STANDARD OPERATING PROCEDURE

FOR

AIR ANALYSIS BY TO-17

PHILIS SOP L-A-601 Rev. 2

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PREPARED BY

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PREPARED FOR

U.S. Environmental Protection Agency
Office of Emergency Management
Washington, DC 20460

Approvals:

PHILIS, Castle Rock Lead Chemist	**September 7, 2023** **Date**
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0	Sang Chung Kevin Makuskie	05/17/2021	Program Issue
1	James Travis	06/09/2022	Revision
2	James Travis Sang Chung	08/11/2023	Annual Review

SOP REVISION FORM

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Purpose: *(Review or Revise)*	*SOP #:*	*Rev. #:* *(Being Reviewed or Revised)*	*Origination / Release Date:*
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For *Revision* : Summary of Revisions (specify sections)

Title Page	Changed Project Manager to Program Manager
Document	Changed from NELAP to EPA format

For *Review*: Comments

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1.0 Scope and Application

1.1 This standard operating procedure (SOP) documents PHILIS application of EPA TO-17, dated January 1999 "Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling On Sorbent Tubes", that will be used in the PHILIS Mobile Labs.

1.2 This SOP is executed in accordance with the U.S. Environmental Protection Agency and National Environmental Laboratory Accreditation Program (NELAP).

1.3 Referenced method reporting limit is 0.5 ppb when using 1.0 liter of sample, however reporting limits may vary depending on compound performance. Referenced method reporting limit is 0.5 ppb when using 1.0 liter of sample, however reporting limits may vary depending on compound performance.

1.4 PHILIS utilizes this method for the determination of subsets of the analytes listed in Table 1 in air & emissions. Not all analytes listed in Table 1 have been monitored by the use of solid sorbents. This method provides performance criteria to demonstrate acceptable performance of the method (or modifications of the method) for monitoring a given compound or set of compounds. Startup data was generated using the Markes Ultra and Unity system and Instrument APL01A in Edison using Universal Absorbent tubes (packed with Tenax TA 35/60, Carbograph 1TD 40/60, and Carboxen 1003 40/60) on a specific subset of compounds.

1.5 This SOP is applied for volatile organic analytes from air & emissions matrices except where a specific Quality Assurance Project Plan's (QAPP) override this method's quality assurance plan.

1.6 Atmospheric Pollutants not Suitable for Analysis by this Method

1.6.1 Inorganic gases not suitable for analysis by this method are oxides of carbon, nitrogen and sulfur, O3 and other permanent gases. Exceptions include C2S and N2O.

1.6.2 Other pollutants not suitable are particulate pollutants, (i.e., fumes, aerosols and dusts) and compounds too labile (reactive) for conventional GC analysis.

2.0 Summary of Method

2.1 The monitoring procedure involves transferring or direct collection a known volume of air onto a sorbent packed tube, thermal desorption onto a cold trap followed by desorption of the cold trap into a GC/MS for analysis. Samples can be collected directly on the tube with the use of a calibrated pump, collected in a Tedlar bag, Summa canister, or mini can. Summa canisters and MiniCans are received at pressures of less than one atmosphere and must be diluted to a positive pressure with moisturized zero air prior for syringe extraction of a measured aliquot of sample through a septa port. Transfer of samples via syringe is accomplished by injection onto the tube followed by running nitrogen through the tube on a special loading rig.

2.2 Regardless of the collection method, key steps of this method are listed below.

2.2.1 Selection of a sorbent or sorbent mix tailored for a target compound list, data quality objectives and sampling environment.

2.2.2 Screening the sampling location for VOCs by taking single tube samples to allow estimates of the nature and amount of sample gases.

2.2.3 Initial sampling sequences with two tubes at 1 and 4 liter nominal sample volumes or appropriate proportional scaling of these volumes to fit the target list and monitoring objectives.

2.2.4 Analysis of the samples and comparison to performance criteria.

2.2.5 Acceptance or rejection of the data.

2.2.6 If rejection, then review of the experimental design and repeat analysis or repeat analysis.

2.3 Key steps in sample analysis are listed below.

2.3.1 Dry purge of the sorbent tube with dry, inert gas before analysis to remove water vapor and air. The sorbent tube can be held at temperatures above ambient for the dry purge.

2.3.2 Thermal desorption of the sorbent tube (primary desorption).

2.3.3 Analyte refocusing on a secondary trap.

2.3.4 Rapid desorption of the trap and injection/transfer of target analytes into the gas chromatograph (secondary desorption).

2.3.5 Separation of compounds by high resolution capillary gas chromatography (GC).

2.3.6 Quantitation by mass spectrometry (MS) or conventional GC detectors (only the MS approach is explicitly referred to in Compendium Method TO-17).

3.0 Definitions

3.1 Batch‡: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A Preparation Batch is composed of between 1 and 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and the last sample in the batch to be 24hours. An Analytical Batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

All batches require one MB, LCS, and MS/MSD pair or MS and Sample Duplicate when possible.

3.2 BFB: 4-bromofluorobenzene or a solution that contains the analyte, 4-bromofluorobenzene, which is used to evaluate the tuning and the performance of the mass spectrometer. The BFB tune is analyzed at the beginning of each 12-hour period during which samples or calibration standards are analyzed.

3.3 Breakthrough Volume (BV): Volume of air containing a constant concentration of analyte which may be passed through a sorbent tube before a detectable level (typically 5%) of the analyte concentration elutes from the non-sampling end. Alternatively, the volume sampled when the amount of analyte collected in a back-up sorbent tube reaches a certain percentage (typically 5%) of the total amount collected by both sorbent tubes. These methods do not give identical results. For purposes in the document the former definition will be used.

3.4 Chain of Custody (COC) ‡: Record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers; the mode of collection; preservation; and requested analyses.

Each time the samples are transferred, the document should be signed by the person releasing the samples and by the person receiving the samples. A date and time must also be recorded.

3.5 Continuing Calibration Verification (CCV): A standard analyzed at the beginning of each analytical sequence that contains all method analytes at a concentration near the mid-range of the calibration curve. Each analyte must have a recovery within a percentage range specified in the method to validate that analyte in the calibration curve. A CCV is not required if a calibration curve is analyzed at the start of an analysis sequence. Some methods require additional CCV's. The CCV frequency will be stated in the method SOP.

3.6 Cryogen: (Also referred to as 'cryogenic fluid'). Typically liquid nitrogen, liquid argon, or liquid carbon dioxide. In the present context, cryogens are used in some thermal desorption systems to cool the focusing tube. The Markes Unity System utilizes a Peltier cooler.

3.7 Duplicates (Field): Identical samples collected at the same time, in the same way, and contained, preserved, and transported in the same manner to determine the reproducibility of the sampling.

3.8 Field Blank: A TD tube of the same tube type and from the same conditioning batch as sample tubes. This tube remains capped with brass Swagelok caps and is carried into the field by sampling team and is stored in the same containment vessel as the sample tube.

3.9 Focusing Tube: Narrow (typically <3mm I.D.) tube containing a small bed of sorbent, which is maintained near or below ambient temperature and used to refocus analytes thermally desorbed from the sorbent tube. Once all the VOCs have been transferred from the sorbent tube to the focusing tube, the focusing tube is heated very rapidly to transfer the analytes into the capillary GC analytical column in a narrow band of vapor.

3.10 High Resolution Capillary Column Chromatography: Conventionally describes fused silica capillary columns with an internal diameter of 320 μm or below and with a stationary phase film thickness of 5 μm or less.

3.11 Holding Time: The maximum amount of time permitted between sampling and sample preparation and/or sample preparation and sample analysis. Also the period of time a sample may be stored prior to analysis when there is no preparation step. See the specific method or SW846 8000B table 4.1.

3.12 Instrument Calibration Standards (ICS): A solution prepared from the primary dilution standard solution or stock standard solutions, internal standards and surrogate analytes. The ICS solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 Internal Standards (IS)[‡]: A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

3.14 Laboratory Control Sample (LCS)‡: (however named, such as laboratory fortified blank, blank spike (BS), or QC check sample). A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known amounts of analytes and taken through all sample preparation and analytical steps of the procedure unless otherwise noted in a reference method. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

The standard source can be the same as the calibration or a second source. The LCS is analyzed exactly like a sample to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.15 Laboratory Duplicate (LD): Two sample aliquots taken in the laboratory and analyzed separately with identical procedures. Analyses of the aliquots indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.16 LIMS: Acronym for the Laboratory Information Management System. PHILIS utilizes Promium Element, LIMS software. This system is used to receive, track, and report sample results.

3.17 Method Blank (MB): A TD tube of the same tube type and from the same conditioning batch as sample tubes. This tube retained by the lab and taken out of containment just prior to analysis.

3.18 Method Detection Limit (MDL): The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined by analyzing seven or more replicates of a spiked analyte free matrix and the resulting statistical calculation, in accordance with 40 CFR 136, Appendix B, Revision 2.

3.19 MS-SCAN: Mode of operation of a GC mass spectrometer detector such that all mass ions over a given mass range are swept over a given period of time.

3.20 MS-SIM: Mode of operation of a GC mass spectrometer detector such that only a single mass ion or a selected number of discrete mass ions are monitored.

3.21 Primary Dilution Standard (PDS): A solution of one or several analytes prepared in the laboratory from SSS and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.22 Reporting Limit (RL): The reporting limit, also known as the LOQ is the minimum concentration that can be reported as a quantitated value for a target analyte in a sample. This value can be no lower than the concentration of the lowest calibration standard.

3.23 Retention Volume (RV): The volume of carrier gas required to move an analyte vapor plug through the short packed column which is the sorbent tube. The volume is determined by measuring the carrier gas volume necessary to elute the vapor plug through the tube, normally measured at the peak response as the plug exits the tube.

3.24 Safe Sampling Volume (SSV): Calculated by halving the retention volume (indirect method) or taking two-thirds of the breakthrough volume (direct method), although these two approaches do not necessarily give identical results. The latter definition is used in this document.

Safe Sampling volume will be determined on a project-specific basis and specified in the QAPP. This information is confirmed with the sampling team prior to the sampling event.

3.25 Sample Custodian: The person assigned to be responsible for receiving samples in compliance with all standard procedures. This individual must be trained in entry of data into Promium Element and know all the functions and checks for sample receiving.

3.26 Sample Delivery Group (SDG): A unit within a single project that is used to identify a group of samples for delivery to the laboratory for chemical analysis. An SDG is a group of 20 or fewer field samples within a project, received over a period of up to 14 calendar days (depending on turnaround time requirements). Data from all samples in an SDG are due concurrently.

3.27 Second Source Calibration Verification (SCV): A solution prepared from a source that is different from the calibration standards. The SCV is immediately following the ICS, and is used to verify calibration standard accuracy.

3.28 Selected Ion Monitoring: A mass spectrometry technique that provides lower detection level capability by monitoring fewer mass scans for longer periods of time that is done in full-scan methods.

3.29 Sorbent Strength: Term used to describe the affinity of sorbents for VOC analytes. A stronger sorbent is one which offers greater safe sampling volumes for most/all VOC analytes relative to another, weaker sorbent. Generally speaking, sorbent strength is related to surface area, though there are exceptions to this. The SSVs of most, if not all, VOCs will be greater on a sorbent with surface area “10n” than on one with a surface area of ?n”. As a general rule, sorbents are described as “weak” if their surface area is less than 50 m2g-1 (includes Tenax®, Carbopack™/trap C, and Anasorb® GCB2), “medium strength” if the surface area is in the range 100-500 m2g-1 (includes Carbopack™/trap B, Anasorb® GCBI and all the Porapaks and Chromosorbs listed in EPA Method TO-17 and “strong” if the surface area is around 1000 m2g-1 (includes Spherocarb®, Carbosieve™ S-III, Carboxen™ 1000, and Anasorb® CMS series sorbents.)

3.30 Sorbent Tube: (Also referred to as 'tube' and 'sample tube') Stainless steel, glass or glass lined (or fused silica lined) stainless steel tube, typically 1/4 inch (6 mm) O.D. and of various lengths, with the central portion packed with greater than 200 mg of solid adsorbent material, depending on density and packing bed length. Used to concentrate VOCs from air.

