GC/MS ANALYSIS OF SORBENT TUBES AND CANISTERS
(EPA TO-15 and TO-17)

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* These sections affected by Revision 3.0

SUPERCEDES: SOP #1814; Revision 2.0; 01/23/06; U.S. EPA Contract EP-C-04-032

1.0 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure (SOP) is to outline the steps for the analysis of air samples collected on either sorbent tubes or in SUMMA® canisters by Gas Chromatography/Mass Spectrometry (GC/MS). This procedure is based on Compendium Methods TO-15 and TO-17 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 by one or both of these media. The VOCs that can be routinely analyzed at the parts per billion by volume (ppbv) are listed in Tables 1and 2, 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

2.1 Sorbent Tubes

Ambient air is drawn through a stainless steel, glass or glass-lined (or fused silica-lined) tube containing solid absorbent material. The absorbent tube is placed in a heated chamber and purged with an inert gas. VOCs are thermally desorbed into a cryogenic trap, cryofocused onto the transfer line, separated by GC and analyzed by a positive ion electron impact Mass Spectrometer (MS).

2.2 Canisters

Ambient air is drawn into a specially-prepared canister. A specific volume of sample is drawn from the canister onto the cryogenic trap. The VOCs are then focused by trapping them on a reduced temperature trap. The sample is then released by thermal desorption and injected onto a GC column for separation and subsequent analysis by MS.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

3.1 Sorbent Tubes

Air samples collected on sorbent tubes are placed in clean culture tubes and shipped to the laboratory. The culture tubes should be labeled and sealed with Teflon tape around the cap. Samples must be accompanied by a chain of custody (COC) record indicating the sampling locations, sample numbers, date collected, sample matrix and sample volumes. The COC record should agree with the information on the culture tube labels, and any discrepancies noted on the COC record at the time of receipt by the laboratory. In addition, any obvious physical damage or potential contamination (e.g., loose culture tube caps, broken cartridges, condensation in the culture tubes or discoloration of the sorbent bed), must also be recorded on the COC record.

The culture tubes containing the air samples collected on sorbent tubes are placed in a cooler maintained at 4 degrees Celsius (°C), and shipped to the laboratory for analysis. Compendium Method TO-17 states that samples should be refrigerated at ≤4°C in a clean environment during storage, and analyzed within 30 days of sample collection. For best results, samples should be analyzed within the first 14 days of collection. The holding time begins when the sample is first drawn onto the tube. All sorbent tubes samples must be handled only with cotton cloth or gloves, and tweezers to avoid contamination.

3.2 Canisters

Samples collected in canisters should arrive at the laboratory with the canister valve closed and the sampling port capped. An identification tag must be attached, and agree with the information documented on the COC record.

One of the advantages of canister samples is that they do not need any refrigeration or special handling until they are analyzed. Most VOCs can be recovered from canisters near the original concentration for up to 30 days.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

- Structural isomers having coeluting 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.
- Sorbent tube samples with excessive moisture will cause the first cryotrap to freeze, restricting sample flow from the desorber oven and resulting in poor recoveries. In general, trapping efficiencies for components with boiling points greater than water are more adversely affected than those with lower boiling points. If excessive moisture is suspected, dry purge the sorbent tube prior to sample desorption.
- Artifacts in sorbent tubes may result from improper cleaning procedures, long term storage of blank sorbent tubes, sampling or sample storage.
- Canister samples suspected of having high concentrations of carbon dioxide (CO_2) will freeze the first cryotrap. Samples collected from landfills or fire plumes cannot be directly analyzed due to high concentrations of CO_2present. Canister samples may be absorbed onto a sorbent tube prior to analysis to eliminate this interference.
- 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 [Hewlett Packard (HP) 6890N GC/5973N MSD equipped with Chemstation software, or equivalent]

- Preconcentrator, capable of a -200 to 250°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 0.25 millimeter (mm), 3.0 micron (µm) film thickness (Restek RTx-Volatile, or equivalent)

- Thermal Heating Controller, with a 0°C to 300°C temperature range, equipped with single tube heater and preconcentrator interface (Valco Instrument Inc., or equivalent)

- Sorbent tubes, greater than 100 milligrams (mg) of sorbent packed into borosilicate glass tubing with Pyrex glass wool on each end and between each phase, provided in sealed glass ampules. The standard size for the single tube desorber is 6 x 120 mm.

