CANISTER CERTIFICATION PROCESS

CONTENTS

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1.0 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure (SOP) is to outline the steps for the certification of SUMMA canisters for VOC sampling and analysis by Gas Chromatography/Mass Spectrometry (GC/MS). This procedure is based on Compendium Method TO-15 and those requirements set forth in the latest approved version of the National Environmental Laboratory Accreditation Committee (NELAC) Quality Systems section. This procedure is applicable to volatile organic compounds (VOCs) that can be sampled using SUMMA canisters. The VOCs that can be routinely analyzed at the parts per billion by volume (ppbv) are listed in Table 1, Appendix A. This list may be modified to include other VOC compounds on a project-specific basis.

This method may not be changed without the expressed approval of the Organic Group Leader, the Analytical Section Leader and the Quality Assurance Officer (QAO). Only those versions issued through the SERAS document control system may be used. Modifications made to the procedure due to interferences in the samples or for any other reason must be documented in the case narrative and on a nonconformance memo.

2.0 METHOD SUMMARY

After air samples in SUMMA canisters have been collected and analyzed, the canisters are cleaned following SERAS SOP #1739, *Automated SUMMA Canister Cleaning Procedures* and then certified as being "clean" by TO-15 analysis. The canisters are considered clean when target compounds and non-target compounds are not detected above 0.2 parts per billion by volume (ppbv) and 2 ppbv, respectively, for the full scan TO-15 analysis. Optionally, canisters may be cleaned down to a site-specific reporting limit (RL) of 70 pptv and are considered clean when target compounds of interest are not detected above this RL. If the criteria for the canisters are not met, the canisters will be returned for re-cleaning and re-certification.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

Once the canisters have gone through the cleaning process, the canisters are pressurized to > 12 pound force per square inch gauge (psig) with zero humidified air (ZHA) and sent to the ERT/SERAS Laboratory for certification.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

- Structural isomers having co-eluting retention times and identical mass spectra will interfere with this method. The most common interference seen in these methods is between meta-xylene and para-xylene.
- Artifacts in canister samples may result from improper cleaning procedures or storage.
- Organic compounds in the carrier gas, the GC/MS system, the sample preparation system or solvent vapors in the laboratory may contribute to contamination problems.

5.0 EQUIPMENT/APPARATUS

- Gas Chromatograph/Mass Selective Detector (GC/MSD) - GC capable of sub-ambient temperature programming interfaced with a MSD [Agilent (HP) 6890N GC/5973N MSD equipped with Chemstation software or equivalent]

- Preconcentrator, capable of a -200 to 250 degrees Centigrade (°C) temperature range, equipped with GC interface (Entech 7100A three-stage preconcentrator, or equivalent)
- Canister autosampler, 16-position tower (Entech 7016CA, or equivalent)
- Chromatographic column, capillary column, 30 meter (m) x 0.32 millimeter (mm), 1.0 micron (µm) film thickness (Restek RTx-1, or equivalent)
- Canisters, passivated 6-Liter (L) and 15-L SUMMA or TOCan® canisters or fused silica-lined 6-15 L Silco can (Andersen Samplers, Inc., Restek Corporation or equivalent)
- Stainless steel vacuum/pressure gauge, capable of measuring 0 to 100 psia (Pennwalt Corp., Wallace and Tiernan Division, Series 1500 dial instrument, or equivalent)
- Chromatographic-grade stainless steel or Teflon® tubing, and stainless steel or brass plumbing fittings
- Stainless steel cylinder regulators, two-stage pressure regulators (Scott Specialty Gases, Inc., or equivalent)
- Septa, 9.5 mm (Supelco, Inc. Microsep F-174, or equivalent)

