# 3M Environmental Laboratory

***Method***

***Analysis of Semivolatile Organic Compounds (SVOCs) Using Sorbent Tubes and Thermal Desorption Gas Chromatography/Mass Spectrometry***

***Method Number: ETS-8-059.0***

***Adoption Date: Upon Signing***

**Effective Date:** 1/3/14

Approved By:

16 DEC 2013

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Date

# 1 Scope and Application

EPA Compendium TO-17 "Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes" provides guidelines and procedures for sorbent tube/thermal desorption/gas chromatography analysis for volatile organic compounds (VOCs).[1] For this method, ambient air is actively sampled through a sorbent tube[2] using a personal sampling pump with the flow rate set within the range of 10 to 200 mL/min. VOCs present in the air are then adsorbed to the sorbent surface within the tube. After sampling, the sorbent tube is heated above the boiling point of the VOCs and purged with helium to desorb the VOCs. The VOCs are then swept to a cold-trap where they are focused prior to injection onto the analytical column of a gas chromatograph equipped with an appropriate detection system (typically mass spectrometer or FID).

ETS-8-59 has been validated to EPA Method TO-17 for the following analytes: phenol, decane, 2-ethylhexyl acetate, naphthalene, naphthalene-$d_8$, 2-ethylhexyl acrylate, and diethyl phthalate.[3] ETS-8-59 is a performance-based method that is generally applicable to the class of VOCs and semivolatile organic compounds (SVOCs) provided the method performance-based quality control acceptance criteria are met. SVOCs are broadly defined as organic compounds with boiling points higher than water that may vaporize when exposed to temperatures above room temperature[4] or organic compounds that evaporate slowly at normal temperatures[5].

The procedures detailed here are applicable to several types of compounds that are amenable to analysis by gas chromatography/mass spectrometery (GC/MS). General classes of compounds that are suited to this type of analysis include, but are not limited to, the following: alkanes, aromatics, acrylates, turpenes, phthalates, acetates/esters, and polycyclic aromatic hydrocarbons (PAHs). Application of this method to any specified target analyte must be demonstrated with sufficient quality control samples that meet method acceptance criteria. Additionally, the procedures outlined here may also be applied to analysis of semivolatile compounds spiked directly onto a sorbent tube (i.e. not actively sampled). Direct tube spiking may be used to perform "large-volume injections" of solvent extracts/solutions containing SVOCs. This document only pertains to the analysis of thermal desorption tubes. Active sampling procedures are not covered.

# 2 Analytical Method Summary

SVOCs are introduced into the gas chromatograph using an automated thermal desorption (ATD) instrumentation. The ATD first applies a helium purge (either with or without heat) to the interior contents of the sorbent tube to remove air, water, and low-boiling compounds (solvents). After the initial purge, elevated heat (typically greater than 300°C) is applied to the tube to desorb the adsorbed analytes. A helium purge of the heated tube sweeps the desorbed analytes to a cold trap (typically held at -30°C). After desorption of the sample tube, the cold trap is rapidly heated to transfer the analytes in tight band to the head of the analytical GC column via a heated transfer

[1] *Compendium Method TO-17 Second Edition "Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes*, Center for Environmental Research Information, Office of Research and Development U. S. Environmental Protection Agency, Cincinnati, OH 45268, January 1999.

[2] Sorbent tube may be referred to as sampling tube or thermal desorption (TD) tube. Several different sorbent materials are available. The sorbent material should be selected depending on the target analytes investigated. Table 1 in TO-17 summarizes the guidelines for sorbent selection.

[3] E13-0558 "Initial Demonstration of Capabilities and Partial Validation of ETS-8-59.0 "Analysis of Semivolatile Organic Compounds (SVOCs) Using Sorbent Tubes and Thermal Desorption Gas Chromatography/Mass Spectrometry".

[4] http://www.epa.gov/iaq/voc2.html

[5] http://www.dtsc.ca.gov/InformationResources/Glossary_of_Environmental_Terms.cfm

line. A GC oven gradient program is typically used to separate the analytes prior to analysis by the mass spectrometer.

Identification of target analytes is accomplished by comparing the retention time and mass spectra to calibration standards prepared on sorbent tubes that undergo the same desorption and analysis process as the samples. Tentative identification of an unknown compound may be made by comparing a full scan spectrum of the unknown to a NIST library mass spectral search. An estimated concentration of a non-target analyte identified in a sample may be made using either the response factor of the total ion chromatogram of the nearest internal standard free of interferences or using the response factor of another calibrated compound.

# 3 Definitions

### 3.1 Analysis Batch

A set of study samples analyzed with calibration standards, laboratory control samples, instrument blanks, and method blanks on the same instrument during a time period that begins and ends with the analysis of the appropriate continuing calibration check standards.

### 3.2 Analytical Sample

A thermal desorption tube that has been actively sampled to collect an air sample. Alternatively, an analytical sample may be a thermal desorption tube spiked with a solution with the intent of analyzing the solution components.

### 3.3 Instrument Calibration Standard

A thermal desorption tube spiked with a known amount of a working or stock solution standard for the purpose of establishing instrument response of a target/surrogate analyte.

### 3.4 Laboratory Control Sample (LCS)

A thermal desorption tube spiked with a known amount of a working or stock standard that then has ambient laboratory air sampled through the tube to mimic the field sampling conditions experienced by the study samples.

### 3.5 Sample Duplicate

A separate thermal desorption tube collected simultaneously with the primary sample. The sample duplicate should be collected at the same sample location/description.

### 3.6 Field Blank (FB)/Trip Blank (TB)

A field blank is a separate thermal desorption tube sent to the sampling location along with tubes designated for sample collection. The caps are removed from the field blank for a brief time and then the tube is recapped. Air is not sampled through the field blank.

### 3.7 Field Matrix Spike (FMS)

A sample to which known quantities of the target analytes are added to the sample tube in the laboratory before the tube is sent to the field for air sampling. The FMS is analyzed to ascertain if any matrix effects, interferences, or stability issues may complicate the interpretation of the sample analysis.

### 3.8 Internal Standard (IS)

A compound added to each study sample, calibration standard, laboratory control samples, and procedural blanks 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.