- Canisters, passivated 6-Liter (L) SUMMA® or TOCan® canisters or fused silica-lined 6-15 L Silco can (Andersen Samplers, Inc., Restek Corporation or equivalent)

- Mass Flow Controller, capable of measuring 0-100 milliliters per minute (mL/min) (Unit Instruments, Inc., UFC-1100 with URS 100 Readout Power Supply, or equivalent)

- Stainless steel vacuum/pressure gauge, capable of measuring 0 to 100 pounds per square inch (psi) (Pennwalt Corp., Wallace and Tiernan Division, Series 1500 dial instrument, or equivalent)

- Chromatographic-grade stainless steel or Teflon® tubing, and stainless steel plumbing fittings

- Stainless steel cylinder regulators (5), two-stage pressure regulators (Scott Specialty Gases, Inc., or equivalent)

- Septa, 9.5 mm (Supelco, Inc. Microsep F-174, or equivalent)

- Pyrex culture tubes

- Teflon® tape, for sealing sorbent tube samples in culture tubes

- Rotameter or Gilibrator, 0-100 mL/min (Matheson Gas Products, Inc./Gilian Instrument Corp., or equivalent)

- Cotton cloths, 9" by 9", for sorbent tube handling (Texwipe, Co., or equivalent)

- Single tube desorber, 9"x1.5" (Tekmar, Co., or equivalent)
- Tweezers, for inserting and removing cartridge samples from thermal desorber
- Syringes, pressure lock, 2.5 - 50 milliliters (mL), for spiking sorbent tubes using the thermal desorber (Dynatech Precision Sampling, Inc., or equivalent)
- O-rings, Viton, [6 mm ID preferred) for retaining sorbent tubes in the thermal desorber (HP 5061-5867 or equivalent).
- Ring stand, 6.5 centimeter (cm) x 11 cm for retaining single tube heater unit connected to Entech 7016A autosampler (Fisher 14-670D or equivalent).

6.0 REAGENTS

- Stock Calibration Standard, approximately 1.0 part per million by volume (ppmv) in nitrogen (Spectra Gases, Inc., or equivalent)
- Intermediate 20 ppbv Calibration Standard - Prepare a nominal 20 ppbv standard from the stock calibration standard in nitrogen using an absolute pressure gauge.
- Intermediate 1.0 ppbv Calibration Standard - Prepare a nominal 1.0 ppbv standard from the stock calibration standard in nitrogen using an absolute pressure gauge.
- Intermediate 0.1 ppbv Calibration Standard - Prepare a nominal 0.1 ppbv standard from the intermediate calibration standard in nitrogen using an absolute pressure gauge.
- Stock 2nd Source Standard, approximately 1.0 ppmv in nitrogen (Scott Specialty Gases Inc., or equivalent)
- Intermediate 20 ppbv 2nd Source Standard - Prepare nominal 20 ppbv standard from the 2nd Source standard in nitrogen using an absolute pressure gauge.
- Intermediate 1.0 ppbv 2nd Source Standard - Prepare nominal 1.0 ppbv standard from the 2nd Source standard in nitrogen using an absolute pressure gauge.
- Intermediate 0.1 ppbv 2nd Source Standard - Prepare nominal standard from the 2nd Source standard in nitrogen using an absolute pressure gauge.
- p-Bromofluorobenzene (BFB) Stock Standard, approximately one ppmv in nitrogen (Scott Specialty Gases, Inc., or equivalent), used as the mass spectrometer performance standard
- BFB Intermediate Standard - Prepare a nominal 100 ppbv standard from the BFB stock standard in nitrogen using an absolute pressure gauge

- Stock Internal Standard Mixture, Bromochloromethane, 1,4-Difluorobenzene, Chlorobenzene-d5 - at approximately one ppmv in nitrogen (Scott Specialty Gases, Inc., or equivalent)

- Intermediate Internal Standard Mixture - Prepare a nominal 1 to 100 ppbv standard from the Stock Internal Standard solution in nitrogen using an absolute pressure gauge

- Perfluorotributylamine (PFTBA), for tuning the mass spectrometer (HP 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.

- Nitrogen, 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

At the beginning of each day, the GC/MS system must be tuned to verify that acceptable performance criteria can be achieved. The mass spectrometer should first be automatically or manually tuned using PFTBA to demonstrate that the instrument is operating properly.

