Prepared for
Nevada Environmental Response Trust
Henderson, Nevada

Prepared by
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QUALITY ASSURANCE PROJECT PLAN ADDENDUM

BHRA WORK PLAN FOR OU-1 AND OU-2 SOIL GAS AND GROUNDWATER MODIFICATION #1 NEVADA ENVIRONMENTAL RESPONSE TRUST SITE HENDERSON, NEVADA

RAMBOLL

Quality Assurance Project Plan Addendum for Modification #1 to the BHRA Work Plan for OU-1 and OU-2 Soil Gas and Groundwater

Nevada Environmental Response Trust
(Former Tronox LLC Site)
Henderson, Nevada

Nevada Environmental Response Trust (Trust) Representative Certification

I certify that this document and all attachments submitted to the Division were prepared at the request of, or under the direction or supervision of the Trust. Based on my own involvement and/or my inquiry of the person or persons who manage the system(s) or those directly responsible for gathering the information or preparing the document, or the immediate supervisor of such person(s), the information submitted and provided herein is, to the best of my knowledge and belief, true, accurate, and complete in all material respects.

Office of the Nevada Environmental Response Trust

Le Petomane XXVII, Inc., not individually, but solely in its representative capacity as the Nevada Environmental Response Trust Trustee

Signature: Not Individually, but Solely as President of the Trustee

Name: Jay A. Steinberg, not individually, but solely in his representative capacity as President of the Nevada Environmental Response Trust Trustee

Title: Solely as President and not individually

Company: Le Petomane XXVII, Inc., not individually, but solely in its representative capacity as the Nevada Environmental Response Trust Trustee

Date: 11/16/21

RAMBOLL

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Nevada Environmental Response Trust
(Former Tronox LLC Site)
Henderson, Nevada

Responsible Certified Environmental Manager (CEM) for this project

I hereby certify that I am responsible for the services described in this document and for the preparation of this document. The services described in this document have been provided in a manner consistent with the current standards of the profession and, to the best of my knowledge, comply with all applicable federal, state and local statutes, regulations and ordinances.

11/16/2021

John M. Pekala, PG
Principal

Date

Certified Environmental Manager
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CEM Expiration Date: September 20, 2022

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RAMBOLL

Project Title	Quality Assurance Project Plan (QAPP) Addendum
Site Name	Nevada Environmental Response Trust Site
Site Location	Henderson, Nevada
Company	Ramboll US Consulting, Inc.
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QAPP Reviewed and Approved:

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CONTENTS

1.	**DATA QUALITY OBJECTIVES**	**1**
1.1	Introduction	1
1.2	Data Quality Objectives	2
2.	**DATA GENERATION AND ACQUISITION**	**4**
2.1	Analytical Methods and Quality Control Requirements	4
3.	**DATA VALIDATION AND USABILITY**	**5**
4.	**REFERENCES**	**6**

TABLES

Table 1	Analytical Methods and Laboratories
Table 2	Air Analytes and Analytical Performance Criteria
Table 3	Water Analytes and Analytical Performance Criteria
Table 4	Analytical Laboratory Calibration Frequencies
Table 5	Sample Preservation, Containers, and Holding Times

APPENDICES

Appendix A	Laboratory Standard Operating Procedures (SOPs)

ACRONYMS AND ABBREVIATIONS

BHRA	Baseline Health Risk Assessment
BMI	Black Mountain Industrial
CEM	Certified Environmental Manager
DQI	Data Quality Indicator
DQO	Data Quality Objective
DVSR	Data Validation Summary Report
EPA	U.S. Environmental Protection Agency
MDL	Method Detection Limit
NDEP	Nevada Division of Environmental Protection
NERT	Nevada Environmental Response Trust
PE	Professional Engineer
PG	Professional Geologist
PQL	Practical Quantitation Limit
QA	Quality Assurance
QAM	Quality Assurance Manual
QAPP	Quality Assurance Project Plan
QC	Quality Control
Ramboll	Ramboll US Consulting, Inc.
RI	Remedial Investigation
RI/FS	Remedial Investigation and Feasibility Study
RPD	Relative Percent Difference
SIM	Selected Ion Monitoring
Site	Nevada Environmental Response Trust (NERT) Site
SOP	Standard Operating Procedure
Trust	Nevada Environmental Response Trust
VOC	Volatile Organic Compound

DISTRIBUTION LIST

This QAPP addendum will be distributed to the entities listed below. The QAPP addendum may also be distributed to other project personnel including, but not limited to, client representatives and consultants, analytical laboratories, remediation contractors, and subcontractors, as needed.

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Project personnel from the organizations listed above are responsible for having the most recent version of the project QAPP (Ramboll 2021a) and this QAPP addendum. The parties should contact Ramboll's Project Manager or Project Quality Assurance/Quality Control Officer for the most recent version. Individual pages include a revision number; any revised pages will be clearly marked with a new revision number and a list of revised pages will be distributed with any revisions.

1. DATA QUALITY OBJECTIVES

1.1 Introduction

The Remedial Investigation (RI) Quality Assurance Project Plan (QAPP) for the Nevada Environmental Response Trust (NERT) RI Study Area, Revision 6, dated February 24, 2021 was approved by the Nevada Division of Environmental Protection (NDEP) on March 11, 2021 (Ramboll 2021a). The QAPP describes the quality assurance/quality control (QA/QC) procedures and performance criteria applicable to data collection tasks associated with the Remedial Investigation and Feasibility Study (RI/FS) for the NERT RI Study Area located in Henderson, Nevada (the Site). The RI QAPP was developed to address soil, soil vapor, surface water, and groundwater sampling. This QAPP Addendum has been prepared to include analytical methodology necessary for conducting sampling under the Baseline Health Risk Assessment (BHRA) Work Plan for OU-1 and OU-2 Soil Gas and Groundwater, Modification #1 (Revision 1), dated October 29, 2021 and approved on November 10, 2021 (BHRA Work Plan Modification No. 1; Ramboll 2021b).

As described in Section 5.1 of the RI QAPP (Ramboll 2021a), consultants are required to evaluate the existing QAPP requirements during the planning phase of a new project. Modifications to the QAPP to incorporate additional RI/FS data collection tasks will be addressed in QAPP Addenda. The structure and the minimum task-specific elements that will be required to prepare a QAPP Addendum are presented in Appendix F of the RI QAPP. The following minimum elements are required information for the preparation of the QAPP Addenda:

- Title, Version, and Approval/Sign-off
- New Data Collection Task Information (includes data quality objectives [DQOs], project organization, sampling design, sampling methods, analytical methods, and field QC procedures)
- Laboratory Requirements (includes laboratory contact information, analytical methods, QC requirements, parameter lists, RLs, screening criteria, Quality Assurance Manual [QAMs], and Standard Operating Procedure [SOPs])
- Data Validation and Usability (identified stage of validation needed, validation subcontractor if necessary, validation criteria, guidance required, validation qualifiers, and reason codes)

Sample collection tasks that will be conducted under the BHRA Work Plan Modification No. 1 will follow the RI QAPP for project organization, field QC procedures, QAMs, and data validation and usability; therefore, QA/QC elements for those areas are not repeated in this QAPP Addendum. The following elements that are not included in the RI QAPP, Revision 6 are included in this addendum:

1. Environmental Protection Agency (EPA) Method 524.2 for volatile organic compounds (VOCs) has been added for the analysis of trihalomethanes in water samples. The analysis will be performed at Eurofins Environment Testing America, Inc. located in Phoenix, Arizona.

2. Sampling indoor, sub-slab, and ambient air are new sample collection tasks that will be conducted. The reporting limits and measurement performance criteria for VOCs by EPA Method TO-15 and TO-15 with selective ion monitoring (TO-15 SIM) for indoor, ambient, and sub-slab air sampling have been included in this addendum.

1.2 Data Quality Objectives

General DQOs for ensuring that comparable and representative data are produced to support the objectives of the RI sampling have been established and are documented in the RI QAPP. The project DQOs provide an internal means for control and review so the environmentally related measurements and data collected by the project team are valid, scientifically sound, and of known, acceptable, and documented quality. For this task-specific QAPP Addendum, DQOs have been developed to ensure data collected meet the objectives of the BHRA and how that data will be used. In addition, this QAPP Addendum discusses supplemental analytical requirements that are used to obtain data of sufficient quality to meet all project DQOs.

The task-specific DQOs for the BHRA Work Plan Modification No. 1 are described in the following sections.

1.2.1 State the Problem

Potential risks from vapor intrusion to indoor air are being evaluated within OU-1 and OU-2 in the NERT RI Study Area for the BHRA.

1.2.2 Identify the Goal of the Study

The objective of the investigation is to confirm that chloroform indoor air levels remain below long-term health-based thresholds and to allow direct comparisons between modeled indoor air estimates and direct indoor air measurements.

1.2.3 Identify the Information Inputs

Data will be collected for indoor air sampling, ambient air sampling, residential water sampling, sub-slab air sampling, and soil vapor sampling. Indoor air, ambient air, and sub-slab air are matrices that were not addressed in the RI QAPP.

1.2.4 Define the Boundaries of the Study

The BHRA Work Plan Modification No. 1 identifies the targeted indoor air sampling areas for the sampling.

1.2.5 Develop the Analytical Approach

The laboratories and methods that will be utilized for sample analyses are listed in Table 1. Project-specific reporting limits (practical quantitation limits [PQLs]), method detection limits (MDLs), and QC limits for the analytes to be tested are provided in Tables 2 and 3. Analytical methods were selected based on comparability to historical data and sensitivity to support screening criteria.

1.2.6 Specify Performance of Acceptance Criteria

To ensure measurement performance criteria are met, data quality indicators (DQIs) for sensitivity, accuracy, precision, completeness, representativeness, and comparability presented in the RI QAPP will be followed. The QA/QC samples to be collected and minimum frequency will follow the specifications of the RI QAPP. One indoor air field duplicate will be collected at each residential location. Field duplicates collected for ambient air and sub-slab air matrices will be collected at the same frequency as field duplicates for soil gas samples, one duplicate per every 10 field samples. Field duplicates collected for indoor air, ambient air, and sub-slab air matrices will also be evaluated by the same goal for precision as soil gas samples. A relative percent difference (RPD) ≤50 will be used for all air sample matrices. Data collected for this sampling will be validated according to the specifications of the RI QAPP and at a level of 90% Stage 2B and 10% Stage 4.

1.2.7 Develop the Detailed Plan for Obtaining Data

The BHRA Work Plan Modification No. 1 details the sampling approach for collecting indoor air, ambient air, residential water, sub-slab air, and soil vapor samples. Samples will be collected within and around residential properties. The BHRA Work Plan specifies the selection of sampling locations, the quantities of samples to be collected per matrix, reporting specifications, and the anticipated schedule.

2. DATA GENERATION AND ACQUISITION

The requirements for sample and field QA/QC identification, labeling, sample handling and transport, sample custody, shipping procedures, transport container receipt, and laboratory deliverables will follow the specifications outlined in the RI QAPP. This section discusses the supplemental requirements for sample collection and analytical methods that will be followed for sample collection tasks for the BHRA Work Plan Modification No. 1.

2.1 Analytical Methods and Quality Control Requirements

The primary methods that will be used to analyze samples are summarized in Table 1. The project-specific MDLs, PQLs, and laboratory QA/QC sample acceptance limits are listed on Table 2 and Table 3. The calibration requirements for the VOC methods are listed in Table 4. The type and frequency of laboratory QA/QC samples will follow the RI QAPP. Laboratory SOPs for the listed methods have been developed and approved by the laboratories performing the analyses. The dates of the current SOPs are summarized for each laboratory on Table 1 and included in Appendix A. Laboratory Quality Assurance Manuals have been provided with the RI QAPP.

2.1.1 Containers, Preservation, and Hold Time

The type of sample containers to be used for each sample type and analysis, preservation requirements for all samples, and holding times are provided in Table 5.

3. DATA VALIDATION AND USABILITY

The procedures for data review, validation, and verification will follow the RI QAPP. All data collected for air matrices and residential water will be validated at a 10% Stage 4 and 90% Stage 2B validation level and included in a Data Validation Summary Report (DVSR). The elements for Stage 4 and Stage 2B data validation are specified in the NERT RI QAPP.

4. REFERENCES

Ramboll (Ramboll US Consulting, Inc.). 2021a. Quality Assurance Project Plan, Revision 6. Nevada Environmental Response Trust Site, Henderson, Nevada. Revised February 24, 2021.

Ramboll. 2021b. BHRA Work Plan for OU-1 and OU-2 Soil Gas and Groundwater, Modification #1 (Revision 1). Nevada Environmental Response Trust Site, Henderson, Nevada. Revised October 29.