### 3.9 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 that 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 highest standard in the calibration curve that meets method acceptance criteria is defined as the ULOQ.

### 3.10 Method Blank

A thermal desorption tube that is sampled with ambient laboratory air using conditions that mimic the field sample collection parameters (flow rate, total time of collection). The method blank is used to determine if test substances or other interferences are present in the laboratory environment or the apparatus.

### 3.11 Surrogate Standard

An isotopically labeled standard, not used as an internal standard, that is added to each sample collection tube prior to being sent to the field for sample collection. The surrogate is also added to laboratory control spike samples and serves as a means to evaluate the method performance (stability, recovery)

## 4 Warnings and Cautions

The operator must be familiar with the ATD and GC/MS systems and their associated hazards, such as high temperature, effluent venting, solvent use, moving autosampler parts, and low-pressure vacuum system. 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.

All exhaust vents, including the ATD split vents and mass spectrometer pump exhaust must be connected to a laboratory hood or vented instrument enclosure to keep potentially hazardous effluent from mixing with laboratory air.

Appropriate protective gloves, eyewear, and clothing must be worn when handling samples or solvents.

## 5 Interferences

Impurities present in solvents, purge gas, and organic compounds out-gassing from the components of the analytical system are potential sources of contamination. Sample integrity can be influenced by diffusion of organic materials present in the ambient air when the sorbent tubes are uncapped.

Contamination by carryover can occur whenever high-concentration and low concentration samples are analyzed sequentially. The analysis of blank samples is used to check for cross-over contamination. Carryover may be reduced by adjusting analytical parameters, such as line and valve temperatures, split flows, and desorption times and temperatures of the sorbent tube and cold trap.

# 6 Instrumentation, Supplies, and Materials

A variety of vendors and models for ATD and GC/MS systems may be used. Any combination of these or other suitable equipment may be used, provided all data quality objectives are met. 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 added at a later date.

## 6.1 ATD Instrumentation

Perkin Elmer (PE) Turbo Matrix 650 (Software controlled pneumatics, tube recollection availability)

Perkin Elmer Turbo Matrix 50 (Manual pneumatics, tube recollection is not available)

Markes International TC-20 (20-place tube conditioner)

## 6.2 GC/MS Instrumentation

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

Agilent Technologies 7890B GC System with 5977 Mass Spectrometer

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

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

Hewlett Packard 5890N GC System with 5973 Mass Selective Detector

## 6.3 Other Equipment

Flow calibration meter: Bios DryCal or other suitable vendor

Sampling manifold for QC samples: 12-place custom built manifold system configured with a primary vacuum pump and individual rotameters to control flow through individual tubes. This custom-built manifold is discussed in detail later in this document.

## 6.4 Supplies and Materials

The following list of supplies and materials is not exhaustive, but rather provides a guide of what the experienced TD-GC/MS operator may use during the course of a study. Refer to the Perkin Elmer instrument manual for additional parts and part numbers.

### 6.4.1 Analytical Column

Phenomenex Zebron ZB-SemiVolatiles (Model No.: 7HG-G027-17) 30m x 0.25mm x 0.5 μm) or other column type, diameter, length or stationery phase that provides suitable analyte retention and resolution.

### 6.4.2 Packed Cold Trap

Low-flow cold trap packed with Tenax TA (Perkin Elmer part number M041-3535) . Different cold trap sorbent material may be used depending on the adsorptive properties of the target analyte(s).

### 6.4.3 Thermal Desorption Tubes

Standard tubes (¼" OD x 3.5" length, glass or stainless steel) compatible with the PE TurboMatrix ATD instruments. Pre-packed tubes are commercially available in a wide range of sorbent materials from various suppliers: Perkin Elmer, Markes International, Suppelco, SKC, etc. Consult the manufacturer's website or the Turbo Matrix instrument manual for a description of the analytes appropriate for a given sorbent material. Stainless steel tubes packed with ~200 mg Tenax TA 35/60 are well-suited for SVOC analyses.

#### 6.4.4 Caps

TurboMatrix PTFE analytical storage caps (PE part number L4270122) are required for sealing tubes while on the ATD carousel. Brass Swagelok caps (1/4") should be used for long-term storage of sample tubes.

#### 6.4.5 GC Carrier Gas

Helium, ultra high purity or equivalent.

#### 6.4.6 Miscellaneous

Other standard laboratory equipment needed to perform the method including, but not limited to, the following : gas-tight glass microsyringes, volumetric flasks, gloves, solvents, analytical balances, etc. Identification of these supplies/equipment will be included in the raw data as appropriate.

## 7 Reagents and Standards

### 7.1 Solvents

Typically Purge and Trap grade methanol is used. Lesser grades may be used, but will likely have trace-level contaminants that will be concentrated during the analysis and could potentially interfere with the analysis. Other solvents may be used or substituted when appropriate (i.e. acetone, methylene chloride, etc.)

### 7.2 Standard Solutions

Stock solutions may be prepared in the lab from neat liquids or solids. Alternatively, custom certified mixes may be purchased (o2si or other appropriate vendor). Stock solutions are prepared in methanol or other appropriate solvent and then further diluted to appropriate working concentrations. Analyte concentrations are adjusted for purity as appropriate. Stock standards may be stored in a refrigerator or freezer to minimize possible losses due to volatility. Standards prepared in the laboratory should follow all appropriate procedures outlined in Chapter 4 "General Laboratory Systems" in the quality system.

### 7.3 Internal Standards (ISTD)

Purchased mixes of deuterated internal standards maybe acquired and diluted appropriately (i.e. EPA 8270 internal standard mix from Restek or custom preparations from o2si, etc). Alternatively, internal standard solutions (single component or mixtures) may be prepared in the lab using isotopically labeled compounds representative of the project's target analytes. The internal standard is added to the sample tube immediately before analysis.

### 7.4 Surrogate Standards

A known amount of a standard mixture may be added separately from the ISTD to selected sample and QC tubes to evaluate accuracy and precision. Surrogate(s) are typically isotopically labeled compounds representative of the target analytes and are not required for all studies. Surrogate(s) are typically added to the sample tubes in the laboratory prior to being sent out in the field for sampling. Surrogate(s) provide a measure of analyte stability as they are subjected to the sampling process and subsequent storage conditions.