Fifty nanogram (50 ng) of BFB is used for the GC/MS performance standard. A single scan is acquired at the apex of the eluted BFB peak. Background subtraction is conducted using a single scan no more than 20 scans prior to the elution of the 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 Table 3, Appendix A must be passed before any standards, blanks or samples are analyzed, and must be repeated every 24 hours of continuous operation. If the software does not indicate what scan was subtracted, the analyst will document the scan number directly on the tune report. If these criteria are not met, the mass spectrometer must be re-tuned. Maintenance or other actions may be necessary to meet the tune acceptance criteria.

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

Initial Temperature : 70°C
Initial Time : 5.0 minutes
Ramp Rate : 25°C/minutes
Final Temperature : 16 minutes

7.2 GC/MS Calibration

7.2.1 Sorbent Tube Initial Calibration

Before any sample or blank analysis, calibrate the GC/MS using sorbent tubes spiked with calibration standards containing all target analytes and internal standards. Typically, the working calibration standards are 0.04, 0.1, 0.2, 1, 10 and 25 ppbv based on 1-L of sample. The typical reporting limit (RL) is based on 250 milliliters (mL) of sample, which is equivalent to 0.16 ppbv. Inject the appropriate volume of standards from 0.04 mL to 25 mL of the nominal 1.0 ppmv stock calibration standard (equivalent to 0.04 nanoliters per liter [nL/L] to 25 nL/L) onto the sorbent tube side that traps the lighter compounds. Internal standards are added by spiking with 1 mL of the nominal 1.0 ppmv internal standard stock mixture (equivalent to 1nL/L). Following analysis of all calibration standard, a calibration report is prepared listing the average relative response factors ($RRF_{average}$) with the corresponding percent relative standard deviation (%RSD), which must be less than or equal to (≤) 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.

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

where:

A_x = Area of the characteristic ion for the compound to be measured
A_{is} = Area of the characteristic ion for the specific internal standard
C_{is} = Concentration of the internal standard (nL/L)
C_x = Concentration of the compound to be measured (nL/L)

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

where:

RRF_i = relative response factor for each initial calibration level
n = total number of initial calibration levels

$$\%RSD = \frac{SD}{\overline{X}} \times 100$$

$$SD = \sqrt{\frac{\sum_{i=1}^{N} (\overline{X} - x)^2}{N-1}}$$

where

N = 6 (number of calibration standards used)
$\overline{X}$ = average RRF
x = individual RRF
SD = standard deviation

7.2.2 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 prepared at 1.0 ppbv and 20 ppbv in nitrogen from the nominal 1.0 ppmv calibration stock standard. A multipoint calibration range is typically 0.04, 0.1, 0.2, 1, 10 and 25 ppbv based on 1-L of sample. Six different volumes of the nominal 1.0 ppbv and 20 ppbv standards are used to trap from 40 mL to 1250 mL. This results in standard concentrations of 0.04, 0.1, 0.2, 1, 10 and 25 ppbv using 1-L of sample. The typical RL is based on 250 mL of sample, which is equivalent to 0.16 ppbv. 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.

7.2.2.2 Selective Ion Monitoring Mode

Before any sample or blank analyses, calibrate the GC/MS using target and internal standards contained in pressurized cylinders prepared at 0.1 ppbv and 1.0 ppbv in nitrogen from the nominal 1.0 ppmv stock calibration standard. A multipoint calibration range is typically

0.02, 0.05, 0.1, 0.2, 0.5 and 0.75 ppbv based on 1-L of sample. Six different volumes of the nominal 0.1ppbv and 1.0 ppbv intermediate calibration standards are used to trap from 200 mL to 750 mL. This results in standard concentrations of 0.02 nL/L (20 picoliters[pL]) to 0.75 nL/L for a 0.08 ppbv (80 pL/L) reporting limit for a 250-mL sample aliquot. Internal standards are added by spiking with 100 mL of 1.0 ppbv (equivalent to 0.1 nL/L). Following the analysis of the calibration standards, a calibration report is prepared listing the $\text{RRF}_{\text{average}}$ 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 1nL/L for the 0.04 nL/L to 25 nL/L calibration range. The continuing calibration is acceptable when all compound abundances in the daily standard are ± 30% of the $\text{RRF}_{\text{average}}$ of the initial calibration curve. A list of the target compounds in the initial and continuing calibration standards is listed in Table 1 and 2, Appendix A, along with the ions used for quantitation.

$$\%D \quad = \quad \frac{|RRF_{Continuing} - RRF_{Average}|}{RRF_{Average}} \quad \times \quad 100$$

7.2.3.2 SIM Mode

For each day of analysis, check the GC/MS calibration prior to sample analysis using a daily standard at 0.1nL/L for the 0.02nL/L to 0.75nL/L calibration range. The continuing calibration is acceptable when all compound abundances in the daily standard are ± 30% of the $\text{RRF}_{\text{average}}$ of the initial calibration curve. A list of the target compounds in the initial and continuing calibration standards is listed in Tables 1 and 2, Appendix A, along with the ions used for quantitation.