3.31 Standard Sorbent (Sample) Tube: Stainless steel, glass or glass lined (or fused silica lined) stainless steel tube, 1/4 inch (6 mm) O.D. and of various lengths, with the central portion packed with 200 mg of solid adsorbent material depending on sorbent density. Tubes should be individually numbered and show the direction of flow.

3.32 Stock Standard Solution (SSS): A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased as certified from a reputable commercial source.

3.33 Temperature Blank: An aliquot of water placed in the sample cooler to aid in determining the temperature of samples at receipt.

3.34 Thermal Desorption: The use of heat and a flow of inert (carrier) gas to extract volatiles from a solid or liquid matrix directly into the carrier gas and transfer them to downstream system elements such as the analytical column of a GC. No solvent is required.

3.35 Time Weighted Average (TWA) Monitoring: If air is sampled over a fixed time period - typically 1, 3, 8, or 24 hours, the time weighted average atmospheric concentration over the monitoring period may be calculated from the total mass of analyte retained and the specific air volume sampled. Constraints on breakthrough volumes make certain combinations of sampling time and flow rates mutually exclusive.

3.36 Total Ion Chromatogram (TIC): Chromatogram produced from a mass spectrometer detector operating in full scan mode.

3.37 Two-stage Thermal Desorption: The process of thermally desorbing analytes from a solid or liquid matrix, reconcentrating them on a focusing tube and then rapidly heating the tube to inject" the concentrated compounds into the GC system in a narrow band of vapor compatible with high resolution capillary gas chromatography.

ǂ EL-V1M2-ISO-2016, 2016 NELAP Standard definition.

4.0 Interferences

4.1 Minimizing Artifact Interference.

4.1.1 Stringent tube conditioning and careful tube capping and storage procedures are essential for minimizing artifacts. System and sorbent tube conditioning must be carried out using more stringent conditions of temperature, gas flow and time than those required for sample analysis.

4.1.2 Reduce artifacts to 10% or less of individual analyte masses retained during sampling. If this level of reduction is not possible then measure levels and document conditions.

4.1.3 Typical artifact levels for 1/4 inch O.D. tubes of 3.5" length range from 0.01 ng and 0.1 ng for carbonaceous sorbents and Tenax® respectively. These levels compare well with the masses of analytes collected, even from sub-ppb atmospheric concentrations. Artifact levels are typically around 10 ng for Chromosorb® Century series and other porous polymer sorbents. However, these types of sorbents can still be used for air monitoring at low ppb levels if selective or mass spectrometer detectors are used or if the blank profile of the tube demonstrates that none of the sorbent artifacts interfere analytically with the compounds of interest.

4.1.4 Some varieties of charcoal contain metals which will catalyze the degradation of certain organic analytes during thermal desorption at elevated temperatures thus producing additional artifacts and resulting in low analyte recoveries.

4.1.5 Artifacts can be formed from long-term storage of blank tubes. Literature reports of the levels of artifacts on (a) Carbotrap/pack™ C, Carbotrap/pack™ B and Carbosieve™ SIII multi-bed tubes and (b) Tenax® GR tubes, by workers sealing the tubes using metal Swagelok®-type caps and PTFE ferrules with multi-tube, glass storage jars are reported to be between 0.01 ng [after 1-2 months and 0.1 ng [after 6 months] for (a) and (b) respectively. Artifact levels reported for other porous polymers are higher; for example 5 ng for Chromosorb 106 after 1 week. More information is given in the Technical Assistance Document (TAD) referred to in EPA Method TO-17.

4.1.6 Artifacts can also be generated during sampling and sample storage. Benzaldehyde, phenol and acetophenone artifacts are reported to be formed via oxidation of the polymer Tenax® when sampling high concentration (100-500 ppb) ozone atmospheres. Tenax® should thus be used with an ozone scrubber when sampling low levels (<10 ppb) of these analytes in areas with appreciable ozone concentrations. Carbotrap™ type sorbents have not been reported to produce this level of artifact formation. Once retained on a sorbent tube, chemically stable VOCs, loaded in laboratory conditions, have been shown to give good recoveries, even under high ozone concentrations for storage of a year or more.

4.2 Minimizing Interference from water. There are three preferred approaches to reducing water interferences during air monitoring using sorbent tubes.

4.2.1 The first is to minimize water collection by selecting, where possible, a hydrophobic sorbent for the sample tube. This is possible for compounds ranging in volatility from n-C5. Tenax®, Carbotrap™ or one of the other hydrophobic sorbents listed in EPA Method TO-17 should be used.

Note: It is essential to ensure that the temperature of the sorbent tube is the same and certainly not lower than ambient temperature at the start of sampling or moisture will be retained via condensation, however hydrophobic the sorbent.

4.2.2 If the sample loading contains a large amount of water, it is usually possible to eliminate sufficient water to prevent analytical interference by using sample splitting. Samples may be split either between the focusing trap and the capillary column (single splitting) during trap (secondary) desorption or between both the tube and the focusing trap during primary (tube) desorption and between the focusing trap and the column during secondary (trap) desorption (double splitting). It may, in fact, be necessary to split the sample in some cases to prevent overloading the analytical column or detector.

4.2.3 The third water management method is to "dry purge" either the sorbent tube itself or the focusing trap or both. Dry purging the sample tube or focusing trap simply involves passing a volume of pure, dry, inert gas through the tube from the sampling end, prior to analysis.

The tube can be heated while dry purging at slightly elevated temperatures. A trap packing combination and a near ambient trapping temperature must be chosen such that target analytes are quantitatively retained while water is purged to vent from either the tube or trap.

5.0 Safety

Laboratory personnel are required to be familiar with the general laboratory safety plan including the location and proper use of safety/emergency equipment

5.1 Employees must abide by the policies and procedures in the Chemical Hygiene Plan and this document. This procedure involves hazardous material, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow the appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are hazardous. Standard laboratory safety procedures should be followed when working with all samples.

5.2 Specific Safety Concerns or Requirements

Eye protection that satisfies ANSI Z87.1, laboratory coat, and disposable nitrile or Silver-Shield gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded. Non-disposable gloves must be cleaned immediately. Latex and Vinyl gloves provide no protection against some organic solvents.

5.3 Each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Procedures involving primary standards and sample preparation must be performed in a fume hood.

5.4 Material Safety Data Sheets (MSDS) for each analyte and reagent used in the mobile laboratory are available to all employees. The MSDS and the PHILIS Chemical Hazard Summary Sheet must be read and understood by the analyst prior to initial use of a chemical.

6.0 Equipment and Supplies

6.1 Sampling equipment

6.1.1 Thermal desorption tubes- based on the analytes to be determined.

6.1.2 Calibrated sampling pump

6.1.3 Pressure gauge

6.1.4 Mass flow meter

6.2 Glassware

6.2.1 Class A volumetric flask – used if liquid calibration standards will be prepared

6.3 Syringes

6.3.1 Gas tight syringes – various sizes

6.4 Instrumentation

6.4.1 Agilent 8890 Gas Chromatograph

6.4.2 Agilent 5977B Mass Spectrometer

6.4.3 Markes International Unity-xr Thermal Desorption platform – or equivalent

6.4.4 Markes International Ultra-xr Thermal Desorption Tube autosampler—or equivalent

6.4.5 Agilent MSD ChemStation G1701 DA or higher version

6.4.6 Markes Instrument Contol Software 2.0 or equvalent.

6.4.7 Alternate instrument LECO Time of Flight (TOF) Mass Spectrometer

6.4.8 Gerstel Thermal Desorption Unit

6.4.9 LECO Chromatography software

6.4.10 NIST spectral library

6.4.11 Restek RTX-VMS capillary column, 20 m x 1.8 mm x 1.0 µm- column used for VOA analysis. Other columns may be used provided required quality assurance parameters can be met.

6.4.12 TDU tube conditioner

6.5 Equipment for Standard Preparation

6.5.1 Markes International Calibration Loading Rig- used to load standards in either the liquid or gas phase.

7.0 Reagents and Standards

7.1 Reagents

7.1.1 Helium- UHP grade or higher

7.1.2 Nitrogen- UHP grade or higher

7.1.3 Methanol-Purge and Trap grade or equivalent

7.2 Gas Standards

Below is a list of suggest gas standards. Other standards than those listed may be used provided they meet analytical requirements. Gas standards used in the Edison application are listed in 10.2.4 and 10.2.5,

7.2.1 Restek TO-14A Internal Standard/Tuning mix, cat#34408- 1 ppmv in nitrogen

7.2.2 Restek BTEX mix, cat#34414- 1 ppmv in nitrogen

7.2.3 Restek TO-15 mix, 65 components, cat#34436- 1 ppmv in nitrogen

7.2.4 Air Liquide Custom 4 component Internal Standard Mix Sales order:2814370 (1ppmv in nitrogen).

7.2.5 Air Liquide Custom 65 component target compound mix Item TQ15-6276 (1ppm in nitrogen).

7.3 Liquid Standards

Below is a list of suggest liquid standards. Standards from other manufacturers may be used provided they meet analytical requirements. 10.3.4 was used in Edison method development for MS performance evaluation

7.3.1 Restek Mega Mix

7.3.2 Restek Internal Standard (optional)

7.3.3 AccuStandard Liquid and Gas mix

7.3.4 Restek Surrogate Mix. 2500ug/ml Catalog #3004. Diluted (40ul diluted in 2ml Purge and Trap grade methanol) to 50ng/ul of 4-Bromofluorobenzene. 1ul loaded onto Markes Universal tube.

7.4 Calibration Standards are listed in Table 2.

7.4.1 Edison start-up data used the following levels 0.5, 1.0, 2.0, 5.0,10,20,30 50 100 and a 5ml ICV. The 80 and 100 levels were removed from individual compounds in the curve where saturation was present in particular, all aromatic compounds eluting after toluene

8.0 Sample Collection, Preservation, and Storage

PHILIS staff typically does not collect samples, but the information below should be considered when setting up a project.

If the field sampling crew does not have a sample collection form to transfer the sampling information to the laboratory, Figure 1 is an example form that may be used.

8.1 Selection of Tube Dimensions and Materials

8.1.1 The laboratory will be providing and conditioning the same tube type for sampling that is used for the instrument calibration.

8.1.2 As an approximate measure, the breakthrough volume for sorbents contained in equal diameter tubes is proportional to the bed-length (weight) of sorbent. Accordingly, doubling the bed-length would approximately double the SSV (15). SSV for specific analytes are listed in Figure 3. SSV's for analytes not listed in Figure 3 may be available in "Application Notes" from tube manufacturers, or will need to be determined. An "Application Note" from Markes gives a detailed description on a procedure to determine SSVs. Safe Sampling volume will be determined for analytes in the QAPP. This is information will be transmitted to the sampling team prior to sampling. Figure 2 lists some sorbent types and Figure 3 lists SSVs.

8.1.3 Stainless steel (304 or "GC" grade) is the most robust of the commonly available tube materials which include, in addition, glass, glass-lined, and fused silica lined tubing. Tube material must be chosen to be compatible with the specifics of storage and transport of the samples. For example, careful attention to packaging is required for glass tubes.

8.1.4 The Edison method for volatile air toxics utilizes 3.5" x .25"O.D treated stainless steel tubes packed with 380mg of Tenax TA 35/60, Carbograph ITD 40/60, and Carboxen 1003 40/60 which are packed and preconditioned by Markes. All tubes are also preconditioned in lab prior to sampling and are traceable to conditioning batch.

8.2 Tube Labeling

Tubes are engraved with a 6 digit serial number which is logged into a spreadsheet containing a batch ID. This batch ID is added to the LIMS batch and the ChemStation sequence log and the sequence log of the instrument control software. so that the conditioning batch is traceable to all standard, QC and samples. Example log book pages for a conditioning batch log can be found in Figure 4. Markes tubes are also engraved with a bar code which will enter the six digit code into a chemStation sequence or the Markes sequence table via bar code scanner.

