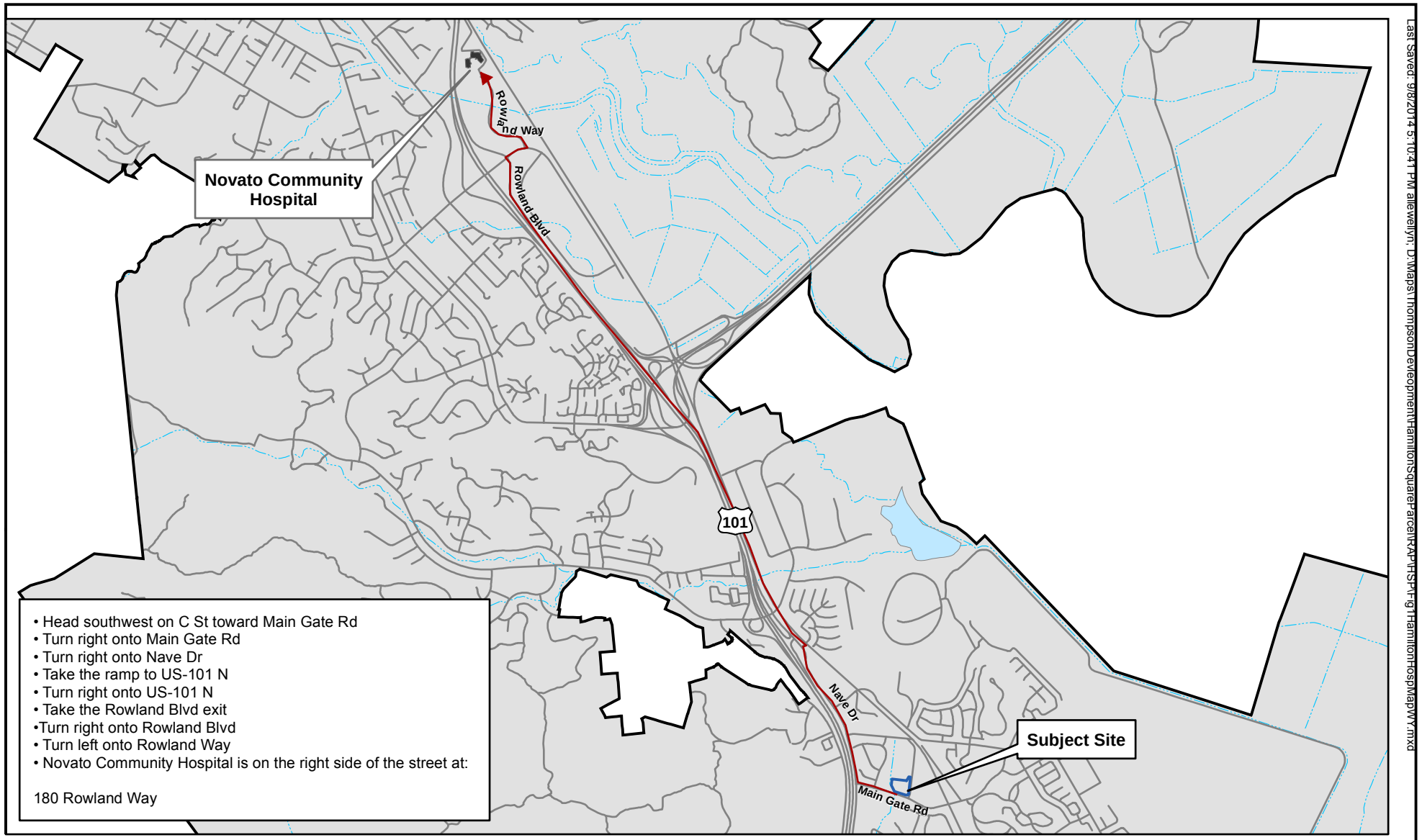

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FIGURE 1

Health and Safety Plan
Hamilton Square
970 C Street, Novato, CA
(T0609592161)