7.2.4 Method or System Blank

A system or method blank must be run after the initial or continuing calibration and prior to sample analysis.

7.2.5 Laboratory Control Sample

A Laboratory Control Sample (LCS) must be run with the frequency of one in 20 samples using 50 mL of the 20 ppbv intermediate 2° standard for the scan mode and 100 mL of the 1.0 ppbv intermediate 2° standard for the SIM mode.

7.2.6 Limit of Quantitation Standard

A Limit of Quantitation (LOQ) standard must be run at one to two times the reporting limit (RL) each time an initial calibration is run. This standard must be run immediately following the calibration before any method blank or samples are analyzed. For the scan mode, prepare either a LOQ standard using either 40 mL or 80 mL of the 1.0 ppbv intermediate 2° standard, representing a 0.04 or a 0.08 nL/L standard. For the SIM mode, prepare either a LOQ standard using 200 mL or 500 mL of the 0.1 ppbv intermediate 2° standard, representing either a 0.02 or a 0.05 nL/L standard. The LOQ standard may be modified if a lower calibration point is inserted into the calibration curve.

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. This unit is equipped with a cryogenic trap (M-1) consisting of a 0.125" stainless tube filled with glass beads, an eight-port switching valve, a sorbent bed trap (M-2) designed to remove water, and a cryofocussing trap (M-3) (Figure 1, Appendix B). A silcosteel transfer line connects M-3 with the analytical column. All preconcentrator parameters are subject to change due to continuous usage of the instrument. The following is a summary of typical preconcentrator parameters:

M-1 Cryotrap Temperature : -120°C to -150°C
Internal Standard Trap Time : 1.0 minute
Internal Standard Flow : 100 to 150 mL/min
Analytical Standard Trap Times : 5 minutes (for sorbent tube)
Analytical Standard Trap Times : 0.33 minutes (1 nL) to 8.33 minutes (25 nL) (for canister)
Analytical Standard/Sample Flow : 100 - 150 mL/min (for sorbent tube)
Analytical Standard/Sample Flow : 150 - 200 mL/min (for canister)
M-1 Cryotrap Desorb Temperature : 10°C to 20°C
M-2 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

7.3.2 Chromatographic Conditions

The chromatographic conditions used are those listed below modified from EPA Compendium Method TO-15 and TO-17:

Unit #1 GC/MS 5890II/5971A MSD
Initial Temperature : 36°C
Initial Time : 4.0 minutes
Ramp Rate : 8.0°C/min to 120°C hold for 1 minute
12°C/min to 185°C hold for 1 minute
20°C/min to 200°C
Final Temperature : 200°C hold for 1minute
Run Time : 23.67 minutes
Mass Scan Range : 35 to 350 Atomic Mass Unit (AMU)

Unit #2 GC/MS 6890N/5973N MSD
Initial Temperature : 5°C
Initial Time : 0.0 minutes
Ramp Rate : 5.0°C/min to 25°C
8.0°C/min to 80°C hold for 1 minutes
9.0°C/min to 120°C hold for 1 minute
12°C/min to 155°C hold for 1 minute
20°C/min to 180°C hold for 1 minute
40°C/min to 220°C
Final Temperature : 220°C
Run Time : 24.49 minutes
Mass Scan Range : 35 to 350 AMU

An example quant report listing internal standards and target compounds in elution order can be found in Figure 2, Appendix B, and the chromatogram in Figure 3, Appendix B.

7.4 Sorbent Tube Analysis

Analysis of a sorbent tube sample is done using a single cartridge thermal desorber. Using a syringe, inject the appropriate volume, 1mL of a nominal 1.0 ppmv internal standard (equivalent to 1nL) onto the sorbent tube side that traps the lighter compounds (vendor will have an indicator on tube). The desorber is connected to a source of ultra-high purity nitrogen at a flow rate of 10 - 20 mL/min. After injection, remove the sorbent tube from the desorber and slide the o-ring to the side that traps the heavier compounds. Insert the side that traps the lighter compounds in the tube desorber, which is connected to the Entech 7016CA autosampler. Set up a single run sequence in the Entech 7000 or 7100A pre-concentrator screen and click on the GO button. The system will initiate the preconcentration steps listed in Section 7.3.1. Turn on the ultra-high purity nitrogen cylinder valve to provide flow into the single tube desorber (do not exceed 200 mL/min). The system will automatically start trapping the sample through the desorber. After 40 to 50 mL of sample has been trapped, turn on the heating controller that is previously set at 240°C. After the sample trapping is complete, the heating controller is turned off and the analysis continues from the stage of transfer (M-1 to M-2).