8.3 Blank and Sampled Tube Storage

8.3.1 Seal clean, blank sorbent tubes and sampled tubes using inert, Swagelok®-type fittings and PTFE ferrules. Use clean, sealable glass jars or metal cans labelled with the conditioning batch designation and containing a small packet of activated charcoal or activated charcoal/silica gel for storage and transportation of multiple tubes. Store the multi-tube storage container in a clean environment at 4°C, or use within 24 hours.

8.3.2 Keep the sample tubes inside the storage container during transportation and only remove them at the monitoring location after the tubes have reached ambient temperature. Store sampled tubes in a refrigerator at 4°C inside the multi-tube container until ready for analysis.

8.3.3 After sampling remove the sampling tubes with clean gloves, recap the tubes with Swagelok® fittings using PTFE ferrules and place the tubes in a clean, airtight container. If not to be analyzed during the same day, place the container in a clean, cool (<4C) organic solvent free environment and leave there until time for analysis. Section 10.10 of compendium method TO-17 January 1999 allows for a holding time of up to 30 days. Based on this the PHILIS holding time will be officially set at 30 days. Due to the unknown nature of the stability of analytes under long term storage and the nature of the sorbent tubes in the current PHILIS developed method (multiple sorbents) it would be prudent for analysis to proceed as soon as possible after collection.

8.4 Samples may be taken in Tedlar® bags and would have a 72 hour holding time. The air from these bags can be transferred to a sorbent tube using a gastight syringe. The volume transferred must be recorded.

9.0 Quality Control

QC requirements include the Demonstration of Capability and ongoing QC requirements that must be met when preparing and analyzing samples.

9.1 DEMONSTRATION OF CAPABILITY (DOC) – must be successfully performed by the analyst prior to analyzing any field samples. This DOC study must be performed every three months or after every 10^{th} series of runs whichever comes first and any time major method modifications are made. DOC result must be provided with the final data package for the project.

9.1.1 Prior to conducting the DOC study, the analyst tunes the instrument and generates an acceptable instrument calibration following the procedure outlined in Section 13 of this SOP. An MB (blank tube) is analyzed to demonstrate that the background contamination is low enough to not interfere with analyte.

9.1.2 Method precision and accuracy are demonstrated by analyzing six replicate LCS's fortified at concentration near the mid-point of the calibration curve and analyzed according to the procedure described in Section 14 of this SOP. Precision and accuracy are calculated using an EXCEL Spreadsheet.

9.1.2.1 Acceptable precision is RSD ≤ 20%. Once adequate points are available, laboratory limits will be established. Analytical precision below 20% for MTBE has been difficult to achieve due to the reactive nature of this compound. RSD limits have been set to 30% for this compound.

9.1.2.2 Acceptable accuracy is mean percent recovery within ± 50%. Once adequate points are available, laboratory limits will be established.

9.1.2.3 Table 3 represents example DOC data for the Edison application of this method.

9.2 MDL Procedure

MDLs and RLs are established by analyzing a minimum of seven replicates of a standard at or near the estimated MDL. Tabulation of results and MDL calculations are performed by the method in 40 CFR, Part 136, Method Update Rule Revision 2.

9.2.1 Initial MDLs

9.2.1.1 Initial MDLs are established by analyzing a minimum of seven replicates of the low-level calibration standard and a minimum of seven blanks prepped and analyzed over three separate days. The MDL should be spiked 1 to 5 times the estimated MDL. Extract and analyze the MDL standards and blanks with the same procedure as regular samples.

9.2.1.2 For each compound, calculate the mean and standard deviation of the replicates in micrograms per liter (µg/L). Then calculate the MDL by multiplying the standard deviation by the Student's t value. The one-sided (single-tailed) Student's t values at the 99% confidence levels are used (e.g., t = 3.143 at the 99% confidence level for n = 7). MDL studies are repeated annually and verified each time they are prepared. MDL results are stored in Element each time they are calculated.

9.2.1.3 Blank MDL's are calculated according to the procedure listed in 40CFR 136 Appendix B After determination of a blank mdl and a mdl based on a low level spike study, use the larger of the two values.

9.2.2 Ongoing MDL Data Collection

9.2.2.1 Ongoing MDL's are determined by preparing and analyzing two spiked standards at 1-5 times the estimated md and two blanks once per quarter for a minimum of seven determinations. The blanks and spikes may be analyzed in the same prep batch, but is not required. If the instruments are being used regularly, the mdl spikes may be added to the routine batches and the regular blanks used. All blanks analyzed during the evaluation period should be used. If samples are not analyzed during a quarter, it is not required to analyze the Ongoing MDLs for that quarter.

9.2.2.2 At least once per year re-evaluate the mdl by, calculating as above in 12.9.1.2. Use the larger of the spiked determinations and blank determinations for the mdl value.

9.2.3 Ongoing MDL Annual Verification

9.2.3.1 At least once every thirteen months, re-calculate the MDL spike and MDL blank from the collected spiked samples and method blank results per 12.9.1.2.

9.2.3.2 Include data generated within the last twenty four months, but only data with the same spiking level. Only documented instances of gross failures (instrument malfunctions, mislabeled samples, cracked vials, etc.) may be excluded from the calculations.

9.2.3.3 Include the initial MDL spiked samples if the data were generated within the last twenty four months.

9.2.3.4 The verified MDL is the larger of the MDL Blank and MDL Spiked samples.

9.2.4 Using MDLs for Multiple Instruments

9.2.5 If the same MDL is to be used for multiple instruments, then MDL spiked samples and MDL blanks from the included instruments must be pooled prior to the mdl calculation. All MDL spiked samples must be at the same prepared level to be included. The same rules for calculations and data gathering that is used for individual instruments are used for the multiple instruments.

9.3 Ongoing QC applied when performing this method includes analyzing acceptable instrument calibration/calibration verification standards, method blanks, duplicates, LCS's, and closing method blanks. Requirements are listed in Table 4. Internal standards and surrogates must be acceptable with all QC samples and with test samples. Example MDL's are listed in Table 5.

10.0 Calibration and Standardization

10.1 Prior to the analysis of samples, performance of the instrument is optimized and an instrument calibration curve is developed. BFB is analyzed prior to instrument calibration and with each analysis batch processed within 24 hours in order to verify that the mass abundance acceptance criteria specified in Table 6 have been achieved.

All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 % that of m/z 95.

10.1.1 Calibration curve regression model and the range of calibration level used in the performance validation (Demonstration of Capability, Section 11) must be used in all routine sample analysis. Either external or internal standard calibration may be used, as long as the same calibration method is used for all project and QC and samples.

10.1.2 Setting Retention Times Extraction Windows and Integration Parameters.

10.1.2.1 Once data has been acquired for the calibration, absolute retention times must be set for the calibration by quantitation of the midpoint followed by qualitative review of the spectral hits and manual setting of the retention times and ion ratios by selecting and integrating the peaks using EasyID.

10.1.2.2 Global updating of the ion extraction windows must be done for first time calibration and after maintenance where a large retention time shift occurs. A default setting of 0.3 minutes is acceptable for most targets in this method. Some compounds will require narrowing of the extraction windows by placement of flags in EasyID where there are peaks with the same ions that elute in close proximity. Widening of retention time windows may be necessary in the case of broader peaks or tailing. Relative ion extraction windows will be maintained when setting retention time on subsequent calibrations.

10.1.2.3 When setting up a calibration curve the RTE integrator should be used with a default parameter file of RTEINT.P for the Edison method. After retention time settings and extraction windows have been properly set recalculate the file and review each compound for accuracy in integration. Some compounds may have choppy peaks or baseline issues where the setting of compound specific integration parameters can be used to assure proper integration. Manual integration is permitted but a reasonable effort to set the proper parameters in the calibration can result in consistent integrations and save time in processing data later.

10.1.3 The instrument is calibrated using a minimum of five concentrations in the following manner: Cal1 – Cal N (number of last calibration standard) are used to generate the calibration curve for all target analytes. The average response factor or a linear regression curve can be used with five points, but a quadratic regression requires a minimum of six points. Calibration points may be dropped from either end of the calibration curve, but a minimum of five points is required for a curve. Calibration points may also be dropped from the middle of a calibration curve for an obvious reason (low internal standards, standard made wrong, etc.). The reason must be documented and the entire point must be removed. The calibration point may be reanalyzed within 24 hours.

10.1.4 The reporting limit (RL) of the analytical method must be at or above lowest point in the initial calibration.

10.1.5 A response factor calibration curve is generated for each target analyte by plotting the response factor as a function of concentration ratio. If the analyte does not meet the 30% variability acceptance criteria, then a regression fit should be used. If linear or quadratic regression is used, the resulting curve fit must be 0.99 or greater.

10.1.6 Response for each of the internal standards in the calibration curve cannot vary more than 40 % when compared to their average responses. The use of internal standards is optional for this procedure.

10.1.7 Retention time for the internal standards may not vary more than 20 seconds in the calibration or subsequent analyses. The use of internal standards is optional for this procedure.

10.1.8 The instrument calibration curve is initially verified by the SCV and continuously verified by the CCV. The concentration of the calibration checks is at or near the midlevel of the calibration curve.

10.1.9 The low and mid points of the curve must be recalculated with the results documented on an "evaluate data file as continuing calibration" report. All target compound calculated values should return an accuracy of 70-130 of the true value,

10.2 Relative Error

If the calibration curve is a Response Factor curve, then the Relative Error is the Average Response Factor.

If the calibration curve is Linear Regression or Quadratic Regression, then run the lowest and midpoint calibration points against the curve and calculate the % difference from the true value. These are the Relative Errors.

10.3 Acceptance criteria for BFB, Instrument Calibration and CCVs, and the required frequency of their analysis are summarized in Table 6.

11.0 Procedure

11.1 Thermal Desorption Tube Conditioning

This procedure must be performed prior to sampling.

11.1.1 Place the TDU tubes into the tube conditioner

11.1.2 Turn on Nitrogen

11.1.3 Markes Universal tubes are loaded into the TC2 Gerstel Tube or TC20 Markes conditioning system, a nitrogen flow of 100ml/min is established and new or newly packed tubes are conditioned at each of the following temperatures in succession for one hour (100C, 200C, 300C) followed by a half hour at 335C. Reconditioning can be done at 15 minutes at the previously mentioned temperatures. For small batches tubes can also be conditioned by running as a blank on the Ultra/Unity system provided that conditioning is documented the same way as if it was conditioned using the Gerstel TC2,

and they are not included in the same conditioning batch. Allow the tube conditioner to cool down to ambient temperature, and then remove the tubes and cap them with Swagelok fittings and PTFE ferrules. An example of the Tube Conditioning Log is Figure 4.

11.1.4 Tube serial numbers from the same conditioning method on the same day must be documented into a conditioning batch log (Figure 4). All samples and QC including method blanks, field blanks, LCS/LSCD's must originate from the same tube conditioning batch.

11.1.5 Stored in a sealed glass or tin container (labelled with the conditioning batch ID containing a silica gel and adsorbent package. Unless used on the same day they must be stored in a refrigerator at less than 4C. Due to the contraction of metal at lower temperatures the Swagelok fittings must be retightened upon cooling.

11.2 Sample Preparation

11.2.1 Remove the sample TDU tubes from the refrigerator.

11.2.2 Verify that the sample has been logged into LIMS and within holding time. If the sample exceeds the holding time, notify the Lead Chemist and follow the corrective action plan.

11.2.3 The sample can now be placed on the Markes International Ultra 2 autosampler or Gerstel TDU.

11.3 Standard Preparation for Tedlar Bags, SUMMA Cannisters, and MiniCans

11.3.1 An aliquot of sample is extracted via gas tight syringe from a Tedlar bag and transferred to a preconditioned sorbent tube attached to a loading rig. The nitrogen valve is turned on prior to removal of the syringe needle from the rig and UHP Nitrogen is allowed to flow though the tube at 100cc/min for 2 min. Tube is removed from the rig and capped with Diff-lock caps and transferred to the Ultra tray for analysis.