6.0 REAGENTS

- Calibration Stock Standard, approximately 1.0 part per million by volume (ppmv) in ZHE (Spectra Gases, Inc., or equivalent)
- Calibration Intermediate Standard - Prepare a nominal 20 ppbv standard from the stock calibration standard in ZHE using an absolute pressure gauge
- Calibration Intermediate Standard - Prepare a nominal 1.0 ppbv standard from the intermediate calibration standard in ZHE using an absolute pressure gauge
- 2nd Source Standard, approximately 1ppmv in ZHE (Scott Specialty Gases Inc., or equivalent)
- 2nd Source Intermediate Standard - Prepare a nominal 20 ppbv standard from the 2nd Source standard in ZHE using an absolute pressure gauge
- p-Bromofluorobenzene (BFB) Stock Standard, approximately 1.0 ppmv in ZHE (Scott Specialty Gases, Inc., or equivalent), used as the MS performance standard
- BFB Intermediate Standard - Prepare a nominal 100 ppbv standard from the BFB stock standard in ZHE using an absolute pressure gauge
- Stock Internal Standard Mixture, Bromochloromethane, 1,4-Difluorobenzene, Chlorobenzene-d5 - at approximately 1.0 ppmv in ZHE (Scott Specialty Gases, Inc., or equivalent)
- Intermediate Internal Standard Mixture - Prepare a nominal 1 ppbv (for selective ion monitoring [SIM]) and 10 ppbv (for Scan or SIM) standard from the Stock Internal Standard solution in zero humidified air using an absolute pressure gauge

- Perfluorotributylamine (PFTBA), for tuning the mass spectrometer (Agilent Inc., or equivalent)
- Nitrogen Refrigerated Liquid, for cryogenic cooling
- Helium, ultra high purity 99.999 percent (%) - 99.9999%, used as carrier gas and as purge gas in the thermal desorber
- ZHE, ultra high purity 99.999% - 99.9999%, for pressurizing canister samples, purging canister analysis train lines and for carrier flow during spiking and desorbing sorbent tubes

7.0 PROCEDURES

7.1 Daily GC/MS Tuning

Prior to analysis, the GC/MS system tune must be checked to verify that acceptable performance criteria can be achieved.

A fifty nanogram (50 ng) standard of BFB is introduced into the GC/MS system. A single scan is acquired at the apex of the eluted BFB peak. Background subtraction is conducted using a single scan within 20 scans of the elution of BFB. If the scan at the apex does not pass the criteria of BFB tuning, three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is conducted in same manner. The performance criteria listed in SERAS SOP #1814, *GC/MS Analysis of Sorbent Tubes and Canisters* must be passed before any standards, blanks or samples are analyzed, and must be repeated every 24 hours. If these criteria are not met corrective action must be taken, (i.e. tuning the MSD, source maintenance/cleaning, etc.). After corrective action has been completed, BFB must be checked and verified to pass performance criteria.

The suggested chromatographic conditions used for the analysis of BFB are those listed below:

Initial Temperature	:	100°C
Initial Time	:	2.0 minutes
Ramp Rate	:	10°C/minutes
Final Temperature	:	200°C
Run Time	:	12 minutes

7.2 GC/MS Calibration

7.2.1 Canister Initial Calibration

7.2.2.1 Scan Mode

Before any sample or blank analyses, calibrate the GC/MS using target and internal standards contained in pressurized cylinders yielding final concentrations of 0.04, 0.1, 0.2, 0.5, 1, 10, 25 ppbv based on 1 L of sample volume. A consistent volume (typically 500 mL) is used for each calibration point and a minimum of five points must be used. The typical RL is based on analyzing 600 mL of sample, which equates to a working RL of 0.0667 ppbv ([1000 mL/600 mL]*0.040 ppbv =0.0667 ppbv). Based on this, the standard RL is set to 0.070 ppbv or 70 pptv. A lower RL can be obtained by analysis of larger volumes of sample. Internal standards are added by spiking 100 mL of the nominal 10 ppbv intermediate internal standard mixture (equivalent to 1nL/L). Following analysis of all calibration standards, a calibration report is prepared listing the $RRF_{average}$ with the corresponding %RSD, which must be ≤30% for each compound. Two compounds may exceed 30% but must be ≤40%. For each compound in the calibration mixture, the retention times and relative abundances of selected ions are stored on the hard disk of the GC/MS computer to be used for compound identification.

7.2.3 Continuing Calibration

7.2.3.1 Scan Mode

For each day of analysis, check the GC/MS calibration prior to sample analysis using a daily standard at 1.0 ppbv (1000 pL). The continuing calibration is acceptable when all target compounds of interest in the daily standard are within ± 30% of the $RRF_{average}$ of the initial calibration curve. .Lists of the target compounds in the initial and continuing calibration standards are listed in Tables 1 and 2, Appendix A, along with the ions used for quantification.

7.2.4 Initial Calibration Verification

A mid-level second source standard must be analyzed to verify the initial calibration curve. This standard must be run prior to the analysis of blanks and samples and is run only after each initial calibration.