TABLES

TABLE 1. ANALYTICAL METHODS AND LABORATORIES
QUALITY ASSURANCE PROJECT PLAN ADDENDUM
Nevada Environmental Response Trust Site; Henderson, Nevada

ANALYTES	MATRIX	ANALYTICAL METHOD	CERTIFICATION	ANALYTICAL LABORATORY	SOP DATE[1]
Volatile Organic Compounds (VOCs) [2]	Water	EPA Method 524.2	NV	Eurofins TestAmerica (Phoenix, AZ)	April 23, 2021
	Indoor, Ambient, and Sub-Slab Air	EPA Method TO-15	NELAC	Eurofins Air Toxics (Folsom, CA)[2]	November 4, 2020
		EPA Method TO-15 SIM	NELAC	Eurofins Air Toxics (Folsom, CA)[2]	November 23, 2020
Helium	Sub-Slab Air	ASTM D1946	Not Applicable	Eurofins Air Toxics (Folsom, CA)[2]	July 13, 2020

Notes:

ASTM = American Society for Testing and Materials

EPA = United States Environmental Protection Agency

NELAC = Laboratory is certified to perform the method listed by an accreditating body of the National Environmental Laboratory Accreditation Conference (NELAC)

NV = Laboratory is certified to perform the method list by the State of Nevada

SIM = Selective Ion Monitoring

SOP = Standard Operating Procedure

(1) SOP Date is the most current review or effective date listed on the laboratory's approved SOPs that will be implemented for this project. Laboratories are responsible for notifying Ramboll of any revisions to the SOPs referenced above. The use of revised SOPs are subject to approval.
(2) Eurofins Air Toxics (Folsom, CA) SOPs are proprietary. For documentation purposes Appendix A of this QAPP includes summaries for Eurofins Air Toxics methods.

TABLE 2. AIR ANALYTES AND ANALYTICAL PERFORMANCE CRITERIA
QUALITY ASSURANCE PROJECT PLAN ADDENDUM
Nevada Environmental Response Trust Site; Henderson, Nevada

ANALYTES	CAS Number	Residential Air[1]	Practical Quantitation Limit (PQL)	Method Detection Limit (MDL)	QUALITY CONTROL LIMITS[(2)]		
					Duplicate	Blank Spike/LCS	
					RPD	%R	RPD
Air Analytes (µg/m^3)							
EPA Method TO-15 (µg/m3)							
Bromodichloromethane	75-27-4	0.076	1.0	0.238	50	70 - 130	25
Bromoform	75-25-2	2.6	1.48	0.275	50	70 - 130	25
Dibromochloromethane	124-48-1	--	1.3	0.164	50	70 - 130	25
EPA Method TO-15 SIM (µg/m3)							
Carbon Tetrachloride	56-23-5	0.47	0.18	0.037	50	60 - 140	25
Chloroform	67-66-3	0.12	0.14	0.015	50	70 - 130	25
Tetrachloroethene	127-18-4	11	0.21	0.010	50	70 - 130	25
Trichloroethene	79-01-6	0.48	0.16	0.031	50	70 - 130	25
ASTM D1946 (%)							
Helium	7440-59-7	--	0.050	--	50	70 - 130	25

Notes:

-- = no value

ASTM = American Society for Testing and Materials

µg/m^3 = micrograms per cubic meter

% = percent

SIM = Selective Ion Monitoring

(1) NDEP July 2017 Basic Comparison Level (BCL) Table

(2) Quality Control Limits for %R (Percent Recovery) of spiked compounds in Laboratory Control Samples (LCS) and surrogate compounds and Relative Percent Difference (RPD) between LCS and LCS Duplicate (LCSD) samples. Matrix spikes (MS) are not performed on soil gas samples. Laboratory historical control limits are subject to change as a result of periodic re-evaluation. Limits in use at the time of sample analysis are available from the laboratory. Duplicate RPDs apply to sample duplicates and field duplicates.

TABLE 3. WATER ANALYTES AND ANALYTICAL PERFORMANCE CRITERIA
QUALITY ASSURANCE PROJECT PLAN ADDENDUM
Nevada Environmental Response Trust Site; Henderson, Nevada

ANALYTES	CAS Number	Screening Level	Screening Level Source[1]	Practical Quantitation Limit (PQL)	Method Detection Limit (MDL)	QUALITY CONTROL LIMITS[2]					
						Surrogate	Duplicate	Matrix Spike		Blank Spike/LCS	
						%R	RPD	%R	RPD	%R	RPD
Volatile Organic Compounds (µg/L)											
EPA Method 524.2											
Bromodichloromethane	75-27-4	0.133	BCL	0.500	0.100	-- --	30	70 - 130	20	70 - 130	20
Bromoform	75-25-2	3.19	BCL	0.500	0.100	-- --	30	70 - 130	20	70 - 130	20
Chloroform	67-66-3	0.219	BCL	0.500	0.050	-- --	30	70 - 130	20	70 - 130	20
Dibromochloromethane	124-48-1	0.8	BCL	0.500	0.170	-- --	30	70 - 130	20	70 - 130	20
Total Trihalomethanes	--	--	--	0.500	0.225	-- --	30	-- - --	--	-- - --	--
4-Bromofluorobenzene (Surrogate)	460-00-4	--	--	--	--	70 - 130	--	-- --	--	-- --	--
1,2-Dichlorobenzene-d4 (Surrogate)	2199-69-1	--	--	--	--	70 - 130	--	-- --	--	-- --	--

Notes:

Shaded PQL exceeds the screening level.

-- = no value

µg/L = micrograms per liter

(1) Basic Contaminant Level (BCL): Residential water basic comparison levels in NDEP July 2017 BCL Spreadsheet.

(2) QC Limits = Quality Control Limits for %R (Percent Recovery) of spiked compounds in Laboratory Control Samples (LCS) and surrogate compounds and Relative Percent Difference (RPD) between Matrix Spike (MS) and MS Duplicate (MSD) samples and LCS and LCS duplicate (LCSD) samples. Laboratory historical control limits are subject to change as a result of periodic re-evaluation. Limits in use at the time of sample analysis are available from the laboratory. Duplicate RPDs apply to sample duplicates and field duplicates.

TABLE 4. ANALYTICAL LABORATORY CALIBRATION FREQUENCIES
QUALITY ASSURANCE PROJECT PLAN ADDENDUM
Nevada Environmental Response Trust Site; Henderson, Nevada

		QUALITY CONTROL CHECK[1]	
Laboratory Analysis	**Instrumentation**	**Initial Calibration Type/Frequency**	**Continuing Calibration Verification Type/Frequency**
Volatile Organic Compounds (VOCs) by EPA 524.2 and TO-15/TO-15 SIM	Gas Chromatography/ Mass Spectrometry	Minimum five points on an as-needed basis with daily verification before sample analysis.	Analyze a CCV standard at the beginning of each 12-hour analytical shift before any samples are analyzed.
Atmospheric Gases by ASTM D194	Gas Chromatography	Minimum five points on an as-needed basis with daily verification before sample analysis.	Analyze a CCV standard at the beginning of each 12-hour analytical shift before any samples are analyzed.

Notes:

ASTM = American Society for Testing and Materials

EPA = United States Environmental Protection Agency

SM = Standard Method

(1) These Quality Control checks are to be considered the minimum frequency and scope of checks and calibrations to be performed. Laboratories may have more stringent requirements as part of their Standard Operating Procedures.

TABLE 5. SAMPLE PRESERVATION, CONTAINERS, AND HOLDING TIMES
QUALITY ASSURANCE PROJECT PLAN ADDENDUM
Nevada Environmental Response Trust Site; Henderson, Nevada

MATRIX	ANALYTES	ANALYTICAL METHOD	PRESERVATION	CONTAINER[1]	TAT	HOLD TIME[2]
Water	Volatile Organic Compounds (VOCs)	EPA Method 524.2	Sodium thiosulfate; no headspace; cool to ≤6 ˚C	3 x 40 mL glass vials with Teflon-lined septum caps	10d	14d
Indoor, Ambient, and Sub-Slab Air	Volatile Organic Compounds (VOCs)	EPA Method TO-15 and TO-15 SIM	None	SUMMA canister	10d	30d
Sub-Slab Air	Helium	ASTM D1946	None	SUMMA canister	10d	30d

Notes:
ASTM = American Society for Testing and Materials
EPA = United States Environmental Protection Agency
SIM = Single Ion Monitoring
TAT = Turnaround Time
d = day(s)
mL = milliliters

(1) Additional volume will be collected for water MS/MSD samples.
(2) Holding time begins from date of sample collection.

APPENDIX A
LABORATORY STANDARD OPERATING PROCEDURES (SOPs)

Title: EPA 524.2
Measurement of Purgeable Organic Compounds in Water and Analyzed by GC/MS
[EPA Method 524.2]

Approvals (Signature/Date):

Emily Langlois	04/21/2021	Lisa Maycock	04/21/2021
Emily Langlois	Date	Lisa Maycock	Date
Volatiles Supervisor		Health & Safety Manager / Coordinator	
Tony Genco	04/21/2021	Stephanie Stimson	04/23/2021
Tony Genco	Date	Stephanie Stimson	Date
Quality Assurance Manager		Laboratory Director	

Facility Distribution No. _____ **Distributed To: *UNCONTROLLED***

1.0 Scope and Application

1.0 This is a general-purpose method for the identification and simultaneous measurement of Purgeable Volatile Organic Compounds in Water by Capillary Column Gas Chromatography-Mass Spectrometry.

1.1 Analytes, Matrix(s), and Reporting Limits

1.1.1 This method is applicable to low water soluble analytes found in surface water, ground water and drinking water in any treatment stage.

1.1.2 Eurofins TestAmerica Environmental Laboratories routinely analyzes the compounds listed in **Attachment 1** by EPA Method 524.2.

1.1.3 The reporting limits for the compounds analyzed by this method can be found in **Attachment 1**.

1.2 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in the Quality Assurance Manual.

2.0 Summary of Method

2.1 An inert gas (helium or equivalent) is bubbled through a 25 ml sample at ambient temperature. The volatiles are efficiently transferred from the aqueous to the vapor phase. The vapor is swept through a sorbent trap where the volatiles are trapped. When purging is completed, the trap is heated and back-flushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the volatiles that are then detected with a mass spectrometer. Comparing the measured mass spectra of each peak to the calibration standards' reference spectra identifies analytes. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using calibration curve.

3.0 Definitions

3.1 Calibration Standard (CAL) – A solution prepared from the primary dilution standard solution(s) or stock standard solutions. Used to calibrate the instrument.

3.2 Initial Calibration Standards (ICAL) – A series of CAL solutions used to initially establish instrument calibration and develop calibration curves.

3.3 Continuing Calibration Verification Standard (CCV/ CCVL) – A CAL solution which is analyzed every 12 hours after BFB, which verifies the previously established calibration curve and confirms accurate analyte quantitation for the previous field samples analyzed. The concentration for the CCV should be at the middle calibration level and the CCVL should be at the lowest calibration level.

3.4 Laboratory Control Sample / Laboratory Control Sample Duplicate (LCS / LCSD) – An aliquot of organic free reagent water, or other blank matrix, to which a known quantity of analyte is added in the laboratory. The LCS / LCSD are analyzed exactly like a sample.

3.5 Matrix Spike / Matrix Spike Duplicate (MS / MSD) – An aliquot of an environmental field sample to which a known quantity of analyte is added in the laboratory. The MS / MSD are analyzed exactly like a sample.

3.6 Method Blank (MB) – An aliquot of organic free reagent water of other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, filtration and reagents that are used with other samples.

3.7 Quality Control Sample (QCS) /Initial Calibration Verification (ICV) – A solution of analyte that is obtained from a source external to the laboratory and different from the source of calibration standards. It is analyzed immediately following calibration, prior to any field sample analysis.

3.8 Relative Percent Difference (RPD) – The difference between two values divided by the average of the values expressed as a percent.

3.9 Internal Standard (IS) – A closely related compound whose presence in environmental samples is highly unlikely. The compounds are often brominated, fluorinated, or stable isotopically labeled analogs of specific target compounds.

3.10 Accuracy: The degree of agreement of a measured quality of concern.

3.11 Precision: The degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions. It is concerned with the closeness of results.

3.12 Duplicate: A second sample randomly selected from a population of interest to assist in the evaluation of sample variance.

3.13 Surrogate – A compound that is added to each sample to monitor extraction and purge efficiency.

3.14 IDOC – Initial Demonstration of Capability. A procedure to establish the ability of the analysts to generate acceptable accuracy.

3.15 Refer to the Quality Assurance Manual Glossary/Acronyms for additional definitions and terms not defined in this section.

4.0 Interferences

4.1 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. A field blank/trip blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.2 Contamination may occur when a low-level sample is analyzed after a high concentration sample. If a sample has high-level detects of target analytes the sample(s) following it should be checked for low-level detects (above the report limit) of the same analytes. If present the sample(s) should be rerun to verify the detects are not due to carryover.

4.3 Contamination may also occur when a sample contains surfactants. Signs of surfactants are foaming and/or bubbling when the sample is purged. After a sample that contains surfactants is analyzed, rinse the system. Look carefully for signs of carry-over in the samples that are analyzed immediately after the surfactant sample.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe and closed-heel, nonabsorbent shoes are a minimum PPE requirement.

5.1 Specific Safety Concerns or Requirements

5.1.1 Since all of the hazards of samples and chemicals used in this procedure are not entirely known, strict adherence to safety rules and use of prescribed personal protection equipment is mandatory. The health hazards of the standards, reagents and samples are not entirely known so caution must be exercised in all cases.

5.1.2 Appropriate PPE must be worn when handling and preparing samples for analysis.

5.1.3 Either nitrile or latex gloves may be used when performing this method.

5.1.4 Analytes detected by this method have been tentatively classified as known or suspected human or mammalian carcinogens. Appendix XIII of the corporate Employee Health and Safety manual lists possible carcinogens.

5.1.5 *Pure standard materials and stock standard solutions of these compounds must be handled in a hood*.

5.1.5.1 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: Benzene; Bromodichloromethane; Carbon tetrachloride; Chloroform; 1,2-Dibromoethane (EDB); 1,4-Dichlorobenzene; 1,2-Dichloroethane (1,2-DCA); cis-1,3-Dichloropropene; Methylene chloride; 1,1,2,2-Tetrachloroethane; Tetrachloroethene; 1,1,2-Trichloroethane; Trichloroethene; 1,2,3-Trichloropropane and Vinyl chloride.

