# 3M Environmental Laboratory

## *Volatile Organic Compound Analysis for Air Samples Collected in Specially Treated Canisters Using Gas Chromatography/Mass Spectrometry*

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Quality Assurance

# 1 Scope and Application

This performance-based method is designed to detect and quantify volatile organic compounds (VOCs) found in ambient air samples and process gas emission samples. The method is based on U.S. Environmental Protection Agency (EPA) Compendium Method TO-15 with quality control modifications to address performance criteria. Modifications and/or improvements to Method TO-15 are incorporated into this method to expand both the list of applicable compounds and the overall quantitation range for samples with analyte concentrations greater than 1 part per million by volume (PPMv). Appendix A3 compares this method, ETS-8-16, to U.S. EPA Compendium Method TO-15.

This method applies to gas chromatography/mass spectrometry (GC/MS) analysis of whole air samples collected in specially prepared canisters. Analyte specificity is determined using chromatographic retention time and the unique component mass spectrum. Method performance is compound dependent and demonstrated by analyzing specific method performance samples.

This method does not address the procedures used to collect the air samples.

# 2 Analytical Method Summary

The recommended canister type for this method is a fused-silica lined (Silonite®) canister or other canisters treated with an inert, non-reactive lining. Electropolished (SUMMA) canisters are applicable, but are limited in suitability due to incompatibility with reactive compounds and susceptibility to variances in sample humidity. Canisters inventoried and maintained by the 3M Environmental Laboratory undergo a canister cleaning and certification procedure as outlined in ETS-8-190 prior to sample collection to verify canister integrity. Upon receipt at the laboratory, the canister is pressurized with a surrogate recovery standard.

VOCs in the collected sample are introduced into the gas chromatograph using a variety of sample introduction techniques depending on the target analyte concentration levels. Sample introduction techniques will be discussed in detail later in this document. Prior to sample transfer to the GC, a mix of deuterated internal standards is added. A GC oven gradient program is used to separate the analytes prior to detection by the mass spectrometer.

Identification of target analytes is accomplished by comparing the retention time and mass spectra to calibration standards prepared in canisters that undergo the same sample introduction process and analysis as the samples. Internal standard quantitation is used to determine the concentration of the target analytes in the analyzed sample.

Tentative identification of an unknown compound may be made by comparing a full scan electron impact (EI) mass spectrum of the unknown to a NIST library mass spectrum and/or a custom library maintained by the 3M Environmental Laboratory via a search algorithm. An estimated concentration of a non-target analyte identified in a sample may be made using the response factor of an internal standard or other calibrated compound. Additional information regarding the chemical structure and functionality of an unknown may be elucidated by collecting mass spectra using chemical ionization (CI) techniques. Analysis using a GC/Q-TOF with either an EI or CI source may be used to obtain an exact mass of an unknown compound.

# 3 Definitions

### 3.1 Volatile Organic Compounds (VOCs)

Defined in U.S. EPA Compendium Method TO-15 as organic compounds having vapor pressures greater than $10^{-1}$ Torr at 25°C and 760 mm Hg.

### 3.2 Parts Per Billion by Volume (PPBv)

Units of air concentration defined below.

$$PPBv = \frac{10^{-9}\text{L of target analyte}}{1\text{ L of air}} = \frac{1\text{ nL of target analyte}}{1\text{L of air}}$$

### 3.3 Parts Per Million by Volume (PPMv)

Units of air concentration defined below.

$$PPMv = \frac{10^{-6}\text{L of target analyte}}{1\text{ L of air}} = \frac{1\ \mu\text{L of target analyte}}{1\text{L of air}}$$

### 3.4 Data Quality Objective (DQO)

A classification of the intended or requested data accuracy and precision for a given sample or project. The specified DQO will dictate what quality control elements and acceptance criteria are required. Three classifications of data quality objectives are addressed in this document.

### 3.5 Lab Ware

The laboratory information management system, or LIMS, used by the 3M Environmental Laboratory.

### 3.6 Pounds per Square Inch Gauge Pressure (psig)

Pressure measured with reference to the surrounding atmospheric pressure, expressed in units of pounds-per-square-inch-gauge (psig). Zero gauge pressure is equal to atmospheric pressure.

### 3.7 Pounds per Square Inch Absolute Pressure (psia)

Pressure measured with reference to absolute zero pressure, expressed in units of pounds-per-square-inch-absolute (psia).

### 3.8 Cryogen

A refrigerant used to obtain very low temperatures for sample concentration. A typical cryogen is liquid nitrogen (bp –195.8°C).

### 3.9 Reference Spectra

Mass spectra used for target analyte identification typically obtained on the same GC/MS system where sample analysis is performed. Reference spectra are typically obtained from calibration standards used for instrument response calibration or calibration verification. Reference spectra generated from calibration standards may be added to a 3M Environmental Laboratory reference library for future project work. Reference spectra for target analyte identification may also be obtained from mass spectral libraries such as NIST14 if interferences exist with spectra generated by the GC/MS or in-house libraries generated from 3M Environmental Laboratory historical data.

### 3.10 Tentatively Identified Compounds (TICs)

Tentatively identified compounds are detected sample components that are not identified as target analytes. Consequently, these components do not have established calibration curves. The mass spectra for these non-target sample components are searched against a mass spectral library such as NIST14 and/or an in-house library. Tentatively identified compounds are not confirmed using

reference standards unless specifically requested by laboratory management or project requesters. Confirmation of TICs largely depends on the availability of a chemical standard and its overall suitability to canister analysis.

## 3.11 Sample Introduction

### 3.11.1 Micro-Scale Purge and Trap (MPT)

MPT is a three-stage sample enrichment or concentration technique where a whole air sample aliquot (typically 100 cc) is concentrated onto a cryogenically cooled glass bead trap under integrated mass flow control. The glass bead trap is heated while purging helium through the trap. The VOCs are swept from the glass bead trap to a cryogenically cooled Tenax trap. This transfer step manages the moisture and carbon dioxide present in the sample. The final concentration step is thermally desorbing the VOCs from the Tenax trap to a cryogenically cooled open tubular trap. This final concentration step simply focuses the concentrated VOCs into a tight band for optimum GC separation. The MPT sample enrichment step has largely been replaced by the cold trap dehydration technique discussed below, but MPT may be used on project-specific basis. MPT is used to analyze sample concentrations in the PPBv range.

### 3.11.2 Cold Trap Dehydration (CTD)

CTD is very similar to microscale purge-and-trap in that three stages or modules are used for sample enrichment. The difference is that the glass bead trap in the first module is replaced with an open tubular trap. Cryogenically cooling an open tubular trap in the first stage to sub-ambient temperature allows the VOCs to pass through to the cryogenically cooled Tenax trap while the water vapor present in the sample is condensed in the open tubular trap. The remaining steps are similar to MPT. CTD was specifically designed for detecting reactive compounds such as aldehydes, specifically formaldehyde. However, the CTD technique has been demonstrated to work well for non-reactive compounds. Therefore, CTD has essentially replaced MTD for routine analyses as the CTD is a suitable for a wider range of analytes. CTD is used to analyze sample concentrations in the PPBv range.

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*NOTE: For formaldehyde analysis, it is critical that specially treated fused silica lined (Silonite®) canisters, concentrator traps, and transfer lines be used.*

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## 3.12 Loop Analysis

Loop analysis is a sample introduction technique that does not involve a sample concentration process. Samples are pressurized and a small volume of sample is used to flush the gas sample loop (typically 1-cc). The sample aliquot is then cryo-focused into a tight band before transfer to the GC for analysis. Loop analysis is used to analyze sample concentrations in the PPMv range.

## 3.13 Analysis Batch

A set of study samples analyzed with calibration standards, a method blank, and instrument blanks on the same instrument during a time period that begins with an initial calibration (or continuing calibration check standard) and ends with a closing continuing calibration check standard.

## 3.14 Analytical Sample

An air sample collected in a specially-treated canister (typically Silonite®).

## 3.15 Instrument Calibration Standard

A gas standard typically prepared in a 6-L canister used to calibrate the instrument response for a given analyte or analytes.

### 3.16 Internal Standard (IS)

A compound added to each study sample, calibration standard, laboratory control sample, and instrument/method blank at a consistent level (typically around the mid-level of the calibration range). The internal standard(s) are typically stable isotopically labeled counterparts of one or more target analytes. If a labeled counterpart is not available, a labeled compound of similar chemical functionality may be used instead. The area count ratio of the target analyte to the internal standard is used for calibration.

### 3.17 Limit of Quantitation (LOQ)

The lower limit of quantitation (LLOQ) for an analytical batch is the lowest concentration that can be reliably quantitated within the specified limits of precision and accuracy. The LLOQ is generally selected as the lowest non-zero standard in the calibration curve that meets method acceptance criteria. The LLOQ for each target analyte is established for each analysis batch as the lowest calibration standard with area counts at meet the established criteria discussed later in this document.

The upper limit of quantitation (ULOQ) for an analytical batch is the highest concentration that can be reliably quantitated within the specified limits of precision and accuracy. The ULOQ for a given analyte is defined as the highest standard in the calibration curve that meets method acceptance criteria. Sample concentrations between 100-110% of the ULOQ may be reported without further justification.

### 3.18 Method Blank

A method blank is a canister that is filled with clean nitrogen (reagent gas) from a liquid nitrogen dewar to 1 atm (0 psig, 14.7 psia). The canister is then pressurized to 10 psig (24.7 psia), or the desired final pressure, with a surrogate standard, typically benzene-$d_6$. See Section 10.1.2 for information regarding this procedure. This method blank doubles as a reagent gas blank.

### 3.19 Surrogate Recovery Standard

An isotopically-labeled standard, not used as an internal standard, which is added to each collected sample canister prior to analysis. The surrogate serves as a means to evaluate the overall method performance (recovery).

## 4 Warnings and Cautions

The operator must be familiar with the canister autosampler and concentrator equipment and GC/MS systems and their associated hazards including, but not limited to the following: electricity, high heat generation, effluent venting, moving autosampler parts, low-pressure vacuum system, cryogens, and compressed gases. All instrument split vents, exhaust vents, and pump exhaust vents should be vented to a hood or the building exhaust ducts. Refer to 3M Environmental Laboratory document ETS-2-001 “General Laboratory Safety Practices and Procedures” and the appropriate equipment procedures, methods, SOPs, or operator manuals for additional information and cautions.

*Some samples may contain hazardous and/or highly toxic compounds. The operator should treat all samples received in the laboratory as such. All canister pressurizations and sample manipulations should be performed in a functioning fume hood.*

# 5 Interferences

Contaminants in solvents, reagents, glassware, and other sample processing or analysis hardware may cause interference. The routine laboratory method blank analyses must be used to demonstrate that there are no such interferences under the analytical conditions.

Water and carbon dioxide may cause interferences, which are dependent on the conditions during sampling and the sample volume injected. For large-volume injections, the three-stage sample preconcentration functions to remove most of the water and carbon dioxide from the sample. Carbon dioxide is eluted early in the chromatogram and may interfere with the most volatile compounds in the sample. Water elutes in the early to mid-range of the chromatogram and may increase or decrease the response of co-eluting analytes, depending on the GC column used. Water may also cause slight retention time shifts and analyte peak splitting. Observed effects due to interference with water vary depending on the column phase. In addition, frozen water and carbon dioxide may plug the traps in the preconcentrator modules and affect observed sample concentrations if not managed correctly. For these reasons, using internal standards and surrogates is required.

Other interferences include co-eluting analytes that have common ions. In this situation, the common ions should not be used as quantitation ions or qualifier ions. Alternate ions should be used. If the co-eluting peaks are the primary peaks of interest, then it may be necessary to select a different analytical column in order to resolve the peaks. For certain isomers, it is appropriate and acceptable to report the concentration as a total. For example, many columns do not separate m-xylene and p-xylene; these compounds would be reported as total for m- and p-xylene.