## 8 Tube Conditioning

All thermal desorption tubes must be conditioned and verified for cleanliness prior to use. Manufacturer's suggested tube conditioning parameters (provided with the purchased tubes or found on the appropriate website) should be followed. Note: tube conditioning parameters vary depending on the sorbent material in the tubes. The analyst must be cognizant of the tubes' sorbent material prior to conditioning. Pre-packed tubes may be purchased unconditioned or

conditioned. Previously unconditioned tubes generally require an extensive conditioning cycle before they are considered ready for first-time use. Newly purchased pre-conditioned tubes should still be re-conditioned prior to use, but typically require only a minimal bake cycle. Typical conditioning parameters for TD tubes with Tenax TA are listed below.

Temp: 320°C

Desorb Flow: 25-100 mL/min

Time: 30 minutes

Tube conditioning may be performed one at time using the "Tube Conditioning Mode" option available on any model of the TurboMatrix ATD instrumentation. When "Tube Conditioning Mode" is selected, the cold trap is isolated from the desorb flow (i.e. the desorb flow is vented out of the instrument). Alternatively, up to 20 tubes may be conditioned simultaineously using the Markes TD-20 tube conditioner. After conditioning, tubes should be sealed using Teflon ferrules and brass caps and stored in a zip-top plastic bag. If tubes are going to be used immediately for laboratory QC samples, the Teflon analytical caps may be used to seal the ends.

After conditioning, each tube should be analyzed to verify that residual contaminants were removed and the tubes are free of potential interferences. Each conditioned tube's chromatogram should be visually inspected to determine if the tube is sufficiently clean. A low-level calibration standard may be included in the instrument batch for a general reference of instrument response. Analyst judgment will dictate whether or not a tube is deemed clean and ready for use. The chromatograms of the cleanliness batches will not be archived with the individual projects; however, tube ID numbers will be included in the sample information section of the GC/MS sequence allowing the analyst to consult the "clean check" chromatogram if questions arise during the subsequent analysis of a tube used to collect a study sample or prepare a QC sample.

# 9 Quality Control and Data Quality Objectives

A general project outline (GPO) or a study protocol will describe the data quality objectives (DQO) for a given study. Unless otherwise specified, the targeted accuracy and precision for a named analyte will be 100±30% with relative standard deviation (RSD) ≤25% as measured by laboratory control spike samples.[6] Studies classified as semi-quantitative, range finding, screening, or method development may have modified acceptance criteria and will be discussed in the general project outline and final report.

## 9.1 Instrument Calibration Standard Preparation

Instrument calibration standards are prepared by spiking μL amounts of working or stock solutions onto the ringed end (sampling end) of the tube. Efforts should be made to minimize the amount of solvent delivered to the tube (in general <50 μL total). Larger volumes may be used if QC elements establish that the solvent does not interfere with the analysis. Typically, the target/surrogate analytes and internal standards are delivered to the tubes as separate spikes. The final amount of the target analyte(s), surrogate(s), and internal standard(s) should be documented appropriately in a standard logbook or LIMS. The solvent will be purged from the tube prior to desorption using the heated dry purge feature on the TurboMatrix ATD. See Figure 1 below.

[6] If collected, recoveries of field spikes will also be considered when determining accuracy and precision.

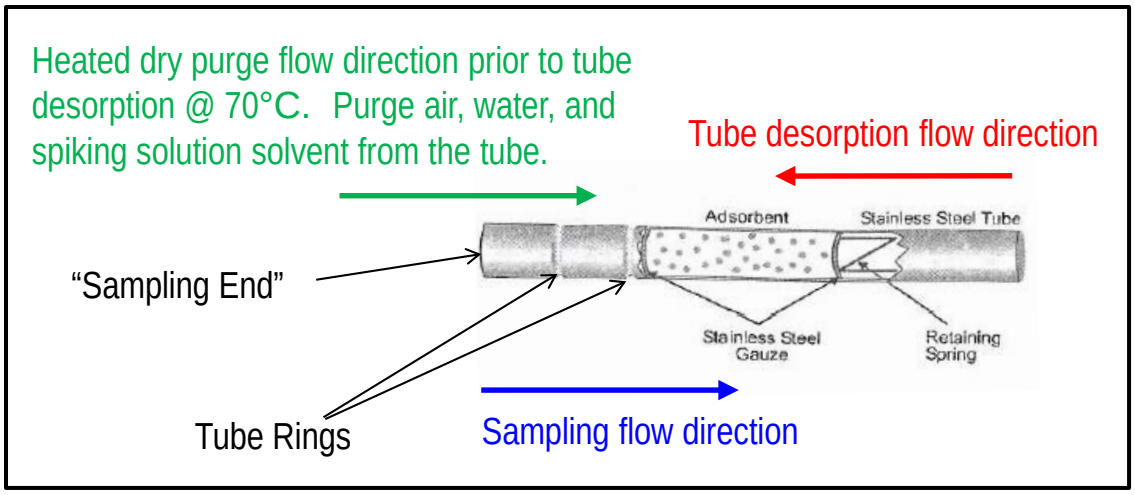


**Figure 1. Thermal Desorption Tube Schematic Showing Sampling and Purge Flow Directions.**

### 9.2 Laboratory Control Spikes (LCSs) and Laboratory Sampling Manifold System

LCSs are typically prepared in triplicate at three different levels[7] that span the anticipated sample range and instrument calibration range. LCSs are prepared by first mounting clean TD tubes onto the sampling manifold pictured in Figure 2. The manifold system is configured with a primary vacuum pump and individual rotameters to control the airflow through each tube. The flow through each tube is calibrated using a Bios DryCal primary flow calibrator or equivalent device and is recorded appropriately in the study documentation. After calibration of flows, the primary flow to the manifold is turned off and the tubes are spiked with a known volume of an appropriate working or stock standard solution of the target/surrogate analyte(s). After spiking, the flow to the manifold is turned on and ambient laboratory air is drawn through the spiked tubes for a documented time period. The flow rate of the individual tubes and the total sampling time should mimic the flows and collection times of the study samples. After the air is drawn through the tubes, the manifold flow is turned off and the tubes are removed and capped appropriately. If analysis is not done immediately, LCS tubes should be capped with brass caps and Teflon ferrules and stored at the same conditions as the study samples. Alternatively, the tubes can be spiked with internal standard, capped with the Teflon autosampler caps, and placed on the thermal desorber unit for analysis.