5.1.6 Additional information about the above listed analytes and all other compounds analyzed by this method is available via a MSDS. All MSDS are available on the company's intranet site OASIS.

5.1.7 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.8 The mass spectrometer is under vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.1.9 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

5.2.1 The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and standards section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effect exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 - Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation (or any equivalent instrument systems)

GCMS 1	GCMS 17	GCMS 26
HP 6890 Series II GC	HP 6890 Series GC	HP 6890 Series GC
HP 5973 MSD	HP 5973 MSD	HP 5973 MSD
OI 4560 Concentrator	OI Eclipse 4760	OI Eclipse 4660 Concentrator
Varian Archon 4552 Autosampler	OI Analytical 4100	OI 4552 Analytical Autosampler

- The autosamplers on these instruments are used in soil mode. The analyst performs the subsampling and addition of IS/Surrogate standard.

- 5 µL of the 100 µg/mL Internal Standard and Surrogate Standard is added to each client sample and QC sample by the analyst during sample preparation before being loaded into the concentrator and purged.

6.1.1 Temperature Program:

	GCMS #1	GCMS #17	GCMS #26
Initial Temperature	40 deg	40 deg	40 deg.
Initial Time	1 min	1 min	3 min.
Rate A	10 deg/min	10 deg/min	18 deg/min
Final Temperature A	120 deg	120 deg	170 deg.
Final Time A	0.0 min	0.0 min	0.5 min.
Rate B	24 deg/ min	24 deg/ min	30 deg/min.
Final Temperature B	220 deg	220 deg	220 deg.
Final Time B	1.0 min	1.0 min	5.89 min.
Final Run Time	14.17 min	14.17 min	18 min.

6.1.2 Instrument Conditions

	GCMS # 1, GCMS # 17	GCMS #26
Column	Rxi-624Sil 30 m x 250 µm x 1.4 µm or equivalent	Rxi-624Sil 60 m x 250 µm x 1.4 µm or equivalent
Carrier Gas (He or equivalent) Flow Rate	1.0 mL/min	1.0 mL/min

6.1.3 Purge and Trap Conditions

	GCMS # 1, GCMS # 17	GCMS # 26
Purge Temp	20 deg	25 deg
Purge Time	11 min.	11 min.
Dry Purge Time	1.0 min.	1.0 min.
Desorb Time	4 min.	4 min.
Desorb Temp	180 deg.	190 deg.
Bake Time	9 min.	10 min.
Bake Temperature	220 deg.	210 deg.

6.1.4 Note: Temperature Programs, Instrument Conditions, and Purge and Trap Conditions are general guidelines and are subject to change based upon instrument performance. The purging time and desorb time are the only parameters that cannot be changed.

6.2 **Supplies**

- Fume hood.
- 10 µL, 25 µL, 50 µL, 100 µL, 250 µL, 500 µL & 1 mL gas tight micro syringes.

- 1 mL, 5 mL, 10 mL, 25 mL gas tight Luerlock or Luertip syringes.
- 1, 2 and 3 mL micro-reaction vessels with mininert valve caps.
- Volumetric flasks.
- 40 mL pre-preserved VOA vials w/septa.
- 40 mL unpreserved VOA vials w/septa.
- pH Test Strips.
- Kimwipes.
- Organic free reagent water.

7.0 Reagents and Standards

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. 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 determination. Standards are subject to change based on performance of standard quality. Catalogue ID's are used for required compound list and additional standards may be added when the required compound list changes. Storage and expiration requirements are based upon the manufacturer's expiration dates and suggested storage conditions.

7.2 Ultrapure Water - water in which no target analytes are observed at or above the Report Limit (RL).

7.3 Purge and Trap Grade Methanol.

7.4 Stock standards:

- Agilent Internal Standard mix 2000 µg/mL (Catalog # STM-320N1) or equivalent
- O2SI 4-Bromofluorobenzene 2000 µg/mL (Catalog # 020135-02-TA) or equivalent
- Crescent Additions with Vinyl Acetate 8260 (custom) Additional compounds (2000 µg/mL) Catalog #CC2239.607, or equivalent. This standard includes Acetone, Carbon Disulfide, Iodomethane, 2-Butanone, 4-Methyl-2-pentanone, 2-Hexanone, Vinyl Acetate, and 2-Chloroethyl vinyl ether.
- Restek Standard Gases Mix (2500 µg/mL) Catalog #569722, or equivalent.
- O2SI EPA Method 502/524 Volatile Standard (54 compounds) 2000 µg/mL (Catalog #93538), or equivalent.
- Absolute Custom 8260 VOC mix (2000 µg/mL) Catalog #96419, or equivalent. This standard includes Methyl tert-Butyl Ether (MTBE), tert-Amyl Methyl Ether (TAME), Ethyl tert-Butyl Ether (ETBE), Di-isopropyl Ether (DIPE), trans-1,4-Dichloro-2-butene, Tetrahydrofuran, n-Hexane, and Freon 113.

Note: The prepared standards are shared with the 8260 method, therefore compounds not specific to this method appear in these standards.

7.5 Standard Preparation

7.5.1 Stock Standards

I. Prepare the standards at the frequency that is specified in SOP PE-QAD-013 Reagent and Standard Preparation, Control and Documentation. Since the vendor and standard type may change, it is important that the analyst reviews the most recent standard preparation logged in TALS LIMS, and make adjustments accordingly. The addition of an isolated standard would require recalculation of the final methanol added.

II. Transfer the stock standards from their 1-mL ampoule to 1-mL micro reaction vessel with a mininert valve cap. The valve cap should be slightly loose when transferring large volumes to prevent backpressure. Use a 1 mL gas tight syringe or a glass pipette to transfer the stock standard into the mininert vessel. This will minimize volatilization of standards. Note: Perform this in a hood.

III. Check mininert caps for wear and replace septa prior to standard preparation. If the cap is not sealing correctly then it may also need to be replaced.

IV. Seal the vials with Teflon tape if necessary.

V. Store the opened stock standards in the appropriate storage conditions recommended by the manufacturer.

VI. See SOP PE-QAD-013 Reagent and Standard Preparation, Control and Documentation for Expiration dates of standards. Replace the standards sooner than the expiration date if a change in response is observed.

VII. Complete the TALS Standard Log. Refer to SOP PE-QAD-013 for the procedure to enter standards into TALS. All standards from receipt, to creating parent (stock) standards, and preparing working standards must be entered into TALS and given an identification number.

7.6 Working standards

7.6.1 4-Bromofluorobenzene standard (25 µg/mL)

I. Add 1975 µL of MeOH with a 1 or 2 mL syringe into an appropriate size mininert vial.

II. Add 25 µL of the 4-Bromofluorobenzene standard (2000 µg/mL)

III. Seal vial by closing mininert valve after the above additions. Store the vial in the freezer with minimal headspace. This applies to all standards prepared from here on.

7.6.2 Internal Standard and Surrogate Standard (100 µg/mL) for autosamplers in soil mode

I. Add approximately 950 µL of MeOH with a 1 or 2 mL syringe into an appropriate size mininert vial.

II. Add 50 µL of the Internal Standard solution (2000 µg/mL)

7.6.3 Primary Calibration standard (50 µg/mL)

I. Add 1810 µL of MeOH with a 1.0 mL syringe into a 2 mL mininert vial.

II. Add 40 µL of the Gases Mix (2500 µg/mL) standard, 50 µL of the Custom VOC Mixture (2000 µg/mL), 50 µL of the 54 compound mix (2000 µg/mL), 50 µL of the 8260 Additions with Vinyl acetate and 2-CEVE mix (2000 µg/mL to the 2 mL mininert vial to attain a final concentration of 50 µg/mL.

7.6.4 Secondary QCS/ICV Standard (50 µg/mL)

I. The Standard must be a different source from the primary calibration standard source. It must be purchased from a different vendor or must be from a different lot number with a certificate from the vendor validating that the primary and secondary standards were prepared from different sources.

II. Add an appropriate amount of MeOH into an appropriate size mininert vial. The amount will be calculated by subtracting the total volume of stock standards that will be added from the final volume.

III. Add 40 µL of the Gases Mix (2500 µg/mL) standard and 50 µL of each of the VOC Mixtures (2000 µg/mL); 54 component, Additions mix and custom mix; to the mininert vial to attain a final concentration of 50 µg/mL.

7.6.5 Primary Calibration Standard (2.5 µg/mL)

I. Add 950 µL of MeOH with a 1.0mL syringe into a 1 mL miniert vial.

II. Add 50 µL of the 50 µg/mL primary calibration standard to attain the final concentration of 2.5 µg/mL.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 All samples must be collected in 40 mL VOA vials with Teflon lined silicon septa screw caps in duplicate or triplicate. The VOA vials should contain no headspace (no visible bubbles greater than pea sized when the vial is inverted)

8.2 All samples must be preserved with HCl to a pH $\leq$ 2.

8.3 If samples are suspected to contain residual chlorine, add about 25 mg of ascorbic acid per 40-mL of sample to each VOA vial before filling. Fill the VOA vial to approximately half, add 5 – 10 drops of 1:1 HCl, then fill the vial completely until there is no headspace. Seal the sample vial and mix for 1 minute

8.4 Samples should be kept at 0 – 6.0°C and promptly delivered to the laboratory after sampling. Once received at TestAmerica, the samples are stored at 0 – 6.0°C, in a refrigerator that has been dedicated for volatile drinking water sample storage.

8.5 Samples must be analyzed within 14 days of sampling.

	Holding Time	Preservation
Preserved	14 Days	pH<2– HCl with or without Ascorbic Acid; 0 – 6.0°C
Unpreserved for any compound other than TTHM compounds;	24 hours	0 – 6.0°C
TTHM Only	14 Days	Sodium thiosulfate; 0 – 6.0°C; acidification not required

8.6 If a sample foams vigorously when HCl is added, discard that sample. Collect a set of duplicate samples but do not acidify them. These samples must be flagged as 'not acidified' and must be stored at 0 – 6.0°C or below. These samples must be analyzed within 24 hours of collection time.

8.7 The usual procedure for 524.2 analyses is to preserve the samples with HCl. In circumstances where samples foam when HCl is added and the client must provide samples unacidified, special arrangements must be made with the laboratory to analyze the samples within 24 hours of sampling. The responsibility to make arrangements for the samples to be analyzed within the 24 hour time frame rests with the client and is dependent on laboratory capacity.

8.8 If samples are found to have a pH >2 for Non-TTHM samples, then the sample must be flagged with a Q3 and/or Q4 qualifier.

9.0 Quality Control

QC Performed	Frequency	Acceptance Criteria	Corrective Action
BFB Tune	Beginning of every 12 hour period	Must pass Table 2 Ion Abundance criteria	1. Re-inject 2. Adjust MS 3. Re-tune 4. Perform maintenance
Minimum 5 point Calibration Curve (for a factor of 100) A minimum 6 points must be used for quadratic curves	Whenever calibration check is out of criteria or whenever major maintenance is performed	≤ 20% RSD, or use curve, $r^2 \geq 0.990$	1. Re-inject curve 2. Prepare new standards 3. Perform maintenance
Daily Minimum Reporting Limit (RLV) Verification Check/Continuing Calibration Check low level (CCVL)	Every analysis batch	Within ± 50% recovery of RF if Ave. RF used, or alternatively ± 50% of true value if linear or second order regression used.	1. Re-inject check once 2. Re-make standard and re-inject 3. Re-run new curve 4. Perform maintenance
Calibration Check (CCV – primary) (at	- Beginning of each 12 hour period	Within ± 30% recovery of RF if Ave. RF used, or	1. Re-inject or flag data

QC Performed	Frequency	Acceptance Criteria	Corrective Action
calibration curve midpoint)	- Shift/maximum of 20 samples (i.e. batch).	alternatively ± 30% of true value if linear or second order regression used.	2. Prepare new standards 3. Re-run new curve 4. Perform maintenance
Method Blank	Each batch	< Reporting limit	1. Re-inject batch 2. Flag data
Surrogate	Each sample	Within ± 30% recovery	1. Re-inject 2. Re-analyze or flag data
Internal Standard	Each sample	IS RT ± 30 seconds IS Area ± 50% of ICAL or ± 30% of CCV	1. Re-inject 2. Re-analyze or flag data
Laboratory Control Sample/Duplicate (LCS / LCSD – primary) (at calibration curve midpoint)	Each batch of 20 samples	Within ± 30% recovery of RF if Ave. RF used, or alternatively ± 30% of true value if linear or second order regression used. ≤ 20% RPD	1. Re-inject Perform maintenance and rerun Flag data / request re-sampling
QCS (Quality Control Sample)/ICV (Initial Calibration Standard) (Secondary Source - midpoint)	At least quarterly	70 – 130% recovery	1. Re-inject QCS/ICV 2. Prepare new standards 3. Re-run new curve 4. Perform maintenance

9.1 Sample QC

9.1.1 Method Blank (MB)

I. Analyze a method blank (MB) after the Continuing Calibration Checks analyzed every 12 hours. Usually the opening MB is assigned as the batch blank associated with 20 samples or less. Analyze a cleanout blank after a highly concentrated sample as a cross-contamination check.

II. Prepare a water MB by adding 25 ml of reagent water to a 40 mL pre-preserved VOA vial with ultrapure water. Process in the same manner as all other samples and QC.