11.3.2 A gauge is attached to a summa canister or MiniCan to determine the pressure. The determined pressure is usually less than 1 atmosphere, Moisturized zero air is added through a secondary port on the canister to raise to a positive (relative to atmospheric pressure) pressure. The new pressure is recorded and a dilution factor is calculated.

11.3.3 An aliquot of sample is extracted via gas tight syringe from a septum fitting on the canister and transferred to a preconditioned sorbent tube attached to a loading rig. The nitrogen valve is turned on prior to removal of the syringe needle from the rig and UHP Nitrogen is allowed to flow though the tube at 100cc/min for 2 min. Tube is removed from the rig and capped with Diff-lock caps and transferred to the Ultra tray for analysis.

11.3.4 Follow the procedure listed in Table 2 using the Markes calibration loading rig or other acceptable procedures.

11.3.5 The Edison method uses a standard mix in a large gas cylinder. Appropriate technique is essential for reproducible results. Prior to tube loading tap the cylinders repeatedly for one or two minutes with a wrench or similar metal object to sonically mix the gases in the cylinder. Using a 250ml syringe withdraw two aliquots (500ml of standard and discard), this is to evacuate the gas in the regulator. Attach the tube to the loading rig and finger tighten nut. For each tube turn on the loading rig open nitrogen valve and attach a flow meter, observe the flow rate and adjust to 100mL +/- 10mL. Turn off valve and remove flow meter. Using the appropriate syringe withdraw gas standard to a mark greater than the desired volume and shut the stopcock on the syringe. Place the syringe under the hood and slowly slide plunger to the point where the syringe barrel is on the desired volume being careful to maintain no pressure on the plunger before closing the luer lock stopcock. Insert the needle into the loading rig and push the needle to just the point you can feel the packing material. Open the syringe stopcock and slowly slide the syringe plunger to load the standard onto the tube taking care to load at a rate no more than 100ml/min. After all of the standard has been loaded and before withdrawing the syringe needle, turn on the nitrogen flow and slowly withdraw the needle. Maintain nitrogen flow for one minute before removing the tube from the loading rig. Cap the inlet end of the tube with an inert end cap, and the outlet end with an untreated end cap. As with all laboratory procedures wear gloves. Handling TD tubes with bare hands can create artifacts which may interfere with analysis.

11.4 Sample Analysis

11.4.1 Analysis is performed using a Thermal Desorption (TD)-GC/MS programmed based on the sorbent tubes and analytes being determined. The program used to generate the calibration must be used for all sample and quality control analyses.

11.4.2 Samples are allowed to equilibrate to room temperature before recapping with Diff -lok caps and being loaded into the Ultra tray. (wear clean gloves when handling tubes to avoid contaminating the tubes with artifacts)

11.4.3 Analysis sequence for EPA Method TO-17 is tune, calibration or CCV, MB, FB, LCS, LCSD. Samples including duplicate and a closing method blank with a different tube from the same conditioning batch.

11.4.4 In the software, ensure that the correct sequence and controlling method is loaded.

11.4.5 In ChemStation, load the “default” sequence and enter the pertinent information into the sequence, making sure the same method used for calibration has been used for analysis. In the Maverick software load the appropriate method and sequence making sure it is the same method used for calibration.

11.4.6 Start the Markes sequence. Tubes are loaded into the Ultra system into and leak checked. Leak check failure results in the trigger of the chemStation sequence to keep the sequence matching the sample. Three leak check failures on separate tube in a row aborts the sequence.

11.4.7 After passing leak check tubes are dry purged for 1 minute followed by the introduction of internal standard through a 1ml standard loop fed by an external cylinder containing 1.00 ppmV each of 1,4-Difluorobenzene, Bromochloromethane, and Chlorobenzene-d5 in Nitrogen. The tube is the desorbed onto a cold trap which is in turn is desorbed into the GC/MS.

11.4.8 After analysis tubes are stored in a sealed glass or tin container (labelled with the condoning batch ID containing a silica gel and adsorbent package Due to the contraction of metal at lower temperatures the Swagelok fittings must be retightened upon cooling

11.4.9 All tubes are subjected to at least one mid-level calibration analysis before being put into circulation, if a large percentage of compounds fail this "CCV" it is retested and if it fails again the tube is taken out of circulation. According to the Markes manual tube lifetime is about 100 cycles which include both analysis and conditioning cycles. The number of cycles will be tracked in the conditioning batch log and tubes will be sent to Markes for repacking.

11.5 Identification of Analytes

11.5.1 The analyte is identified by comparison of its mass spectrum to a reference spectrum in the instrumental method and comparing its retention time to the retention time observed for the same analyte in the most recent CCV or calibration.

11.5.2 Analytes above the calibration range are flagged and reported as estimated.

12.0 Data Analysis and Calculations

12.1 Identification of Analytes

12.2 Percent recovery for LCS and LCSD are calculated using the following equation:

$$\%R = \left[\frac{\left(C_{spk} - C_x\right)}{C_t}\right]100$$

where:
C_{spk} = the concentration of the analyte in the spiked sample
C_x = the concentration of the analyte in the reference (parent) sample; (Cx = 0 for LCS.)
C_t = the theoretical spike concentration.

The concentration of each analyte is calculated using Agilent MSD ChemStation software using an average response factor or linear regression curve as established in Section 13 of this SOP. Response factors and analyte concentrations are calculated by the equations below when internal standards are not used:

12.3 Calibration factor (CF):

$$CF = \frac{(A_x)}{mass\ of\ std}$$

where:
A_x = Area of the Analyte being measured
Mass of std = Total mass of standard injected in nanograms

Average CF ($\overline{\mathrm{CF}}$): $\overline{CF} = \frac{\sum_1^n CF}{n}$

where
n = number of initial calibration standards

12.4 Percent relative standard deviation (%RSD):

$$\%RSD = (^{S}/_{\overline{x}})100$$

where:
$\overline{\mathrm{x}} = \overline{\mathrm{CF}}$: $\overline{\mathrm{CF}} = \frac{\sum_1^{\mathrm{n}} \mathrm{CF}}{\mathrm{n}}$
where:

s = standard deviation: $= \sqrt{\frac{\sum_{\mathrm{i}=1}^{\mathrm{n}}(\mathrm{x_i} - \bar{\mathrm{x}})^2}{\mathrm{n}-1}}$

12.5 Sample concentration using CF:

$$Conc\left(\frac{\mu g}{m^3}\right) = \frac{A_x}{(\overline{CF})(V_o)}$$

where :
A_x = peak area for compound being measured
$\overline{CF}$ =mean calibration factor for compound being measured
V_o = volume of air collected in L

The concentration of each analyte is calculated using Agilent MSD ChemStation software using an average response factor or linear regression curve as established in Section 13 of this SOP. Response factors and analyte concentrations are calculated by the equations below when internal standards are used:

12.6 Relative response factor (RRF):

$$RRF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

where:
A_x = Area of the quantitation ion for the surrogate or compound being measured.
A_{is} = Area of the quantitation ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard.
C_x = Concentration of the compound being measured.

12.7 Average RRF $\left(\overline{RRF}\right)$:

$$\overline{RRF} = \frac{\sum_{1}^{n} RRF}{n}$$

where,
n = number of initial calibration standards

12.8 Percent relative standard deviation (%RSD):

$$\%RSD = \left(\frac{s}{\bar{x}}\right)100$$

where:

$\bar{x} = \overline{RRF}$: $\overline{RRF} = \frac{\sum_{1}^{n} RRF}{n}$

s = standard deviation: $s = \sqrt{\frac{\left(\sum_{i=0}^{n}(\bar{x}-x_i)^2\right)}{n-1}}$

12.9 Sample concentration using RRF:

$$C(ppbv) = \frac{I_s A_x}{\overline{RRF} A_{Is} V_o}$$

where :
A_x = area of quantitation ion for compound being measured
I_s = amount of internal standard injected onto the tube (nL)
A_{is} = area of quantitation ion for the internal standard
$\overline{RRF}$ = mean relative response factor for compound being measured
V_o = volume of air sampled on the tube (L) accounting for dilutions

12.10 Percent recovery for CCV, and, LCS are calculated using the following equation:

$$\%R = \left[\frac{\left(C_{spk} - C_x\right)}{C_t}\right]100$$

where:
C_{spk} = the concentration of the analyte in the spiked sample
C_x = the concentration of the analyte in the reference (parent) sample;
(C_x = 0 for CCV and LCS.)
C_t = the theoretical spike concentration.

12.11 Relative percent difference for duplicate is calculated using the following equation:

$$RPD = \left[\frac{\left|C_1 - C_2\right|}{\left(C_1 + C_2\right)/2}\right]100$$

where:
C_1 = concentration of the first sample
C_2 = concentration of the second sample

13.0 Method Performance

13.1 MDL's are analyzed on an annual basis. Lab Accuracy and Precision data are used to calculate lab specific acceptance criteria. Precision and Accuracy data are recalculated and evaluated every six months. Limit acceptance criteria will be established no tighter than 50 % to 150 %. Precision and Accuracy data and acceptance limits will be evaluated based on ongoing QC produced over time.

Other specific Quality Assurance Objectives (QAO) may be found in the appropriate statement-of-work or Quality Assurance Project Plan (QAPP) for specific projects.

13.2 Analytical data generated by the instrument software is reviewed and evaluated by the analyst as follows:

13.2.1 BFB, instrument calibration, calibration verifications, IS/SS, QC measures are evaluated and the results documented on the separate forms:

13.2.2 The tune evaluation of BFB.

13.2.3 The instrument calibration relative response factors and percent relative standard deviations.

13.2.4 QA-QC check report for internal standard area counts and percent recoveries for the surrogates.

13.2.5 Analyze percent recoveries for the SCV, CCV, LCS, and % RPD for the sample duplicate.

13.2.6 In order for the analytical data to be acceptable, the calibration standards and quality control measures must meet the criteria listed in Sections 12 and 13 of this SOP.

13.2.7 All false positives are Q-Deleted, and all positively identified target analytes are reported to LIMS.

13.3 Manual integration is applied in cases when the instrument data processing software produces integrated areas that are not valid. The manual adjustments to the chromatographic peak must be performed in a consistent manner for the calibration standards, QC and field samples.

Manual integration should not be substituted for proper maintenance of the instrument or setup of the method (e.g. retention time updates), integration parameter files, etc.

The analyst should seek to minimize manual integrations by proper instrument maintenance, retention time updates, and configuring peak integration parameters.

13.4 If the QAPP requires it, chromatograms of all field samples are examined to detect additional peaks, which were not identified as target analytes. If such peaks are present, generate a Library Search Report and report a tentatively identified compound (TIC) if the percent match is greater than the 50%. The Lead Chemist should be notified immediately in that case.

13.5 Anytime the analyst alters the instrument generated quantitation report, the hardcopies of both reports (original and analyst corrected) must be retained (e.g., manual integration). The altered report must be initialed and dated with a reason for altering.

13.6 Discrepancies in the analytical run are described in “QC Summary Form” and discussed with the Lead Chemist.

13.7 Reviewed data is entered into LIMS, hard copies of LIMS report is printed and compared to the original data.

13.8 All records derived from the analytical process are assembled in the analytical data packages that consist of:

13.8.1 LIMS work list.

13.8.2 Analytical run sheet.

13.8.3 BFB tune evaluation report.

13.8.4 QA-QC check report.

13.8.5 Quantitation Report for each Sample and QCS.

13.8.6 Evaluation reports for CCV, SCV, LCS and Initial calibration form.

13.9 Data is stored on the server and is backed up.

13.10 In cases where quality control measures do not meet acceptance criteria, the quality of the analytical data is not acceptable and the analyst does the following:

13.10.1 When tuning and instrument calibration fail to meet acceptance criteria, the analysis does not start. The problem is investigated and the necessary instrument maintenance is performed, followed with tuning and calibration.

13.10.2 If the acceptance criteria listed in Table 4 of this SOP are not met for MB, CCV, FB, LCS/LCSD, ICV, internal standards, and surrogates, the affected QCs and associated samples should be treated as per laboratory or QAPP protocols.

13.10.3 If after analysis, any of the criteria for quality control are not met, or the sample is not available for reanalysis, the analyst must notify the Lead Chemist. The Lead Chemist will implement the corrective action plan.