The current manifold system consists of 12 individual rotameters. This allows for triplicate LCSs at three different levels and three manifold blanks (unspiked tubes) to be sampled simultaneously. Typically, the highest level LCSs will have a back-up tube attached in series to monitor for break-through of the target analytes. (Figure 2). If fewer than 12 tubes are sampled, the flow to the empty slots should be turned off prior to the flow calibration.

Current 3M Environmental Laboratory procedures indicate that LCSs should be prepared at the same time as the study samples. While this policy is justifiable to study samples requiring extraction, dilution, or other forms of manipulation once received in the laboratory, it is not applicable for this method. Study samples described here are collected in the field outside of the laboratory and no further "sample" preparation is done except to spike internal standard. Spiking of the internal standard for both the laboratory generated QC samples and the study samples will be done at the same time. Although LCSs in theory could be prepared at the same time/on the same day as study samples, this will rarely be feasible as the exact day/time/flow rates/and collection times of field samples will not be known until after the sampling event is completed.

[7] The replicate number of LCSs and the number of LCS levels can be adjusted accordingly to meet the data quality objectives of the given study. For example, tube availability may only allow for duplicate spikes and two levels.

LCS recoveries will be used to assess the accuracy and precision of the analytical method. The mean recovery of the pooled LCSs (all replicates from levels within the final established calibration range) should be within 100±30% with a relative standard deviation ≤25% for the data to be used without further technical justification or bias adjustment. LCS recoveries may reveal analyte losses dependent on the air sampling through the tube (i.e. analyte detected in the back-up tube or significant analyte losses with increased sampling time or rate). In these circumstances, the LCS recoveries may be used to bias adjust the sample results with proper discussion in the report.

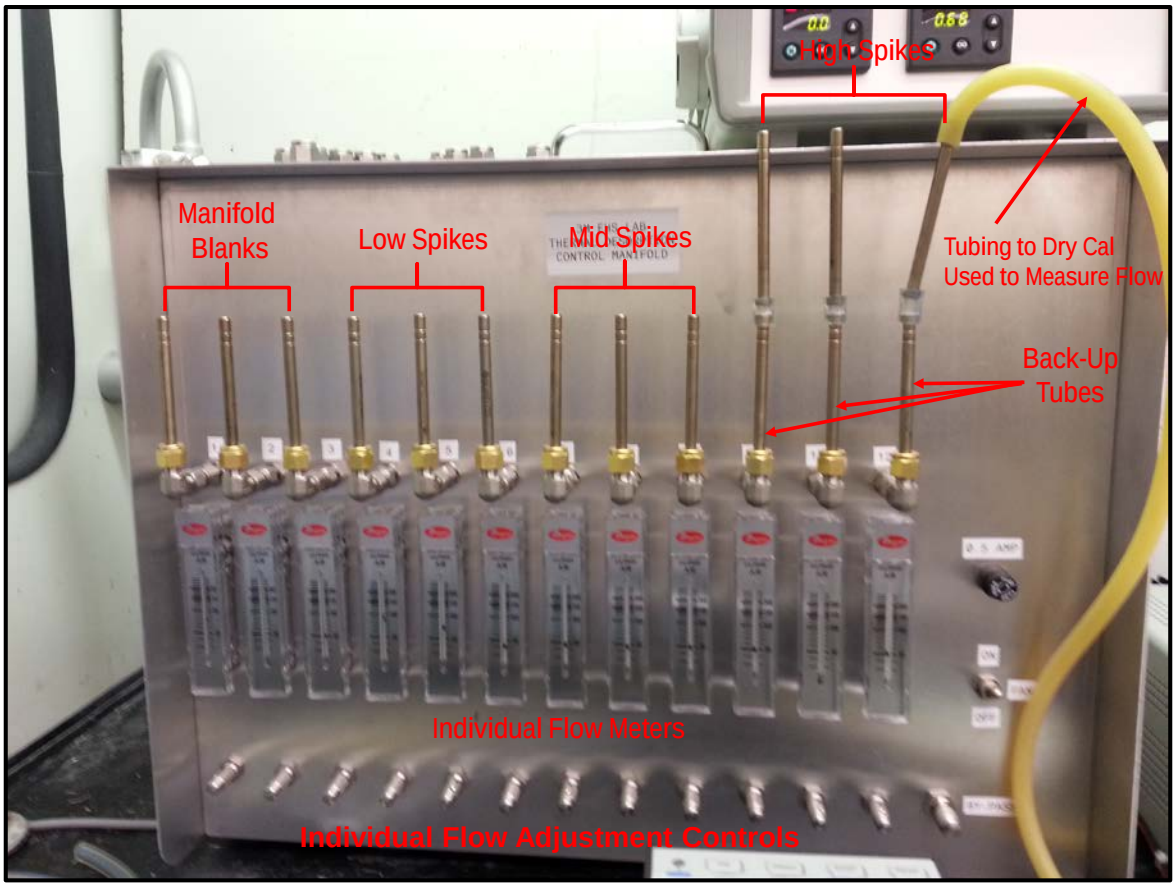


**Figure 2. Manifold System.**

### 9.3 Blanks

Preparation of field blanks and manifold (method) blanks are described above. Instrument blanks are prepared by spiking clean tubes with internal standard only. Empty tubes and clean tubes without internal standard can also be prepared and analyzed as well.

### 9.4 Sample Duplicate

Duplicate samples may be collected using two separate pumps to simultaneously collect two individual tubes at a given sample location/description. (These, technically are not duplicates, but may provide some indication of sampling reproducibility.) Alternatively, TO-17 provides information regarding “distributed volume pairs” where two samples are collected simultaneously at two different total sampled volumes (e. g. 1 L and 4 L). Relative percent deviations (RPD) of sample duplicates or distributed volume pairs of <30% are deemed acceptable. RPDs >30% may still be reported, but should be flagged appropriately

in the report. Sample duplicates and/or distributed volume pairs are not required unless specified in the general project outline.