III. The method blank results must be below the Report Limit (RL). Avoid carry over by cleaning a system contaminated by saturated samples (see **Section 4**).

9.1.2 Laboratory Control Sample/Laboratory Control Sample Dup (LCS/LCSD)

I. Prepare a LCS or LCSD by adding 25 µL of the 50 mg/L primary calibration standard to a pre-preserved VOA vial containing 25mL of ultrapure water. Process the same as all other samples and QC.

II. The LCS / LCSD must recover within ± 30% of RF if Ave. RF used, or alternatively ± 30% of true value if linear or second order regression used. LCSD RPD must be ≤ 20%.

Note: Method 524.2 does not require the routine analysis of a MS/MSD. If requested or required follow the procedures in **Section 9.1.2** using a matrix sample instead of ultrapure water. Also the CCV/LCS/LCSD are made the same and may be used in conjunction to meet quality control requirements; minimum of two are required.

9.1.3 Surrogates (Surr.)

I. Surrogates are added to each sample, method blank and QC. The analyst adds 5µL of IS/Surr standard (100 ppm) during prep.

II. The surrogate recoveries must fall within the acceptance limits of 70 – 130%. If any surrogates are outside of the acceptance limits the sample must be re-analyzed or flagged.

9.1.4 Internal Standards (ISTD)

I. Determine that the absolute areas of the quantitation ions of the internal standards in each sample have not changed by more than 30% from the areas measured during the last daily calibration check or by more than 50% from the areas measured during initial calibration.

9.2 Instrument QC - The following quality control samples are prepared with each batch of samples.

9.2.1 BFB Tune

I. Method 524.2 requires a BFB tune to be analyzed every 12-hours before analysis of any quality control or samples.

II. Prepare the mass spectrometer tune verification by directly injecting 1 µL of the 25 ppm BFB standard (GCMS #1/#26). Alternatively, purge 10 mLs of a BFB solution prepared by adding 4µL of BFB standard to 10mLs of reagent water in an unpreserved VOA vial (GCMS #17).

III. The mass spectrometer must produce a mass spectrum for BFB that meets all the relative ion abundance criteria in Table 3 of the 524.2 method as follows:

Table 3

M/z	Relative abundance
50	15 to 40% of m/z 95
75	30 to 80% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

Note: For instruments that analyze both method 8260B and method 524.2 the tighter criteria for mass 75 from the 8260 method will be utilized. M/z 75 must have a relative abundance that is 30 to 60% of m/z 95.

IV. Evaluating the BFB **must** include a minimum of three scans including the peak apex with a background subtract using a scan just outside the BFB peak.

V. If the BFB mass spectrum does not meet all the criteria, re-inject the BFB one more time. If the BFB mass spectrum still does not meet all the criteria, re-make the standard. If it still fails, then adjust the MS parameters or do injection port maintenance. For example: replace the liner, gold seal, septa etc., then bake the column and try the BFB tune verification again.

VI. If the criteria are still not met, then perform a system autotune using PFTBA (perfluorotributylamine) followed by two passing BFB tune verifications. Tuning with PFTBA is a last resort since this compound prematurely contaminates the ion source.

9.2.2 Continuing Calibration Verification (CCV)

I. Verify the initial calibration at the beginning of each 12 hour sample analysis period (after the tune check) and at the end of any cycle of continuous instrument operation.

II. Analyze a 50 ppb and/or 2.0 ppb calibration standard fortified with 20 ppb Internal Standard and Surrogates. (Note: 1,2-Dibromo-3-chloropropane and 1,2,3-Trichloropropane must be analyzed at 2.0 ppb, and the remaining analytes at either 2.0 or 50 ppb).

III. Determine that the absolute areas of the quantitation ions of the internal standards in the CCV(s) have not changed by more than 50% from the areas measured during the last calibration midpoint 50 ppb).

IV. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration or, if linear or second order regression was used, the concentration measured must be within 30% of true value.

V. The Continuing Calibration Verification may also be used as LCS or LCSD. See Sample QC **Section 9.1.2**.

9.2.3 Reporting Limit Verification Check (RLV) In TALS (CCVL 0.5 & CCV 2.0)

I. Verify the Report limit for each analyte every 12 hour sample analysis period.

II. Analyze a 0.5 ppb and/or 2.0 ppb calibration standard fortified with 20 ppb Internal Standard and Surrogates. (Note: 1,2-Dibromo-3-chloropropane and 1,2,3-Trichloropropane must be analyzed at 2.0 ppb, and the remaining analytes at 0.5 ppb).

III. The RF for each analyte must be within 50% of the mean value measured in the initial calibration if average response factor was used. If the linear or second order regression was used, the concentration measured must be within 50% of true value.

9.2.4 Quality Control Sample (QCS)

I. At least quarterly, analyze a 20 ppb second source standard. Acceptable recovery is 70 – 130%.

10.0 Procedure

10.1 Sample Preparation

10.1.1 Take a 25 mL aliquot of sample and transfer it into an unpreserved VOA vial using a 25 mL gas tight syringe. Add 5µL of the IS/Surr standard (100 ppm) to the aliquot and cap the vial. Check historical data for dilutions that may be needed. Use the remaining sample to check for foaminess and pH.

10.1.2 Document the sample number, dilution factor, container letter, and any other necessary information such as headspace or strong smell in the printed run log from CHROM. If the sample has a pH > 2, check the remaining vials pH and run another vial that is pH $\leq$ 2. If all vials are pH > 2, notify the PM and flag the sample accordingly.

10.1.3 Prepare dilutions for samples that have target analytes detected above the calibration range. Perform the dilution by taking the appropriate aliquot of sample and adding it to the appropriate amount of ultrapure water to equal 25 mL. Proceed with the preparation in the same manner as an undiluted sample.

10.1.4 Enter the port numbers corresponding to the samples to be analyzed into the autosampler. Verify all settings are correct. Press start.

10.2 Calibration

10.2.1 Perform initial calibrations on an as needed basis. Initial calibration is required after any major instrument maintenance or after failing calibration checks that cannot be rectified by corrective actions. Major maintenance includes, but is not limited to, the following: Detector maintenance and column replacement.

10.2.2 The number of calibration levels needed, according to the method, depends on the calibration range desired. A minimum of three calibration levels is required to calibrate a range of a factor of 20. For a factor of 50, use a least four calibration standards, and for a factor of 100 at least five calibration standards. Use a minimum of six standards for quadratic curves.

10.2.3 Calibration standards are made into 25 mL of ultrapure water in 40 mL VOA vials pre-preserved with HCl. Listed below are the typical concentrations used for calibration. Additional or other concentrations can be used as required.

	FINAL CONCENTRATIONS (ppb)		SPIKE AMOUNTS (µL)	SPIKE AMOUNTS (µL)	SPIKE AMOUNTS (µL
Calibration number	ISTD / Surrogates	Target Compounds	Calibration standard 2.5 ppm	Calibration standard 50 ppm	Second Source 50 ppm standard
1	5	0.5	5		
2	5	1	10		
3	5	2		1	
4	5	5		2.5	
5	5	10		5	
6	5	20		10	
7	5	50		25	
8	5	75		37.5	
9	5	100		50	
ICV – Second Source	5	50			25
CCVL – Primary Source	5	0.5	5		
CCV – Primary Source	5	50		25	

10.2.4 All of the calibration curve must run within the 12 hour clock established by the BFB tune run prior to the curve.

10.2.5 A method blank must be run prior to the calibration to verify that the instrument is free from contamination. The blank run prior to the calibration should be re-calculated using the new method and any analytes that are detected must be less than the Report Limit.

10.2.6 Analyze the initial calibration curve in the same manner as samples as described in the sample preparation section. An example of how to prepare the calibration levels is in the table above.

10.2.7 Check the calibration standards frequently for signs of degradation or evaporation, especially just prior to preparing a calibration.

10.2.8 Process all calibration points by reviewing the chromatography. Check for any integrations and delete any peaks that are non-spectral matches (NSM) or that have a peak height < 3 times the height of the baseline. Print the data files for all curve points and the before and after chromatograms/spectra for any manual integrations that are performed. See Data analysis **Section 10.4** for further information on manual integrations.

10.2.9 Check the %RSD and examine the curve plots for each analyte. Per method 524.2 the RFs from the initial calibration curve should have an RSD ≤ 20% for all compounds.

10.2.10 If one or more of the compounds have an RSD >20% then:

I. A first order (linear) regression or second order (quadratic) may be used for quantitation.

II. For a 5 point minimum linear curve or 6 point minimum quadratic curve the Coefficient of Determination (r^2) must be ≥ 0.990 (Correlation Coefficient (r) ≥ 0.995) for the curve to be acceptable. If r^2 < 0.990 then the instrument must be re-calibrated for that compound.

10.2.11 If 1st or 2nd order curves are not allowed to be forced through the origin as inaccuracies may be present near the low end of the curve or negative values may be obtained at the reporting limit.

10.2.12 The accuracy at the low end of the curve can be verified by re-quantitating the calibration standard at (or below) the reporting limit against the new calibration method. The result must be ± 50% of the true value.

10.2.13 Due to bending in a quadratic curve inaccuracies may be present at the high end of the curve as well. Analysts must be especially careful to scan the chromatogram for unidentified peaks when this type of curve fit has been used because compounds with a concentration above the calibration range may not be identified.

10.3 Sample Analysis

10.3.1 Perform a BFB tune, analyze calibration/ICV and/or check(s), and analyze an instrument blank/method blank before running any samples. The Reporting Limit Verification (CCVL) can be run after the CCV and prior to the instrument blank. Analyzing the instrument blank prior to running samples ensures the instrument is free of contamination and minimizes reanalysis of samples due to contamination.

An example sequence follows:

Tune Check	BFB – 12 hour Tune Window
Calibration Standards	Standards 1-8
ICV/QCS	20 ppb Second Source
Tune Check	BFB – 12 hour Tune Window
CCVL/RLV	0.5 ppb Primary source
CCVIS	50 ppb Primary Source
LCS/LCSD	50 ppb Primary Source
Method Blank	Reagent Water
20 Samples	1-20 samples

10.3.2 All samples and QC must run within the 12-hour clock established by the BFB tune at the beginning of the run.

10.4 Data Analysis

10.4.1 Reports and their corresponding chromatograms are printed out after each QC sample and client sample is analyzed and has been electronically reviewed.

10.4.2 Perform a manual integration when a peak has a co-elution, has been misidentified, or has interferences. All manual integrations must undergo second level review. Print graphics before and after the integration and document the reason for integration on the before graphics (This is done electronically in TALS) TALS provides graphics of the before and after integrations, electronically attached to each QC and sample analyzed. See the Manual Integration SOP, PE-QAD-009, for further information.

10.5 Compound Identification

10.5.1 Identify a sample component by comparing its mass spectrum (after background subtraction) to a reference spectrum in the Lab-created database. 50 ppb standard spectrum is used to update the reference spectrum database each time the instrument is calibrated. Sample component mass spectrum must compare with the standard as follows:

I. All ions present in the standard mass spectra at a relative intensity greater than 10% (major abundant ion in the spectrum equals 100%) **must** be present in the sample spectrum.

II. The relative intensities of these ions must agree within ±20% of the sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30% and 70%).

III. Ions greater than 10% in the sample spectra but not present in the standard spectrum must be considered and accounted for by the analyst. All compounds meeting the identification criteria must be reported.

IV. If a compound cannot be verified by the above criteria, and in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the compound value will be reported.

10.6 Entering the Data into TALS LIMS

10.6.1 Create an analytical batch creating a new Work List (WL). In TALS use the “Analyst” drop down menu and select “Chrom Toolbar”, then select “Worklist Editor”

10.6.2 When a Work List is saved a batch number will be automatically assigned to the batch.

10.6.3 Fill in the appropriate information including the Worklist Name, Sample Info, Sample Reagents, Run Reagents, check all appropriate boxes, etc…

10.6.4 Choose the client samples that are included in the batch by using the scanners and scanning in the barcode assigned at login.

10.6.5 Query the batch and review the data by using “Chrom Toolbar” and select “Review”. Check the integration, QC recoveries, RPDs, correct identification of analyte peaks, etc .

10.6.6 Once the “Review” is completed in “Chrom” send the data over to TALS by changing the status from “UnReviewed” to “Reviewed”. After processing the batch in TALs, adding the sample pH to the worklist tab, adding/correcting any needed flags, NCMs and assuring data links are correct, be sure to update the batch to “1st Level Review” in TALS, this locks the cells after the initial review of the data has been completed. Lastly be sure the printed

run log is attached to the batch and has the documented pH sample values and sample prep loader analyst initials present. The prep and loader analyst initials must also be added to the batch review comments sections.

10.6.7 Before the Project Manager can report the results to the client the data must be second level reviewed. After the review has been completed, be sure that the batch has been updated to the "2nd Level Review" status.

10.6.8 A copy of the Worklist, instrument sequence, run log, data review checklist and ICAL checklist must be included along with the raw data.

10.6.9 Enter each new standard that is prepared or purchased into the TALS "Reagent" list.

10.7 Reporting Results

10.7.1 Sample results are reported to two significant figures. QC data is reported to a minimum of three significant figures.

10.7.2 The analytical data is uploaded directly into the TALS LIMS. The analyst is the first reviewer of the data for accuracy / completeness and the Department Supervisor (or other authorized reviewer) performs the secondary review.

10.7.3 Client final reports are generated using the TALS LIMS. The reports include: a) the Eurofins TestAmerica project number and associated sample number(s); b) the analyte names; c) the sample results and reporting limits for all target analytes; d) any dilution factors; and e) the date of analysis.