13.11 The analyst shall report to the Lead Chemist and indicate on the "QC Summary form" any out of control event. Such events include:

13.11.1 Damage to the sample.

13.11.2 Holding time exceeded.

13.11.3 Inadequate sample preservation.

13.11.4 Sample results exceeds the Agency's action limit

13.11.5 Samples do not reflect historical data.

13.11.6 Upward trending or sample results approaching interval warning limits.

13.11.7 Any non-target analyte peak present on the instrument generated chromatogram, if required.

13.12 The Lead Chemist will implement the corrective action plan described in the PHILIS corrective action plan document or the associated SAPP.

13.13 Contingencies for Handling Out of Control or Unacceptable Data

See the QAPP that the samples were analyzed under for guidance.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. The EPA places pollution prevention as the management option of first choice with regard to laboratory waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 The Environmental Protection Agency requires that laboratory waste management practices be compliant with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult the PHILIS Chemical Hygiene Plan.

14.3 The waste produced from EPA Method TO-17 consists of waste collected from excess sample, standards (stock mixes, PDS, WS), and methanol.

14.4 Excess reagents are disposed following the MSDS instructions or the site waste disposal plan.

14.5 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036.

15.0 Waste Management

Waste management procedures are specified in the Hazardous Waste Management Plan.

16.0 References

16.1 EPA Method TO-15, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, January, 1999.

16.2 EPA Method TO-17, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, January, 1999.

17.0 Tables, Figures, and Attachments

Table 1. Title III Clean Air Act Amendment Compounds and Characteristic Masses (M/Z) Used for Quantifying

Compound	CAS#	Primary Ion	Secondary Ion
Methyl chloride (chloromethane); CH3Cl	74-87-3	50	52
Carbonyl sulfide; COS	463-S8-1	60	62
Vinyl chloride (chloroethene); C2H3Cl	7S-01-4	62	64
Diazomethane; CH2N2	334-88-3	42	41
Formaldehyde; CH2O	50-00-0	29	30
1,3-Butadiene; C4H6	106-99-0	39	54
Methyl bromide (bromomethane); CH3Br	74-83-9	94	96
Phosgene; CCl2O	75-44-5	63	65
Vinyl bromide (bromoethene); C2H3Br	593-60-2	106	108
Ethylene oxide; C2H4O	75-21-8	29	44
Ethyl chloride (chloroethane); C2H5Cl	75-00-3	64	66
Acetaldehyde (ethanal); C2H4O	75-07-0	44	29, 43
Vinylidene chloride (1,1-dichloroethylene);	75-35-4	61	96
Propylene oxide; C3H6O	75-56-9	58	57
Methyl iodide (iodomethane); CH3I	74-88-4	142	127
Methylene chloride; CH2Cl2	75-09-2	49	84, 86
Methyl isocyanate; C2H3NO	624-83-9	57	56
Allyl chloride (3-chloropropene); C3H5Cl	107-05-1	76	41, 78
Carbon disulfide; CS2	75-15-0	76	44, 78
Methyl tert-butyl ether; C5H12O	1634-04-4	73	41, 53
Propionaldehyde; C2H5CHO	123-38-6	58	29, 57
Ethylidene dichloride (1,1-dichloroethane);	75-34-3	63	65, 27
Chloroprene (2-chloro-1,3-butadiene);	126-99-8	88	53, 90
Chloromethyl methyl ether; C2H5ClO	107-30-2	45	29, 49
Acrolein (2-propenal); C3H4O	107-02-8	56	55
1,2-Epoxybutane (1,2-butylene oxide);	106-88-7	42	41, 72
Chloroform; CHCl3	67-66-3	83	85, 47
Ethyleneimine (aziridine); C2H5N	151-56-4	42	43
1,1-Dimethylhydrazine; C2H8N2	57-14-7	60	45, 59
Hexane; C6H14	110-54-3	57	41, 43
1,2-Propyleneimine (2-methylazindine);	75-55-8	56	57, 42
Acrylonitrile (2-propenenitrile); C3H3N	107-13-1	53	52
Methyl chloroform (1,1,1 trichloroethane);	71-55-6	97	99, 61
Methanol; CH4O	67-56-1	31	29
Carbon tetrachloride; CCl4	56-23-5	117	119

Compound	CAS#	Primary Ion	Secondary Ion
Vinyl acetate; C4H6O2	108-05-4	43	86
Methyl ethyl ketone (2-butanone); C4H8O	78-93-3	43	72
Benzene; C6H6	71-43-2	78	77,50
Acetonitrile (cyanomethane); C2H3N	75-05-8	41	40
Ethylene dichloride (1,2-dichloroethane);	107-06-2	62	64, 27
Triethylamine; C6H15N	121-44-8	86	58, 101
Methylhydrazine; CH6N2	60-34-4	46	31, 45
Propylene dichloride (1,2-dichloropropane);	78-87-5	63	41, 62
2,2,4-Trimethyl pentane; C8H18	540-84-1	57	41, 56
1,4-Dioxane (1,4 Diethylene oxide);	123-91-1	88	58
Bis(chloromethyl) ether; C2H4Cl2O	542-88-1	79	49, 81
Ethyl acrylate; C5H8O2	140-88-5	55	73
Methyl methacrylate; C5H8O2	80-62-6	41	69, 100
1,3-Dichloropropene; C3H4Cl2 (cis)	542-75-6	75	39, 77
Toluene; C7H8	108-88-3	91	92
Trichloethylene; C2HCl3	79-01-6	130	132, 95
1,1,2-Trichloroethane; C2H3Cl3	79-00-5	97	83, 61
Tetrachloroethylene; C2Cl4	127-18-4	166	164, 131
Epichlorohydrin (l-chloro-2,3-epoxy	106-89-8	57	49, 62
Ethylene dibromide (1,2-dibromoethane);	106-93-4	107	109
N-Nitrso-N-methylurea; C2H5N3O2	684-93-5	60	44, 103
2-Nitropropane; C3H7NO2	79-46-9	43	41
Chlorobenzene; C6H5Cl	108-90-7	112	77, 114
Ethylbenzene; C8H10	100-41-4	91	106
Xylenes (isomer & mixtures); C8H10	1330-20-7	91	106
Styrene; C8H8	100-42-5	104	78, 103
p-Xylene; C8H10	106-42-3	91	106
m-Xylene; C8H10	108-38-3	91	106
Methyl isobutyl ketone; C6H12O	108-10-1	43	58, 100
Bromoform (tribromomethane); CHBr3	75-25-2	173	171, 175
1,1,2,2-Tetrachloroethane; C2H2Cl4	79-34-5	83	85
o-Xylene; C8H10	95-47-6	91	106
Dimethylcarbamyl chloride; C3H6ClNO	79-44-7	72	107
N-Nitrosodimethylamine; C2H6N2O	62-75-9	74	42
Beta-Propiolactone; C3H4O2	57-57-8	42	43
Cumene (isopropylbenzene); C9H12	98-82-8	105	120
Acrylic acid; C3H4O2	79-10-7	72	45, 55
N,N-Dimethylformamide; C3H7NO	68-12-2	73	42, 44

Compound	CAS#	Primary Ion	Secondary Ion
1,3-Propane sultone; C3H6O3S	1120-71-4	58	65, 122
Acetophenone; C8H8O	98-86-2	105	77,120
Dimethyl sulfate; C2H6O4S	77-78-1	95	66,96
Benzyl chloride (a-chlorotoluene); C7H7Cl	100-44-7	91	126
1,2-Dibromo-3-chloropropane; C3H5Br2Cl	96-12-8	57	155, 157
Bis(2-Chloroethyl)ether; C4H8Cl2O	111-44-4	93	63, 95
Chloroacetic acid; C2H3ClO2	79-11-8	50	45, 60
Aniline (aminobenzene); C6H7N	62-53-3	93	66
1,4-Dichlorobenzene (p-); C6H4Cl2	106-46-7	146	148, 111
Ethyl carbamate (urethane); C3H7NO2	51-79-6	31	44, 62
Acrylamide; C3H5NO	79-06-1	44	55, 71
N,N-Dimethylaniline; C8H11N	121-69-7	120	77, 121
Hexachloroethane; C2Cl6	67-72-1	201	199, 203
Hexachlorobutadiene; C4Cl6	87-68-3	225	227, 223
Isophorone; C9H14O	78-59-1	82	138
N-Nitrosomorpholine; C4H8N2O2	59-89-2	56	86, 116
Styrene oxide; C8H8O	96-09-3	91	120
Diethyl sulfate; C4H10O4S	64-67-5	45	59, 139
Cresylic acid (cresol isomer mixture);	1319-77-3		
o-Cresol; C7H8O	95-48-7	108	107
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	110	64
Phenol; C6H6O	108-95-2	94	66
1,2,4-Trichlorobenzene; C6H3Cl3	120-82-1	180	182, 184
Nitrobenzene; C6H5NO2	98-95-3	77	51, 123
Naphthalene	91-20-3	128	

Table 2. Example of Preparation of Working Standards

Working Standard Name	Vol Gas Std Primary Lot (mL)	Vol Gas Std. Alt Lot (mL)	Amt spiked (nL)	Conc. In 1L air (ppbv)
L1	0.50	x	0.50	0.50
L2	1.00	x	1.00	1.00
L3	2.00	x	2.00	2.00
L4	5.00	x	5.00	5.00
L5	10.0	x	10.0	10.0
L6	25.0	x	25.0	25.0
L7	50.0	x	50.0	50.0
CCV	5.00	x	5.00	5.00
LCS	X	5.00	5.00	5.00

Table 3. Example Precision and Accuracy for Six 5nl injections Into Markes Universal TD Tubes Using APL01A

EPA Method TO-17: Precision and Accuracy Data for APL01A

Prep Date: 10/03/17
Analysis Date: 10/03/17
Analyst: Kevin Makuskie
Matrix: Air
Limits: Mean Recovery 50 to 150%, RSD ≤= 20% MTBE ≤= 30%
Batch: E7J0303
Preparation: LCS 10ml E17D115 injected over 30 seconds into Universal Tube. Nitrogen turned on after injection and run at 100ml/min for 1minute.