Potential sample matrix interference will be addressed on a project-by-project basis. For example, if an ambient air sample collected in a canister was found to have an extremely high concentration for a particular VOC, measures will be taken to confirm that the VOC did not condense on the canister wall. This may include referencing the compound's vapor pressure or preparing a lab control spike at a similar concentration to document acceptable recovery. If specified in the general project outline or dictated by laboratory management, matrix spikes may also be prepared to assess sample matrix effects.

# 6 Instrumentation, Supplies, and Materials

The instruments listed below are examples of the equipment available at the time this document was created. Newer models and different vendors of equipment may be used without updating this method. Additionally, the supplies and materials provided below are not meant to be an exhaustive list, but rather, a guide of what the experienced canister GC/MS operator may use during the course of a study. Refer to the appropriate manual(s) for additional parts and part numbers.

## 6.1 Preconcentrator and Autosampler

Entech 7100 or 7200 preconcentrator, with 7032 or 7650 canister autosampler, or equivalent.

## 6.2 GC/MS Instrumentation

Agilent Technologies 7890B GC System with 5977 Mass Spectrometer

Agilent Technologies 7890A GC System with 5975C Inert XL EI/CI MSD with Triple-Axis Detector

Agilent Technologies 7890B GC System with 7200B Q-TOF Mass Spectrometer with EI and CI sources and a thermal conductivity detector (TCD)

Agilent Technologies 6890A GC System with 5973 Network Mass Selective Detector

Agilent Technologies 6890N GC System with 5973 Inert XL Mass Selective Detector

## 6.3 Analytical Column

The following analytical columns have been successfully used for VOC analyses. Alternative columns may be used as long as method performance criteria are satisfied.

**Agilent GS-GasPro**, 30 m x 0.32 mm (no film) capillary column (recommended column for volatile organic fluorochemical analyses)

**Agilent DB-624**, 60 m x 0.32 mm with a 1.4 µm film thickness.

**Agilent DB-1**, 60 m x 0.32 mm with a 1 µm or 3 µm film thickness (recommended for general use and for formaldehyde).

**Agilent DB-5MS**, 60 m x 0.32 mm with a 1 µm film thickness.

### 6.4 Canisters

Fused silica lined canisters equipped with a Nupro® valve, or Micro-QT quick-connect fitting: 0.4 liter, one liter, three liter, six liter, or fifteen liter capacity, and 40 psig maximum pressure, certified (refer to ETS-8-190). Manufacturers of these types of canisters include the following:

- Entech Instruments, Inc (Simi Valley, CA)
- Restek Corporation (Bellefonte, PA)

### 6.5 Pressure/Vacuum Gauge

Temperature compensated high accuracy dual pressure/vacuum gauge, Omega Engineering, Inc. accuracy grade 3A or equivalent.

### 6.6 Carrier Gas

"High Purity" grade, or better, high-pressure helium cylinder for column carrier gas, equipped with a dual stage pressure regulator.

### 6.7 Cryogen

Liquid nitrogen (bp –195.8°C) dewar, 50 psig, equipped with a nitrogen regulator, as a source of clean nitrogen gas; also used for cryogenically cooling the GC oven and preconcentrator modules.

### 6.8 Chemical Ionization Gas

"High Purity" grade, or better, high pressure methane cylinder for chemical ionization techniques, or other appropriate reaction gas.

### 6.9 Gas Tight Syringes

Gas tight syringes for standard preparation and sample dilution.

### 6.10 Fittings

1/16-inch Swagelok union for connecting the analytical column and the transfer line from the preconcentrator.

Various sized Swagelok fittings for connecting instrument gas lines, canisters, etc.

Fused silica lined transfer line in varying internal diameters.

Graphite/Vespel ferrules for the GC/MS interface, of appropriate diameter for the GC column in use.

## 7 Reagents and Standards

### 7.1 Reagent Gas

Nitrogen gas obtained from the gas outlet on a liquid nitrogen dewar is used as a balance gas for all gas standard preparation, for all sample canister secondary pressurizations, and for method blanks. Nitrogen gas from a liquid nitrogen dewar is a clean nitrogen source. Any volatile organic compounds present in the dewar will remain in the liquid nitrogen (bp: -195.8°C). For this reason, the nitrogen used as a balance gas and to pressure sample canisters is not analyzed before use. The nitrogen gas from a liquid nitrogen dewar is analyzed, however, as a system/method blank.

### 7.2 Gas Standards

Gas standards are prepared according to the most current version of ETS-8-196. Prepare standards in cleaned and humidified canisters.

### 7.3 Calibration Standards

Gas standards for instrument calibration are prepared in humidified canisters (suggested humidity is approximately 0.7% v/v). Gas calibration standards should bracket the expected sample concentration range. Since the low level calibration standard is used to set the limit of quantitation, it is important to make sure that the low level standard concentration will meet the data quality objectives. See ETS-8-196 "Gas Standard Preparation" regarding humidification and preparation of gas standard canisters.

### 7.4 Internal Standard

An internal standard is a compound(s) added to each sample to monitor instrument detector performance. The internal standard amount added during analysis is the same for all calibration standards, blanks, samples, and quality control samples. The internal standard is prepared in a separate canister and is added to the sample flow-path by the autosampler prior to sampling the sample canister.

Choose an internal standard compound that is free of chromatographic interferences and is not expected to be in the whole air samples. A deuterated compound is typically chosen because it can be easily distinguished by its mass spectrum and deuterated compounds are not found in air samples. Quantitation for target analytes is based on the analyte's response relative to a chosen internal standard compound's response. The internal standard that elutes nearest to a target analyte is typically used to quantitate that analyte. This quantitation technique compensates for minor instrument detector fluctuations during an analytical sequence.

The recommended internal standard for this method should contain methylene chloride-$d_2$ at approximately 50 PPBv (MPT, CTD) and 10 PPMv (loop), and toluene-$d_8$ and o-xylene-$d_{10}$ at approximately 25 PPBv (MPT, CTD) and 5.0 PPMv (loop). Other compounds or concentrations may be used as internal standards as necessary.

## 8 Data Quality Objectives

A general project outline (GPO) or a study protocol will describe the data quality objectives (DQO) for a given study. Three levels of DQO are outlined here. If the DQO specified in the GPO cannot be met for any reason, the data must be qualified appropriately and discussed in the final report. Industrial Hygiene (IH) samples will be analyzed under the most-current standing IH GPO.[1] Specific GPOs will not be written for IH samples unless it is deemed necessary by laboratory management, the GC/MS analyst(s), or the IH requester. Specific examples of IH projects that may need a specific GPO include, but are not limited to, the following: projects that require method development to evaluate new compounds, projects that will span several sampling events over an extended timeframe, projects that require a large number of canisters, or any project that requires unique sampling or analytical procedures not described within this document.

### 8.1 Quantitative

Results associated with DQO category "Quantitative" will have analytical results within ±30% accuracy. The accuracy is based on, but not limited to, statistical data generated from instrument target analyte calibration, continuing calibration verification samples, replicate analyses (if appropriate), surrogate recovery, and other quality control samples if available. Specific method

[1]The standing IH GPO specifies "Quantitative" data with a targeted LLOQ of 1/10 the occupational exposure limit (OEL) – if available. Target analytes for IH projects will be specified on the sample media request. If "VOC scan" or "unknowns" is specified, the samples will be analyzed against the current calibration mix for "quantitative" results and concurrently analyzed for TICs (unknowns) that will be classified as "screening" quality data.

acceptance criteria required for “Quantitative” data will be discussed in detail. Furthermore, all method QC criteria must be met before results are classified as “Quantitative”. Accuracy for “Quantitative” data will likely be better than ±30% based upon control chart data of CCVs.

#### 8.1.1 Qualified Quantitative

In many instances, samples may be analyzed with the intent of generating “Quantitative” results yet one or more of the QC elements required for “Quantitative” results do not meet method acceptance criteria. When this occurs, the results may be given a “Qualified Quantitative” distinction. Under these circumstances, the affected results will be “qualified” with an appropriate footnote to delineate the non-compliant aspect of the method. When appropriate, the results may be given an expanded uncertainty assignment dependent upon what QC requirement did not meet criteria. “Qualified Quantitative” is not intended to be a data quality objective as the goal would be to meet all aspects of “Quantitative” data. The “Qualified Quantitative” designation is meant as a provision to report results with a greater level of analytical accuracy than what the “Screening” designation (described below) would imply.

### 8.2 Estimated or Semi-Quantitative

The DQO category “Estimated” will apply to projects where target anaylte(s) are specified, but the method’s QC aspects are intentionally minimized. For example, samples analyzed against a one-point calibration curve would be considered to have estimated or semi-quanitative quality results. In this instance, the method accuracy cannot be ascertained; however, the results are deemed more reliable than if no calibration was established.

### 8.3 Screening

The DQO classification of “Screening” is reserved for those projects where no target analytes are specified and reported results are for tentatively identified compounds (TICs) only. Concentration of TICs are typically estimated using the response factor of an internal standard or other calibrated analyte. Analytical accuracy of TICs cannot be ascertained as the accuracy of the estimation method will not be evaluated and will likely be vastly different for a wide range of compounds.

## 9 Instrument Performance, Calibration, and Quality Control

This section delineates the following calibration and QC elements associated with this method. For projects classified with the “Quantitative” DQO, all QC elements listed must be included. For projects classified as “Estimated” or “Screening”, some of the elements may be optional and will be clarified as such.

### 9.1 Instrument Tuning

#### 9.1.1 Electron Impact (EI) Ionization

The instrument should be tuned using perfluorotributyl amine (PFTBA) using autotuning options available in the instrument operation software (MassHunter or Chemstation). Before each analysis batch, a tune report or tune evaluation report should be generated to verify that the relative abundances and corresponding isotopic ratios of m/z=69, m/z=219, and m/z=502 are within the manufacturer’s criteria. Additionally, the percentages of the following ions indicative of air and/or water should be monitored as an overall indicator of the system being leak-tight: m/z=18 (water), m/z=28 (nitrogen), m/z=32 (oxygen), m/z=44 (carbon dioxide). Note: given the complexity of the canister autosampler and concentrator sample introduction system, the presence of air and/or water may be above Agilent’s recommended levels for operation (>20%). In these instances the tune evaluation report may state that tune fails for air and water indicating that a leak is present. It is up to the analyst to critically review the levels of air and water and determine if the system is satisfactory to run or if a significant leak needs to be addressed.

### 9.1.2 Chemical Ionization (CI)

If the mass spectrometer is operated using chemical ionization (CI) using methane as a reagent gas, running a chemical ionization autotune where a summary report for PCICH4.U (positivie chemical ionization) or NCICH4.U (negative chemical ionization) is generated is sufficient. The manufacturer does not have specific CI tuning criteria. However, the manufacturer recommends that a positive CI tune be run first even if the intent is to run in negative CI mode. Also, it is highly recommended that a tune be generated in EI mode prior to switching the source to verify system performance. If a reagent gas other than methane is used (ammonia or isobutene), consult the instrument operation manual for guidance on appropriate tuning procedures.

### 9.1.3 System Performance Check (50 ng p-bromofluorobenze) - *OPTIONAL*

A standard of p-bromofluorobenzene (BFB) may be analyzed to demonstrate acceptable instrument mass spectral performance. BFB is commonly used for most EPA volatile organic compound GC/MS analytical methods and is designed to standardize mass spectra. BFB tuning is currently required by U. S. EPA Compendium Method TO-15, but is deemed *optional* for the method described here if an appropriate tune described above is used.[2] A BFB tune may be required on an individual project basis. An example of a project requiring a BFB tune would be an interlaboratory comparison study where either replicate samples or the same set of samples would be analyzed by an outside laboratory specifically running U. S. EPA Compendium Method TO-15. The information below describes method acceptance criteria if a BFB performance check is analyzed.

- The on-column amount of BFB should be 50 ng or less.
- The mass spectrum for the p-bromofluorobenzene peak is obtained by averaging the apex with the two adjacent scans and the background spectrum must be taken before the peak elutes as a single spectrum. Table 1 lists the required ion abundance criteria.