10.8 Preventative Maintenance

10.8.1 Record all performed maintenance in the instrument maintenance logbook.

10.8.2 If an instrument is unusable or has limitation to its use it must be tagged accordingly until such a time the problem has been corrected. Record the problem, solution and verification of proper operation into the instrument maintenance logbook.

10.8.3 Replace traps, dry purge valves, water-management units, and bulkhead fittings as needed or by the following recommendations: Trap replacement approximately quarterly, water management approximately bi-annually and dry purge valve approximately annually.

10.8.4 Flush transfer line from concentrator to GC as needed.

10.8.5 Replace injector septa, liner approximately quarterly and gold seal when necessary.

10.8.6 Clean ion source and replace filaments approximately quarterly or more often when necessary. For 5973, check repeller ceramic insulator.

10.8.7 Flush the purge needle and purge valve with Methanol whenever needed (after high level or surfactant containing samples).

10.8.8 Replace the sparge tube as necessary or approximately quarterly.

10.8.9 Check the diffusion pump oil at least annually and replace as necessary.

10.8.10 Replace the carrier gas trap when necessary.

10.8.11 Preventative maintenance for the autosamplers:

I. Wipe the slide rails down with a Kimwipe and Methanol when necessary.

II. Perform a calibration for the XYZ axis whenever the system fails to retrieve or return vials from their position.

III. Flush the transfer line from the autosampler to the concentrator approximately quarterly.

11.0 Calculations / Data Reduction

11.1 **Calibration:** Calibration calculations are performed by instrument software. Alternatively, the calculations can be performed using the equations found in PE-QAD-022, Good Calibration Practices.

11.2 **Concentration:** Calculate the analyte and the surrogate concentrations:

$$\text{Concentration } (\mu g/L) = \frac{Ax \times Cis}{Ais \times RF} \times DF$$

Where:

As = Area of the characteristic ion for the parameter to be measured.
Ais = Area of the characteristic ion for the internal standard.
Cis = Concentration of the internal standard.
Cs = Concentration of the parameter to be measured.
RF = Mean response factor of the analyte from the initial calibration.
DF = Dilution factor (if necessary).

Note: The RF is used only for cases where a linear regression calibration curve is not being used. When the linear regression is used as the calibration criteria, the slope of line is used in the calculation.

11.3 Mean ($\bar{x}$): Adding together the numerical values (a, b, c, etc.) of an analysis and dividing this sum by the number *n* of measurements used yields the mean.

$$\bar{x} = \frac{a + b + c}{n}$$

11.4 Standard Deviation (s): The standard deviation is calculated by taking the square root of the quotient from the sum of all the squared individual deviations divided by one less than the number of measurements ($n - 1$) used in the analysis. Statistically it has been

determined that as the number of measurements *n* exceeds 30, the *n* – 1 term can be simplified to *n*.

$$s = \sqrt{\frac{x^2 + y^2 + z^2 \ldots}{n - 1}}$$

The standard deviation can be calculated in five steps:

1. Determine the mean ($\bar{x}$).
2. Subtract the mean from each measured data item.
3. Square each difference.
4. Find the average of the squared terms in step 3.
5. Calculate the square root of the average found in step 4 by dividing by one less than the actual number of measurements.

11.5 Relative Standard Deviation (RSD).

$$\%RSD = \frac{\text{Standard deviation}}{\text{Mean}} \times 100$$

11.6 Relative Percent Difference (RPD).

$$RPD = \left| \frac{A - B}{(A + B)/2} \right| x\,100$$

A = Measured concentration of the first sample or spike aliquot
B = Measured concentration of the second sample or spike aliquot

11.7 Percent Recovery (% Recovery).

$$\%Recovery = \frac{SSR - SR}{SA} \times 100$$

SSR = Spike sample result
SR = Sample result
SA = Spike added from spiking standard

11.8 Percent Difference and Percent Drift

$$\%\ Drift = \frac{(Calculated\ concentration - True\ concentration)}{True\ concentration} \times 100$$

$$\%\ Difference = \frac{RFv - RFa}{True\ concentration} \times 100$$

RFv = RF value for the compound of interest in the verification standard
RFa = mean RF for the compound of interest in the calibration

11.9 Calculate a response factor (RF) for each analyte of interest and surrogate using the internal standard method.

$$RF = \frac{Ax \times Cis}{Ais \times Cx} \times 100$$

Ax = Integrated abundance of quantitation ion of the analyte
Ais = Integrated abundance of quantitation ion of internal standard
Cx = Concentration of analyte purged
Cis = Concentration if internal standard purged

12.0 Method Performance

12.1 **Method Detection Limit Study (MDL) –** See CA-Q-S-006 Detection Limits for complete details

12.1.1 Additional information can be found in the QA Manual.

12.2 **Training Requirements – Method SOPs**

12.2.1 Refer to the QA Manual or to SOP PE-QAD-008 – Personnel Certification and Training. At a minimum before an analyst can perform the method independently, they must have:

a. Read the analytical method(s);
b. Read the applicable SOP(s); and
c. Acceptably performed and documented the data for four QCS.

12.3 **Demonstration of Capabilities (DOC)**

12.3.1 Refer to the QA Manual for general procedures and any specific concentrations that must be used. See PE-QAD-015 Demonstration of Capability for complete details.

12.3.2 IDOC limits for method 524 are 80-120%

12.3.3 A Demonstration of Capability form shall be completed initially and annually thereafter.

12.4 **Control Limits (Procedure/Method Acceptance Criteria)**

12.4.1 Once control limits have been established (in-house or by method), they are verified, reviewed, and updated if necessary on an annual basis unless the method or regulatory authority requires more frequent updating. Control limits are established per method (as opposed to per instrument) regardless of the number of instruments utilized.

12.4.2 More information concerning Control Limits can be found in the QA Manual.

12.4.3 Current Control limits for this method can be found in **Appendix 1** of this SOP.

13.0 Pollution Control

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Section 13 – Waste Management and Pollution Prevention of the Corporate Environmental Health and Safety Manual (CW-E-M-001) or the current Waste Management SOP.

14.2 The following waste streams are produced when this method is carried out:

14.2.1 Following analysis, all samples are stored in the EPA 524.2 sample storage refrigerator. Approximately one month later, samples are moved to the warehouse.

14.2.2 **Acidic waste** (Closed Top Poly Drum): Acidic waste is stored in appropriately labeled hazardous waste containers in satellite storage areas throughout the lab, and should be emptied as often as possible. The waste should be transferred to the storage area in these exact same containers. The snorkel valve on the fume hood exhaust tubing should be turned 90 degrees clockwise to direct flow to the snorkel. The drum openings should then be opened with a wrench. The carboy placed over one opening and the snorkel placed over the other opening. The valve for the carboy should then be opened thereby transferring the contents of the carboy into the waste drum.

I. **All acidic aqueous instrument waste in the VOAs Department is neutralized to a pH of 6 to 7 and then dumped down the drain.**

14.2.3 **Mixed solvent waste** (Closed Top Metal Drum): Solvent waste is stored in appropriately labeled hazardous waste containers in satellite storage areas throughout the lab, and should be emptied as often as possible. The waste should be transferred to the storage area in these exact same containers. The snorkel valve on the fume hood exhaust tubing should be turned 90 degrees clockwise to direct flow to the snorkel. The drum openings should then be opened with a wrench. The carboy placed over one opening and the snorkel placed over the other opening. The valve for the carboy should then be opened thereby transferring the contents of the carboy into the waste drum.

14.2.4 **Contaminated solid material utilized for sample preparation (i.e. glass ASE vials, transfer pipettes, plastic materials, sodium sulfate)**. If the solid material is estimated to contain <5% of the original material, they can be disposed of in the trash, unless they exhibit RCRA characteristics such as ignitability, reactivity, corrosivity or toxicity.

14.2.5 Expired primary and working standards:

I. Low concentration (<1000 PPM): Dispose of in the solvent waste stream.
   a. If the standard is prepared in water, dispose in the acidic waste stream.
II. High concentration: (>1000 PPM) Lab pack.

14.3 Any waste, which does not fit into any of the waste streams or cannot be disposed of in any of the other drums, should be brought directly to the department and/or waste manager's attention.

15.0 References / Cross-References

15.1 National Exposure Research Laboratory – Cincinnati, EPA, Pub. No. EPA/600/R-95/131, Methods for the Determination of Organic Compounds in Drinking Water: Supplement III (August 1995), Method 524.2 – Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, 1995, Revision 4.1.

15.2 EPA 815-R-05-004, Manual for the Certification of Laboratories Analyzing Drinking Water, EPA, 5th Edition, January 2005.

15.3 Arizona Department of Health Services

- Director Approved Method Modifications, Revision 1, dated 2/19/2008
- Information Update #13, dated July 6, 1995
- Information Update #18, dated September 15, 1995
- Information Update #31, dated August 27, 1996
- Information Update #87, dated July 7, 2005
- Information Update #89, dated May 15, 2006

15.4 TestAmerica – Corporate

- Environmental Health and Safety Manual, CW-E-M-001.
- CA-Q-S-002 Manual Integrations
- QA-S-005 Calibration Curves (General)
- CA-Q-S-006 Detection Limit

15.5 TestAmerica – Phoenix

- PX-QAD-011 Quality Assurance Manual
- PE-QAD-013 Reagent and Standard Preparation, Control and Documentation
- PE-QAD-023 Measurement Traceability
- PE-QAD-022 Good Calibration Practices
- PE-QAD-009 Manual Integrations/Data Integrity
- PE-QAD-006 Logbook Documentation
- PE-QAD-011 Significant Figures
- PE-SFT-001 Sample Disposal and Waste Management

16.0 Method Modification

16.1 For instruments that analyze both method 8260B and method 524.2 the tighter criteria for mass 75 from the 8260 method is utilized.

17.0 Attachments

Attachment 1: Target Analyte List

18.0 Revision History

Revision 0, dated June 27, 2008
- Integration of TestAmerica and STL operations.

Revision 1, dated January 27, 2010
- Conversion to the TestAmerica Laboratories, Inc. SOP template.
- Purge volume changed from 20 mL to 25 mL.
- BFB Tune criteria explanation expanded.
- Expanded how to handle non-preserved samples.

Revision 2, dated March 10, 2011
- Annual Review.
- Updated to reflect current practices.

Revision 3, dated April 19, 2012

Section	Change
6.1	Updated instrumentation section. Added note that routine conditions are listed and that they are subject to change
7.4	Revised standards information
7.6.2	Updated Internal Standard preparation information
7.6.3	Updated ICAL standard preparation information
9.2.2	Added that the CCV is also used as the LSC
10.2	Added ICV information
10.6	Updated information required for raw data package
10.8	Revised maintenance procedures
12.3	Changed IDOC recovery limits to 80 – 120% per method requirement
14.0	Updated disposal information
15.0	Updated references
16.0	Added information on BFB evaluation

Revision 4, dated November 26, 2012
- Section 6.1 – Updated Instrumentation to reflect current configurations and remove GCMS 9.
- Section 7.6 - Updated standard preparation descriptions to reflect current practice.
- Section 9.2.2 – Changed all references of the 5 ppb CCV to 20 ppb.
- Section 10.1 – Updated sample preparation procedures to reflect current practice.
- Section 10.2.3 – Updated Calibration standard preparation table to reflect current practice.

- Section 10.3.1 – Added recommendation for running CCV approximately halfway through the 12 hour clock when no analysts are present.
- Removed Attachment 2 – Data Review Checklist

Revision 5, dated March 31, 2014
- Revised Section 3.3 – Included CCVL
- Revised section 10.6 – Entering data into TALS
- Replaced all references to Element with TALS.

Revision 6, dated April 7, 2015
- Section 6.1 – Updated Instrumentation list
- Section 6.1.3 – Updated Purge and Trap conditions
- Section 7.4 – Standards updated
- Section 7.6.3 – Updated Primary Calibration Standard (50 µg/mL) section
- Section 7.6.5 – Added Primary Calibration Standard (2.5 µg/mL) section
- Section 9.2.2.II – Added analytes to “Note”.
- Section 10.2.3 – Updated Calibration Standard Table

Revision 6, dated April 7, 2015

5/12/16 Annual SOP Review – No changes necessary.

Revision 7, dated January 4, 2017
- Section 10.2.3 – Removed the 200 ppb standard from list of calibration standards.

Revision 8, dated February 28, 2018
- Section 9.2.2.II and 9.2.3 II – Removed Vinyl Chloride.
- Removed section on Method of Uncertainty

Revision 8.1, dated November 2, 2018
- Updated signatures only

Revision 9 dated November 9, 2019
- Section 6.1.1 / 6.1.2 / 6.1.3 – Updated operating conditions
- Attachment 1 – Updated reporting limits

Revision 10 dated December 4, 2020
- Section 6.1 – Updated instrumentation list, temperature program and instrument conditions,
- Section 6.2 – Removed Teflon tape
- Section 7.4 – Updated vendors for standards.
- Section 7.6.2/7.6.3/7.6.4 – updated preparation of standards,
- Section 8.5 – Inserted table for holding time and preservations.
- Section 8.8 – Inserted section on TTHMs
- Section 9.0 – Updated table on Quality Control
- Section 9.1.1 – Updated preparation of method blanks
- Section 9.1.2 – updated preparation of LCS/LCSD. Added last sentence,
- Section 9.2.1 II – Updated preparation of BFB
- Section 10.2.3 – Updated table
- Section 10.3.1 – Updated table

- Section 10.6.6 – Added requirements for pH. Added requirements regarding printed runs and initials.