### 9.5 Field Spike

A field spike is prepared by spiking a tube with a known amount of the target analyte(s) in the laboratory prior to field sampling. If a field spike is prepared, a duplicate, unspiked, sample of the same process/sample description must be collected as well. The amount of the target analyte resulting from the collected air sample is subtracted from the value obtained from the spiked tube to determine recovery. The amount of the field spike must be appropriate for the given sample concentration. Field spike amounts should be in the range of 0.5-10 times the resultant amount from the collected air sample to be deemed appropriate. Field spike recoveries of 100±30% are considered acceptable without further justifications. Field spike recoveries outside of this range may still be reported, but need to be flagged and discussed appropriately in the report. Field spikes are not required unless specified in the general project outline.

## 10 Calibration and Standardization

### 10.1 Instrument Calibration

Samples are quantitated against a standard curve containing varying amounts of target/surrogate analyte and a fixed amount of internal standard[8]. The curve is calculated from the plot of individual calibration points using Target ™, MassHunter, or equivalent chromatography and/or data reduction software. A minimum of six calibration standards is analyzed at the beginning of each analytical study and within a study if Continuing Calibration Verification (CCV) standards do not meet the criteria (see next section). The acceptance criterion for the residual of each standard is 100±25%, except at the lower limit of quantitation (LLOQ) where 100±30% is considered acceptable. Low or high curve points may be deactivated, depending on instrument sensitivity, linearity of response, and levels required to bracket sample concentrations. Curve points not at either end of the curve may be deactivated or re-prepared if there is evidence of instrument malfunction or preparation error.

The average relative response factor may be used for quantitation if the relative standard deviation (RSD) of the relative response factors (RRF) is <20% for any analyte as it is assumed that the RRF is constant over the calibration range. However, this should be confirmed by inspection of the calibration curve for consistent deviations at the high or low ends. If the RSD of any target analyte is greater than 20%, a linear or quadratic curve fit with or without weighting are options for quantitation. The regression fit may include, but not be forced through, the origin. A minimum correlation coefficient (r) of 0.995 is required ($r^2$=0.990).

### 10.2 Continuing Calibration Verification (CCV)

After a successful initial calibration curve, the continued accuracy of the curve may be shown by the analysis of, one or more calibration check standards at the beginning of a new analytical sequence, after every ten study samples or fewer, after an elapsed time of 12 hours (environmental samples only), and at the end of the analytical sequence.

Only samples bracketed by a successful CCV (recovery within 100±25%) may be reported without technical justification. If evidence exists that the instrument malfunctioned, or that an anomaly existed during CCV analysis, the standard may be re-prepared. If two or more successive CCVs were analyzed to demonstrate continued accuracy of the calibration, the successful CCV may be used to accept results. If this should happen, it will be discussed in the final report.

[8] External calibration (exclusion of an internal standard) may be used if the project lead or laboratory management deems it acceptable given the data quality objectives of the project.

The CCV concentration is typically near the mid range of the curve, but may be varied. For example, low level CCVs may be used for low level samples, whereas a low and a high CCV may be analyzed in succession to further document the continued accuracy of the entire curve range.

### 10.3 Independent Calibration Verification (ICV)

If a secondary standard source of the target analyte is available, a stock standard solution may be prepared from the separate source material. Analysis of tube spikes prepared with dilutions (if necessary) of the secondary stock standard will verify the integrity of the primary calibration preparation. ICV recoveries within 100±25% will demonstrate that the primary calibration standard used to establish the calibration curve was accurate. ICV tube spikes are not required, but should be included if a secondary source of the target analyte(s) is readily available in the laboratory. If prepared, ICV tube spikes should be prepared in duplicate, preferably triplicate. Average recovery and %RSD or %RPD should be calculated and reported.

### 10.4 Limits of Quantitation and Blank Evaluation

The limit of quantiation (LOQ) is defined as the lowest calibration standard in the final calibration curve. As discussed above, the back-calculated LOQ standard must meet an accuracy requirement of 100±30% when compared to the true value of the standard. The LOQ standard must also have target analyte area counts at least twice those of the manifold blanks and the back-up tubes linked in series behind the high LCSs. (The back-up tubes should only be used in LOQ determination if break-through of the target analytes was not detected.) The average area count of the manifold blanks and back-up tubes (if included) should be used to evaluate the LOQ standard if the area count %RSD is less than 40%. If the %RSD of the average blank area counts is greater than 40%, then the maximum blank area value should be used. If the LOQ standard produces acceptable accuracy, but does not meet the 2X blank criteria, the lowest standard must be excluded from the calibration curve and the LOQ raised to the next calibration standard and the evaluation process repeated. Instrument blanks (tubes spiked with internal standards) should also be considered when evaluating the LOQ. However, instrument blanks that follow high level calibration standards, LCSs, or samples will likely exhibit instrument carry-over and need to be considered with great care. A minimum of two instrument blanks (preferably three) following the highest calibration standard and samples of known high concentrations is strongly suggested. When more than one instrument blank is analyzed sequentially, the last blank should be the one used to evaluate the cleanliness of the system. Alternate ways of evaluating the study blanks relative to the LOQ standard may be performed as long as the procedure is documented in the raw data.

### 10.5 System Suitability

The thermal desorption GC/MS system is deemed suitable for use if the GC/MS generates an acceptable perfluorotributylamine (PFTBA) autotune[9] and if an initial calibration or CCV meets the data quality objectives. An autotune (or check tune) should be performed before the start of the study. The Agilent autotune or check tune report should be inspected and verified that the criteria listed below in Table 1 are within Agilent's specified acceptance ranges and that the overall system is leak free with minimal levels of m/z=18 ($H_2O$), m/z= 28 ($N_2$), m/z =32 ($O_2$), m/z= 40 (Ar), and m/z= 44 ($CO_2$). Ideally, these levels should be less than 20% of the base peak (usually m/z=69) for the system to be considered "leak" free. The "Tune Evaluation" macro in the Agilent software may be run to determine if the tune file is acceptable. Acceptable instrument tunes are necessary when performing mass spectral library searches to identify and estimate unknowns.