**Table 1: BFB Performance Criteria.**

| m/z | Ion Abundance Criteria |
|---|---|
| 95 | Base peak, 100% relative abundance |
| 50 | 8.0-40.0% of mass 95 |
| 75 | 30.0-66.0% of mass 95 |
| 96 | 5.00-9.0% of mass 95 |
| 173 | Less than 2.0% of mass 174 |
| 174 | 50.0-120.0% of mass 95 |
| 175 | 4.0-9.0% of mass 174 |
| 176 | 93.0-101.0% of mass 174 |
| 177 | 5.0-9.0% of mass 176 |

*Note: The criteria listed above are those specified in EPA TO-15. Newer etune and low mass tune options available on the Agilent 5977's offer greater overall sensitivity, but can produce ion abundances just outside of the historical EPA criteria.

- If BFB tuning is included for a given project, it must be analyzed and deemed compliant before any standard, blank, or sample can be analyzed. The BFB system performance check sample is required every 24 hours during a continuous analytical sequence. The evaluation parameters listed above can be entered into the tune evaluation module in the MassHunter data reduction software. The "Tune Evaluation Report" will summarize a "Pass/Fail" result for each criteria listed in Table 1. The pdf of the "Tune Evaluation Report" should be included in the raw data package.

## 9.2 Calibration

For quantitative data, it is recommended that a calibration curve be generated using a minimum of five or six points to allow for flexibility in establishing a linear range. When possible, the curve should bracket the expected sample concentration range. A typical calibration range is

[2] E16-0400 compared relative and raw abundances of the BFB ions using four different tuning options available on the Agilent 5977 GC/MS system: atune.u, etune.u, bfb_atune.u, and bfb.u. This investigation concluded that etune.u, which uses PFTBA, has increased sensitivity and performs equivalent or better than using the bfb tuning option when generated spectra of known analytes were searched against the NIST14 mass spectral library.

approximately 0.002 PPMv to 0.2 PPMv for high volume sample analysis (CTD) and 0.5 PPMv to 100 PPMv for low volume (loop) injection, or an appropriate sub-range. The instrument must be calibrated for each target compound prior to sample analysis and the calibration must meet the linearity requirements listed below in Section 9.2.1. Calibration criteria for "Estimated" data is provided in Section 9.2.2.

An internal standard quantitation technique is used to demonstrate instrument linearity. The ratio for the quantitation ion reconstructed chromatogram area for the analyte and the associated internal standard are plotted relative to the analyte concentration and internal standard concentration ratio using an appropriate regression analysis. The regression fit used is up to the analyst's discretion as long an equation exists to describe the curve and the minimum accuracy requirements are satisfied. Regression fit types include, but are not limited to, the following: linear, weighted linear ($1/x$, $1/x^2$), quadratic, and weighted quadratic ($1/x$, $1/x^2$). The origin may be included, but should not be "forced".

### 9.2.1 Quantitative Calibration Criteria

Calibration criteria include a coefficient of determination ($r^2$) greater than or equal to 0.985 and accuracy for each plotted point between 70 and 130% (also referred to as residuals). Any level outside the 70 to 130% accuracy must be deactivated, and the regression re-calculated. All levels must show a response (target area counts) greater than two times that of the blank. The calibration curve must contain a minimum of five calibration levels for a linear fit and a minimum of six for a quadratic fit. Mid-level points may be deactivated from the curve with documented technical justification from the analyst. Points at the low and high ends of the curve may be deactivated as needed to establish a better fit to bracket the concentrations of the samples.

Calibration curve point accuracy is typically evaluated in the data reduction software program (Agilent MassHunter Quantitative Analysis, Target, or other appropriate program).

Agilent MassHunter Quantitative Analysis (for GCMS) uses the following equation to determine the %Accuracy of each curve point[3].

$$\%\text{Accuracy} = \frac{\text{Calculated Concentration}}{\text{Expected Concentration}} * 100\%$$

The internal standard area response for each calibration level must be at least 60% of the mean internal standard area response for the points comprising the final calibration curve.

### 9.2.2 Estimated Calibration Criteria

"Estimated" DQO may use a reduced number of calibration levels (i.e. single-point or three-point). There are no internal standard response criteria or coefficient of determination ($r^2$) for "Estimated" data.

In the case of a single-point calibration, the calibration standard must be analyzed once before and once after the applicable project samples. The two one-point standard analyses can be averaged, but the %Accuracy for both analyses must be between 50% and 150% to maintain the classification as "Estimated". If more than one point is used for an estimated calibration, the %Accuracy for each point must be between 50% and 150% to maintain the classification "Estimated".

### 9.2.3 Screening

No calibration curve is required for "Screening" data (TICs only).

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[3] Note other data reduction programs, namely Target, may use different names for the same terms. Target reports the "Percent Difference" which is calculated using the following equation

$$\text{Pct. Diff} = \frac{(\text{Cal Conc} - \text{Quant Conc})}{\text{Cal Conc}} * 100\%$$

where Cal Conc=Expected or "theoretical" concentration and Quant Conc=the calculated concentration the software determines using the area responses and the regression equation. If using Target, the Pct. Diff should be within ±30%.

### 9.2.4 Continuing Calibration Verification (CCV)

A continuing calibration verification (CCV) is analyzed to verify the instrument stability and that the previously established calibration curve is still valid. Typically, a calibration standard near the mid-range of the calibration curve is analyzed as a CCV.

The accuracy of each CCV must be within 100±30% for the bracketed data to be considered acceptable for "Quantitative" data and 100±50% for "Estimated" data. The CCV accuracy is calculated in the same manner as the curve point accuracy. If a CCV does not meet the acceptance criteria, a new calibration curve may be established or the DQO will be classified as "Qualified Quantitative" in the case of Quantitative DQO or "Screening" in the case of "Estimated" DQO. When more than one CCV is analyzed within a given analytical batch, the relative percent difference of the two CCVs is calculated using the following equation:

$$\%RPD=\left(\frac{|\text{Conc. of Opening CCV-Conc of Closing CCV}|}{\text{Average of Opening and Closing CCVs}}\right)*100\%$$

DQO "Quantitative" mandates that %RPD of subsequent CCVs within a given batch be ≤25% for data to be reported without qualification. There is no %RPD criteria for "Estimated" DQO.

CCVs should be analyzed at the following time intervals:

- At the end of an analytical batch that includes the initial calibration curve followed by project samples.
- At the beginning and end of an analytical batch that does NOT include the initial calibration curve.
- After analysis of no more than fifteen study samples (excluding blanks).

## 9.3 Internal Standards

Internal standards will be used for sample quantitation and as a system reproducibility indicator. Internal standards are added to each instrument injection at the same concentration. Internal standards are added from a separate canister by the autosampler prior to loading the sample, standard, or blank. Analytes are associated with a particular internal standard for quantitation.

The area response for each calibration level must be greater than 60% of the average area response from the initial calibration range for each internal standard.

All internal standard responses observed throughout a sequence must be greater than 60% of the average internal standard responses observed in the most recent valid initial calibration. If the internal standard area counts are not greater than 60% of the average, the analytical system should be checked for errors and samples reanalyzed. If the internal standard areas for the reanalysis meet the criteria, report the results from the reanalysis.

All internal standard retention times will be monitored throughout the run and evaluated by the analyst.

If the criteria detailed above fail for any reason, the sample data may still be reported as "Quantitative" if the analyst and the technical lead deem that the overall quality is not compromised. Technical justification for acceptance of the non-compliant internal standard should be documented in a Note to File or Method Deviation. There are no internal standard method acceptance criteria for "Estimated" or "Screening" analytical data.

Internal standards are added to all standards, samples, blanks, and other QC samples at the time of analysis.

## 9.4 Blanks

### 9.4.1 Method Blank

A method blank is a canister that is filled with clean nitrogen (reagent gas) from a liquid nitrogen dewar to 1 atm (0 psig, 14.7 psia). The canister is then pressurized to 10 psig (24.7 psia), or the desired final pressure, with a benzene-$d_6$ surrogate standard. See Section 10.1.2 for information regarding this procedure. The concentration of the surrogate will depend on the type of analysis to be performed. This method blank doubles as a reagent gas blank.

Method blanks should result in target analyte area on column calculated concentrations less than one half the lowest calibration standard. If a method blank does not meet this criteria, identify and eliminate the source of the contamination.

If the contaminant cannot be eliminated and samples are analyzed, the associated sample data may be flagged. The analyte detected above the LOQ in the blank and sample may be qualified using the "B" qualifier. The "B" qualifier is commonly used in EPA methods to indicate the analyte detected in the sample was detected in the blank. Alternatively, low-level calibration standards may be deactivated from the final calibration curve until the lowest standard in the calibration curve has target analyte area counts at least twice those of the method blank.

A single, uniquely-identified, method blank is required prior to the analysis of samples. The method blank is used to evaluate the limit of quantitation. The method blank does not need to be in sequence right after the opening CCV or right after the last calibration point. See Section 9.5.

### 9.4.2 Instrument Blanks

Instrument blanks are the same as method blanks except they are used to assess instrument carry-over and cleanliness. Instrument blanks are not used to evaluate the limit of quantitation (See Section 9.5). If samples are expected to contain high VOC concentrations, it is recommended that at least one instrument blank be analyzed after each sample to avoid carry over.

## 9.5 Limit of Quantitation

The limit of quantitation (LOQ) for each analyte is equal to the analyte's lowest calibration standard concentration. The expected concentration ('true value') of the lowest calibration standard must be greater than two times the observed method blank concentration. The LOQ is adjusted for each sample to reflect any dilution factor. For example, the lowest calibration standard for compound A is 2.0 PPBv and the sample dilution factor due to pressurization is 1.7, the sample LOQ for compound A would be 3.4 PPBv (2.0 PPBv X 1.7). If a compound is not detected at or above the LOQ, the analytical result reported will be listed as less than LOQ (<LOQ).

LOQs based off established calibration curves are reported for "Quantitative" or "Qualified Quantitative" data only. Arbitrary LOQs defined by the analyst for "Estimated" or "Screening" may be included in the report. Typical examples of arbitrary LOQs established by the analyst are given below.

- "Only results with a signal-to-noise ratio greater than 10 are reported for Compound X" (Estimated Data, 1-point calibration curve).
- "The reported concentration of TICs is based on the base peak response of the internal standard toluene-$d_8$ and the deconvoluted base peak of the TIC. In general, only TICs with an estimated concentration of 0.005 PPMv on-column (before any dilution factor is applied) were reported." (Screening Results – See 13.3 for additional information.)

Although not routinely done, sample results may be reported below the LOQ with an accompanying "J" flag when deemed appropriate by the analyst when considering the needs of the project requester/client.

## 9.6 Surrogate Recovery Standard

A surrogate is added to each canister to monitor sample matrix effects and as an analytical quality control measure. Benzene-$d_6$ is typically used as a surrogate compound because it does not interfere analytically and is not present in a typical whole air sample. An alternative surrogate compound may be used as long as that compound does not interfere with the analysis. See Section 10.1.2 for the surrogate addition procedure.

Surrogate addition to a canister is not addressed in U.S. EPA Compendium Method TO-15. Based upon 3M Environmental Laboratory historical data, surrogate recoveries should be within 100±30% for "Quantitative" data. "Estimated" and "Screening" data have no surrogate recovery criteria.

Surrogate recovery is calculated using the following equation

$$\text{Surrogate Recovery} = \frac{\text{Measured Surrogate Concentration}}{\text{Surrogate Spike Concentration}} * 100\%$$

Surrogate is added to every sample canister at a level appropriate for the VOC content of the sample. There may be times where surrogate is added to canister at low (PPBv) levels and the high (PPMv) sample concentration may prohibit surrogate detection. Conversely, there may be instances where surrogate is added to the canister at high (PPMv) levels and the samples ultimately require low (PPBv) level analysis. For this type of situation, the detector may be turned off during the elution of the surrogate to extend the lifetime of the filament (avoid detector saturation). When this occurs, the surrogate recovery is typically reported from the initial loop-level (PPMv) analysis, while the results for the other analytes are reported from the low-level (PPBv) analysis.