Revision 11 dated March 23, 2021
- Section 6.1.1 – Updated Temperature Program
- Section 6.1.3 – Updated Purge and Trap Conditions
- Section 6.1.4 – Reworded. Only purging time and desorb time cannot be changed.
- Section 9.1.2 – Updated preparation of standards.
- Section 9.2.2/10.5.1 – Changed all references of the 20 ppb CCV to 50 ppb.
- Section 10.2.3 – Updated table
- Section 10.3.1 – Updated table

ATTACHMENT 1

TARGET ANALYTE LIST, QUANTITATION IONS AND REPORTING LIMITS (RL)

Compound	Primary Quantitation Ions	Secondary Quantitation Ions	RL (µg/L)
Internal Standard			
Fluorobenzene	96	77	
Surrogates			
4-Bromofluorobenzene	95	174, 176	
1,2-Dichlorobenzene-d_4	152	115	
Target Analytes			
Benzene	78	77	0.50
Bromobenzene	156	77, 158	0.50
Bromochloromethane	128	93, 130	0.50
Bromodichloromethane	83	85, 127	0.50
Bromoform	173	175	0.50
Bromomethane	94	96	0.50
n-Butylbenzene	91	134	0.50
sec-Butylbenzene	105	134	0.50
tert-Butylbenzene	119	91	0.50
Carbon Tetrachloride	117	119	0.50
Chlorobenzene	112	77, 114	0.50
Chloroethane	64	66	0.50
Chloroform	83	85	0.50
Chloromethane	50	52	0.50
2-Chlorotoluene	91	126	0.50
4-Chlorotoluene	91	126	0.50
1,2-Dibromo-3-chloropropane	157	155	2.0
1,2-Dibromoethane	107	109, 188	0.50
Dibromochloromethane	129	127	0.50
Dibromomethane	93	95, 174	0.50
1,2-Dichlorobenzene	146	111, 148	0.50
1,3-Dichlorobenzene	146	111, 148	0.50
1,4-Dichlorobenzene	146	111, 148	0.50
Dichlorodifluoromethane	85	87,101	0.50
1,1-Dichloroethane	63	65, 83	0.50
1,2-Dichloroethane	62	98	0.50
1,1-Dichloroethene	96	61, 63	0.50
cis-1,2-Dichloroethene	96	61, 98	0.50
trans-1,2-Dichloroethene	96	61, 98	0.50

ATTACHMENT 1 (cont'd)

TARGET ANALYTE LIST, QUANTITATION IONS AND REPORTING LIMITS (RL)

Compound	Primary Quantitation Ions	Secondary Quantitation Ions	RL (µg/L)
1,2-Dichloropropane	63	112	0.50
1,3-Dichloropropane	76	78	0.50
2,2-Dichloropropane	77	97	0.50
1,1-Dichloropropene	75	110, 77	0.50
cis-1,3-Dichloropropene	75	110	0.50
trans-1,3-Dichloropropene	75	110	0.50
Ethylbenzene	91	106	0.50
Hexachlorobutadiene	225	260	0.50
Isopropylbenzene	105	120	0.50
4-Isopropyltoluene	119	134, 91	0.50
Methylene Chloride	84	86, 49	0.50
Methyl-t-butyl Ether	73	57	1.0
Naphthalene	128		0.50
Propylbenzene	91	120	0.50
Styrene	104	78	0.50
1,1,1,2-Tetrachloroethane	131	133, 119	0.50
1,1,2,2-Tetrachloroethane	83	131, 85	0.50
Tetrachloroethene	166	168, 129	0.50
Toluene	92	91	0.50
1,2,3-Trichlorobenzene	180	182	0.50
1,2,4-Trichlorobenzene	180	182	0.50
1,1,1-Trichloroethane	97	99, 61	0.50
1,1,2-Trichloroethane	83	97, 85	0.50
Trichloroethene	95	130, 132	0.50
Trichlorofluoromethane	101	103	0.50
1,2,3-Trichloropropane	110	97	2.0
1,2,4-Trimethylbenzene	105	120	0.50
1,3,5-Trimethylbenzene	105	120	0.50
Vinyl Chloride	62	64	0.50
m,p-Xylene	106	91	1.0
o-Xylene	106	91	0.50

ANALYTICAL METHODS

Section 12.0

Method: EPA Method TO-14A/TO-15 Volatile Organic Compounds (Low-Level)

Eurofins Air Toxics SOP #83 Revision 22 Effective Date: November 4, 2020 Methods Manual Summary

Description: This method involves full scan gas chromatograph/mass spectrometer (GC/MS) analysis of whole air samples collected in evacuated stainless steel canisters. Samples are analyzed for volatile organic compounds (VOCs) using EPA Method TO-14A/TO-15 protocols. An aliquot of up to 400 mL of air is withdrawn from the canister utilizing a mass flow controller. This volume is loaded onto a hydrophobic multibed sorbent trap to remove water and carbon dioxide and to concentrate the vapor sample. The focused sample is then flash-heated to sweep adsorbed VOCs onto a GC/MS for separation and detection. Compounds are detected using a mass spectrometer operating in full scan mode.

Eurofins Air Toxics maintains a suite of TO-14A/TO-15 methods, each optimized to efficiently meet the data objectives for a wide range of targeted concentration ranges. The methods, their reporting limits, and typical applications are summarized in the table below. This method summary describes TO-14A/TO-15 (Low-Level).

Eurofins Air Toxics Method	Base Reporting Limits	Typical Application
TO-14A/TO-15 (5&20)	5 – 20 ppbv	Soil gas and ppmv range vapor matrices
TO-14A/TO-15 (Standard or Quad)	0.5 – 5.0 ppbv	Ambient air, soil gas, and ppbv level vapor matrices
TO-15 (Extended)	0.2 – 5.0 ppbv	Ambient air and ppbv level vapor matrices
TO-14A/TO-15 (Low-level)	0.1 – 1.0 ppbv	Indoor and outdoor air
TO-14A/TO-15 (SIM)	0.01 – 0.5 ppbv	Indoor and outdoor air
TO-15 HSS	0.01 – 0.1 ppbv	Soil gas and other high concentration matrices

Certain compounds are not included in Eurofins Air Toxics' standard target analyte list. These compounds are communicated at the time of client proposal request. Unless otherwise directed, Eurofins Air Toxics reports these non-routine compounds with partial validation. Validation may include a 3-point calibration with the lowest concentration defining the reporting limit, no second source verification analyzed, and no method detection limit study performed unless previous arrangements have been made. In addition, stability of the non-standard compound during sample storage is not validated. Full validation may be available upon request.

Since Eurofins Air Toxics applies TO-15 methodology to all Summa™ canisters regardless of whether TO-14A or TO-15 is specified by the project, Eurofins Air Toxics performs a modified version of method TO-14A as detailed in Table 1. Please note that Methods TO-14A and TO-15 were validated for specially treated canisters. As such, the use of Tedlar bags for sample collection is outside the scope of the method and is not recommended for ambient or indoor air samples. It is the responsibility of the data user to determine the usability of TO-14A and TO-15 results generated from Tedlar bags.

All samples submitted for TO-15 Low-Level are screened prior to analysis. If samples contain high concentrations of target and/or non-target VOCs, samples may be analyzed by an alternative TO-15 method (i.e., Standard or 5&20) with a higher dynamic calibration range.

Table 1. Summary of TO-14A Method Modifications

Requirement	TO-14A	Eurofins Air Toxics Modifications
Sample Drying System	Nafion Dryer	Multibed hydrophobic sorbent
Blank acceptance criteria	< 0.2 ppbv	< RL
BFB ion abundance criteria	Ion abundance criteria listed in Table 4 of TO-14A	Follow abundance criteria listed in TO-15.
BFB absolute abundance criteria	Within 10% when comparing to the previous daily BFB	CCV internal standard area counts are compared to ICAL; corrective action taken when recovery is less than 60%.
Blanks and standards	Zero Air	UHP Nitrogen provides a higher purity gas matrix than zero air for trace level measurements.
Initial Calibration	≤ 30% RSD for listed 39 VOCs	≤ 30% RSD with 4 compounds allowed out to ≤ 40%

Table 2. Summary of Method TO-15 Modifications

Requirement	TO-15	Eurofins Air Toxics Modifications
Initial Calibration	≤ 30% RSD with 2 compounds allowed out to < 40% RSD	≤ 30% RSD with 4 compounds allowed out to ≤ 40%
Blanks and standards	Zero Air	UHP Nitrogen provides a higher purity gas matrix than zero air for trace level measurements.

The standard target analyte list, reporting limits (RL), also referred to as Limit of Quantitation (LOQ), Quality Control (QC) criteria, and QC summary can be found in tables 3 through 6.

Table 3. Method TO-14A/TO-15 Standard Analyte List (Low-Level) and QC Limits

Analyte	RL/LOQ (ppbv)	QC Acceptance Criteria			
		ICAL (%RSD)	CCV (%R)	ICV/LCS* (%R)	Precision Limits (Max. RPD)
1,1,2,2-Tetrachloroethane	0.1	≤ 30%	70 – 130	70 – 130	± 25
1,1,2-Trichloroethane	0.1	≤ 30%	70 – 130	70 – 130	± 25
1,1-Dichloroethane	0.1	≤ 30%	70 – 130	70 – 130	± 25
1,1-Dichloroethene	0.1	≤ 30%	70 – 130	70 – 130	± 25
1,2,4-Trichlorobenzene	0.5	≤ 30%	70 – 130	70 – 130	± 25
1,2,4-Trimethylbenzene	0.1	≤ 30%	70 – 130	70 – 130	± 25
1,2-Dibromoethane (EDB)	0.1	≤ 30%	70 – 130	70 – 130	± 25
1,2-Dichlorobenzene	0.1	≤ 30%	70 – 130	70 – 130	± 25
1,2-Dichloroethane	0.1	≤ 30%	70 – 130	70 – 130	± 25
1,2-Dichloropropane	0.1	≤ 30%	70 – 130	70 – 130	± 25
1,3,5-Trimethylbenzene	0.1	≤ 30%	70 – 130	70 – 130	± 25
1,3-Dichlorobenzene	0.1	≤ 30%	70 – 130	70 – 130	± 25
1,4-Dichlorobenzene	0.1	≤ 30%	70 – 130	70 – 130	± 25
Benzene	0.1	≤ 30%	70 – 130	70 – 130	± 25
Bromomethane	0.5	≤ 30%	70 – 130	70 – 130	± 25
Carbon Tetrachloride	0.1	≤ 30%	70 – 130	70 – 130	± 25
Chlorobenzene	0.1	≤ 30%	70 – 130	70 – 130	± 25
Chloroethane	0.5	≤ 30%	70 – 130	70 – 130	± 25
Chloroform	0.1	≤ 30%	70 – 130	70 – 130	± 25
Chloromethane	0.5	≤ 30%	70 – 130	70 – 130	± 25
Chlorotoluene (Benzyl Chloride)	0.1	≤ 30%	70 – 130	70 – 130	± 25
cis-1,2-Dichloroethene	0.1	≤ 30%	70 – 130	70 – 130	± 25
cis-1,3-Dichloropropene	0.1	≤ 30%	70 – 130	70 – 130	± 25
Dichloromethane (Methylene Chloride)	0.2	≤ 30%	70 – 130	70 – 130	± 25
Ethylbenzene	0.1	≤ 30%	70 – 130	70 – 130	± 25
Freon 11 (Trichlorofluoromethane)	0.1	≤ 30%	70 – 130	70 – 130	± 25
Freon 113 (Trichlorotrifluoroethane)	0.1	≤ 30%	70 – 130	70 – 130	± 25
Freon 114	0.1	≤ 30%	70 – 130	70 – 130	± 25
Freon 12 (Dichlorodifluoromethane)	0.5	≤ 30%	70 – 130	70 – 130	± 25
Hexachlorobutadiene	0.5	≤ 30%	70 – 130	70 – 130	± 25
m,p-Xylene	0.1	≤ 30%	70 – 130	70 – 130	± 25