7.5 Canister Sample Analysis

Canister samples are usually collected at or near atmospheric pressure. To allow the sample to flow from the canister, the canister pressure must be raised above one atmosphere with ultra-high purity nitrogen. Typically, sample pressure is doubled from approximately one atmosphere to two atmospheres for ease of calculation.

1. Before attaching the canister containing the sample, purge the pressurizing line with nitrogen as indicated in Figure 4, Appendix B. Attach the canister sample to the pressurizing apparatus and close the regulator to the nitrogen cylinder. Open the canister valve, allow the pressure to equilibrate, and record the initial pressure (P_i) on the pressurization log.

2. Open the cylinder regulator slowly so the pressure gradually increases. When the canister pressure SERAShes the desired final pressure P_f, close the regulator, close the canister valve, and record the final pressure (P_f) on the pressurization log.

3. Attach the canister samples to the appropriate positions on the canister autosampler (Figure 5, Appendix B) and follow the analysis procedure in Section 7.3.1.

7.6 Analysis of Canister Samples Adsorbed on Sorbent Tubes

Canister samples are adsorbed on sorbent tubes if samples are suspected of containing high levels of carbon dioxide or other permanent gases that would freeze the cryotraps.

1. Follow the procedure in Section 7.5, steps 1 and 2, for the pressurization of the canister sample.

2. Place a sorbent tube in the thermal desorber with the side that traps the heavier compounds in first. Attach the canister to the analysis train as shown in Figure 6, Appendix B.

3. With the mass flow controller valve closed, open the canister valve to allow the sample to come to equilibrium in the sample train. Open the mass flow controller valve and let the desired sample volume adsorb onto the cartridge.

4. After the sample has been adsorbed, close the canister and mass flow controller valves, place the sorbent tube in the thermal desorber with the sorbent tube side that traps the lighter compounds (Figure 7, Appendix B), and follow the sorbent tube analysis procedure in Section 7.4.

8.0 CALCULATIONS

8.1 Target Compounds

Concentrations of target compounds are calculated by the GC/MS computer software as follows

$$C_c(nL/L) = \frac{(A_c)(I_{is})(DF)}{(A_{is})(RRFavg)}$$

where:

$\mathbf{C_c}$ = Compound concentration in nL/L
$\mathbf{A_c}$ = Area of the characteristic ion for the compound
$\mathbf{I_{is}}$ = Amount of internal standard , nL/L
DF = Dilution factor
$\mathbf{A_{is}}$ = Area of the characteristic ion for the internal standard
$\mathbf{RRF_{avg}}$= Average Relative Response Factor

8.2 Reporting Limits

Reporting Limits (RL) are calculated for each sample and are calculated by the following equation:

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

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

8.3 Canister Sample to Sorbent Tube

The following equation calculates the adsorb time (minutes) necessary for a given sample volume and flow rate (in mL/min):

$$\textit{Adsorb Time} = \frac{\textit{Sample Volumes x DF}}{\textit{Flow Rate}}$$

where:

Sample volume = milliliters
DF = dilution factor (from above)
Flow rate = mL/min

For example, with a DF of two and a flow rate of 40 mL/min, it would take five minutes to adsorb 100 mL of unpressurized sample (equivalent to 200 mL of pressurized sample). For larger sample volumes, it may be necessary to extend the adsorb time.

8.4 MS/MSD Sample Recoveries

Accuracy is calculated from the recovery of the MS/MSDs. Precision is calculated from the relative percent difference (RPD) of the recoveries measured for the MS/MSD pair. Matrix spike recoveries and RPD will be calculated by the following equations:

$$\textit{Matrix Spike Recovery } (\%R) = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Concentration of target analyte in spike sample (spiked)
SR = Concentration of target analyte in sample (unspiked)
SA = Concentration of spike added

and

$$RPD = \frac{|Sample - SampleDup|}{(Sample + SampleDup)/2} \times 100$$

where:

RPD = Relative percent difference

Note: RPD is always expressed as a positive value.