Alternatively, samples may be spiked with low-level surrogate (PPBv) regardless of the VOC content with analytical data generated using the simultaneous SIM/Scan function on the mass spectrometer. In this instance, the SIM chromatogram could accurately quantitate low-level surrogate and the full-scan data could be used for the PPMv level VOC quantitation, or the canister could then be overspiked with PPMv level surrogate and reanalyzed. Other surrogate spiking and measurement techniques may be used and documented accordingly in the data package.

## 9.7 Laboratory Control Spikes and Laboratory Matrix Spikes

### 9.7.1 Laboratory Control Spikes (LCSs)

Analysis of LCSs demonstrates acceptable analyte recovery from a canister and stability over a defined time range. LCSs are not required for routine execution of this method. Preparation and analysis of any LCS will be prescribed by a project-specific GPO. LCSs are typically prepared when evaluating compounds not previously analyzed by this method. All LCS preparation conditions (concentration(s), humidity, etc.) will be outlined in the GPO. Analysis time points to establish stability will also be outlined in the GPO. Since LCSs are usually prepared to evaluate new compounds, acceptance criteria for LCS recoveries are not defined here. Recoveries from initial LCS investigations may be used to define compound specific criteria moving forward.

### 9.7.2 Laboratory Matrix Spikes (LMSs)

Matrix spike samples are prepared to evaluate sample matrix effects. LMSs are not required for routine execution of this method. Preparation and analysis of any LMS will be prescribed by a project-specific GPO or specifically dictated by laboratory management.

Matrix spike samples may require a sample canister to be spiked in the lab after sampling and initial analysis. The sample canister to be spiked is first analyzed to determine sample component concentration. Once accurate and precise sample data are obtained, the canister is vented to slightly less than atmospheric pressure, spiked with a known concentration gas standard, and reanalyzed.

Alternatively, if a larger canister is used to collect the sample gas (1L, 3L, or 6L), matrix spikes may also be prepared by pressurizing a separate mini canister (0.38 L) pre-spiked with a known amount of analyte with the sample gas from the larger vessel.

Prescribed acceptance criteria for matrix spikes are not defined here. Rather, observed matrix spike recoveries will be included in the project report and the impact to the overall sample data will be discussed accordingly.

# 10 Procedures

This section lists recommended procedures for sample handling (surrogate pressurization, etc.) and typical operating parameters for the GC/MS, autosampler, and sample concentrator. Due to the method's wide scope and application, it is not feasible to list the recommended instrument parameters for each potential analyte. Any modification, no matter how extreme, to these recommended conditions is acceptable as long as method performance criteria are met and the conditions are documented in the data package.

The analyst can use LabWare LIMS to search for historical analyte data. Once a reference to a lab request is found in LabWare LIMS, the analyst can then obtain the instrument parameters from the lab request record in the archive database. The archive database contains a document that lists the instrument parameters. Copies of instrument run logs paper or electronic (PDF) and saved copies of instrument methods are also a suitable starting place for determining acceptable instrument parameters for historical analytes.

## 10.1 Sample Handling

The items below describe how an air sample collected in a canister is processed once it is received at the laboratory.

### 10.1.1 Canister Inventory Tracking

Canister inventory is maintained using the LabWare Laboratory Information Management System (LIMS). When preparing canisters for sampling and receiving canisters after sampling, the canisters should be scanned into the appropriate inventory category in the database.

Canisters returning to the laboratory after sampling in the field are received by Sample Custody personnel and the chain-of-custody form is signed. Canister samples are then delivered to the analyst by Sample Custody.

### 10.1.2 Sample Canister Pressurization and Surrogate Addition

Sample canisters are pressurized prior to analysis to ensure sufficient sample volume. A vendor prepared high-pressure cylinder containing a surrogate, with nitrogen as the balance gas, is used to pressurize sample canisters. Follow the steps below to pressurize sample canisters prior to analysis:

1. Adjust the high accuracy pressure gauge to zero.
2. Open the surrogate standard cylinder and adjust the dual stage pressure regulator to the desired pressure.
3. Attach the valved transfer line from the surrogate standard cylinder to the pressurization assembly and flush the lines briefly with the surrogate standard.
4. Close the valve prior to connecting the canister.
5. Attach the canister to the pressurization assembly and record the sample canister pressure (psia) in LabWare LIMS under initial pressure. The gauge used may read vacuum in inches of Hg and pressure in psig. At the

pressurization work area, a pressure conversion table is available to convert to psia if needed.

6. Open the surrogate standard transfer line valve on the pressurization assembly to pressurize the system.
7. Carefully fill the canister to the desired final pressure, by adjusting the surrogate standard transfer line valve.
8. Once the final pressure is reached, close the canister valve remove the sample canister from the pressurization assembly and record the final canister pressure (psia) in LabWare LIMS under final pressure.
9. Purge the pressurization assembly with surrogate a few times to prevent contamination of the next sample.
10. Set the canister aside to equilibrate for at least two hours before analysis.

#### 10.1.3 Sample Holding Time

A recommended holding time is up to 30 days from the date sampled to analysis. This holding time may be compound dependent and should be evaluated as dictated by the GPO. If data have been published indicating compound stability over time in SUMMA canisters, the same stability, at a minimum, will be observed in a fused-silica lined canister. Performance samples such as lab control spikes (Section 9.7.1) can be used to document compound stability in a canister over time. See the References (Section 16) in this method for publications related to compound stability when stored in canisters.

In lab request E03-0265, it was demonstrated that FCs routinely analyzed are stable in canisters for greater than five months at approximate concentrations of 20 PPMv. At 2 PPMv, all but two of the FCs (perfluoromethane and PFTBA) were stable for greater than five months. See the E03-0265 final report for more information.

### 10.2 Pre-run Steps

#### 10.2.1 Following instrument maintenance

After a mass spectrometer maintenance event or if the analyzer was vented for any reason, complete the following steps before beginning sample analyses.

Check the mass spectrometer tune or perform a new tune according to the vendor's recommendations to assure that the selected criteria are met. Generate a mass spectrometer tune report.

Perform an air/water check and review. Verify that the system passes the air/water check. Inspect the mass spectrum for m/z=18 (water), 28 (nitrogen), 32 (oxygen), and 44 (carbon dioxide). Levels of these ions greater than 20% of m/z=69 or 219 (from PFTBA tune gas) may indicate that a leak is present or the system is still pumping down.

#### 10.2.2 For daily, routine analyses

Use the Entech model 7032/7100/7200 software to flush and bake the autosampler/preconcentrator.

Run the instrument manufacture's tune evaluation report for the type of tune selected (atune.u, etune.u, etc.) *or* analyze and evaluate an aliquot (equivalent to 50 ng or less) of the BFB performance check standard. Only one of these two evaluation methods is required, not both. Verify that the performance criteria were met for *either* the appropriate tune or for BFB (Table 1). Regardless of the evaluation method, verify that the criteria are met before proceeding with standards and sample analyses.

An instrument blank may be analyzed from the method blank canister to ensure that the analytical system is free of significant contamination and that the internal standard pressure and system pressures and temperatures are stabilized from any period of inactivity. The

instrument blank analysis is not subject to the acceptance criteria of the method blank in Section 12.4.3.

Set up the preconcentrator and the GC/MS. Operating conditions provided below are recommended and may be adjusted to optimize system performance.

## 10.3 GC Conditions

**Table 2: GC Oven Program Using DB-1 Column.**

| Step | Initial Temperature | Rate | Final Temperature | Hold |
|---|---|---|---|---|
| 1 | -10°C | 0°C/min | -10°C | 0.00 |
| 2 | -10°C | 10°C/min | 250°C | 2.75 |

**Table 3: Example GC Oven Program Using GasPro Column.**

| Step | Initial Temperature | Rate | Final Temperature | Hold |
|---|---|---|---|---|
| 1 | 25°C | 0°C/min | 25°C | 2.00 |
| 2 | 25°C | 5°C/min | 60°C | 0.00 |
| 3 | 60°C | 10°C/min | 255°C | 1.50 |

## 10.4 MS Conditions.

**Table 4: Example Quadrupole Mass Spectrometer(1) Settings: Full Scan.**

| Condition | Setting |
|---|---|
| Acquisition mode: | (2)Scan |
| Scan range: | 30.0 to 550.0 m/z |
| MS source temperature: | (3)230°C |
| MS quadrupole temperature: | 150°C |
| Interface temperature: | 250°C |
| Multiplier voltage: | Adjust to give required low standard sensitivity |
| Electron energy: | 70 eV (nominal) |

(1) The conditions provided are for a single quad mass spectrometer operating in electron impact (EI) ionization. Please consult instrument manuals for appropriate conditions for chemical ionization (CI) or if using the Agilent 7200 GC/Q-TOF.

(2) Agilent GC/MS models 5975 and 5977 are equipped to perform simultaneous SIM/SCAN. If this option is used, the appropriate ions for selected ion monitoring (SIM) should be entered for the compounds of choice. Dwell times (SIM) and scan rates (SCAN) should be balanced to ensure enough data points are collected across the chromatographic peak.

(3) Extractor sources on the Agilent GC/MS model 5977 may be operated at elevated temperatures.

## 10.5 Preconcentrator Conditions.

**Table 5: Suggested Microscale Purge-and-Trap Parameters.**

| **During concentration** | | **Temperature (°C)** |
|---|---|---|
| Module No. 1, Glass Bead or Glass Bead/Tenax Cryo trap | | -150 |
| Module 1 Bulkhead | | 30 |
| Module No. 2, Sorbent Packed Cryo trap | | -100 |
| Module 2 Bulkhead | | 30 |
| Focusing Trap | | -180 to -200 |
| **Desorb/transfer/inject** | **Preheat (°C)** | **Final temp (°C)** |
| Module No. 1, Glass Bead or Glass Bead/Tenax Cryo trap | -50 | 20 |
| Module 1 Bulkhead | NA | 100 |
| Module No. 2, Sorbent Packed Cryo trap | No | 180 |
| Module 2 Bulkhead | NA | 100 |
| Focusing Trap | NA | 100 |
| **Media concentrated /transferred** | **Volume (cc)** | **Flow rate (cc/min)** |
| Internal Standard | 40 to 200 | 100 |
| Sample | 10 to 1000 | 100 |
| Sweep/Dry Purge | 75 | 100 |
| Transfer to Packed Column | 40 | 10 |
| **Sample Transfer Times** | | |
| Line conditioning sample flush time before trapping | | 5 sec. |
| Sample transfer to focusing trap time | | 1.5 to 4 min. |
| Sample injection time | | 1.5 to 5 min. |
| Total cycle time | | Generally 15 min |
| **System bakeout** | **Temperature (°C)** | **Time (min.)** |
| Module No. 1 | 130 | 7 |
| Module 1 Bulkhead | 150 | 7 |
| Module No. 2 | 190 | 7 |
| Module 2 Bulkhead | 150 | 7 |
| Module No. 3 | 100 | 7 |
| **Regulated zones** | | **Temperature (°C)** |
| 8-port valve | | 120 |
| GC transfer line | | 120 |
| 16-position select valve | | 120 |
| Sample container | | ambient |