7.2.5 Method or System Blank

A method blank must be run after the initial or continuing calibration and prior to sample analysis. The blank must be non-detect for target compounds at or below the target RL.

7.3 Analysis Conditions

7.3.1 Sample Preconcentration

All samples are prepared for GC/MS analysis by using a three-stage desorption/cryogenic trapping preconcentrator, Entech 7100A or equivalent. The 7100A is equipped with two trapping modules (M1 and M2) and a cryofocusing module (M3). Modules 1 and 2 can be configured with different traps (i.e. empty, glass bead, Tenax) based upon sample conditions (i.e. high concentrations of analytes, CO2, Methane, etc.). Suggested configurations for MPT (Microscale Purge and Trap) and CTD (Cold Trap Dehydration) are shown below. A silcosteel transfer line connects M-3 with the analytical column.

Suggested Conditions:

Microscale Purge and Trap (MPT)

Module 1 (M-1) (Glass Bead Trap, Entech trap #2)	
Trapping Temp:	: -120°C to -150°C
Internal Standard Trap Time:	: 1.0 minute
Internal Standard Flow Rate:	: 100 mL/min
Analytical Standard Flow Rate:	: 20-150 mL/min (based on trapping volume)
M-1 Cryotrap Desorb Temperature:	: 10°C to 20°C
Module 2 (M-2) (Tenax Trap, Entech trap #3)	
Cryotrap Temperature:	: -10°C to -20°C
Transfer (M-1 to M-2) Time:	: 4.5 minutes
M-2 Cryotrap Desorb Temperature:	: 180°C
M-3 Cryotrap Temperature:	: -150°C to -180°C
Transfer (M-2 to M-3) Time:	: 3.5 minutes
Injection Time:	: 2.5 minutes
Injection Temp:	:Default Temp (Not programmable)

Cold Trap Dehydration (CTD)

M-1 (Empty Trap, Entech Trap #1)	
Trapping Temp:	: -40°C
Internal Standard Trap Time:	: 1.0 minute
Internal Standard Flow Rate:	: 100 mL/min
Analytical Standard Flow Rate:	: 50-150 mL/min (based on trapping volume)
M-1 Cryotrap Desorb Temperature:	: 10°C
Module 2 (Tenax Trap #3)	
Cryotrap Temperature:	: -50°C
Transfer (M-1 to M-2) Time:	: 2 minutes @ 5mL/min
M-2 Cryotrap Desorb:	: 200°C for 3.5 min
M-3 Cryotrap Temperature:	: -150°C to -180°C
Transfer (M-2 to M-3) Time:	: 3.5 minutes
Injection Time:	: 2.5 minutes
Injection Temp:	: Default Temp. (Not programable)

7.3.2 Chromatographic Conditions

The suggested chromatographic conditions used are those listed below modified from U.S. EPA Compendium Method TO-15:

GC/MS (Agilent 6890N/5973 or 5975 MSD or equivalent)

Initial Temperature	: 35°C
Initial Time	: 4 minutes
Ramp Rate	: 10.0°C/min to 180°C Post run 280°C
Run Time	: 18.5 min
Mass Scan Range	: 35 to 350 AMU

7.4 Canister Sample Analysis

7.4.1 Attach the canister samples to the appropriate positions on the canister autosampler and follow the analysis procedure in Section 7.3.1.

8.0 CALCULATIONS

8.1 Target Compounds

Concentrations of target compounds are calculated by the GC/MS computer software. Reporting Limits (RL) are calculated for each sample and are calculated by the following equation:

$$RL = \frac{\textit{Lowest Calibration Volume x Standard Concentration x DF}}{\textit{Sample Volume}}$$

where:

Lowest Calibration Volume	=	milliliters of standard
Sample volume	=	milliliters
Standard Concentration	=	parts per billion volume
DF	=	Dilution Factor (for canister samples only)

When the canister pressure is increased, the dilution factor (DF) is calculated by the following equation:

$$DF = \frac{P_f}{P_i}$$

where:

P_f	=	canister pressure (psi) after pressurization; and
P_i	=	canister pressure (psi) before pressurization

8.2 LCS Recoveries

The recoveries of target compounds are calculated by the following equation:

$$\%\ Recovery = \frac{2^{nd}\ source\ Standard\ Concentration\ x100}{Calibration\ standard\ Concentration}$$

where:

Concentration = parts per billion volume

9.0 QUALITY ASSURANCE/QUALITY CONTROL

The following quality assurance/quality control procedures apply:

9.1 GC/MS Tuning and Performance Criteria

Prior to analysis and at least once every 24-hour period of operation, the GC/MS tune must be verified to meet the abundance criteria for BFB as listed in Compendium Method TO-15 (Table 2, Appendix A).