Analyte	RL/LOQ (ppbv)	QC Acceptance Criteria			
		ICAL (%RSD)	CCV (%R)	ICV/LCS* (%R)	Precision Limits (Max. RPD)
Methyl Chloroform (1,1,1-Trichloroethane)	0.1	≤ 30%	70 – 130	70 – 130	± 25
o-Xylene	0.1	≤ 30%	70 – 130	70 – 130	± 25
Styrene	0.1	≤ 30%	70 – 130	70 – 130	± 25
Tetrachloroethene	0.1	≤ 30%	70 – 130	70 – 130	± 25
Toluene	0.1	< 30%	70 – 130	70 – 130	± 25
trans-1,3-Dichloropropene	0.1	≤ 30%	70 – 130	70 – 130	± 25
Trichloroethene	0.1	≤ 30%	70 – 130	70 – 130	± 25
Vinyl Chloride	0.1	≤ 30%	70 – 130	70 – 130	± 25
1,3-Butadiene	0.1	≤ 30%	70 – 130	70 – 130	± 25
1,4-Dioxane	0.1	≤ 30%	70 – 130	70 – 130	± 25
2-Butanone (Methyl Ethyl Ketone)	0.5	≤ 30%	70 – 130	70 – 130	± 25
2-Hexanone	0.5	≤ 30%	70 – 130	70 – 130	± 25
4-Ethyltoluene	0.1	≤ 30%	70 – 130	70 – 130	± 25
4-Methyl-2-Pentanone (MIBK)	0.1	≤ 30%	70 – 130	70 – 130	± 25
Acetone	1.0	≤ 30%	70 – 130	70 – 130	± 25
Bromodichloromethane	0.1	≤ 30%	70 – 130	70 – 130	± 25
Bromoform	0.1	≤ 30%	70 – 130	70 – 130	± 25
Carbon Disulfide	0.5	≤ 30%	70 – 130	70 – 130	± 25
Cumene	0.1	≤ 30%	70 – 130	70 – 130	± 25
Cyclohexane	0.5	≤ 30%	70 – 130	70 – 130	± 25
Dibromochloromethane	0.1	≤ 30%	70 – 130	70 – 130	± 25
Ethanol	0.5	≤ 30%	70 – 130	70 – 130	± 25
Heptane	0.5	≤ 30%	70 – 130	70 – 130	± 25
Hexane	0.5	≤ 30%	70 – 130	70 – 130	± 25
Isopropanol	0.5	≤ 30%	70 – 130	70 – 130	± 25
Methyl tert-Butyl Ether (MTBE)	0.1	≤ 30%	70 – 130	70 – 130	± 25
Propylbenzene	0.1	≤ 30%	70 – 130	70 – 130	± 25
Tetrahydrofuran	0.5	≤ 30%	70 – 130	70 – 130	± 25
trans-1,2-Dichloroethene	0.1	≤ 30%	70 – 130	70 – 130	± 25
2,2,4-Trimethylpentane	0.5	≤ 30%	70 – 130	70 – 130	± 25
3-Chloroprene	0.5	≤ 30%	70 – 130	70 – 130	± 25
Naphthalene**	0.5	≤ 40%	60 – 140	60 – 140	± 25

Analyte	RL/LOQ (ppbv)	QC Acceptance Criteria			
		ICAL (%RSD)	CCV (%R)	ICV/LCS* (%R)	Precision Limits (Max. RPD)
TPH (Gasoline)***	10	1- Point Calibration	N/A	ICV only: 60 – 140	± 25
NMOC (Hexane/Heptane)***	2.0	1- Point Calibration	N/A	N/A	± 25

*See Table 6.

**Due to its low vapor pressure, Naphthalene does not meet TO-15 performance requirements. The wider QC limits reflect typical performance. Although Naphthalene is not on Eurofins Air Toxics "standard" TO-15 list, it is commonly requested and therefore included in Table 3.

***TPH and NMOC are not on Eurofins Air Toxics' standard TO-15 list, but are included in Table 3 due to common requests.

Table 3 is the list of Standard compounds, reporting limits and QC acceptance criteria. Each project may be customized as needed. Additional compounds and different reporting limits may be obtainable and/or achieved upon request

Table 4. Internal Standards

Analyte	Accuracy (% R)
Bromochloromethane	60 – 140
1,4-Difluorobenzene	60 – 140
Chlorobenzene-d_5	60 – 140

Table 5. Surrogates

Analyte	Accuracy (% R)
1,2-Dichloroethane-d_4	70 – 130
Toluene-d_8	70 – 130
4-Bromofluorobenzene	70 – 130

Table 6. Summary of Calibration and QC Procedures for Methods TO-14A/TO-15 Low-Level

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Tuning Criteria	Every 24 hours	TO-15 ion abundance criteria	Correct problem then repeat tune.
Minimum 5-Point Initial Calibration (ICAL)	Prior to sample analysis	% RSD ≤ 30 with 4 compounds allowed out to ≤ 40% RSD	Correct problem then repeat Initial Calibration curve.
Initial Calibration Verification and Laboratory Control Spike (ICV and LCS)	After each Initial Calibration curve, and daily prior to sample analysis	Recoveries for 85% of Standard compounds must be 70–130%. No recovery may be < 50%. ICV is evaluated on a full list basis at the time of calibration. If specified by the project, in-house generated control limits may be used.	Check the system and re-analyze the standard. Re-prepare the standard if necessary to determine the source of error. Re-calibrate the instrument if the primary standard is found to be in error.
Initial Calibration Verification and Laboratory Control Spike (ICV and LCS) for Non-standard Compounds	Per client request or specific project requirements only	Recoveries of compounds must be 60–140%. No recovery may be <50%.	Check the system and re-analyze the standard. Re-prepare the standard if necessary to determine the source of error. Re-calibrate the instrument if the primary standard is found to be in error.
Continuing Calibration Verification (CCV) for Standard compounds	At the start of each analytical clock (24-hours) after the tune check	70–130%	Compounds exceeding this criterion and associated data will be flagged and narrated with the exception of high bias associated with non-detects. If more than 4 compounds from the standard list recover outside of 70–130% or >10% of VOCs if short list is used (40 compounds or less), corrective action will be taken. If any compound exceeds 60–140%, samples are not analyzed unless data meets project needs. Check the system and re-analyze the standard. Re-prepare the standard if necessary. Re-calibrate the instrument if the criteria cannot be met.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Continuing Calibration Verification (CCV) for Non-Standard compounds	Per client request or specific project requirements only	Recoveries of compounds must be 60–140%. No recovery may be <50%.	Check the system and re-analyze the standard. Re-prepare the standard if necessary to determine the source of error. Re-calibrate the instrument if the primary standard is found to be in error.
Laboratory Blank	After analysis of standards and prior to sample analysis, or when contamination is present	Results less than the laboratory reporting limit	Inspect the system and re-analyze the blank. "B"-flag data for common contaminants.
Internal Standard (IS)	As each standard, blank, and sample is being loaded	Retention time (RT) for blanks and samples must be within ±0.33 min of the RT in the CCV and within ± 40% of the area counts of the daily CCV internal standards.	**For blanks:** Inspect the system and reanalyze the blank. **For samples:** Re-analyze the sample unless obvious matrix interference is documented. If the ISs are within limits in the re-analysis, report the second analysis. If ISs are out-of-limits a second time, report data from first analysis and narrate.
Surrogates	As each standard, blank, and sample is being loaded	70–130% R If specified by the project, in-house generated control limits may be used.	**For blanks:** Inspect the system and re-analyze the blank **For samples:** Re-analyze the sample unless obvious matrix interference is documented. If the %Rs are within limits in the re-analysis, report the second analysis. If %Rs are out-of-limits a second time, report data from first analysis and narrate.
Laboratory Duplicates - Laboratory Control Spike Duplicate (LCSD)	One per analytical batch	RPD ≤25%	Narrate exceedances. If more than 5% of compound list is outside criteria or if compound is >40% RPD, investigate the cause and perform maintenance as required. If instrument maintenance is required, calibrate as needed.

ANALYTICAL METHODS

Section 13.0

Method: EPA Method TO-14A/TO-15 Volatile Organic Compounds by SIM

Eurofins Air Toxics SOP #38 Revision 25 Effective Date: November 23, 2020 Methods Manual Summary

Description: This method involves Selective Ion Monitoring (SIM) gas chromatograph/mass spectrometer (GC/MS) analysis of whole air samples collected in evacuated stainless steel canisters. Samples are analyzed for volatile organic compounds (VOCs) using EPA Method TO-14A/TO-15 protocols. An aliquot of the sample is withdrawn from the canister through a mass flow controller and concentrated onto a hydrophobic drying system that removes water from the sample stream. The sample is then focused onto a cryogenic-cooled column prior to analysis by GC/MS in the SIM mode.

Mass spectrometer detectors can be set to acquire both SIM and full scan data simultaneously. This generates two separate data files in the analytical software. One file contains full scan data and the other contains SIM data for selected compounds. The results for each sample in a report will be from two separate data files originating from the same analytical run. The two data files have the same base file name and are differentiated with a "sim" extension on the SIM data file.

Eurofins Air Toxics maintains a suite of TO-14A/TO-15 methods, each optimized to efficiently meet the data objectives for a wide range of targeted concentration ranges. The methods, their reporting limits, and typical applications are summarized in the table below. This method summary describes TO-14A/TO-15 SIM.

Eurofins Air Toxics Method	Base Reporting Limits	Typical Application
TO-14A/TO-15 (5&20)	5 – 20 ppbv	Soil gas and ppmv range vapor matrices
TO-14A/TO-15 (Standard or Quad)	0.5 – 5.0 ppbv	Ambient air, soil gas, and ppbv level vapor matrices
TO-15 (Extended)	0.2 – 5.0 ppbv	Ambient air and ppbv level vapor matrices
TO-14A/TO-15 (Low-level)	0.1 – 1.0 ppbv	Indoor and outdoor air
TO-14A/TO-15 SIM	0.01 – 0.5 ppbv	Indoor and outdoor air
TO-15 HSS	0.01 – 0.1 ppbv	Soil gas and other high concentration matrices

Certain compounds are not included in Eurofins Air Toxics' standard target analyte list. These compounds are communicated at the time of client proposal request. If full validation of the required compound(s) is not available, the laboratory will present Quality Control (QC) options to the client based on the project objectives.

Please note that Methods TO-14A and TO-15 were validated for specially treated canisters. As such, the use of Tedlar bags for sample collection is outside the scope of the method and not recommended for ambient or indoor air samples. It is the responsibility of the data user to determine the usability of TO-14A and TO-15 results generated from Tedlar bags.

All samples submitted for TO-15 SIM are screened prior to analysis. If samples contain high concentrations of target and/or non-target VOCs, samples may be analyzed by an alternative TO-15 method (i.e. Standard or 5&20) with a higher dynamic calibration range.

Eurofins Air Toxics performs a modified version of TO-15 SIM as detailed in Table 1. Additionally, since Eurofins Air Toxics applies TO-15 methodology to all Summa™ canisters regardless of whether TO-14A or TO-15 is specified by the project, Eurofins Air Toxics performs a modified version of method TO-14A as described in Table 2. The default SIM target list, reporting limits (RL), QC criteria and QC summary may be found in tables 3 through 7.

Table 1. Summary of TO-15 SIM Method Modifications

Requirement	TO-15	Eurofins Air Toxics Modifications
Blank and standards	Zero Air	UHP Nitrogen provides a higher purity gas matrix than zero air for trace level measurements.

Table 2. Summary of TO-14A SIM Method Modifications

Requirement	TO-14A	Eurofins Air Toxics Modifications
Sample Drying System	Nafion Dryer	Multibed hydrophobic sorbent
ICAL %RSD acceptance criteria	≤ 30% RSD for listed 39 VOCs	Follow TO-15 requirements of ≤ 30%RSD with 2 of standard compound list allowed out to ≤ 40%RSD
Blank and standards	Zero air	UHP Nitrogen provides a higher purity gas matrix than zero air for trace level measurements.
BFB ion abundance criteria	Ion abundance criteria listed in Table 4 of TO-14A	Follow abundance criteria listed in TO-15.
BFB absolute abundance criteria	Within 10% when comparing to the previous daily BFB	CCV internal standard area counts are compared to ICAL; corrective action when recovery is less than 60%

Table 3. Method TO-14A/TO-15 Standard Analyte List (SIM) and QC Limits

Analyte	RL/LOQ (ppbv)	QC Acceptance Criteria			
		ICAL (%RSD)	CCV (%R)	ICV/LCS (%R)	Precision Limits (Max. RPD)
Dichlorodifluoromethane (Fr12)	0.020	≤ 30%	70 – 130	70 – 130	± 25
Freon 114	0.020	≤ 30%	70 – 130	70 – 130	± 25
Chloromethane	0. 50	≤ 30%	70 – 130	70 – 130	± 25
Vinyl Chloride	0.010	≤ 30%	70 – 130	70 – 130	± 25
Chloroethane	0.050	≤ 30%	70 – 130	70 – 130	± 25
Freon 11	0.02	≤ 30%	70 – 130	70 – 130	± 25
Freon 113	0.02	≤ 30%	70 – 130	70 – 130	± 25
1,1-Dichloroethene	0.010	≤ 30%	70 – 130	70 – 130	± 25
Trans-1,2-Dichloroethene	0.100	≤ 30%	70 – 130	70 – 130	± 25
Methyl tert-Butyl Ether	0.100	≤ 30%	70 – 130	70 – 130	± 25
1,1-Dichloroethane	0.020	≤ 30%	70 – 130	70 – 130	± 25
cis-1,2-Dichloroethene	0.020	≤ 30%	70 – 130	70 – 130	± 25
Chloroform	0.020	≤ 30%	70 – 130	70 – 130	± 25
1,1,1-Trichloroethane	0.020	≤ 30%	70 – 130	70 – 130	± 25
Carbon Tetrachloride	0.020	≤ 40%	60 - 140	60 - 140	± 25
Benzene	0.050	≤ 30%	70 – 130	70 – 130	± 25
1,2-Dichloroethane	0.020	≤ 30%	70 – 130	70 – 130	± 25
Trichloroethene	0.020	≤ 30%	70 – 130	70 – 130	± 25
Toluene	0.050	≤ 30%	70 – 130	70 – 130	± 25
1,1,2-Trichloroethane	0.020	≤ 30%	70 – 130	70 – 130	± 25
Tetrachloroethene	0.020	≤ 30%	70 – 130	70 – 130	± 25
1,2-Dibromoethane	0.020	≤ 30%	70 – 130	70 – 130	± 25
Ethyl Benzene	0.020	≤ 30%	70 – 130	70 – 130	± 25
m,p-Xylene	0.040	≤ 30%	70 – 130	70 – 130	± 25
o-Xylene	0.020	≤ 30%	70 – 130	70 – 130	± 25
1,1,2,2-Tetrachloroethane	0.020	≤ 30%	70 – 130	70 – 130	± 25
1,4-Dichlorobenzene	0.020	≤ 30%	70 – 130	70 – 130	± 25
Naphthalene	0.050	≤ 40%	60 – 140	60 – 140	± 25

Table 3 is the list of Standard compounds, reporting limits and QC acceptance criteria. Each project may be customized as needed. Additional compounds and different reporting limits may be obtainable and/or achieved upon request.