**Table 6: Suggested Cold Trap Dehydration Parameters.**

| **During concentration** | | **Temperature (°C)** |
|---|---|---|
| Module No. 1, Glass Bead or Glass Bead/Tenax Cryo trap | | -40 |
| Module 1 Bulkhead | | 30 |
| Module No. 2, Sorbent Packed Cryo trap | | -40 |
| Module 2 Bulkhead | | 30 |
| Focusing Trap | | -180 to -200 |
| **Desorb/transfer/inject** | **Preheat (°C)** | **Final temp (°C)** |
| Module No. 1, Glass Bead or Glass Bead/Tenax Cryo trap | NA | NA |
| Module 1 Bulkhead | NA | NA |
| Module No. 2, Sorbent Packed Cryo trap | No | 180 |
| Module 2 Bulkhead | NA | 100 |
| Focusing Trap | NA | 100 |
| **Media concentrated /transferred** | **Volume (cc)** | **Flow rate (cc/min)** |
| Internal Standard | 40 to 200 | 100 |
| Sample | 10 to 1000 | 100 |
| Sweep/Dry Purge | 75 | 100 |
| Transfer to Packed Column | 40 | 10 |
| Line conditioning sample flush before trapping | | 5 sec. |
| Sample transfer to focusing trap | | 1.5 to 4 min. |
| Sample injection | | 1.5 to 5 min. |
| Total cycle time | | Generally 15 min. |
| **System bakeout** | **Temperature (°C)** | **Time (min.)** |
| Module No. 1 | 130 | 7 |
| Module No. 2 | 190 | 7 |
| Module No. 3 | 100 | 7 |
| **Regulated zones** | | **Temperature (°C)** |
| 8-port valve | | 120 |
| GC transfer line | | 120 |
| 16-position select valve | | 120 |
| Sample container | | ambient |

### 10.6 Sample Screening

If samples are received without any indication of their contamination level, they may be screened by loop injection or loop with split injection analyses to determine the appropriate calibration range and proper Entech injection method for the reportable analyses. Because minute gas volumes can be transferred between canisters via the dead volume of the multi-port autosampler valve, care must be taken to prevent cross-contamination from sample or standard canisters containing compounds at high concentrations to canisters that may require concentration prior to injection for target analyte concentrations below 0.1 PPMv. The following steps should be taken to avoid potential cross contamination during screening analyses or for samples that contain wide concentration ranges of compounds such that they require both loop and concentrated injection analyses.

1. Autosampler ports following standards and between samples should be left open to allow venting of potential contaminants from the valve dead space before it rotates to the next sample position; or,
2. Any samples following a standard or other high concentration sample must be at a pressure of at least 5 psig and within 2 psig of the preceding standard or sample. Samples should be loaded on the autosampler at approximately equal pressures because cross contamination is less likely without large pressure differences.
3. Standard canisters and potentially high concentration sample canisters should not be loaded on the autosampler with pressures >15 psig.

Note: These precautions are only necessary if microscale purge and trap or cold trap dehydration concentration analyses are required following the loop injection analyses. The potential cross contamination for reporting sample concentrations >1 PPMv is not significant.

### 10.7 Sample Analysis

Set up the instrument acquisition method and create an analytical sequence. The sequence includes a sample list documenting the methods used and data files created. Document the sequence in the instrument run log.

Analyze all standards, blanks, samples, and spiked samples using the same analytical conditions. Document the autosampler/concentrator and GC/MS methods in the run log. Aliquots sampled may vary in volume from the standard volume in order to obtain dilution. The sample aliquot must be recorded in the instrument run log.

### 10.8 Data Reporting

After initial analysis, a sample canister may require dilution to bring the concentration of the analyte(s) of interest to within the established calibration range. The re-analysis of diluted samples will consequently produce multiple result concentrations from multiple data files for any given analyte. When this situation occurs, the analyst should report *only* the analyte result (including surrogate) from the least diluted sample that produced an on-column amount still within the established calibration range. In the final report, the “date/time analyzed” stamp and the resulting LOQ for each individual analyte will indicate from which analytical run (dilution) the reported result was extracted. Analyte concentrations generated from multiple analyses of sample dilutions should not be averaged unless required by the GPO.

## 11 Data Analysis and Calculations

### 11.1 Data Processing

When data acquisition is complete, transfer the data files to a file server for processing. Each batch of data files from an analytical run should be transferred to an appropriate batch directory on the server, depending on the instrument and run date. When possible, use automated macro scripts to transfer the data files to the server upon run completion.

Analyze the data using appropriate data reduction software such as Agilent MassHunter, Target, or other suitable alternative. Integration parameters should be set to minimize the number of manual integrations required yet still result in uniform integration of peaks at all concentration levels. It is acceptable to perform manual integrations for any or all standards, samples, or blanks if appropriate integration parameters cannot be found, especially when near baseline resolved isomers are present. All integrations must be done consistently for all standards, samples, and blanks and in compliance with ETS-12-010. The concentration of a target analyte in the canister will be quantitated using the established internal standard calibration curve.

### 11.1.1 Target Analytes

Target analytes are identified by retention time and by matching the mass spectrum with a reference mass spectrum for the analyte. The analyst should visually inspect the mass spectra carefully and consider the following *guidelines* during the evaluation.

All ions present in the standard mass spectrum at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

The relative intensities of ions specified above should agree within ±40% between the standard and sample spectrum. Ion ratios between sample and reference spectra can vary considerably when the sample co-elutes with another analyte and when the sample concentration differs significantly from the concentration of the standard used to create the reference spectra. Examples of co-eluting analytes commonly encountered include the following:

- methanol and acetaldehyde
- ethyl acetate, methyl acrylate and n-hexane
- 1-bromopropane and tetrahydrofuran
- benene-$d_6$ and benzene
- m-xylene and p-xylene
- o-xylene-$d_{10}$ and styrene
- hexafluoropropene and chlorotrifluoroethylene
- 2H-heptafluoropropane and 1,1-difluoroethane
- methylene chloride-$d_2$ and 2,2-difluoropropane

Ions with relative abundances greater than 10% in the sample spectrum, but not present in the standard spectrum must be carefully considered by the analyst. These ions may be present due to co-eluting peaks or background system contamination. The verification process should favor false positives.

Target analytes are quantitated using an internal standard quantitation technique. Each analyte is assigned to a specific internal standard to determine a relative response. The nearest eluting internal standard is typically used, but the analyst may select a different internal standard if deemed appropriate. The extracted ion chromatogram profile area for an individual ion selected from the mass spectrum for both the analyte and internal standard is used to establish a calibration curve. Appropriate ions for target analyte quantitation are chosen at the analyst's discretion. The analyst must balance sensitivity and selectivity needs when choosing ions. See Table 9 for suggested quantitation and qualifier ions.

MassHunter Quantitative Analysis is currently the data reduction software program of choice used for quantitating target analytes in analyzed samples. For each injection, MassHunter will provide a match factor of the target analyte relative to the reference

spectrum in the method. The analyst should use this match factor as an additional guideline to substantiate the presence of a target analyte in a sample.

For MassHunter Quantitative Analysis, there are multiple ways of creating batches, processing methods, etc. The built-in help menu should be consulted. Modification of an existing quantitation method is also acceptable and may be preferable. Additionally, Agilent has created several instructional videos that can be found on the installation CDs. Other software programs may be used when appropriate, i.e. Target, Excel.

The highest concentration standard in the calibration curve is considered the upper limit of quantitation. Samples that contain target analytes at on-column concentrations higher than the upper limit of the calibration curve must be diluted such that the on-column concentration is within the calibration range, or they must be reported as minimum estimated concentrations. In this instance, an "E" flag is typically used to indicate that the reported value "exceeded" the instrument calibration. Samples with on-column concentrations within 110% of the highest calibration standard may be reported without additional technical justification.

### 11.1.2 Tentatively Identified Compounds (TICs)

Use a NIST mass spectral library to tentatively identify components present in the chromatogram that are attributed to target analytes. The most-current NIST mass spectral library should be used (i.e. NIST14). The available NIST libraries are available on a laboratory shared drive or may be copied to the hard drive of the analyst's personal workstation for faster searching. Components identified via library search will be noted as such in the final report with an "N" qualifier indicating presumptive identification based on a mass spectral library search. Custom-built mass spectral libraries can be searched along with the NIST library.

If using Agilent MassHunter for data reduction, a separate program module called "Unknowns Analysis" will be used for component identification and estimation. Unknowns Analysis is utilized after the data has been quantitated for target analytes using MassHunter Quantitative Analysis. Unknowns Analysis will compare detected components against the targets specified in Quantitative Analysis (using retention time, quant and qual ions, CAS#, and/or library search name). Unknowns will then segregate the "Targets" from "Non-Targets" allowing the analyst to focus on "unknowns" present in the chromatogram.

The information that follows is intended to provide *high-level information* for Unknowns Analysis, and not prescriptive instructions for creating a method and analysis of samples. Several parameters exist in Unknowns Analysis that can be manipulated to customize the analysis and subsequent estimation. *This document does not address all parameters.* Depending on the complexity of the chromatograms and the desired estimation level, the analyst will need to alter parameters as needed. The "help" menu should be consulted when creating and adjusting an Unknowns method. Likely, the method creation will be an iterative process with a selected sample chromatogram until the produced results meet the DQO and needs of the project requester/management. A few of the high-level parameters/components of Unknowns Analysis are discussed below.

#### 11.1.2.1 Deconvolution

Deconvolution is a mathematical algorithm that the MassHunter software applies to the raw mass spectral data to extract ions from a complex total ion chromatogram. Peak shapes and apex retention times for extracted ions are then mathematically evaluated to determine if multiple components are present within a retention window. Deconvolution can clean background noise from spectra and help spectrally separate out co-elutions.

The RT window size factor is a key parameter for deconvolution. A smaller RT window size (i.e. 25) will likely result in more peaks being detected and

should be used when co-elutions are suspected. A larger RT window size will likely result in fewer peaks. The analyst should visually inspect the detected components and the corresponding retention times to determine if the selected RT window size is either missing co-elutions or producing deconvolution "artifacts" (erroneous peaks typically just off-set from the main component). Multiple RT window sizes can be included in a single method (default setting is 25, 50, 100, 200); however, the analysis speed will decrease as additional processing will be required.

Note: Deconvolution is the preferred approach for "peak detection", but TIC (total ion chromatogram) analysis may be performed as well and is the standard approach used by Target data reduction software.

#### 11.1.2.2 Library Search

The library search tab allows the analyst to enter the libraries to be searched. It is recommended that the user created library generated in Quantitative Analysis which stores the reference spectra generated from calibration standards be used as well as the most current NIST library. Inclusion of the user created library will typically produce better identifications of targets, especially for isotopically labeled compounds used as surrogates or internal standards.

#### 11.1.2.3 Compound Identification

This tab allows the analyst to specify the number of possible identifications per component peak and the minimum match factor. It is recommended that the "Max Hit Count" be something greater than 1 (default setting) so the analyst can view multiple library hits if he/she suspects that the "best hit" is not appropriate. Also, if the "Min Match Factor" is too high, there is a risk that peaks may not be identified. The analyst should always review the chromatogram to visually verify that the program did not miss obvious peaks because the library search could not produce an identification with sufficient match quality. If, in the technical judgment of the analyst, no valid identification can be made, report the compound as an unknown with possible classification, such as hydrocarbon.

#### 11.1.2.4 Target Match

This tab allows the analyst to specify how the program determines if a component is a target analyte. It is recommended that "Target Ion", "Qualifier Ion(s)", "Compound Name", "Within target RT window", and/or "Use CAS#" be selected. The "Target Requirements" check boxes should not be selected.

The estimation response factor is also selected in this tab. There are several estimation approaches available in the pull down menu. Consult the help menu for a full description of each approach. Typically, the "RF of closest ISTD" is used, but other types of estimation may be used at the analyst's discretion. "RF of closest ISTD" uses the following equation to estimate the concentration of the tentatively identified compound:

$$\text{Estimated Concentration} = \text{Multiplier} \times \left( \frac{\text{Area of the Deconvoluted Base Peak of the Component}}{RF_{ISTD}} \right)$$

where

$$RF_{ISTD} = \frac{\text{Average ISTD area count from the calibration curve samples}}{\text{Concentration of the ISTD}}$$

$$\text{Multiplier} = \frac{\text{Sample Concentration}}{\text{On-column calculated concentration}}$$

Note: This estimation approach is very different from what is typically done with Target.