9.2 GC/MS Initial Calibration

Initial calibration acceptance criteria must be met prior to the analysis of any samples or blanks. A calibration is acceptable when the RSD is ≤30% for each compound with no more than 2 compounds exceeding 40%. Samples are quantitated on the average response factors from the initial calibration curve. The calibration must be verified by analyzing an ICV made from a source other than the one used for the calibration, at a concentration equal to the mid-point of the calibration curve (i.e. 1000 pptv for scan mode). The ICV recovery must be within 50-150% for all compounds for the calibration to be valid.

9.3 GC/MS Continuing Calibration

A continuing calibration standard (1ppbv in scan mode, 0.10 ppbv in SIM mode) must be run for each day of analysis. Response factors are calculated and compared against the $RRF_{average}$ obtained from the initial calibration. If any target compound varies more than ±30% of the average response factor, the continuing calibration standard must be rerun. If the second continuing calibration standard still exceeds the ±30% criteria, a new initial calibration will be run.

9.4 Internal Standard Evaluation

Internal standards of bromochloromethane (BCM), 1,4-difluorobenzene, and chlorobenzene -d5 are added to all standards , blanks and samples. The internal standard area response must be within ±40% (60% - 140%) between the sample and the respective internal standard area in the appropriate calibration standard. In addition, retention times must be within 20 seconds of its retention time in the latest daily (24-hour) calibration check standard.

9.5 Method or System Blank

For canister samples, the method blank is a volume of zero humidified air in a certified clean canister analyzed immediately after calibration. A system blank is a volume of zero humidified air run through the system after the analysis of samples containing high levels of target or non-target compounds. Typically, these volumes are 600 mL.

9.6 Laboratory Control Sample

Once within every 24 hour window of certification, the laboratory must analyze a Laboratory Control Sample (typically a 1nL/L for the scan mode and 0.5nL/L for the SIM mode of the 2nd source analytical standard is analyzed as LCS). The laboratory will use 50-150% as interim acceptance criteria for recovery of LCS samples until the upper and lower LCS control limits are developed. The LCS limits shall be calculated as follows:

Calculate average percent recovery (p) and standard deviation (s) of 15-20 LCS samples.

Upper control limit = p + 3s
Lower control limit = p - 3s

9.10 Target Compound Identification

Two criteria must be satisfied to verify the identification of a target compound:

- Retention Time - A sample component's retention time (RT) must be within ±0.50 minutes of the RT of the standard component. For reference, the standard must be run on the same day as the sample.

- Spectra (Scan Only)

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

  The relative intensities of the ions specified above must agree within ±20% between the sample and the reference spectra.

9.11 Non-Target Compound Identification (Scan Only)

When requested, a library search shall be executed for non-target compounds present in method blanks and samples for the purpose of tentative identification. In this case, the Wiley7N Mass Spectral Library version D.03.00 (or equivalent) will be used for identification search.

1. Guidelines for making tentative identification of a non-target compound:

   - Relative intensities of major ions greater than 10% of the most abundant ion in the reference spectrum should be present in the sample spectrum.

   - For example, if an ion has an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30-70%.

   - Molecular ions present in reference spectrum should be present in sample spectrum.

   - Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

   - Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds.

   NOTE: Data system library reduction programs can sometimes create these discrepancies.

2. If all of the above conditions for a compound are met and if the Q value of the search is ≥80%, that compound will be reported as a tentatively identified compound (TIC). If the Q value is < 80% or the mass spectral interpretation specialist indicates that no valid tentative identification can be made, the compound should be reported as *unknown*. The mass spectral interpretation specialist should give additional classification of the unknown compound, if possible. Up to twenty (20) compounds of greatest apparent

concentration that are not target.

An estimated concentration for tentatively identified compounds (TICs) must be calculated by the internal standard method. The nearest internal standard free of interferences must be used. All non-target concentrations are reported to two significant figures for concentrations >10 ppbv and one significant figure for concentrations <10 ppbv.