Site Vicinity and Hospital Location Map

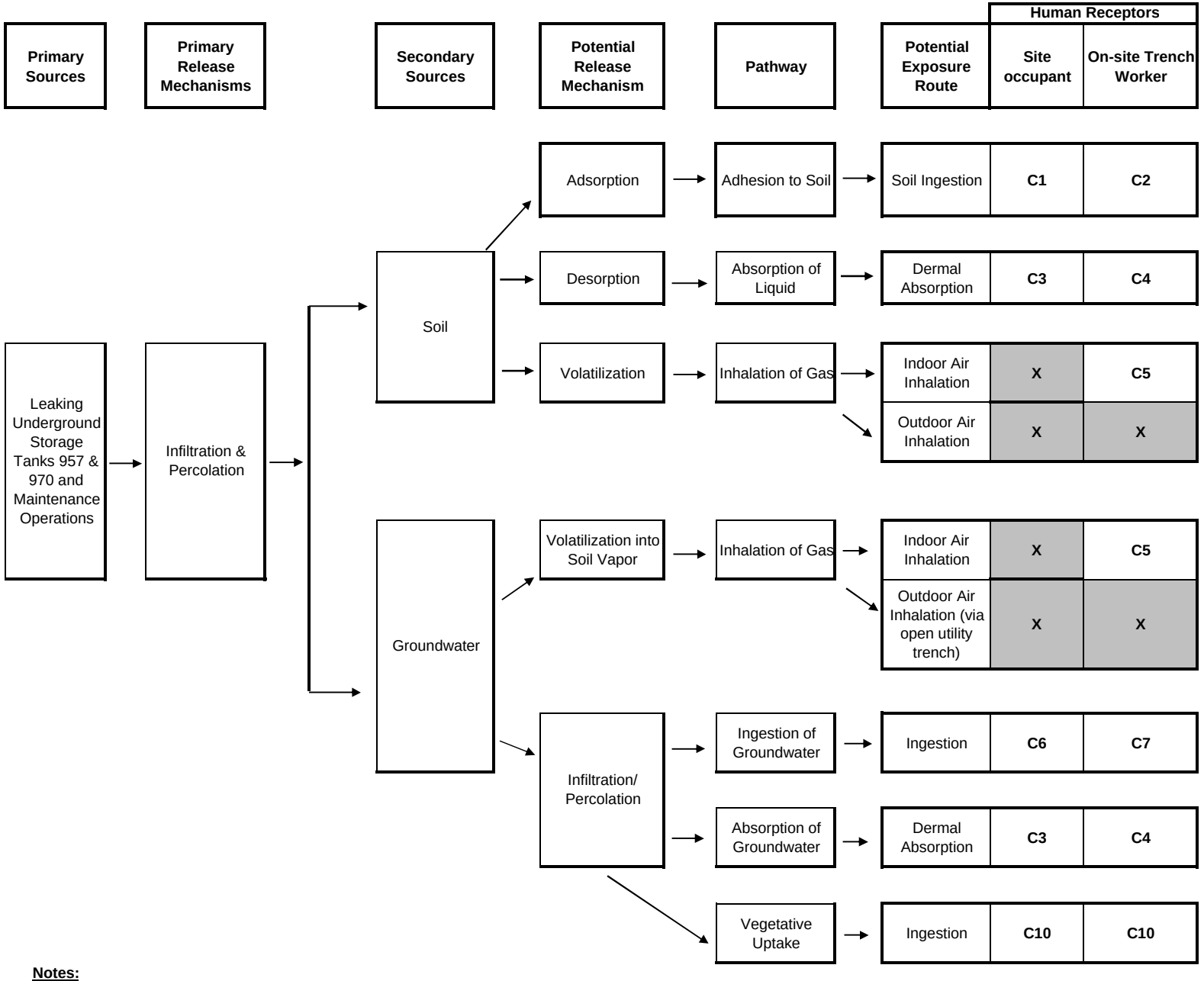
THOMPSON DEVELOPMENT INC.
AN AFFILIATE OF WEST BAY BUILDERS INC.

WEST YOST ASSOCIATES

APPENDIX B

Exposure Pathway Flow Chart

Plate 2. Conceptual Site Model
Hamilton Air Force Base
Parcels 1A and 1B



Notes:

"X" Indicates Complete Exposure Pathway to be Considered in PEA.

"C" indicates that pathway is considered, but incomplete, and therefore not considered. Explanation presented in Section 9.0.