- Target uses the response factor from the total ion chromatogram of the toluene-$d_8$ ISTD. Target did not perform spectral deconvolution.
- Target uses the toluene-$d_8$ response factor for the given sample. MassHunter uses the average response factor from the calibration curve. If the ISTD response for the sample in question is significantly different than the average response of the calibration curve, estimated results may be biased high or low. In such instances, the analyst may elect to use a different estimation scheme such as a manually entered response factor when using MassHunter.

All estimated TIC concentrations should be reported with a qualifier of "J" to reiterate that the reported concentration is a screening level result. A brief description of how the TIC concentrations were estimated should be included in the raw data and/or final report.

## 11.2 Dilution Equations

### 11.2.1 Pressure Dilution

$$\text{Dilution Factor} = \frac{P_f}{P_i}$$

where,

$P_f$ = Final canister pressure in psia

$P_i$ = Initial canister pressure in psia

### 11.2.2 Injection Volume Dilution Factors

$$\text{Dilution Factor} = \frac{V_a}{V_n}$$

where,

$V_a$ = Actual sample volume injected (cc)

$V_n$ = Normal sample injection volume (cc)

### 11.3 Percent Accuracy and Difference (Calibration Curve Points and CCVs)

$$\text{Percent Accuracy} = \frac{C_{quant}}{C_{actual}} * 100\%$$

$$\text{Percent Difference} = \frac{C_{quant} - C_{actual}}{C_{actual}} * 100\%$$

where,

$C_{quant}$ = Quantitated concentration in PPMv

$C_{actual}$ = Theoretical standard concentration in PPMv

### 11.4 Surrogate Recovery

$$\text{Percent Surrogate Recovery} = \frac{C_{quant}}{C_{spk}} * 100\%$$

where,

$C_{quant}$ = Quantitated sample surrogate concentration in PPMv;

$C_{spk}$ = Surrogate spike amount added in PPMv.

$$C_{spk} = \frac{(\text{Final Pressure} - \text{Initial Pressure})}{\text{Final Pressure}} * DF1 * DF2 * \text{Surrogate Standard Conc.}$$

where

DF1 equals the dilution factor arising from injecting a different sample volume than the normal volume used to establish the method. See Section 11.2.2.

DF2 equals the secondary dilution factor arising from a subsequent pressure dilution of the sample canister or serial dilution from the sample canister to another canister. (A secondary pressure dilution is often performed if sample concentrations exceed the upper calibration range during the initial analysis). See Section 11.2.1. If only a single pressurization occurs, then DF2 =1.

For example, a sample canister arrives in the laboratory with an initial pressure of 13.8 psia (slight vacuum). It is then pressurized to 24.7 psia using a 25 ppb benzene-$d_6$ surrogate standard. A 50 cc injection volume is used to analyze the sample when the standard injection volume is 100 cc. The theoretical surrogate concentration is calculated below.

$$C_{spk} = \frac{(24.7 \text{ psia} - 13.8 \text{ psia})}{24.7 \text{ psia}} * \frac{50cc}{100cc} * 1 * 25 \text{ PPMv} = 5.52 \text{ PPMv}$$

In MassHunter, the surrogate dilution is calculated as follows:

$$\text{"Surrogate Dil."} = \frac{C_{spk}}{\text{Surrogate Standard Concentration}}$$

### 11.5 Replicate Precision

$$\text{Relative Percent Difference} = \frac{|C_1 - C_2|}{C_a} * 100\%$$

where,

$C_1$ = Concentration for replicate number 1 in PPMv;

$C_2$ = Concentration for replicate number 2 in PPMv;

$C_a$ = The average of replicate number 1 and number 2.

### 11.6 Laboratory Control Samples

$$\text{Percent Recovery} = \frac{C_q}{C_a}(100)$$

where,

$C_q$ = Quantitated concentration of compound *x* in PPMv;

$C_a$ = Actual concentration of compound *x* in PPMv.

### 11.7 Matrix Spike Recovery

$$\text{Matrix Spike Percent Recovery} = \frac{(C_m - C_s)}{C_a} * 100\%$$

where,

$C_m$ = Matrix spike sample concentration in ppmv;

$C_s$ = Sample concentration in ppmv;

$C_a$ = Matrix spike amount added in ppmv.

### 11.8 Pressure Conversion Factor Calculations

| ***Present Units*** | ***Operation*** | ***Outcome Units*** |
|---|---|---|
| "Hg (vacuum) | 14.696 – ("Hg/2.036) | psia |
| "Hg (gauge pressure) | 14.696+("Hg/2.036) | psia |
| psig (gauge pressure) | psig+14.696 | psia |
| atm (absolute) | atmx14.696 | psia |

## 12 Analysis Batch Method Performance Criteria for Quantitative Data

Any method performance parameters that are not achieved must be considered during evaluation of the data. If "Quantitative" data quality objectives are requested in the GPO, particular attention must be given to the criteria described below. Also, intended use of the results (if provided) should also be considered. For example, if the intended use of the data is an exploratory/method development investigation, stringent adherence to method acceptance criteria summarized below may not be required. On the contrary, if the data is going to a regulatory agency for permitting work, any nonconformance to general method acceptance criteria or to the data quality objectives set forth in the GPO must be described and discussed in the final report. Additionally, if results are to be reported when performance criteria have not been met, the data must be footnoted appropriately in corresponding tables based on the DQO requested.

### 12.1 System Performance Mass Spectrometer Tuning (EI only)

A mass spectrometer PFTBA tune report and air/water diagnostic report are generated after a mass spectrometer maintenance event, or after the analyzer is vented for any reason, to document mass spectral resolution and peak shape and to demonstrate that the system is leak-free. The percent nitrogen (m/z 28) should be <20% relative to the base peak (m/z 69) of the tuning compound (PFTBA). If the air/water check does not meet these criteria, a leak may be present in the system and should be corrected before proceeding with the analysis. However, for some air analytical instruments, the normal air present in the system is elevated. The analyst should critically review the air/water and determine if the level is normal or if a leak is present. Save .pdf files of the reports on the file server in an appropriate folder under the Instrument.i folder.

### 12.2 Sensitivity

Method Detection Limits (MDLs) as per 40 CFR 136 have not yet been established for this analysis, but will be summarized and referenced in analytical reports when available. Sensitivity is addressed on a project basis based on the data quality objectives. An important DQO parameter to establish, preferably prior to sample collection, is the limit of quantitation. All attempts will be made to make the low-level calibration standard concentration equal to or near the LOQ stated in the GPO. In some cases, the LOQ will far exceed the GPO requirements. For industrial hygiene sample analysis, the general goal is to obtain an LOQ equal to or near a concentration that is 10 times less than the specified occupation exposure limit (OEL). Inversely, samples requesting sub-PPMv LOQs, but contain high PPMv analytes may not be suitable for high-volume (CTD / MPT) analysis. The requestor should be contacted to inform him or her that the LOQ specified in the GPO will not be attainable.

### 12.3 System Repeatability

System repeatability is determined by variability in internal standard response in calibration standards. The area response for each calibration level must be greater than 60% of the average area response from the initial calibration range for each internal standard. The area response for all internal standard responses observed throughout a sequence (blanks, samples, CCVs) must be >60% of the average internal standard responses observed in the most recent valid initial calibration.

### 12.4 Calibration and Limit of Quantitation (LOQ) – Analysis Batch for Quantitative Data

#### 12.4.1 Calibration Curve – Analysis Batch (Quantitative)

If a linear, quadratic, or other fit is applied to the calibration data (with or without weighting), then the coefficient of determination ($r^2$) value for the calibration curve must be greater than or equal to 0.985. Each point included in the final calibration curve must be within ±30% of the theoretical concentration.

#### 12.4.2 CCV Performance – Analysis Batch (Quantitative)

The calibration standards that are interspersed throughout the analytical sequence are evaluated as continuing calibration verifications (CCV). CCVs may also be used at the beginning of an analytical batch if an acceptable calibration curve was established in a previous analytical batch. The accuracy of each CCV must be within 30% of the theoretical value. Samples that are bracketed by CCVs not meeting these criteria must be flagged appropriately.

#### 12.4.3 Limits of Quantitation (LOQ) – Analysis Batch (Quantitative)

The lower LOQ (LLOQ) is the lowest active standard in the calibration curve. The peak area of the LLOQ must be carefully evaluated against the method blank and verified to have target analyte area counts at least 2X of a blank free from instrument carryover.

#### 12.4.4 Blanks – Analysis Batch (Quantitative)

Instrument blanks should be interspersed throughout the analytical batch. Instrument blanks are typically analyzed both before and after the instrument calibration curve or CCV injections. It is highly recommended to run more than one instrument blank after the highest calibration curve point or after samples suspected to have high target analyte concentrations. Instrument blanks are intended to be used as system "clean up" blanks and are not explicitly used to evaluate the LOQ as is the method blank (See Section 12.4.3).

### 12.5 Data Accuracy and Precision – Analysis Batch

#### 12.5.1 Surrogate Recovery – Analysis Batch (Quantitative)

Surrogate recoveries should be within 100±30% for each project sample for the data to be reported without further technical justification or qualifications.

## 13 Method Uncertainty and Reporting

### 13.1 Quantitative

All batch data is uploaded into Labware LIMS. CCV recoveries for each target analyte and surrogate recoveries are available for control charting for each instrument and sample introduction technique (i.e. loop vs. ambient). Using the "Run Control Chart" option in LIMS, a control chart can be generated which will provide the method uncertainty. However, analyte-specific calculated method uncertainty from the control chart will not be provided in the final report for "Quantitative" data if CCV recoveries for the given batch/project are within 100±30%. For "Qualified Quantitative" data, the stated method uncertainty will likely address any CCV non-compliances.

### 13.2 Estimated

For "Estimated" results, a statement saying that method uncertainty cannot be ascertained should be included, but the analyst should include commentary on the level of calibration or QC included (i.e. "estimated value based off a single-point calibration".

### 13.3 Screening

For "Screening" results (TICs only), a statement saying that method uncertainty cannot be ascertained will be included in the report. The analyst should also include verbiage that discusses the library match factor, the method used for estimation, and reporting limit. Example text to be included is given below, but may be modified to meet the reporting needs of a given project.

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*Non-target (non-calibrated) compounds were tentatively identified in the samples on the basis of a mass spectral library search. Mass spectra of tentatively identified compounds (TICs) were compared to the NIST14 reference spectral library. Quality fit factors are included in the report to indicate the confidence level of matches. The quality fit factors range from 0% for no spectral correlation to 100% for a perfect match. The quality fit factor is less reliable for TICs at lower concentrations and for those with low primary fragment ion masses. This is because their fragment ion ratios are more easily biased by background subtraction or other factors such as a limited scan range that may produce spectra which are less representative of the unknown sample components. The reported concentration of TICs is based on the base peak response of the internal standard toluene-$d_8$ and the deconvoluted base peak of the TIC. In general, only TICs with an estimated concentration of 0.005 PPMv on-column (before any dilution factor is applied) were reported. This arbitrary LLOQ is dependent on several factors which include instrument sensitivity and canister certification cleanliness. A TIC may not be reported due to low library match quality, estimated concentration below the LLOQ, and poor model peak signal to noise ratio. Other factors such as the compatibility of the compound to canisters (i.e. volatility, chemical functionality, etc.), how it reacts during introduction to the gas*

*chromatograph, compound retention, or spectral fragmentation affinity adds to the uncertainty of its presence or non-presence. Therefore, reported TICs may be considered as the presence of additional chemical species. However, the absence of additional species cannot be confirmed given the reasons previously mentioned.*

*Since the response factors of the TICs relative to the internal standard are unknown, the reported TIC concentrations are considered estimates at best. The analytical method uncertainty of TICs cannot be ascertained, and TIC results should be used for screening purposes only.*

## 14 Pollution Prevention and Waste Management

The toxicity and carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard.