9.12 Manual Integrations

Manual integration of all target analytes, surrogates, and internal standards shall be submitted for review. The manual integration results shall be flagged with "m" if not performed by the software, and initialed and dated by the analyst and group leader. Documentation of the manual integration of quantitation ion peaks must be included in the data package. Refer to SERAS SOP# 1001, *Chromatographic Peak Integration Procedures*.

9.13 Reporting Limit

The lowest concentration of the calibration standard that is analyzed during the initial calibration determines the method RL.

9.14 Limit of Detection Studies

Limit of detection (LOD) studies will be run once on every instrument for the air matrix to verify the minimum concentration that can be measured and reported with 99% confidence. A minimum of seven replicates will be used for the study (EPA 1984).

9.15 Limit of Quantitation Standard

The validity of the Limit of Quantitation (LOQ) will be performed on annual basis, or any time a major change is made to the method or instrument, using the 2nd source standard. The concentration of the LOQ standard will be 1 to 2 times the lowest calibration point (i.e. the reporting limit). The acceptance criteria for accuracy must be between 70% - 130%.

9.16 Nonconformance Memo

A nonconformance memo will be generated any time an employee notices a deficiency suspected of being a nonconformance. This nonconformance memo will be forwarded to the QAO for verification of corrective action.

9.17 Initial Demonstration of Capability

Initial proficiency for air analysis must be demonstrated by each analyst initially and each time significant changes are made in the procedure or for instrumentation. Each analyst will generate precision and accuracy data using a reference standard other than the source used for calibration. Four replicates are analyzed using the procedures outlined in this SOP. Calculate the average mean in ppbv and the standard deviation (S) in ppbv. The QAO will tabulate the results from all of the analysts per matrix per parameter, and calculate control limits.

10.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow EPA, Occupational Safety and Health (OSHA) and laboratory health and safety practices. More specifically refer to SERAS SOP #3013, *SERAS Laboratory Safety Program* and SERAS SOP #1501, *Hazardous Waste Management*.

11.0 REFERENCES

NELAC. *Quality Systems*, current approved version.

United States Environmental Protection Agency, Office of Environmental Research and Development. 1999. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. EPA /625/R-96/010b. Compendium Methods TO-15

EPA. 1984. Federal Register, 40 Code of Federal Regulations (CFR) Part 136, Appendix B, *Definition and Procedure of the Determination of the Method Detection Limit - Revision 1.11*, October 26, 1984.

12.0 APPENDICES

TABLE 1. Target Compounds Analyzed for Calibration (55 Compounds)

Compound	Quantitation Ions
Propylene	41
Dichlorodifluoromethane	85
Chloromethane	50
Dichlorotetrafluoroethane	85
Vinyl Chloride	62
1,3 Butadiene	39
Bromomethane	94
Chloroethane	64
Acetone	43
Trichlorofluoromethane	101
Isopropyl Alcohol	45
1,1 Dichloroethene	61
Methylene Chloride	49
Trichlorotrifluoroethane	151
trans 1,2 Dichloroethene	61
1,1 Dichloroethane	63
MTBE	73
Vinyl Acetate	43
2 Butanone	43
cis 1,2 Dichloroethene	61
Ethyl Acetate	43
Hexane	57
Chloroform	83
Tetrahydrofuran	42
1,2 Dichloroethane	62
1,1,1 Trichloroethane	97
Benzene	78
Carbon Tetrachloride	117
Cyclohexane	84
1,2 Dichloropropane	63
1,4 Dioxane	88
Trichloroethene	130
Heptane	43
cis 1,3 Dichloropropene	75
Methyl Isobutyl Ketone	43
trans 1,3 Dichloropropene	75
1,1,2 Trichloroethane	97
Toluene	91
2 Hexanone	43
Dibromochloromethane	129
1,2 Dibromoethane	107
Tetrachloroethene	166
Chlorobenzene	112
Ethylbenzene	91
m&p Xylene	91
Bromoform(Tribromomethane)	173

Styrene	104
1,1,2,2 Tetrachloroethane	83
o Xylene	91
Ethyltoluene	105
1,3,5 trimethylbenzene	105
1,2,4 Trimethylbenzene	105
1,3 Dichlorobenzene	146
1,4 Dichlorobenzene	146
1,2 Dichlorobenzene	146