Instrument: **APL01A**

Analyte	Data Files:	1A100317017.D	1A100317018.D	1A100317019.D	1A100317020.D	1A100317021.D	1A100317022.D	Mean Amt. (nl)	Mean Recovery (%)	STDEV	Precision as RSD (%)
	Spiked Amt. (nl)	LCS 1 (nl)	LCS 2 (µnl)	LCS3 (nl)	LCS 4 (nl)	LCS 5 (nl)	LCS 6 (nl)				
Propene	10.0	9.27	9.29	9.20	9.44	8.94	9.32	9.2	92.4	0.1	1.1
Dichlorodifluoromethane	10.0	9.41	9.54	9.28	9.53	9.24	9.31	9.4	93.9	0.1	1.3
Freon 114	10.0	9.29	9.79	9.31	9.47	9.39	9.16	9.4	94.0	0.2	2.5
Chloromethane	10.0	11.18	9.78	12.04	10.80	8.80	11.10	10.6	106.2	0.9	8.8
1,3-Butadiene	10.0	10.72	9.12	10.80	10.36	8.73	10.62	10.1	100.6	0.8	7.7
Vinyl chloride	10.0	9.64	9.79	9.62	9.50	9.38	9.55	9.6	95.8	0.1	1.2
Chloroethane	10.0	9.88	9.63	9.99	9.66	8.64	9.66	9.6	95.8	0.2	1.8
Trichlorofluoromethane	10.0	9.43	9.58	9.30	9.46	9.03	9.04	9.3	93.1	0.1	1.2
1,1-Dichloroethene	10.0	9.53	9.45	9.29	9.52	9.30	9.14	9.4	93.7	0.1	1.2
Freon 113	10.0	9.46	10.90	9.41	9.48	9.15	9.08	9.6	95.8	0.7	7.6
Acrolein	10.0	10.14	9.95	9.72	10.11	9.29	9.53	9.8	97.9	0.2	2.0
Isopropyl alcohol	10.0	9.50	10.12	9.25	9.03	9.65	8.40	9.3	93.3	0.5	5.1
Methylene Chloride	10.0	9.21	9.05	9.07	9.16	8.85	8.92	9.0	90.4	0.1	0.8
Acetone	10.0	9.56	8.98	9.36	9.64	8.54	9.30	9.2	92.3	0.3	3.2
trans-1,2-Dichloroethene	10.0	9.58	9.68	9.51	9.58	9.30	9.17	9.5	94.7	0.1	0.7
Hexane	10.0	9.53	10.37	9.32	9.68	10.11	9.45	9.7	97.4	0.5	4.7
Methyl tert-butyl Ether	10.0	9.10	14.79	9.13	9.29	15.93	11.29	11.6	115.9	2.8	24.2
1,1-Dichloroethane	10.0	9.75	9.36	9.68	9.72	9.40	9.37	9.5	95.5	0.2	1.9
Vinyl acetate	10.0	9.97	9.70	9.80	9.82	9.41	9.63	9.7	97.2	0.1	1.1
cis-1,2-Dichloroethene	10.0	9.61	9.67	9.48	9.66	9.29	9.28	9.5	95.0	0.1	0.9
Cyclohexane	10.0	9.47	9.67	9.19	9.48	9.14	9.15	9.4	93.5	0.2	2.1
Chloroform	10.0	9.69	9.37	9.48	9.74	9.36	9.29	9.5	94.9	0.2	1.8
Carbon Tetrachloride	10.0	9.75	9.86	9.85	10.13	9.23	9.66	9.7	97.5	0.2	1.7
Tetrahydrofuran	10.0	9.86	9.63	9.48	9.62	9.46	9.28	9.6	95.6	0.2	1.6
Ethyl Acetate	10.0	9.67	9.49	9.49	9.67	9.25	9.15	9.5	94.5	0.1	1.1
1,1,1-Trichloroethane	10.0	9.70	9.31	9.50	9.66	9.42	9.35	9.5	94.9	0.2	1.9
2-Butanone	10.0	9.93	9.47	9.55	9.59	9.54	9.67	9.6	96.3	0.2	2.1
Heptane	10.0	9.72	9.74	9.52	9.99	9.35	9.44	9.6	96.3	0.2	2.0
Benzene	10.0	9.41	9.36	9.09	9.46	9.11	9.00	9.2	92.4	0.2	1.8
1,2-Dichloroethane	10.0	9.80	9.62	9.50	9.76	9.42	9.17	9.5	95.5	0.1	1.4
Trichloroethene	10.0	9.56	9.49	9.34	9.55	9.08	9.13	9.4	93.6	0.1	1.1

Analyte	Data Files:	1A100317017.D	1A100317018.D	1A100317019.D	1A100317020.D	1A100317021.D	1A100317022.D	Mean Amt. (nl)	Mean Recovery (%)	STDEV	Precision as RSD (%)
	Spiked Amt. (nl)	LCS 1 (nl)	LCS 2 (µnl)	LCS3 (nl)	LCS 4 (nl)	LCS 5 (nl)	LCS 6 (nl)				
1,2-Dichloropropane	10.0	9.86	8.96	9.60	9.55	9.05	9.34	9.4	93.9	0.4	4.0
Bromodichloromethane	10.0	9.81	9.09	9.75	9.77	9.20	9.45	9.5	95.1	0.3	3.6
1,4-Dioxane	10.0	9.27	8.39	9.32	9.10	9.05	8.94	9.0	90.1	0.4	4.8
Methyl Methacrylate	10.0	10.29	9.23	10.02	10.00	9.55	9.75	9.8	98.1	0.5	4.7
cis-1,3-Dichloropropene	10.0	10.20	9.24	9.86	9.92	9.44	9.61	9.7	97.1	0.4	4.2
4-Methyl-2-pentanone	10.0	10.56	9.50	10.06	9.95	9.82	9.93	10.0	99.7	0.4	4.4
Toluene	10.0	10.07	9.27	9.79	9.88	9.21	9.51	9.6	96.2	0.3	3.6
trans-1,3-Dichloropropene	10.0	11.06	9.91	10.74	10.72	9.94	10.36	10.5	104.6	0.5	4.7
1,1,2-Trichloroethane	10.0	10.35	9.47	10.08	10.03	9.39	9.76	9.8	98.5	0.4	3.8
Tetrachloroethene	10.0	10.26	9.29	9.78	9.80	9.22	9.48	9.6	96.4	0.4	4.1
2-Hexanone	10.0	11.36	9.97	11.07	10.96	10.60	10.83	10.8	108.0	0.6	5.6
Dibromochloromethane	10.0	10.38	9.54	10.10	10.13	9.44	9.68	9.9	98.8	0.4	3.6
1,2-Dibromoethane	10.0	10.56	9.57	10.24	10.21	9.75	9.95	10.0	100.5	0.4	4.1
Chlorobenzene	10.0	10.40	9.31	9.90	9.88	9.36	9.73	9.8	97.6	0.4	4.6
Ethylbenzene	10.0	10.39	9.33	9.82	10.19	9.07	9.78	9.8	97.6	0.5	4.8
m,p-Xylene	20.0	20.86	18.59	19.71	20.50	18.17	19.47	19.6	97.8	1.0	5.1
o-Xylene	10.0	10.42	9.22	9.79	10.10	8.94	9.67	9.7	96.9	0.5	5.3
Styrene	10.0	11.23	9.84	10.57	10.85	9.59	10.52	10.4	104.3	0.6	5.6
Bromoform	10.0	10.45	9.26	9.81	10.01	9.09	9.68	9.7	97.2	0.5	5.1
1,1,2,2-Tetrachloroethane	10.0	10.91	9.52	10.10	10.50	9.33	10.19	10.1	100.9	0.6	5.9
4-Ethyltoluene	10.0	11.01	9.55	10.07	10.54	9.49	10.29	10.2	101.6	0.6	6.2
1,3,5-Trimethylbenzene	10.0	10.63	9.23	9.82	10.25	9.22	9.96	9.9	98.5	0.6	6.1
1,2,4-Trimethylbenzene	10.0	10.78	9.34	9.89	10.37	9.39	10.17	10.0	99.9	0.6	6.2
1,3-Dichlorobenzene	10.0	11.47	9.64	10.28	10.69	9.80	10.76	10.4	104.4	0.8	7.3
1,4-Dichlorobenzene	10.0	11.44	9.53	10.19	10.70	9.75	10.48	10.3	103.5	0.8	7.8
Benzyl Chloride	10.0	11.82	9.84	10.68	10.93	10.13	10.99	10.7	107.3	0.8	7.6
1,2-Dichlorobenzene	10.0	11.25	9.30	9.99	10.51	9.56	10.59	10.2	102.0	0.8	8.1
Hexachlorobutadiene	10.0	11.63	9.46	9.95	11.19	10.27	11.60	10.7	106.8	1.0	9.6
1,2,4-Trichlorobenzene	10.0	12.09	9.67	10.36	11.38	10.67	11.99	11.0	110.3	1.1	9.7
Naphthalene	10.0	12.53	9.94	10.74	11.65	10.98	12.41	11.4	113.8	1.1	9.9

Table 4. TO-17 Method Criteria

Item	Measure	Action
Instrument Tune	Outside Acceptance Criteria	Re-tune.
	Repeated failure indicates a need for system maintenance.	Perform system maintenance and re-tune the instrument. No analyses should be performed until the system is tuned correctly.
Internal Standard(s)—(IS) Optional	± 40 % of the average of the most recent initial calibration	If the nonconformance is on a calibration or QC sample, evaluate the system (repair) and reanalyze. Remake the standard if an error is suspected.
		If the nonconformance is on a field sample, reanalyze. If the reanalysis is within limits, report the results within limits. If the reanalysis is outside limits, dilute and reanalyze. Report the diluted results.
Internal Standard(s)—(IS) Optional	Retention times of the internal standards may not vary more than ± 20 seconds from the ICAL average retention time.	Evaluate the system for leaks or other problems. Affected samples must be reanalyzed.
Initial Calibration (ICAL) for both internal and external calibration	Average Response Factor > 30.0 % RSD. Recalculation of low and midpoint of the curve must return an accuracy of 70-130% of the true value for regression fits.	Evaluate points in the curve for use of linear or quadratic regression (r2 must be ≥ 0.99). Also evaluate upper and lower points for removal. Criteria still not met, recalibrate if compound is an analyte of interest.
Initial Calibration Verification	Not within ± 30% of true value for deviation or drift	Reanalyze and or recalibrate if % deviation or drift is not met and the compound is an analyte of interest.
Continuing Calibration Verification	Not within ± 30% of true value for deviation or drift.	Reanalyze and or recalibrate if % deviation or drift is not met and the compound is an analyte of interest
Method Blank and closing Method blank	Analyte(s) at or above reporting limit	If the associated samples are non-detect, no action is required. If the analyte(s) is detected in the sample, flag with a "b" or reanalyze. If the analyte level in the sample is 10 times or greater than the blank contamination, the results are not affected. Locate the source of the contamination.
Laboratory Control Spike (LCS)	% Recovery ± 50 %	If the LCS % Recovery is high and the sample is non detect, no action is required. If the LCS is high and the sample has detects, reanalyze the sample. If the LCS is low, the sample(s) should be reanalyzed.
Surrogate(s) Optional	% Recovery. Laboratory acceptance criteria are evaluated every six months. Acceptable values are stored in LIMS.	If the % Recovery is outside laboratory acceptance criteria on a QC sample, evaluate the system. Surrogate recalibration may be necessary. Reanalyze the QC samples.
		If the % Recovery is on a client sample, reanalyze. If the % Recovery is within criteria, report the sample within limits. If the % Recovery outside criteria is confirmed, there is a matrix effect. Flag the results as estimated and report both results.
Laboratory Duplicate (LD)	Acceptance criteria is 20% for RPD	If the RPD value is above 20%, then evaluate the system for possible problems. Reanalyze samples as necessary.
Field blank	Analyte(s) at or above reporting limit	If the associated samples are non-detect, no action is required. If the analyte(s) is detected in the sample then notify the client and flag the any results associated with false positive with “b” in final report

Table 5. Example Compound List and MDL Results from Seven 0.5nl Spikes onto Markes Universal TD Tubes Using APL01

Analyte	CAS #	RL (ppbv)*	Calculated MDL (ppbv)*	Precision as RSD (%)
Propene	115-07-1	0.5	0.10	5.1
Dichlorodifluoromethane	75-71-8	0.5	0.08	5.1
Freon 114	76-14-1	0.5	0.1	4.4
Chloromethane	74-87-3	0.5	0.2	11.4
1,3-Butadiene	106-99-0	0.5	0.1	5.8
Vinyl Chloride	75-01-4	0.5	0.10	6.5
Bromomethane	74-83-9	0.5	0.41	24.8
Chloroethane	75-00-3	1.0	0.28	16.7
Trichlorofluoromethane	75-69-4	0.5	0.08	5.0
1,1-Dichloroethene	75-34-4	0.5	0.09	6.1
Acrolein	107-02-8	0.5	0.18	10.6
Freon 113	76-13-1	0.5	0.10	6.8
Isopropyl alcohol	67-63-0	0.5	0.17	11.8
Methylene Chloride	75-09-2	1.0	0.47	22.0
Acetone	67-64-1	0.5	0.29	13.3
trans-1,2-Dichloroethene	156-60-5	0.5	0.14	10.3
Hexane	110-54-3	0.5	0.15	11.1
Methyl tert-butyl ether	1634-04-4	0.5	0.33	32.1
1,1-Dichloroethane	75-34-3	0.5	0.10	6.8
Vinyl acetate	108-05-4	0.5	0.2	13.3
cis-1,2-Dichloroethene	156-59-2	0.5	0.12	8.3
Cyclohexane	110-82-7	0.5	0.10	7.3
Chloroform	67-66-3	0.5	0.13	9.1
Carbon Tetrachloride	56-23-5	0.5	0.11	8.0
Tetrahydrofuran	109-99-9	0.5	0.24	18.0
Ethyl acetate	141-78-6	0.5	0.20	15.5
1,1,1-Trichloroethane	71-55-6	0.5	0.13	9.5
2-butanone	78-93-3	0.5	0.13	9.5
Heptane	14-82-5	0.5	0.13	10.1
Benzene	71-43-2	0.5	0.16	12.0
1,2-Dichloroethane	107-06-2	0.5	0.15	10.3