[9] The standard autotune (Atune.u) or the gain autotune (Atune.u + HiSense.u) may be used on the Agilent GC/MS systems.

**Table 1. PFTBA Autotune *Criteria.**

| Tune Parameter | Acceptance Criteria |
|---|---|
| Base peak | m/z = 69 or 219 |
| Ratio of m/z=70 to m/z =69 | (0.5-1.6%) |
| Ratio of m/z=220 to m/z=219 | (3.2-5.4%) |
| Ratio of m/z=503 to m/z=502 | (7.9-12.3%) |
| Ratio of m/z = 219 to m/z=69 | >40% |
| Ratio of m/z=502 to m/z=69 | >2.4% |
| Ratio of m/z=18 to m/z=69 | <20% |
| Ratio of m/z=28 to m/z=69 | <10% |

*Acceptance criteria listed in the table were extracted from the Tune Evaluation report.

## 11 Procedures

ATD and GC/MS parameters are set to provide sufficient desorption of the analytes from the tube and suitable chromatography and sensitivity for the intended purpose. Analytical conditions used for a study need to be adjusted to meet the data quality objectives of a given project. Factors that strongly influence the instrument conditions used include the following: expected analyte levels on the tubes, required limits of quantitation, boiling points of the target analytes, chromatographic resolution of target/surrogate/internal standards, and instrument carryover.

The TurboMatrix 50 and 650 is capable of splitting the flow from the desorbed sample tube at two different points. The "Inlet Split" vents a known ratio of the tube desorb flow prior to the analytes entering the cold trap. The "Outlet Split" vents a known ratio of the cold-trap desorb flow prior to the transfer line to the GC. The combination of the "Inlet" and "Outlet" split flows allows for a range of 0.001% to 60% of the tube sample to reach the GC column and the MS detector. The instrument manual for the TurboMatrix should be consulted for suggested split flow settings to use for a given transfer ratio of analytes on the tube to the detector.

All calibration standards, CCVs, blanks, study samples, and control samples must be analyzed using the same settings. The following analytical conditions and settings are provided as an example, only. These conditions were successfully used to calibrate for phenol, decane, d-limonene, 2-ethylhexyl acetate, naphthalene, naphthalene-$d_8$, 2-ethylhexyl acrylate, and diethyl phthalate in the *approximate* range of 0.02 μg[10] to 3 μg on tube in the initial demonstration of capability study E13-0558 "Initial Demonstration of Capabilities and Partial Validation of ETS-8-059.0 *Analysis of Semivolatile Organic Compounds (SVOCs) Using Sorbent Tubes and Thermal Desorption Gas Chromatography/Mass Spectrometry*". Care must be given to select desorption conditions (i.e. temperature, time, flow rate) that are compatible with the tube's sorbent material.

[10] The minimum reporting level (MRL) was between approximately 0.02 μg and 0.05 μg for the listed analytes.

**Table 2. Representative ATD Instrument Parameters.**

| Instrument Make and Model | Perkin Elmer TurboMatrix 650 |
|---|---|
| **Temperatures (°C)** | |
| Tube Desorption | 320 |
| Transfer Line | 280 |
| Valve | 260 |
| Cold Trap Low | -30 |
| Cold Trap High | 300 |
| Trap Heating Rate (°C/sec) | 40 |
| Heated Purge | 70 |
| **Times (minutes)** | |
| Tube Desorption | 10 |
| Trap Hold | 2.5 |
| Cycle | 25 |
| Purge | 5 |
| Trap Desorb | 1 |
| **Options** | |
| Inlet Split | On |
| Outlet Split | On |
| Injections per tube | 1 |
| Split Mode | Flow |
| Heated Purge | On |
| Dry Purge | On |
| **Pneumatics (Flow) (mL/min)** | |
| Inlet Split | 50 |
| Outlet Split | 75 |
| Tube Desorb | 50 |
| Column (Mode = Flow) | 2.0 |
| Dry Purge | 50 |

**Table 3. Representative GC/MS Instrument Conditions.**

| **Instrument Make and Model** | **Agilent 5973 mass spectrometer with 6890A gas chromatograph – or equivalent** |
|---|---|
| Analytical Column | Phenomenex Zebron ZB-SemiVolatiles (Model No: 7HG-G027-17) 30 m x 0.25 mm x 0.5 μm |
| Oven Program | 70°C for 3 min, 5°C/min to 120°C, 25°C min to 260°C |
| Thermal Auxiliary Temperature (MSD Transfer Line) | 280°C |
| Solvent Delay | 3.5 minutes |
| Scan Range (amu) | 40-350 |
| Threshold | 150 |
| Sample # | 2 |
| MS Source | 230°C |
| MS Quad | 150°C |

The GC/MS scan range may be adjusted depending on the molecular weight of the target analytes. The mass spectrometer may also be operated in selected ion monitoring (SIM) mode to improve sensitivity and lower detection limits of target analytes. Identification of unknowns cannot be performed if only the SIM mode is used. Some models of Agilent GC/MS systems allow for the simultaneous collection of SIM/scan data. Dwell times and sample number may need to be adjusted to optimize peak shape if the dual SIM/scan functionality is used.

All ATD and GC/MS conditions used for a project will be documented in the raw data and archived with the project.

## 12 Data Analysis and Calculations

Each dataset should be processed using chromatography software (e.g. Target Falcon integrator, Agilent Chemstation, Agilent MassHunter, Applied Biosystems Analyst). 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 amount of a target analyte on a tube will be quantitated using the established internal standard calibration curve.

### 12.1 Unknowns

If peaks not attributable to calibrated compounds, surrogates, or internal standards are present in the sample chromatograms, these peaks maybe tentatively identified and the concentrations estimated. Tentative identification of the unknown peak will be done by spectral library searching the mass spectrum of unknown peak (typically, an average of three or more scans across the peak's apex, background subtracted) against the NIST library (i.e. NIST11 or previous version). The data analyst will need to use his/her best judgment and experience to evaluate if the assigned identification is reasonable. If necessary, the analyst may need to select a different search result or give the peak an alternate classification such as "Unknown Hydrocarbon". Non-target compounds are commonly referred to as "tentatively identified compounds" or TICs.