8.5 LCS Standard Recoveries

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

$$\textit{Laboratory Control Sample Recovery } (\%R) = (LCSR)/SA \times 100$$

where:

LCSR = Concentration of target analyte in LCS
SA = Concentration of spike added

9.0 QUALITY ASSURANCE/QUALITY CONTROL

The following quality assurance/quality control procedures apply:

9.1 GC/MS Tuning and Performance Criteria

The GC/MS is tuned each day with PFTBA to meet the abundance criteria for BFB as listed in Table 3, Appendix A. The tune is adjusted when necessary. The BFB must be analyzed initially and once per 24-hour period of operation.

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.

9.3 GC/MS Continuing Calibration

A continuing calibration standard (1ppbv in scan mode and 0.1ppbv 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 standard component 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 sorbent tube samples, a system blank is analyzed immediately following a calibration standard to ensure that the system is free of any target analytes. A method blank may be run using an unopened sorbent tube from the same lot used for the collection of samples spiked with internal standards. The method blank is analyzed if a lot blank is not submitted from the field with a sampling event.

For canister samples, the method blank is a volume of nitrogen gas analyzed immediately after calibration. A system blank is a volume of nitrogen gas run through the system after the analysis of samples containing high levels of target or non-target compounds. Typically, these volumes are 250 mL or an equivalent volume as that used for samples.

For canister samples adsorbed onto sorbent tubes, a method blank is a volume of nitrogen equal to the sample volumes adsorbed on the sorbent tubes spiked with internal standards.

9.6 Duplicates

Ten percent (10%) of all sorbent tube samples received are analyzed in duplicate. The relative percent difference (%RPD) must be within 25% and are calculated as in Section 8.4.

9.7 Replicates

Ten percent (10%) of all canister samples received are to be analyzed in replicate. The %RPD must be within 25% and are calculated as in Section 8.4.

9.8 Matrix Spike Analysis

Ten percent (10%) of all sorbent tube samples received are spiked with 50 mL of 20ppbv of calibration standard, which is equivalent to 1 nL/L and analyzed as a matrix spike (MS). If samples were not collected for the MS analysis, a blank spike (BS) is run. Ten percent (10%) of all canister samples received are analyzed as a matrix spike/matrix spike duplicate (MS/MSD). Typically the spike concentrations are 1 nL/L for the scan mode and 0.1 nL/L for the SIM mode. Recoveries must be within 60 - 140% and are calculated as in Section 8.4.

9.9 Laboratory Control Sample

The LCS must be obtained from an independent source, and must be run with the frequency of one in 20 samples. Typically the LCS concentrations are 1 nL/L for the scan mode and 0.1 nL/L for the

SIM mode. LCS results for each analyte must be within 70 - 130% and are calculated as in Section 8.5.

9.10 Dilution Analysis

All target analyte concentrations must be within the linear range for canister samples. Use the results of the initial analysis to determine the appropriate dilution factor (DF). The DF should bring the target compounds within the upper half of the initial calibration.

9.11 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
  1. 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.
  2. The relative intensities of the ions specified above must agree within ±20% between the sample and the reference spectra.

9.12 Non-Target Compound Identification

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 coeluting 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 coeluting 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.

3. 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.

9.13 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*.

9.14 Reporting Limit

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

9.15 Method Detection Limit Studies

Method detection limit (MDL) studies will be run on an annual basis 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).

9.16 Limit of Quantitation Standard

The validity of the Limit of Quantitation (LOQ) will be performed each time the initial calibration is run using the intermediate 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 LOQ standard must be run immediately following the initial calibration and prior to any samples. The acceptance criteria for accuracy should be between 70% - 130%.

9.17 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.

9.18 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 DATA VALIDATION

Data will be assessed in accordance with the guidelines set forth in the most current version of SERAS SOP #1015, Data Validation Procedures for Routine Organic Analysis. However, the data is considered satisfactory for submission when all requirements in Section 9.0 are met.

11.0 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.*

12.0 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 and TO-17.

United States Environmental Protection Agency. *"Standard Operating Procedure for Preparation of Clean Absorbent Cartridges"* EMSL/RTP-SOP-EMD-013.

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.