Table 4. Method TO-15 Additional Analyte List (SIM) and QC Limits

Analyte	RL/LOQ (ppbv)	QC Acceptance Criteria			
		ICAL (%RSD)	CCV (%R)	ICV/LCS (%R)	Precision Limits (Max. RPD)
1,2,3-Trichloropropane	0.040	≤30%	70 - 130	70 - 130	± 25
1,2,4-Trichlorobenzene	0.050	≤30%	70 - 130	70 - 130	± 25
1,2,4-Trimethylbenzene	0. 040	≤30%	70 - 130	70 - 130	± 25
1,2-Dichlorobenzene	0.050	≤30%	70 - 130	70 - 130	± 25
1,2-Dichloropropane	0.040	≤30%	70 - 130	70 - 130	± 25
1,3,5-Trimethylbenzene	0.040	≤30%	70 - 130	70 - 130	± 25
1,3-Butadiene	0.200	≤30%	70 - 130	70 - 130	± 25
1,3-Dichlorobenzene	0.100	≤30%	70 - 130	70 - 130	± 25
1,4-Dioxane	0.100	≤30%	70 - 130	70 - 130	± 25
2-Butanone	0.200	≤30%	70 - 130	70 - 130	± 25
2-Hexanone	0.200	≤30%	70 - 130	70 - 130	± 25
2-Propanol	0.040	≤30%	70 - 130	70 - 130	± 25
4-Ethyltoluene	0.040	≤30%	70 - 130	70 - 130	± 25
4-Methyl-2-Pentanone	0.040	≤30%	70 - 130	70 - 130	± 25
Acetone	0.200	≤30%	70 - 130	70 - 130	± 25
Acetonitrile	0.200	≤30%	70 - 130	70 - 130	± 25
Acrolein	0.200	≤30%	70 - 130	70 - 130	± 25
Acrylonitrile	0.010	≤30%	70 - 130	70 - 130	± 25
alpha-Chlorotoluene	0.100	≤30%	70 - 130	70 - 130	± 25
Bromodichloromethane	0.012	≤30%	70 - 130	70 - 130	± 25
Bromoform	0.040	≤30%	70 - 130	70 - 130	± 25
Bromomethane	0.040	≤30%	70 - 130	70 - 130	± 25
Chlorobenzene	0.020	≤30%	70 - 130	70 - 130	± 25
cis-1,3-Dichloropropene	0.020	≤30%	70 - 130	70 - 130	± 25
Cyclohexane	0.040	≤30%	70 - 130	70 - 130	± 25
Dibromochloromethane	0.010	≤30%	70 - 130	70 - 130	± 25
Ethyl Acetate	0.040	≤30%	70 - 130	70 - 130	± 25
Heptane	0.040	≤30%	70 - 130	70 - 130	± 25
Hexachlorobutadiene	0.020	≤30%	70 - 130	70 - 130	± 25
Hexane	0.040	≤30%	70 - 130	70 - 130	± 25
Methylene Chloride	0.200	≤30%	70 - 130	70 - 130	± 25
Propylene	0.200	≤30%	70 - 130	70 - 130	± 25

Styrene	0.030	≤30%	70 - 130	70 - 130	± 25
Tetrahydrofuran	0.040	≤30%	70 - 130	70 - 130	± 25
trans-1,3-Dichloropropene	0.020	≤30%	70 - 130	70 - 130	± 25
Vinyl Acetate	0.040	≤30%	70 - 130	70 - 130	± 25

Table 4 is the list of additional Method TO-15 SIM compounds that may be requested upon request with full QC – 5-point calibration, second source calibration verification, continuing calibration verification, laboratory control spike, and method detection limit study.

Table 5. Internal Standards

Analyte	Accuracy (% R)
Bromochloromethane	60 – 140
1,4-Difluorobenzene	60 – 140
Chlorobenzene-d_5	60 – 140

Table 6. Surrogates

Analyte	Accuracy (% R)
1,2-Dichloroethane-d_4	70 – 130
Toluene-d_8	70 – 130
4-Bromofluorobenzene	70 – 130

Table 7. Summary of Calibration and QC Procedures for Methods TO-14A/TO-15 by SIM

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Tuning Criteria	Every 24 hours	TO-15 Ion Abundance criteria	Correct problem then repeat tune.
Multi-point Calibration (Minimum of 5 points)	Prior to sample analysis	≤ 30% for standard compounds with 2 compounds allowed out to ≤ 40% RSD	Correct problem then repeat Initial Calibration Curve.
Initial Calibration Verification and Laboratory Control Spike (ICV and LCS)	After each initial calibration curve, and daily prior to sample analysis	Recoveries for 85% of standard compounds must be 70–130% 60–140% for Carbon Tetrachloride and Naphthalene). No recovery may be < 50%. ICV evaluated on a full list basis at the time of calibration. If specified by the project, in-house generated control limits may be used.	Check the system and re-analyze the standard. Re-prepare the standard if necessary to determine the source of error. Re-calibrate the instrument if the primary standard is found to be in error.
Initial Calibration Verification and Laboratory Control Spike (ICV and LCS) for Non-Standard Compounds	Per client request or specific project requirements only	Recoveries of compounds must be 60–140%. No recovery may be < 50%.	Check the system and re-analyze the standard. Re-prepare the standard if necessary to determine the source of error. Re-calibrate the instrument if the primary standard is found to be in error.
Continuing Calibration Verification (CCV)	At the start of each day after the BFB tune check	70–130%D; 60-140% D for Carbon Tetrachloride and Naphthalene.	Compounds exceeding this criterion and associated data will be flagged and narrated with the exception of high bias associated with non-detects. If more than two compounds from the standard list recover outside of 70–130%, corrective action will be taken. If any compound exceeds 60–140%, samples are not analyzed unless data meets project needs. Check the system and re-analyze the standard. Re-prepare the standard if necessary. Re-calibrate the instrument if the criteria cannot be met.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Continuing Calibration Verification (CCV) for Non-Standard Compounds	Per client request or specific project requirements only	Recoveries of compounds must be 60–140%. No recovery may be < 50%.	Check the system and re-analyze the standard. Re-prepare the standard if necessary to determine the source of error. Re-calibrate the instrument if the primary standard is found to be in error.
Laboratory Blank	After analysis of standards and prior to sample analysis, or when contamination is present.	Results less than the laboratory reporting limit (Tables 3 and 4) or project required reporting limit.	Inspect the system and re-analyze the blank. "B" flag data for common contaminants.
Internal Standard (IS)	As each standard, blank, and sample is being loaded	Retention time (RT) for blanks and samples must be within ±0.33 min of the RT in the CCV and within ±40% of the area counts of the daily CCV internal standards.	**For blanks:** Inspect the system and re-analyze the blank. **For samples:** Re-analyze the sample. If the ISs are within limits in the re-analysis, report the second analysis. If ISs are out-of-limits a second time, dilute the sample until ISs are within acceptance limits and narrate.
Surrogates	As each standard, blank, and sample is being loaded	70–130% If specified by the project, in-house generated control limits may be used.	**For blanks:** Inspect the system and re-analyze the blank. **For samples:** Re-analyze the sample unless obvious matrix interference is documented. If the %Rs are within limits in the re-analysis, report the second analysis. If %Rs are out-of-limits a second time, report data from first analysis and narrate.
Laboratory Duplicates - Laboratory Control Spike Duplicate (LCSD)	One per analytical batch	RPD ≤ 25%	Narrate exceedances. If more than 5% of compound list outside criteria or if compound is > 40%RPD, investigate the cause and perform maintenance as required. If instrument maintenance is required, calibrate as needed.

ANALYTICAL METHODS

Section 4.0

Method: ASTM D1946 – Atmospheric Gases

Eurofins Air Toxics SOP #8 Revision 28 Effective Date: July 13, 2020 Methods Manual Summary

Description: This method involves gas chromatograph (GC) analysis of soil gas, landfill gas, ambient air, or stack gas collected in Summa™ canisters, Tedlar bags, or any vessel that has been demonstrated to be clean and leak free. Samples are analyzed for Methane, fixed gases, and Non-Methane Organic Carbon (NMOC) using modified ASTM D1946 protocols. Because the sample is withdrawn from the vessel by positive pressure, rigid containers are first filled to positive pressure using UHP Helium or Nitrogen. Samples are then analyzed using a GC equipped with a FID and a TCD.

Certain compounds are not included in Eurofins Air Toxics' standard target analyte list. These compounds are communicated at the time of client proposal request. Unless otherwise directed, the laboratory reports these non-standard compounds with partial validation. Validation includes a 3-point calibration with the lowest concentration defining the reporting limit, no second source verification is analyzed, and no method detection limit study is performed unless previous arrangements have been made. In addition, stability of the non-standard compound during sample storage is not validated. Full validation may be available upon request.

Since the protocols in the ASTM D1946 standard were designed for the analysis of reformed gas, the laboratory has taken modifications to apply the method to environmental samples covering a wide concentration range and to implement standard NELAP and EPA calibration criteria. The method modifications, standard target analyte list, reporting limits (RL), Quality Control (QC) criteria, and QC summary can be found in the following tables.

Table 1. Summary of Method Modifications for ASTM D1946

Requirement	ASTM D1946	Eurofins Air Toxics Modifications
Calibration	A single-point calibration is performed using a reference standard closely matching the composition of the unknown.	A minimum 5-point calibration curve is performed. Quantitation is based on the initial calibration, which may or may not resemble the composition of the associated samples.
Reference Standard	The composition of any reference standard must be known to within 0.01 mol % for any component.	The standards used by Eurofins Air Toxics are blended to a ≥ 95% accuracy.
Sample Injection Volume	Components whose concentrations are in excess of 5% should not be analyzed by using sample volumes greater than 0.5 mL.	The sample container is connected directly to a fixed volume sample loop of 1.0 mL. Linear range is defined by the calibration curve. Bags may be loaded by vacuum or by positive pressure.
Normalization	Normalize the mole percent values by multiplying each value by 100 and dividing by the sum of the original values. The sum of the original values should not differ from 100% by more than 1.0%.	Results are not normalized. The sum of the reported values can differ from 100% by as much as 15%, either due to analytical variability or an unusual sample matrix.

Requirement	ASTM D1946	Eurofins Air Toxics Modifications
Precision	Precision requirements established at each concentration level.	Duplicates should agree within 25% RPD for detections >5X the RL.

Table 2. ASTM D1946 Method Compound List and QC Limits

Compound	Reporting Limit (%)	ICAL Criteria (%RSD)	ICV/LCS Criteria (%R)	CCV Criteria (%D)	Precision Limits (RPD)**
Carbon Dioxide	0.010	≤ 15%	85 – 115	± 15%	± 25%
Carbon Monoxide	0.010	≤ 15%	85 – 115	± 15%	± 25%
Methane	0.00010	≤ 15%	85 – 115	± 15%	± 25%
Ethene	0.0010	≤ 15%	85 – 115	± 15%	± 25%
Ethane	0.0010	≤ 15%	85 – 115	± 15%	± 25%
Nitrogen	0.10	≤ 15%	85 – 115	± 15%	± 25%
NMOC	0.010	≤ 15%	85 – 115	± 15%	± 25%
Oxygen	0.10	≤ 15%	85 – 115	± 15%	± 25%
Helium	0.050	≤ 15%	85 – 115	± 15%	± 25%
Hydrogen	0.010*	≤ 15%	85 – 115	± 15%	± 25%

*Reporting limit is 1.0% when sample is pressurized with Helium.
**For detections greater than 5 times the reporting limit.

Note: Results are reported in units of mol %. If required to report volume % or ppmV, a compressibility factor of 1 for all gases will be assumed. As a result, mol % is assumed to be equivalent to volume %. This assumption may result in a bias for highly compressible gases at high concentrations and pressures.

Table 3. Summary of Calibration and QC Procedures for Mod. ASTM Method D1946

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration Curve (ICAL)	Prior to sample analysis	RSD ≤ 15%	Correct problem then repeat Initial Calibration.
Second Source Verification (LCS)	All analytes: once per Initial Calibration, and with each analytical batch	%R between 85–115%	Check the system and re-analyze the standard. Verify the accuracy of standards as needed. Re-prepare erroneous standards and/or re-calibrate the instrument if the criteria cannot be met.
Continuing Calibration Verification (CCV)	Daily prior to sample analysis and after every 20 reportable samples.	%D ±15%	Check the system and re-analyze the standard. Re-calibrate the instrument if the criteria cannot be met.
Laboratory Blank (He) (N_2 for He and H_2 analysis)	After each daily check standard and prior to sample analysis, or when contamination is present.	Results below the RL	Inspect the system and re-analyze the Blank.
End Check	At the end of analytical sequence. It can be primary (CCV) or Independent Source (LCS).	%R between 85–115%	Check system and re-analyze the standard. If the 2nd analysis fails, identify and correct the problem. Samples analyzed after the last acceptable CCV are re-analyzed.
Sample Duplicates - Laboratory Control Spike Duplicate (LCSD)	One per analytical batch	RPD ≤ 25%	Narrate exceedances. Investigate the cause and perform maintenance as required and re-calibrate as needed.