Estimation of the unknown/TIC can be performed in a few different ways. Typically, the peak area (response) of the unknown compound from the total ion chromatogram is compared to the total ion chromatogram response of an internal standard. Alternative

methods for TIC estimation include, but are not limited to, the following: assigning a fixed/arbitrary response factor, using the response factor of the closest eluting target compound, using the response factor of a target compound with similar chemical composition, or using the response factor of a surrogate compound. The methodology used for TIC estimation will be documented in the raw data and discussed in the report. When TICs are reported, the data table should include the match quality factor of the library search as this gives a level of confidence regarding the TIC assignment. Additionally, TICs need to be clearly identified as such in all data tables with a suitable data flag if appropriate ("J"). The report should also clearly indicate that the accuracy of the TIC estimation cannot be ascertained.

The general project outline should discuss whether or not TICs should be evaluated and to what level. For samples with several TICs, the project lead may decide to report only the ten (or other specified number) most abundant TICs based on total ion chromatogram response. Another common reporting guideline is to exclude the reporting of TICs with a total ion chromatogram response less than a specified percentage (i.e. 10%) of the internal standard response (or other compound) used for estimation.

## 12.2 Calculations

### 12.2.1 Air Concentration

The resulting amount on the tube will be converted to a time-weighted air concentration in PPMv using the following equation assuming ambient temperature and pressure (~25°C and 1 atm).

$$\text{Air Concentration (PPMv)} = \frac{\mu\text{g on tube} * 24.45\left(\frac{\text{L}}{\text{mol}}\right)}{\text{molecular weight}\left(\frac{\text{g}}{\text{mol}}\right) * \text{total volume sampled(L)}}$$

$$\text{PPMv} = \frac{\mu\text{L analyte}}{\text{L of air}}$$

$10^6\ \mu\text{L} = 1\text{L}$

Total air volume sampled = flow rate (LPM)*time (min)

### 12.2.2 Laboratory Control Spikes (LCS)

LCS recovery is calculated using the following equation.

$$\text{LCS Recovery (\%)} = \frac{\text{Amount Detected on Tube } (\mu\text{g})}{\text{Amount Spiked on Tube } (\mu\text{g})} * 100$$

### 12.2.3 Field Matrix Spikes (FMS)

To determine the recovery of a FMS, the air concentration must first be calculated from the corresponding non-spiked tube collected concurrently with the spiked tube.

$$\text{FMS Recovery (\%)} = \frac{\text{Amount Detected on FMS Tube } (\mu\text{g}) - \text{PPMv} * (\text{Volume Sampled}) * \left(\frac{\text{Molecular Weight}}{24.45}\right)}{\text{FMS Spike Amount } (\mu\text{g})}$$

Note: For this equation, the PPMv is the concentration determined from the unspiked sample and the volume sampled is from the *spiked* tube. This is especially critical if a different flow rate and sampling duration was used to collect the spiked tube relative to the unspiked tube.

### 12.2.4 Other QC Calculations

Means (averages) will be calculated by adding the individual entities and dividing the resultant sum by the number of individual entities.

Standard deviations will be calculated using Microsoft Excel ®. The Microsoft® built-in function STDEV (or equivalent) is typically used.

Sample and LCS precision will be reported as % relative standard deviation (%RSD) for three or more replicates, and relative percent difference (RPD) for duplicate data. Sample %RSD and %RPD will be calculated using the following equations:

$$\%RSD=\left(\frac{\text{Standard Deviation}}{\text{Average}}\right)*100$$

$$\%RPD=\left(\frac{\text{absolute value(Replicate 1-Replicate 2)}}{\text{Average (Replicate1\&Replicate2)}}\right)*100$$

The Dixon's Q-Test described in the next section may be used for identification and rejection of outliers.

### 12.3 Dixon's Q-Test:

A data point may be excluded if "$Q_{observed}$" is greater than "$Q_{tabulated}$" with 95% confidence.

$$Q_{observed}=\frac{gap}{range}$$

where "gap" is the difference between the questionable data point and the closest value of the data set, and "range" is the difference between the highest and lowest value of the data set. The following table provides $Q_{tabulated}$ values to compare $Q_{observed}$. If Confidence Levels of greater than 95% are calculated, the "Q" Values from the same source will be used and documented in the raw data and the report.

**Table 4. Dixon Q Test Values for $Q_{tabulated}$.**

| $^{(1)}Q_{tabulated}$ Values: | |
|---|---|
| **Number of Observations:** | **Confidence Level= 95% Percentile** |
| 3 | 0.970 |
| 4 | 0.829 |
| 5 | 0.710 |
| 6 | 0.625 |
| 7 | 0.568 |
| 8 | 0.526 |
| 9 | 0.493 |

(1) David B. Rorabacher, Statistical Treatment for Rejection of Deviant Values: Critical Values of Dixon's "Q" Parameter and Related Subrange Ratios at the 95% Confidence Level, Anal. Chem. 1991, 63, 139-146.

If an outlier value is rejected, and if technical justification exists for the outlier, exclude the result from further data reporting and calculate the average and %RSD or RPD for the remaining values. If data points cannot be excluded and the results do not meet acceptance criteria necessary for the project's data quality objectives, the data may be used, but the impact of non-compliant results must be discussed in the report. Document

the non-compliant data and technical justification for rejecting the outlier with the final results.

# 13 Analysis Batch Method Performance Criteria

Any method performance parameters that are not achieved must be considered in the evaluation of the data. The data quality objectives provided in the general project outline (GPO) should be considered. For example, screening studies or method development type analyses may not require stringent adherence to method acceptance criteria summarized below. 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

## 13.1 Calibration and Limit of Quantitation (LOQ) – Analysis Batch

### 13.1.1 Calibration Curve – Analysis Batch

If an average response factor is used for quantitation then the %RSD of the response factors must be less than 20%. If a linear or quadratic 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 0.990 corresponding to a correlation coefficient (r) = 0.995. Each point included in the final calibration curve must be within ±25% of the theoretical concentration with the exception of the LLOQ, which may be within ±30%.

### 13.1.2 CCV Performance – Analysis Batch

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 25% of the theoretical value (within 30% for lowest curve point). Samples that are bracketed by CCVs not meeting these criteria must be flagged appropriately.