Sample canisters will not be cleaned until at least one week after final report distribution. Sample canisters may be vented in a functioning fume hood prior to cleaning if it is appropriate to do so (i.e. no current "workers on the roof" notices or "no-vent" notices from building safety.)

Refer to 3M Waste Stream policies for further information.

## 15 Records

Document all analytical sequences in the instrument run log.

## 16 References


1. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition: "Compendium Method TO15: Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)" Center for Environmental Research Information, January 1999. (http://www.epa.gov/ttn/amtic/airtox.html)
2. "32-Week Holding Time Study of SUMMA Polished Canisters and Triple Sorbent Traps Used to Sample Organic Constituents in Radioactive Waste Tank Vapor Headspace," J. C. Evens et al, Environmental Science and Technology, 1998, 32, 3410-3417.
3. "Development of an Analytical Technique and Stability Evaluation of 143 C3-C12 Volatile Organic Compounds in SUMMA Canisters by Gas Chromatography-Mass Spectrometry," Della Wai-mei Sin et al, Analyst, 2001, 126, 310-321.
4. "Formaldehyde and VOCs in Indoor Air Quality Determinations by GCMS," D. Cardin, Entech Instruments, Inc., Application Note:101.
5. "Theoretical Evaluation of Stability of Volatile Organic Chemicals and Polar Volatile Organic Chemicals in Canisters," R. W. Coutant (Batelle), Atmospheric Research and Exposure Assessment Laboratory U.S. Environmental Protection Agency, February 18, 1992.
6. "Viability of Using SUMMA Polished Canisters for the Collection and Storage of Parts per Billion by volume Level Volatile Organics," D. A. Betmer et al, Environmental Science and Technology, 1996, 30, 188-195.
7. 3M Environmental Laboratory Lab Request W1289, "Report on the Stability Study of Perfluorooctane Sulfonyl Fluoride (POSF), Perfluorohexane Sulfonyl Fluoride (PHSF), and α-hydro Perfluoroethane Sulfonyl Fluoride (HESF) in Silcosteel Canisters," March 12, 1999.

8. 3M Environmental Laboratory Lab Request E03-0265, “Stability of the Fluorochemical Calibration Standard Mix in Canisters,” May, 2003.
9. 7032-L Operators’ Manual, version 1.0. Entech Instruments, Inc.
10. 7100 Operators’ Manual, version 2.0. Entech Instruments, Inc.
11. ETS 1-009 “General Project Outline (GPO)”
12. ETS-4-026 “Control Charts for Laboratory Analyses”
13. ETS-8-190 “Canister Cleaning and Certification Procedure”
14. ETS-8-196 “Gas Standard Preparation Using Canisters”
15. ETS-9-019 “Entech Canister Air Sample Preconcentrator and Autosampler and Entech Canister Cleaning System”
16. ETS-9-039 “Operation and Maintenance of the HP/Agilent 6890 or 7890 Gas Chromatograph/5973, 5975, or 5977 Mass Spectrometer”
17. ETS-9-004 “Working with Compressed Gases”
18. ETS-12-012 “Estimation of Uncertainty of Measurements”

# 17 Appendices

## A1. Example Applicable Volatile Organic Compounds.

**Table 7: Example Applicable Volatile Organic Compounds.**

| Analyte | CAS Number | Estimated LOQ (PPBv) |
|---|---|---|
| 1,1,1-Trichloroethane | 71-55-6 | 2 |
| 1,1,2,2-Tetrachloroethane | 79-34-5 | 2 |
| 1,1,2-Trichloroethane | 79-00-5 | 2 |
| 1,1,2-Trichlorotrifluoroethane | 76-13-1 | 2 |
| 1,1-Dichloroethane | 75-34-3 | 2 |
| 1,1-Dichloroethene | 75-35-4 | 2 |
| 1,2,4-Trichlorobenzene | 120-82-1 | 2 |
| 1,2,4-Trimethylbenzene | 95-36-3 | 2 |
| 1,2-Dibromoethane | 106-93-4 | 2 |
| 1,2-Dichloro-1,1,2,2-tetrafluoroethane | 76-14-2 | 2 |
| 1,2-Dichlorobenzene | 95-50-1 | 2 |
| 1,2-Dichloroethane | 107-06-2 | 2 |
| 1,2-Dichloropropane | 78-87-5 | 2 |
| 1,3,5-Trimethylbenzene | 108-67-8 | 2 |
| 1,3-Dichlorobenzene | 541-73-1 | 2 |
| 1,4-Dichlorobenzene | 106-46-7 | 2 |
| 2-Butanone (MEK) | 78-93-3 | 5 |
| 3-Methyl hexane | 589-34-4 | 5 |
| Acetone | 67-64-1 | 5 |
| Acetonitrile | 75-05-8 | 5 |
| Benzaldehyde | 100-52-7 | 5 |
| Benzene | 71-43-2 | 2 |
| Carbon Tetrachloride | 56-23-5 | 2 |
| Chlorobenzene | 108-90-7 | 2 |
| Chloroform | 67-66-3 | 2 |
| Chloromethane | 74-87-3 | 2 |
| cis-1,2-Dichloroethene | 156-59-2 | 2 |
| cis-1,3-Dichloropropene | 10061-01-5 | 2 |
| Cyclohexane | 110-82-7 | 5 |
| Cyclohexanone | 108-94-1 | 5 |
| Dichlorodifluoromethane | 75-71-8 | 2 |
| Ethanol | 64-17-5 | 5 |
| Ethyl acetate | 141-78-6 | 5 |
| Ethyl acrylate | 140-88-5 | 5 |
| Ethyl benzene | 100-41-4 | 2 |

**Table 7 continued.**

| Analyte | CAS Number | Estimated LOQ (PPBv) |
|---|---|---|
| Ethylene Oxide | 75-21-8 | 100 |
| Formaldehyde | 50-00-0 | 15 |
| Heptane | 142-82-5 | 5 |
| Hexachloro-1,3-butadiene | 87-68-3 | 2 |
| Hexane | 110-54-3 | 5 |
| Isopropyl alcohol | 67-63-0 | 5 |
| m,p-Xylene | 108-38-3/106-42-3 | 2 |
| Methanol | 67-56-1 | 5 |
| Methyl methacrylate | 80-62-6 | 5 |
| Methylene chloride | 75-09-2 | 2 |
| o-Xylene | 95-47-6 | 2 |
| Styrene | 100-42-5 | 2 |
| t-Butyl alcohol | 75-65-0 | 5 |
| Tetrachloroethylene | 127-18-4 | 2 |
| Toluene | 108-88-3 | 2 |
| trans-1,3-Dichloropropene | 10061-02-6 | 2 |
| Trichloroethene | 79-01-6 | 2 |
| Trichlorofluoromethane | 75-69-4 | 2 |

**Table 8: Example Applicable Volatile Organic Fluorochemicals.**

| Analyte | CAS Number | Estimated LOQ (PPBv) |
|---|---|---|
| 1,1,1,2,2-Pentafluoropropane | 1814-88-6 | 2 |
| 1,1,1,2,3,3-Hexafluoropropane | 431-63-0 | 2 |
| 1,1,1,2-Tetrafluoroethane | 811-97-2 | 2 |
| 1,1,1,3,3,3-Hexafluoropropane | 690-39-1 | 2 |
| 1,1,1-Trifluoroethane | 420-46-2 | 2 |
| 1,1,2,2-Tetrafluoroethane | 359-35-3 | 2 |
| 1,1,2-Trifluoroethane | 430-66-0 | 2 |
| 1,1-Difluoroethane | 75-37-6 | 2 |
| 1,1-Difluoroethylene (VDF) | 75-38-7 | 2 |
| 1H-Heptafluoropropane | 2252-84-8 | 2 |
| 2H-Heptafluoropropane | 431-89-0 | 2 |
| alpha-Hydroperfluoroethane sulfonyl fluoride (HESF) | 2127-74-4 | 2 |
| Chlorotrifluoroethylene | 79-38-9 | 2 |
| Difluoromethane | 75-10-5 | 2 |
| Fluoroethane | 353-36-6 | 2 |
| Hexafluoropropene (HFP) | 116-15-4 | 2 |
| Methyl fluoride | 593-53-3 | 2 |
| Octafluoro-2-butene | 360-89-4 | 2 |
| Perfluoroisobutene (PFIB) | 382-21-8 | 2 |
| Pentafluoroethane | 354-33-6 | 2 |
| Perfluorobutane | 355-25-9 | 2 |
| Perfluorobutane sulfonyl fluoride (PBSF) | 375-72-4 | 2 |
| Perfluoroethane | 76-16-4 | 2 |
| Perfluoroethane sulfonyl fluoride (PESF) | 354-87-0 | 2 |
| Perfluoroethylhexyl sulfonyl fluoride (PEHSF) | NA | 2 |
| Perfluoroheptane, tech. –90% | 335-57-9 | 2 |
| Perfluorohexane | 355-42-0 | 2 |
| Perfluorohexane sulfonyl fluoride (PHSF) | 423-50-7 | 2 |
| Perfluoromethane sulfonyl fluoride (PMSF) | 335-05-7 | 2 |
| Perfluoromethylmorpholine (PMM) | 382-28-5 | 2 |
| Perfluorooctane | 307-34-6 | 2 |
| Perfluorooctane sulfonyl fluoride (POSF) | 307-35-7 | 2 |
| Perfluoropentane | 678-26-2 | 2 |
| Perfluoropropane | 76-19-7 | 2 |
| Perfluoropropane sulfonyl fluoride (PPSF) | 423-40-5 | 2 |
| Perfluoropropyl vinyl ether (PPVE) | 1623-05-8 | 2 |
| Perfluorotributylamine (PFTBA) | 311-89-7 | 2 |

**Table 8 Continued.**

| Analyte | CAS Number | Estimated LOQ (PPBv) |
|---|---|---|
| Sulfur dioxide | 7446-09-5 | 4 |
| Sulfur hexafluoride | 2551-62-4 | 2 |
| Sulfuryl fluoride ($SO_2F_2$) | 2699-79-8 | 2 |
| Tetrafluoroethylene (TFE) | 116-14-3 | 2 |
| Trifluoromethane | 75-46-7 | 2 |
| Trifluoromethylsulfurpentafluoride | 373-80-8 | 2 |

## A2. Quantitation and Qualifier Ions

### Table 9: Suggested Quantitation and Qualifier Ions.

| Analyte | Quantitation Ion | Qualifier Ion(s) |
|---|---|---|
| 1,1,1-Trichloroethane | 97 | 99, 61 |
| 1,1,2,2-Tetrachloroethane | 83 | 85, 131 |
| 1,1,2-Trichloroethane | 97 | 83, 85 |
| 1,1,2-Trichlorotrifluoroethane | 101 | 103, 151 |
| 1,1-Dichloroethane | 63 | 65, 83 |
| 1,1-Dichloroethene | 96 | 61, 98 |
| 1,2,4-Trichlorobenzene | 180 | 182, 145 |
| 1,2,4-Trimethylbenzene | 105 | 120 |
| 1,2-Dibromoethane | 107 | 109, 79 |
| 1,2-Dichloro-1,1,2,2-tetrafluoro- | 85 | 135, 87 |
| 1,2-Dichlorobenzene | 146 | 111, 148 |
| 1,2-Dichloroethane | 62 | 64, 100 |
| 1,2-Dichloropropane | 63 | 65 |
| 1,3,5-Trimethylbenzene | 105 | 120 |
| 1,3-Dichlorobenzene | 146 | 111, 148 |
| 1,4-Dichlorobenzene | 146 | 111, 148 |
| 2-Butanone (MEK) | 72 | 57, 43 |
| 3-Methyl hexane | 43 | 57 |
| Acetone | 43 | 58 |
| Acetonitrile | 41 | 40 |
| Benzaldehyde | 77 | 106 |
| Benzene | 78 | NA |
| Carbon Tetrachloride | 117 | 119, 121 |
| Chlorobenzene | 112 | 114 |
| Chloroform | 83 | 85, 87 |
| Chloromethane | 50 | 52 |
| cis-1,2-Dichloroethene | 96 | 61, 98 |
| cis-1,3-Dichloropropene | 75 | 110, 77 |
| Cyclohexane | 56 | 84 |
| Cyclohexanone | 55 | 98 |
| Dichlorodifluoromethane | 85 | 87 |
| Ethanol | 31 | 45 |
| Ethyl acetate | 61 | 70, 43 |
| Ethyl acrylate | 55 | 85 |
| Ethyl benzene | 106 | 91 |
| Heptane | 43 | 71 |
| Hexachloro-1,3-butadiene | 225 | 223, 227 |
| Hexane | 57 | 41 |