13.0 APPENDICES

A - Tables
B - Figures

APPENDIX A
Tables
SOP #1814
March 2006

TABLE 1. Target Compounds Analyzed for Calibration (27 Compounds)

Compound	RL (Scan)*	RL (SIM)*	Quantitation Ion
Benzene	0.04	0.02	78
Bromodichloromethane	0.04	0.02	83
Carbon Tetrachloride	0.04	0.02	117
Chloroethane	0.04	0.02	64
Chloromethane	0.04	0.02	50
Dibromomethane	0.04	0.02	93
1,1-Dichloroethane	0.04	0.02	63
1,2-Dichloroethane	0.04	0.02	62
1,1-Dichloroethene	0.04	0.02	61
trans-1,2-Dichloroethene	0.04	0.02	61
Ethylbenzene	0.04	0.02	91
Methylene Chloride	0.10	0.05	49
Styrene	0.04	0.02	104
1,1,2,2-Tetrachloroethane	0.04	0.02	83
Tetrachloroethene	0.04	0.02	166
1,1,1-Trichloroethane	0.04	0.02	97
1,1,2-Trichloroethane	0.04	0.02	97
Trichloroethene	0.04	0.02	130
Trichlorofluoromethane	0.04	0.02	101
Trichloromethane	0.04	0.02	83
1,3,5-Trimethylbenzene	0.04	0.02	120
Toluene	0.04	0.02	91

Vinyl Chloride	0.04	0.02	62
m-Xylene	0.04	0.02	91
o-Xylene	0.04	0.02	91
cis-1,2- Dichloroethene	0.04	0.02	61

NOTE: RLs are in nL/L and are based on 1-L of sample

TABLE 2. Target Compounds Analyzed for Calibration (55 Compounds)

Compound	RL (Scan)*	RL (SIM)*	Quantitation Ion
Propylene	0.04	0.02	41
Dichlorodifluoromethane	0.04	0.02	85
Chloromethane	0.04	0.02	50
Dichlorotetrafluoroethane	0.04	0.02	85
Vinyl Chloride	0.04	0.02	62
1,3-Butadiene	0.04	0.02	39
Bromomethane	0.04	0.02	94
Chloroethane	0.04	0.02	64
Acetone	0.10	0.05	43
Trichlorofluoromethane	0.04	0.02	101
Isopropyl Alcohol	0.04	0.02	45
1,1-Dichloroethene	0.04	0.02	61
Methylene Chloride	0.10	0.05	49
Trichlorotrifluoroethane	0.04	0.02	151
trans-1,2-Dichloroethene	0.04	0.02	61
1,1-Dichloroethane	0.04	0.02	63
MTBE	0.04	0.02	73
Vinyl Acetate	0.04	0.02	43
2-Butanone	0.04	0.02	43
cis-1,2-Dichloroethene	0.04	0.02	61
Ethyl Acetate	0.04	0.02	43
Hexane	0.04	0.02	57

Chloroform	0.04	0.02	83
Tetrahydrofuran	0.04	0.02	42
1,2-Dichloroethane	0.04	0.02	62
1,1,1-Trichloroethane	0.04	0.02	97
Benzene	0.04	0.02	78
Carbon Tetrachloride	0.04	0.02	117
Cyclohexane	0.04	0.02	56
1,2-Dichloropropane	0.04	0.02	63
1,4-Dioxane	0.10	0.05	88
Trichloroethene	0.04	0.02	130
Heptane	0.04	0.02	43
cis-1,3-Dichloropropene	0.04	0.02	75
Methyl Isobutyl Ketone	0.04	0.02	43

NOTE: RLs are in nL/L and are based on 1-L of sample

TABLE 2. Target Compounds Analyzed for Calibration (55 Compounds)
(cont'd)

Compound	RL (Scan)*	RL (SIM)*	Quantitation Ion
trans-1,3-Dichloropropene	0.04	0.02	75
1,1,2-Trichloroethane	0.04	0.02	97
Toluene	0.04	0.02	91
2-Hexanone	0.04	0.02	43
Dibromochloromethane	0.04	0.02	129
1,2-Dibromoethane	0.04	0.02	107
Tetrachloroethene	0.04	0.02	166
Chlorobenzene	0.04	0.02	112
Ethylbenzene	0.04	0.02	91
m&p-Xylene	0.04	0.02	91
Bromoform(Tribromomethane)	0.04	0.02	173
Styrene	0.04	0.02	104
1,1,2,2-Tetrachloroethane	0.04	0.02	83
o-Xylene	0.04	0.02	91
Ethyltoluene	0.04	0.02	105
1,3,5-trimethylbenzene	0.04	0.02	105
1,2,4-Trimethylbenzene	0.04	0.02	105
1,3-Dichlorobenzene	0.04	0.02	146
1,4-Dichlorobenzene	0.04	0.02	146
1,2-Dichlorobenzene	0.04	0.02	146