### 13.1.3 ICV Performance – Analysis Batch

If prepared, independent calibration standards (ICVs) prepared using a different source of stock/working standard solutions should produce recoveries within 25% of the theoretical value.

### 13.1.4 Limits of Quantitation (LOQ) – Analysis Batch

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 (manifold)blanks, back-up tubes, and instrument blanks and verified to have target analyte area counts at least 2X of blanks free from instrument carryover. Refer to Section 9.3 for a more in-depth discussion regarding blank evaluation. By definition, the measured value of the LLOQ must be within 30% of the theoretical value.

## 13.2 Blanks – Analysis Batch

Instrument blanks (tubes spiked with internal standards) should be interspersed throughout the analytical batch. Instrument blanks are analyzed both before and after the instrument calibration curve or opening CCV injection, after every ten study or QC samples, and at the end of the batch. 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. Method (manifold) blanks and back up tubes should be analyzed after instrument blanks or low level samples to minimize LOQ inflation due to instrument carryover. Each sampling campaign should have at least one field blank included in the sample set.

The results of the field blank should be included in the final report with the rest of the study sample results.

In general, the average area counts of all blanks should have target anlayte area counts less than one-half the area counts of the LOQ standard. Refer to Section 9.3 for a more comprehensive discussion regarding blank evaluation. The procedure used to evaluate blanks should be documented in the raw data and discussed in the report if it deviates from the general 50% of the LOQ standard criteria.

### 13.3 Data Accuracy and Precision – Analysis Batch

#### 13.3.1 Lab Control Spikes – Analysis Batch

The average recovery (accuracy) of the pooled LCSs (all levels considered collectively) should be within 100±30% with a %RSD (precision) of ≤25% for the data to be used without further technical justification or bias adjustment.

#### 13.3.2 Field Duplicates – Analysis Batch

If field duplicates or distributed volume pairs are collected, the calculated %RPD should be less than 30% for the data to be used without further technical justification. As true field duplicates are challenging to collect with this method, duplicate data with %RPDs greater than 30% may be reported, but the results should be flagged appropriately.

#### 13.3.3 Field Matrix Spike (FMS) – Analysis Batch

If collected, field matrix spikes should produce recoveries within 100±30% to be considered acceptable without further technical justification if the spike level is appropriate for the resultant sample concentration. As expected sample concentrations will likely not be known at the time of collection, generation of appropriate FMS can be challenging. Therefore, non-compliant FMS recoveries should not preclude the reporting of data unless other factors are known and discussed in the report.

#### 13.3.4 Surrogate Recovery – Analysis Batch

Surrogate recoveries should be within 100±30% for the data to be reported without further technical justification. Because surrogates are spiked in the laboratory prior to sampling, they provide the only measure of stability and sorbent capacity when non-validated target analytes are analyzed.

### 13.4 Method Uncertainty

Analytical method uncertainty for each target analyte and surrogate is determined with control charted historical analysis batch LCS data for the method and reported with each analysis batch.[11] Uncertainty determinations are based on INTERNATIONAL ANS/ISO/IED STANDARD 17025 reference (GUM, Guide to the Expression of Uncertainty in Measurement) and described in ETS-12-012 “Estimation of Uncertainty of Measurements”. At least thirty data points are required for determining analytical method uncertainty. While all LCS data points are control charted, only the most recent fifty data points are used for determining the method uncertainty.

When less than thirty LCS data points have been generated for a given analyte (which will likely be the case for this method), the analysis batch LCSs (and any other available batch LCS results) are used to determine the data uncertainty.

[11] Method uncertainty based on INTERNATIONAL ANS/ISO/IED STANDARD 17025 reference (GUM, Guide to the Expression of Uncertainty in Measurement). Method application demonstrated in ETS-12-012, citing references: a.) EURACHEM/CITAC Guide, “Quantifying Uncertainty in Analytical Measurement,” Second Edition; Editors: S.L.R. Ellison, M. Rosslein, and A. Williams. b.)Georgian, Thomas, “Estimation of Laboratory Analytical Uncertainty Using Laboratory Control Samples,” Environmental Testing & Analysis, November/December 2000. c.)Taylor, B.N. and CE. Kuyatt, NIST Technical Note 1297, 1994 Edition: “Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results.”d.)Adams, T.M., “A2LA Guide for the Estimation of Measurement Uncertainty in Testing”, July 2002.

## 14 Pollution Prevention and Waste Management

Dispose of sample vials in low BTU and flammable solvent in high BTU containers.

Dispose of glass pipette waste in broken glass containers located in the laboratory.

Follow 3M policies for all sample handling and disposal. Zero headspace aqueous samples that have an aliquot removed generally lose sample integrity for reanalysis after one hour. Sample vials with an aliquot removed may be disposed of at the discretion of the analyst. Alternatively, the remaining aqueous sample may be transferred to a smaller zero-head space vial for future analysis within one hour of opening the original vial.

## 15 Records

Analytical records needed to reconstruct the sample preparation, sample analysis, and to reconstruct the results calculations must be included in the final data package or kept as facility records. The required documents may include, but are not limited to, the following handwritten or electronic records:

Standard Preparation Log Book Records

Sample Preparation Worksheet(s)

ATD Instrument Settings

Gas Chromatograph and Mass Spectrometer Identification and Settings

Analytical Sequence(s)

Initial Calibration Results Summary

Chromatograms

Quantitation Reports for Analyses

Notes to File

## 16 Attachments

None

## 17 References

Several references were provided as footnotes or mentioned directly in the text of this document. The two most significant references that are not part of the Environmental Laboratory's quality system or an instrument manual are listed below.

[1] *Compendium Method TO-17 Second Edition* "Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes, Center for Environmental Research Information, Office of Research and Development U. S. Environmental Protection Agency, Cincinnati, OH 45268, January 1999.

[2] **E13-0558** "Initial Demonstration of Capabilities and Partial Validation of ETS-8-059.0 Analysis of Semivolatile Organic Compounds (SVOCs) Using Sorbent Tubes and Thermal Desorption Gas Chromatography/Mass Spectrometry".

## 18 Affected Documents

None.

## 19 Revisions

| Revision Number | Summary of Changes |
|---|---|
| 0 | Original Document |