**Table 9 Continued.**

| Analyte | Quantitation Ion | Qualifier Ion(s) |
|---|---|---|
| Isopropyl alcohol | 45 | 43 |
| m,p-Xylene | 106 | 91 |
| Methanol | 31 | 32 |
| Methyl methacrylate | 69 | 100 |
| Methylene chloride | 84 | 49, 51 |
| o-Xylene | 106 | 91 |
| Styrene | 104 | 103 |
| t-Butyl alcohol | 59 | 41 |
| Tetrachloroethylene | 166 | 164, 129 |
| Toluene | 92 | 51 |
| trans-1,3-Dichloropropene | 75 | 110, 77 |
| Trichloroethene | 130 | 95, 97 |
| Trichlorofluoromethane | 101 | 103, 105 |
| 1,1,1,2,2-Pentafluoropropane | 115 | 65, 45 |
| 1,1,1,2,3,3-Hexafluoropropane | 82 | 51, 69 |
| 1,1,1,2-Tetrafluoroethane | 83 | 69 |
| 1,1,1,3,3,3-Hexafluoropropane | 64 | 133, 69 |
| 1,1,1-Trifluoroethane | 65 | 69 |
| 1,1,2,2-Tetrafluoroethane | 83 | 101 |
| 1,1,2-Trifluoroethane | 65 | 51 |
| 1,1-Difluoroethane | 65 | 51 |
| 1,1-Difluoroethylene (VDF) | 64 | 45 |
| 1H-Heptafluoropropane | 151 | 69, 51 |
| 2,2-Difluoropropane | 65 | 45 |
| 2H-Heptafluoropropane | 82 | 151 |
| alpha-Hydroperfluoroethane sulfonyl fluoride (HESF) | 101 | 51 |
| Chlorotrifluoroethylene | 116 | 118 |
| Difluoromethane | 33 | 51 |
| Fluoroethane | 47 | 33 |
| Hexafluoropropene (HFP) | 131 | 69 |
| Methyl fluoride | 33 | NA |
| Pentafluoroethane | 51 | 101 |
| Perfluorobutane | 131 | 219 |
| Perfluorobutane sulfonyl fluoride (PBSF) | 67 | 131 |
| Perfluoroethane | 119 | 69 |
| Perfluoroethane sulfonyl fluoride (PESF) | 67 | 119 |
| Perfluoroethylhexyl sulfonyl fluoride (PEHSF) | 181 | 231 |
| Perfluoroheptane, tech. –90% | 119 | 131 |

**Table 9 Continued.**

| Analyte | Quantitation Ion | Qualifier Ion(s) |
|---|---|---|
| Perfluorohexane | 131 | 119 |
| Perfluorohexane sulfonyl fluoride (PHSF) | 67 | 69 |
| Perfluoromethane sulfonyl fluoride (PMSF) | 67 | 69 |
| Perfluoromethylmorpholine (PMM) | 100 | 114 |
| Perfluorooctane | 119 | 131 |
| Perfluorooctane sulfonyl fluoride (POSF) | 169 | 181, 67 |
| Perfluoropentane | 131 | 119 |
| Perfluoropropane | 169 | 69 |
| Perfluoropropane sulfonyl fluoride (PPSF) | 67 | 169 |
| Perfluoropropyl vinyl ether (PPVE) | 119 | 266 |
| Perfluorotributylamine (PFTBA) | 264 | 414 |
| Sulfur dioxide | 48 | 64 |
| Sulfur hexafluoride | 127 | 89 |
| Sulfuryl fluoride ($SO_2F_2$) | 83 | 102 |
| Tetrafluoroethylene (TFE) | 81 | 100 |
| Trifluoromethane | 69 | 51 |

### A3. Method Comparison: ETS-8-16 and EPA Compendium Method TO15

| Method Parameter | ETS-8-16 | TO15 |
|---|---|---|
| Scope | Same with provisions added for expanding analyte list and quantitation range (<0.001 PPMv to >500 PPMv). | Subset of 97 VOCs from the 189 HAPs listed in Title III of the Clean Air Act Amendments of 1990 (0.0005 PPMv to 0.200 PPMv). |
| Mass Spectral Tuning | Appropriate PFTBA tune may be used instead of a BFB tune. | BFB tune required. |
| Calibration curve | Minimum 5 levels (linear regression); 6 levels (quadratic fit) ($R^2 \geq 0.985$, % residuals ≤ 30%). 1/x or $1/x^2$ weighting factors may be applied as appropriate. | Minimum 5 levels, average relative response factor plotted (%RSD ≤ 30%). |
| Internal standard area reproducibility in calibration curve | Response must be at least 60% of the average ISTD response from the calibration curve. | Response for each calibration level within 40% of mean. |
| Continuing calibration verification | Response compared to curve (≤ 30% difference). Using regression, the %D is based on actual standard concentration versus determined concentration. The percent recovery for each CCV is control charted. | RRF compared to curve (≤ 30% difference). TO15 uses the following equation:<br>%D = (RRF – Ave RRF)/(Ave RRF)<br>TO15 requires that these %D values be charted. |
| Continuing calibration verification frequency | Required and must be compliant at beginning and end of analytical sequence. | Required and must be compliant one per 24 hour period. |
| Sample quantitation | Internal standard linear regression | Internal standard average relative response factor |
| Performance criteria - MDL | No MDL study required. LOQ is based on low-level standard. For analytes not having documented acceptable performance, a LCS is used to demonstrate recovery and stability over time. Required quantitation limit dictated by GPO; strive for low-level calibration to be equal to 10 times less than the exposure limit. | MDL study according to 40 CFR Part 136 Appendix B. Requires MDL ≤ 0.0005 PPMv. |
| Performance criteria – replicate precision | ≤ 25 relative percent difference for the opening and closing continuing calibration verification. | ≤ 25 relative percent difference for a sample |
| Performance criteria – audit accuracy | In-house proficiency testing protocol in place. | ≤ 30% accuracy. Based on internal EPA audit accuracy samples for specific EPA monitoring programs. Audit gas standards are generally not as available as are liquid or solid audit samples. |
| Sample surrogate spike | Required (70 to 130% recovery). | Not addressed. |
| Matrix spike | Recommended for unusual sample matrices or challenging analytes. Project dependent, specified in the GPO. | Not addressed. |

## 18 Affected Documents

None.

# 19 Revisions

| Revision Number | Reason For Revision |
|---|---|
| 1 | Removed system suitability requirement.<br>Added Appendix A.3.<br>Added percent relative difference requirement for opening and closing continuing calibration verification standards. |
| 2 | 7.1.2: Added requirement for the BFB background spectrum to be a single scan before the peak elutes. Previously stated that the background spectrum was an average spectrum before and after the peak.<br>7.5.2: Removed the statement allowing for method blank subtraction and replaced it the data must be qualified using the “B” qualifier.<br>9: Added comment allowing for extreme modifications to the recommended conditions as long as method performance criteria are met and the conditions are documented in the data package.<br>9.1.2: Added step-by-step instructions for canister sample pressurization/surrogate addition.<br>9.1.4: Added a section to discuss the 21-day holding time requirement for air samples collected in canisters for formaldehyde analysis. (Removed 9.1.4 in Rev. 4) |
| 3. | 1.2.2: Added reference to the GPO SOP. Project instructions may be documented in other written communications. Stated that IH canisters usually fall under the standing IH GPO.<br>1.2.7: Added statement explaining that FAST canisters are cleaned and certified by a contract facility.<br>2.9 and 9.8.2: NIST98 library updated to NIST02 library.<br>7.3.3. Added statement that opening CCV is not necessary if samples are analyzed in the same batch as the initial calibration.<br>7.4.2: Added statement that data may be acceptable when internal standard criteria fail.<br>7.6.1: Added descriptions for other means of matrix spiking.<br>7.8.2: Added statement that data would not be corrected for surrogate recoveries outside of the arbitrary acceptance range.<br>8.4.2. Removed internal standard criteria for retention time and area response for Level 2 DQO.<br>9.8: Added statement addressing how data should be reported when multiple dilutions of a single sample are analyzed.<br>10.13: Corrected “Hg to psia conversion factor for positive pressure samples. Added “Hg to psia” conversion factor for samples under vacuum. |
| 4. | 7.5.1: Amended to allow pressurization of samples to pressures other than 10 psig.<br>8: Added clarification of the analytical accuracy for reporting tentatively identified compounds.<br>8.9: Added clarification for determining the LOQ for reporting tentatively identified compounds.<br>9.1.4: Deleted this section specifying a different holding time requirement for formaldehyde samples. |

9.2: Rearranged and designated pre-run items as either requirements following instrument maintenance (10.2.1) or for daily, routine analyses (10.2.2).

9.2.1: Air/water and tune checks are required only after instrument maintenance events.

9.2.2: Added clarification of the difference between an instrument blank and method blank.

9.6: New section describing sample screening by loop injection analysis.

9.8.1: Defined upper limit of calibration as 110% of highest calibration standard.

11.1.1: Changed air/water and tune check requirements to agree with section 9.2.1.

5. 1.2.7: Removed reference to the FAST Lab.

2.10: Removed all temperature references because they are method specific, not technique specific.

2.11: Removed all temperature references because they are method specific, not technique specific. Replace the word “condensed” with “deposited”.

4.2.1: Added the words “or equivalent”. Corrected the URLs in the company links.

4.2.3: Added the words “or better”.

4.2.5: Added the words “or better”.

5.1: Removed reference to LN2 pressure. Added the word secondary “. . . for all sample canister secondary pressurizations, for all canister certification, and for method blanks.” Surrogate gases are used for the initial sample pressurizations.

5.2: Removed the word “certified”.
7.1.3: Clarified the BFB frequency criteria.
7.3.3: Reworded the section to clarify the frequency at which a CCV must be run.
7.5.1: Removed the word “certified”. Removed reference to LN2 Dewar pressure.
7.5.2: Removed confusing verbiage.
8: Removed 100±50% accuracy reference to TICs since there is no data to back this up.
8.5.1: Removed the word “certified”. Removed reference to LN2 Dewar pressure.
8.5.2: Removed confusing verbiage.
9.1.1: Updated the data base location for canister tracking.
9.1.2: Various changes to make the attachment of the sample container generic regardless of the type of fittings.
9.8.1: Added clarification of relative ion intensities as they pertain to coelutions and because of coelutions, removed the statement, “The relative intensities of ions specified above must agree within ± 20% between the standard and sample spectrum.” Added examples of co-eluting analytes.
11.1.2: Revised the BFB aliquot volume(s) and concentration to reflect 50ng or less.
12: Added a reference and a link to the 3M CLIF intra web-site for MSDS referrals.

6. Extensive revisions throughout the whole document.

Sections were revamped to be more consistent with other laboratory method SOP documents.

- Reclassification of data quality objectives (Section 8).
- Allowed provisions for PFTBA tuning instead of BFB tuning. (Section 9.1)
- Added information regarding chemical ionization mass spectrometry. (Section 9.1)
- Updated internal standard requirements. (Section 9.3)
- Added information regarding MassHunter as a data reduction software platform. (Section 11)
- Added “Analysis Batch” criteria section for Quantitative Data. (Section 12)
- Updated “Method Uncertainty” – provided verbiage to be included with TIC analysis (Section 13)
- Updated Appendix A.3 accordingly