Analyte	CAS #	RL (ppbv)*	Calculated MDL (ppbv)*	Precision as RSD (%)
Trichloroethene	79-01-6	0.5	0.13	10.1
1,2-Dichloropropane	78-87-5	0.5	0.18	12.6
Bromodichloromethane	75-27-4	0.5	0.14	11.1
1,4-Dioxane	123-91-1	0.5	0.27	18.6
Methyl methacylate	80-62-6	0.5	0.19	15.7
cis-1,3-Dichloropropene	10061-01-5	0.5	0.17	14.1
4-Methyl-2-pentanone	108-10-1	0.5	0.19	14.8
Toluene	108-88-3	0.5	0.18	13.8
trans-1,3-Dichloropropene	10061-02-6	0.5	0.20	18.2
1,1,2-Trichloroethane	79-00-5	0.5	0.19	14.8
Tetrachloroethene	127-18-4	0.5	0.15	11.6
2-Hexanone	591-78-6	0.5	0.24	18.3
Dibromochloromethane	124-48-1	0.5	0.14	12.5
1,2-Dibromoethane	106-93-4	0.5	0.17	14.4
Chlorobenzene	108-90-7	0.5	0.17	13.7
Ethylbenzene	100-41-4	0.5	0.18	14.2
m,p-Xylene	106-42-3	1.0	0.33	13.3
o-Xylene	95-47-6	0.5	0.20	14.7
Styrene	100-42-5	0.5	0.14	13.5
Bromoform	75-25-2	0.5	0.13	7.0
1,1,2,2-Tetrachloroethane	79-34-5	0.5	0.18	14.4
4-Ethyltoluene	622-96-8	0.5	0.19	16.2
1,3,5-Trimethylbenzene	108-67-8	0.5	0.19	14.6
1,2,4-Trimethylbenzene	95-63-6	0.5	0.22	16.9
1,3-Dichlorobenzene	541-73-1	0.5	0.22	18.6
1,4-Dichlorobenzene	106-46-7	0.5	0.21	18.4
Benzyl Chloride	100-44-7	0.5	0.19	9.9
1,2-Dichlorobenzene	95-90-41	0.5	0.17	13.3
Hexachlorobutadiene	87-68-3	0.5	0.27	20.3
1,2,4-Trichlorobenzene	120-82-1	0.5	0.27	18.9
Naphthalene	91-20-3	0.5	0.32	22.4

*Based on a one Liter sample volume.

Table 6. BFB Relative Abundance Criteria (From EPA Method TO 17)

BFB Relative Abundance Criteria	
m/z	**Relative Abundance Criteria**
50	8 to 40 % of 95
75	30 to 66% of 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of 95
173	<2% of 174
174	50 to 100% of 95
175	4 to 9% of 174
176	93 to 101% of 174
177	5 to 9% of 176

Figure 1. Compendium Method TO-17
Field Test Data Sheet (FTDS)

VOCs — Method TO-17

COMPENDIUM METHOD TO-17
FIELD TEST DATA SHEET (FTDS)

I. GENERAL INFORMATION

PROJECT:_____ DATE(S) SAMPLED:_____
SITE:_____ TIME PERIOD SAMPLED:_____
LOCATION:_____ OPERATOR:_____
INSTRUMENT MODEL NO.:_____ CALIBRATED BY:_____
PUMP SERIAL NO.:_____ RAIN: ____YES _____NO

ADSORBENT CARTRIDGE INFORMATION:

	Tube 1	Tube 2
Type:		
Adsorbent:		
Serial No.:		
Sample No.:		

II. SAMPLING DATA

Tube Identification	Sampling Location	Ambient Temp., °F	Ambient Pressure, in Hg	Flow Rate (Q), mL/min		Sampling Period		Total Sampling Time, min.	Total Sample Volume, L
				Tube 1	Tube 2	Start	Stop		

III. FIELD AUDIT

	Tube 1	Tube 2
Audit Flow Check Within 10% of Set Point (Y/N)?	_ pre- / post-	_ pre- / post-

CHECKED BY:_____
DATE:_____

Figure 1. Compendium Method TO-17 Field Test Data Sheet.

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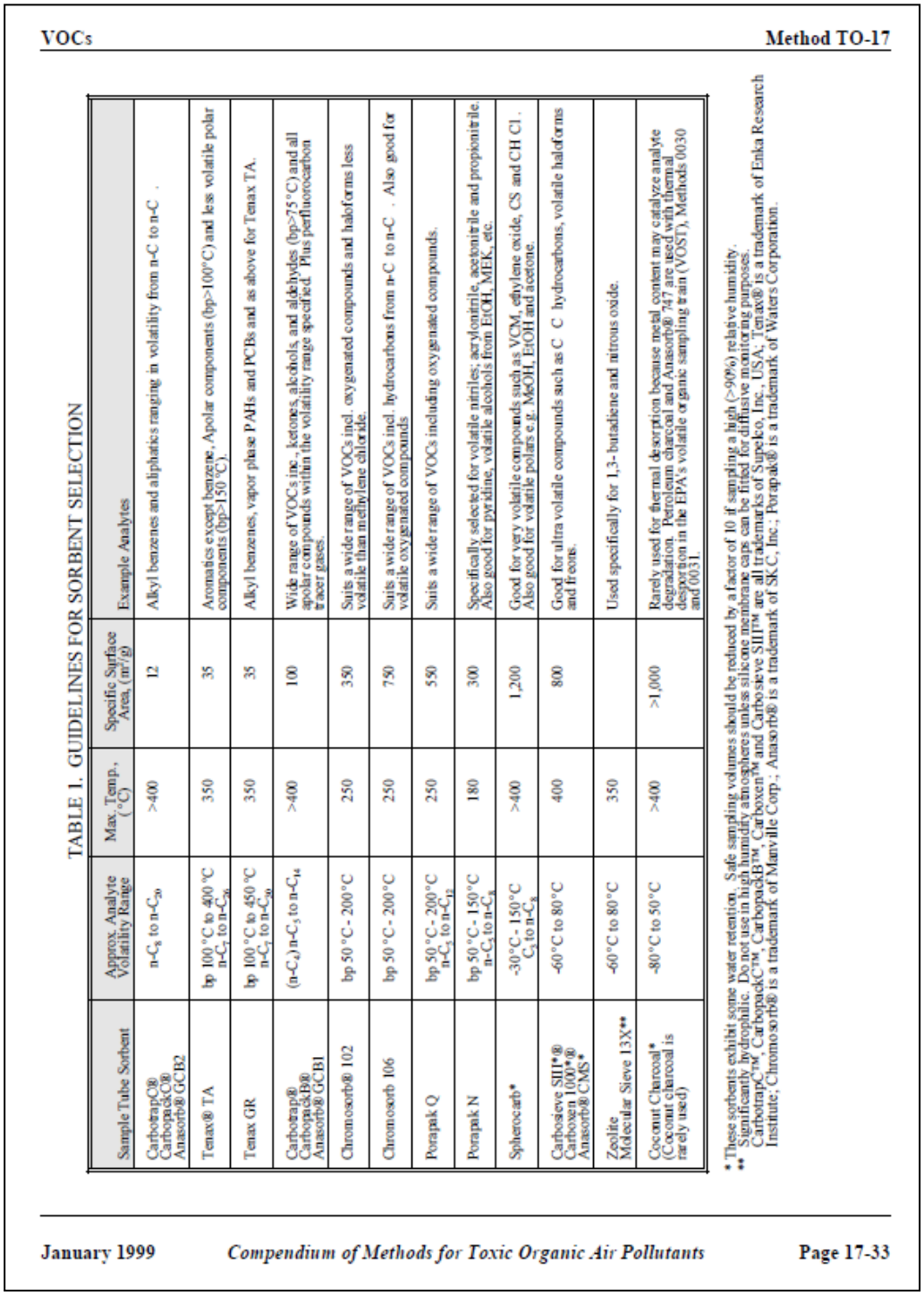
Figure 2. Guidelines for Sorbent Selection



VOCs — Method TO-17

TABLE 1. GUIDELINES FOR SORBENT SELECTION

Sample Tube Sorbent	Approx. Analyte Volatility Range	Max. Temp., (°C)	Specific Surface Area, (m^2/g)	Example Analytes
Carbotrap®C® CarbopackC® Anasorb® GCB2	n-C_4 to n-C_{20}	>400	12	Alkyl benzenes and aliphatics ranging in volatility from n-C to n-C .
Tenax® TA	bp 100 °C to 400 °C n-C_7 to n-C_{30}	350	35	Aromatics except benzene, Apolar components (bp>100°C) and less volatile polar components (bp>150 °C).
Tenax GR	bp 100 °C to 450 °C n-C_7 to n-C_{30}	350	35	Alkyl benzenes, vapor phase PAHs and PCBs and as above for Tenax TA.
Carbotrap® CarbopackB® Anasorb® GCB1	(n-C_4) n-C_5 to n-C_{14}	>400	100	Wide range of VOCs inc. ketones, alcohols, and aldehydes (bp>75°C) and all apolar compounds within the volatility range specified. Plus perfluorocarbon tracer gases.
Chromosorb® 102	bp 50 °C - 200 °C	250	350	Suits a wider range of VOCs incl. oxygenated compounds and haloforms less volatile than methylene chloride.
Chromosorb 106	bp 50 °C - 200 °C	250	750	Suits a wider range of VOCs incl. hydrocarbons from n-C to n-C . Also good for volatile oxygenated compounds
Porapak Q	bp 50 °C - 200 °C n-C_5 to n-C_{12}	250	550	Suits a wider range of VOCs including oxygenated compounds.
Porapak N	bp 50 °C - 150 °C n-C_5 to n-C_8	180	300	Specifically selected for volatile nitriles; acrylonitrile, acetonitrile and propionitrile. Also good for pyridine, volatile alcohols from EtOH, MEK, etc.
Spherocarb*	-30°C - 150°C C_3 to n-C_8	>400	1,200	Good for very volatile compounds such as VCM, ethylene oxide, CS and CH Cl . Also good for volatile polars e.g. MeOH, EtOH and acetone.
Carbosieve SIII*® Carboxen 1000*® Anasorb® CMS*	-60 °C to 80 °C	400	800	Good for ultra volatile compounds such as C C hydrocarbons, volatile haloforms and freons.
Zeolite Molecular Sieve 13X**	-60°C to 80°C	350		Used specifically for 1,3- butadiene and nitrous oxide.
Coconut Charcoal* (Coconut charcoal is rarely used)	-80°C to 50°C	>400	>1,000	Rarely used for thermal desorption because metal content may catalyze analyte degradation. Petroleum charcoal and Anasorb® 747 are used with thermal desorption in the EPA's volatile organic sampling train (VOST), Methods 0030 and 0031.

* These sorbents exhibit some water retention. Safe sampling volumes should be reduced by a factor of 10 if sampling a high (>90%) relative humidity.
** Significantly hydrophilic. Do not use in high humidity atmospheres unless silicone membrane caps can be fitted for diffusive monitoring purposes.
CarbotrapC™, CarbopackC™, CarbopackB™, Carboxen™ and Carbosieve SIII™ are all trademarks of Supelco, Inc., USA; Tenax® is a trademark of Enka Research Institute; Chromosorb® is a trademark of Manville Corp., Anasorb® is a trademark of SKC, Inc., Porapak® is a trademark of Waters Corporation.

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Figure 3. Safe Sample Volumes

APPENDIX 1.

The following list includes safe sampling volume data generated by the UK Health and Safety Executive (4) on single sorbent bed 1/4 inch O.D. stainless steel tubes and compatible with a thermal desorption - capillary GC analytical procedure. It is provided as a resource to readers only. The recommendation for Tube Style 2 is based on the specific tube referenced in Section 6.1.2 and Table 3. Where tubes are not listed with safe sample volumes they have not been tested and their inclusion represents a suggestion only. Application to air sampling is subject to criteria listed in Section 14 of Compendium Method TO-17.

[Note: Combination tubes 1, 2, and 3 referenced in this Appendix are those adsorbent tubes described in Section 9.1.3.]

Compound	Suitable sorbents and SSV's where available
Hydrocarbons	
This procedure is suitable for all aliphatic, aromatic and cyclic hydrocarbons less volatile than ethane and more volatile than n-C20. These include:	
n-Butane	CS III, C 1000, Combination Tubes 2 or 3 or Spherocarb (SSV 820L).
n-Pentane	CS III, C 1000, Spherocarb (SSV 30,000L), Combination Tubes 2 or 3 or Chromosorb 106 (SSV 5.5L).
n-Hexane	Carbopack™ B, Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 30L).
Benzene	Carbopack™ B, Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 26L) or Tenax (SSV 6L).
n-Heptane	Carbopack™ B, Tenax (SSV 17L), Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 160L).
Toluene	Carbopack™ B, Tenax (SSV 38L), Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 80L).
n-Octane	Carbopack™ B, Tenax (SSV 700L) Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 1000L).
Ethylbenzene	Carbopack™ B, Tenax (SSV 180L), Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 360L).
all Xylenes	Carbopack™ B, Tenax (SSV 300L), Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 770L).
n-Nonane	Carbopack™ C/B, Tenax (SSV 700L), Combination Tubes 1, 2 or 3 or Chromosorb 106 (SSV 7000L).
Styrene	Carbopack™ C/B, Tenax (SSV 300L) or Combination Tubes 1, 2 or 3.
Isopropylbenzene	Carbopack™ C/B, Tenax (SSV 480L) or Combination Tubes 1, 2 or 3.
n-Propylbenzene	Carbopack™ C/B, Tenax (SSV 850L) or Combination Tubes 1, 2 or 3.
1-Methyl-3-ethylbenzene	Carbopack™ C/B, Tenax (SSV 1000L) or Combination Tubes 1, 2 or 3.
1-Methyl-4-ethylbenzene	Carbopack™ C/B, Tenax (SSV 1000L) or Combination Tubes 1, 2 or 3.

Compound	Suitable sorbents and SSV's where available
1,3,5-Trimethylbenzene	Carbopack™ C/B, Tenax (SSV 1800L), Combination Tubes 1, 2 or 3 or Chromosorb 106 (SSV 2800).
Methylstyrene	Carbopack™ C/B, Tenax (SSV 1200L) or Combination Tubes 1, 2 or 3.
Methyl-2-ethylbenzene	Carbopack™ C/B, Tenax (SSV 1000L) or Combination Tubes 1, 2 or 3.
1,2,4-Trimethylbenzene	Carbopack™ C/B, Tenax (SSV 1800L) or Combination Tubes 1, 2 or 3.
n-Decane	Carbopack™ C/B, Tenax (SSV 2100L), Combination Tubes 1, 2 or 3 or Chromosorb 106 (SSV 37,000L).
1,2,3-Trimethylbenzene	Carbopack™ C/B, Tenax (SSV 1800L) or Combination Tubes 1, 2 or 3.
n-Undecane	Carbopack™ C/B, Tenax (SSV 12,000L) or Combination Tubes 1, 2 or 3.
n-Dodecane	Carbopack™ C, Tenax (SSV 63,000L) or Combination Tubes 1 or 3.

Halogenated Hydrocarbons including PCBs

This procedure is suitable for all aliphatic, aromatic and cyclic halogenated hydrocarbons more volatile than n-C20. Examples include:

Dichloromethane	CS III, C 1000, Spherocarb (SSV 200L) or Combination Tubes 2 or 3.
1,2-Dichloroethane	CS III, C 1000, Spherocarb, Chrom. 106 (SSV 17L), Carbopack™ B, Tenax (SSV 5.4L) or Combination Tubes 1, 2 or 3.
1,1,1-Trichloroethane	Spherocarb (SSV 8,000L), Chrom. 106 (SSV 8L), Carbopack™ B, or Combination Tubes 1, 2 or 3.
Carbontetrachloride	Chrom. 106 (SSV 22L), Carbopack™ B, Tenax (SSV 6.2L) or Combination Tubes 1, 2 or 3.
Trichloroethylene	Chrom. 106, Carbopack™ B, Tenax (SSV 5.6L) or Combination Tubes 1, 2 or 3.
1,1,2-Trichloroethane	Chrom. 106, Carbopack™ B, Tenax (SSV 34L) or Combination Tubes 1, 2 or 3.
Tetrachloroethylene	Chrom. 106, Carbopack™ B, Tenax (SSV 48L) or Combination Tubes 1, 2 or 3.
Chlorobenzene	Chrom. 106, Carbopack™ B, Tenax (SSV 26L) or Combination Tubes 1, 2 or 3.
1,1,1,2-Tetrachloroethane	Chrom. 106, Carbopack™ B, Tenax (SSV 78L) or Combination Tubes 1, 2 or 3.
1,1,2,2-Tetrachloroethane	Chrom. 106, Carbopack™ B, Tenax (SSV 170L) or Combination Tubes 1, 2 or 3.

Compound	Suitable sorbents and SSV's where available
Alcohols	
This procedure is suitable for alcohols more volatile than n-C20 and sufficiently stable to be analyzed by conventional GC techniques. Examples include:	
Methanol	CSIII, C1000, Spherocarb (SSV 130L) or Combination Tubes 2 or 3.
Ethanol	CSIII, C1000, Spherocarb (SSV 3500L) or Combination Tubes 2 or 3.
n-Propanol	Porapak N (SSV 20L), Chrom 106 (SSV 8L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Isopropanol	Chrom 106 (SSV 44L), Carbopack™ B or Combination Tubes 1, 2 or 3.
n-Butanol	Chrom 106 (SSV 50L), Carbopack™ B, Porapak N (SSV 5L), Tenax (SSV 5L) or Combination Tubes 1, 2 or 3.
iso-Butanol	Chrom 106 (SSV 30L), Carbopack™ B, Tenax (SSV 2.8L) or Combination Tubes 1, 2 or 3.
Octanol	Tenax (SSV 1400L), Carbopack™ C or Combination Tubes 1 or 3.
Esters and Gycol Ethers	
This procedure is suitable for all esters and glycol ethers more volatile than n-C20 and sufficiently stable to be analyzed by conventional GC techniques. Examples include:	
Methylacetate	Chromosorb 106 (SSV 2.6L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Ethylacetate	Chromosorb 106 (SSV 20L), Carbopack™ B, Tenax (SSV 3.6L) or Combination Tubes 1, 2 or 3.
Propylacetate	Chromosorb 106 (SSV 150L), Carbopack™ B, Tenax (SSV 18L) or Combination Tubes 1, 2 or 3.
Isopropylacetate	Chromosorb 106 (SSV 75L), Carbopack™ B, Tenax (SSV 6L) or Combination Tubes 1, 2 or 3.
Butylacetate	Chromosorb 106 (SSV 730L), Carbopack™ B, Tenax (SSV 85L) or Combination Tubes 1, 2 or 3.
Isobutylacetate	Chromosorb 106 (SSV 440L), Carbopack™ B, Tenax (SSV 130L) or Combination Tubes 1, 2 or 3.
Methyl-t-butyl ether	Chromosorb 106 (SSV >6L), Carbopack™ B or Combination Tubes 1, 2 or 3.
t-Butylacetate	Chromosorb 106 (SSV 160L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Methylacrylate	Chromosorb 106, Carbopack™ B, Tenax (SSV 6.5L) or Combination Tubes 1, 2 or 3.

Compound	Suitable sorbents and SSV's where available
Ethylacrylate	Chromosorb 106, Carbopack™ B, Tenax (SSV 60L) or Combination Tubes 1, 2 or 3.
Methylmethacrylate	Chromosorb 106, Carbopack™ B, Tenax (SSV 27L) or Combination Tubes 1, 2 or 3.
Methoxyethanol	Chromosorb 106 (SSV 5L), Carbopack™ B, Tenax (SSV 3L) or Combination Tubes 1, 2 or 3.
Ethoxyethanol	Chromosorb 106 (SSV 75L), Carbopack™ B, Tenax (SSV 5L) or Combination Tubes 1, 2 or 3.
Butoxyethanol	Chromosorb 106, Carbopack™ B, Tenax (SSV 35L) or Combination Tubes 1, 2 or 3.
Methoxypropanol	Chromosorb 106, Carbopack™ B, Tenax (SSV 13L) or Combination Tubes 1, 2 or 3.
Methoxyethylacetate	Chromosorb 106 (SSV 860L), Carbopack™ B, Tenax (SSV 8L) or Combination Tubes 1, 2 or 3.
Ethoxyethylacetate	Chromosorb 106 (SSV 4000L), Carbopack™ B, Tenax (SSV 15L) or Combination Tubes 1, 2 or 3.
Butoxyethylacetate	Chromosorb 106, Carbopack™ B, Tenax (SSV 150L) or Combination Tubes 1, 2 or 3.

Aldehydes and Ketones

This procedure is suitable for all aldehydes and ketones more volatile than n-C20 and sufficiently stable to be analyzed using conventional GC techniques. Examples include:

Acetone	CSIII, C1000, Spherocarb, Chrom 106 (SSV 1.5L) or Combination Tubes 2 or 3.
Methylethylketone (2-butanone)	Chromosorb 106 (SSV 10L), Tenax (SSV 3.2L), Porapak N (SSV 50L) Carbopack™ B or Combination Tubes 1, 2 or 3.
n-Butanal	Chromosorb 106, Carbopack™ B, Porapak N (SSV 50L) or Combination Tubes 1, 2 or 3.
Methylisobutylketone	Chromosorb 106 (SSV 250L), Tenax (SSV 26L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Cyclohexanone	Chromosorb 106, Tenax (SSV 170L), Carbopack™ B or Combination Tubes 1, 2 or 3.
3,5,5-Trimethylcyclohex-2-enone	Tenax (SSV 5600L), Carbopack™ B or Combination Tubes 1 or 3.
Furfural	Tenax (SSV 300L), Carbopack™ B or Combination Tubes 1, 2 or 3.

Compound	Suitable sorbents and SSV's where available
Miscellaneous VOCs	
This procedure is suitable for the analysis of most VOCs in air. It is generally compatible with all organics less volatile than ethane, more volatile than n-C20 and sufficiently stable to be analyzed using conventional GC techniques. Examples include:	
Acetonitrile	Porapak N (SSV 3.5L), CSIII, C1000 or Combination Tubes 2 or 3.
Acrylonitrile	Porapak N (SSV 8L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Propionitrile	Porapak N (SSV 11L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Maleic anhydride[a]	Tenax (SSV 88L), Chrom. 106, Carbopack™ B or Combination Tubes 1, 2 or 3.
Pyridine	Tenax (SSV 8L), Porapak N (SSV 200L) Chrom. 106, Carbopack™ B or Combination Tubes 1, 2 or 3.
Aniline	Tenax (SSV 220L), Chrom. 106, Carbopack™ B or Combination Tubes 1, 2 or 3.
Nitrobenzene	Tenax (SSV 14,000L) Carbopack™ C or Combination Tubes 1 or 3.
Acetic acid	Porapak N (SSV 50L), Carbotrap™ B or Combination Tubes 1, 2 or 3.
Phenol	Tenax (SSV 240L) or combination tube 1.

Figure 4. Tube Conditioning Log

Batch ID:

Date:

Tube Type (PAH or Universal)

Conditioning methods:

(1)Universal-TC2 Short Cycle (15minutes ea @ 100,200,300,335)

(2)Univesal-TC2 Long Cycle (1 hour ea @ 100,200,300 and 30 min @335)

(3)Universal-Running as blank On Ultra.

(4)-PAH-Long Cycle 2Hours @330C.

(5)-PAH-Short Cycle 15-30mins @330C.

Serial#	Tube Type	Conditioning Method	Sequence ID	Cycle

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