NOTE: RLs are in nL/L and are based on 1-L of sample

TABLE 3. GC/MS Performance Criteria for p-Bromofluorobenzene

m/z	Ion Abundance Criteria [1]
50	8.0 - 40% of mass 95
75	30 - 66% of mass 95
95	Base Peak, 100% relative abundance
96	5.0 - 9.0% of mass 95
173	Less than 2.0% of mass 174
174	50 - 120% of mass 95
175	4.0 - 9.0% of mass 174
176	93 - 101% of mass 174
177	5.0 - 9.0% of mass 176

[1] 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.

APPENDIX B
Figures
SOP #1814
March 2006

FIGURE 1. 7001A or 7000 Preconcentrator Trapping Pathway

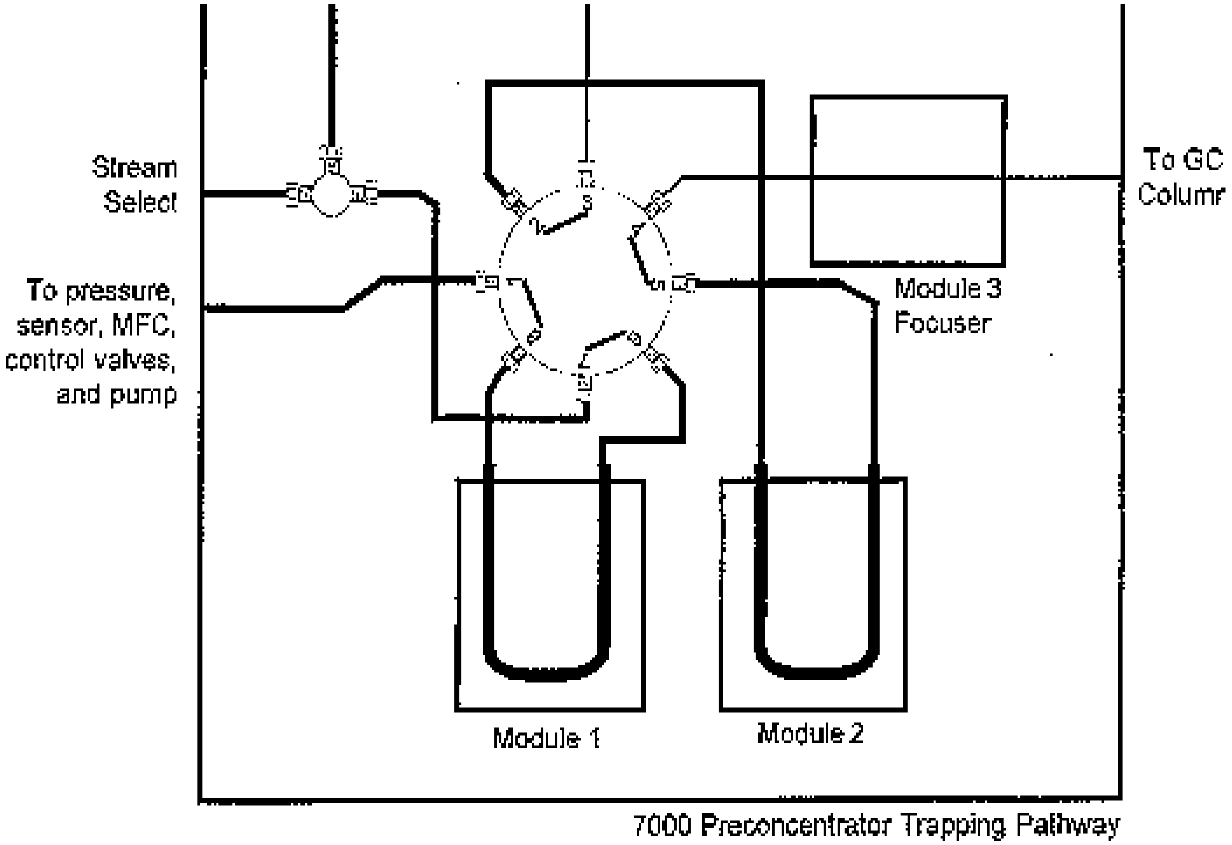
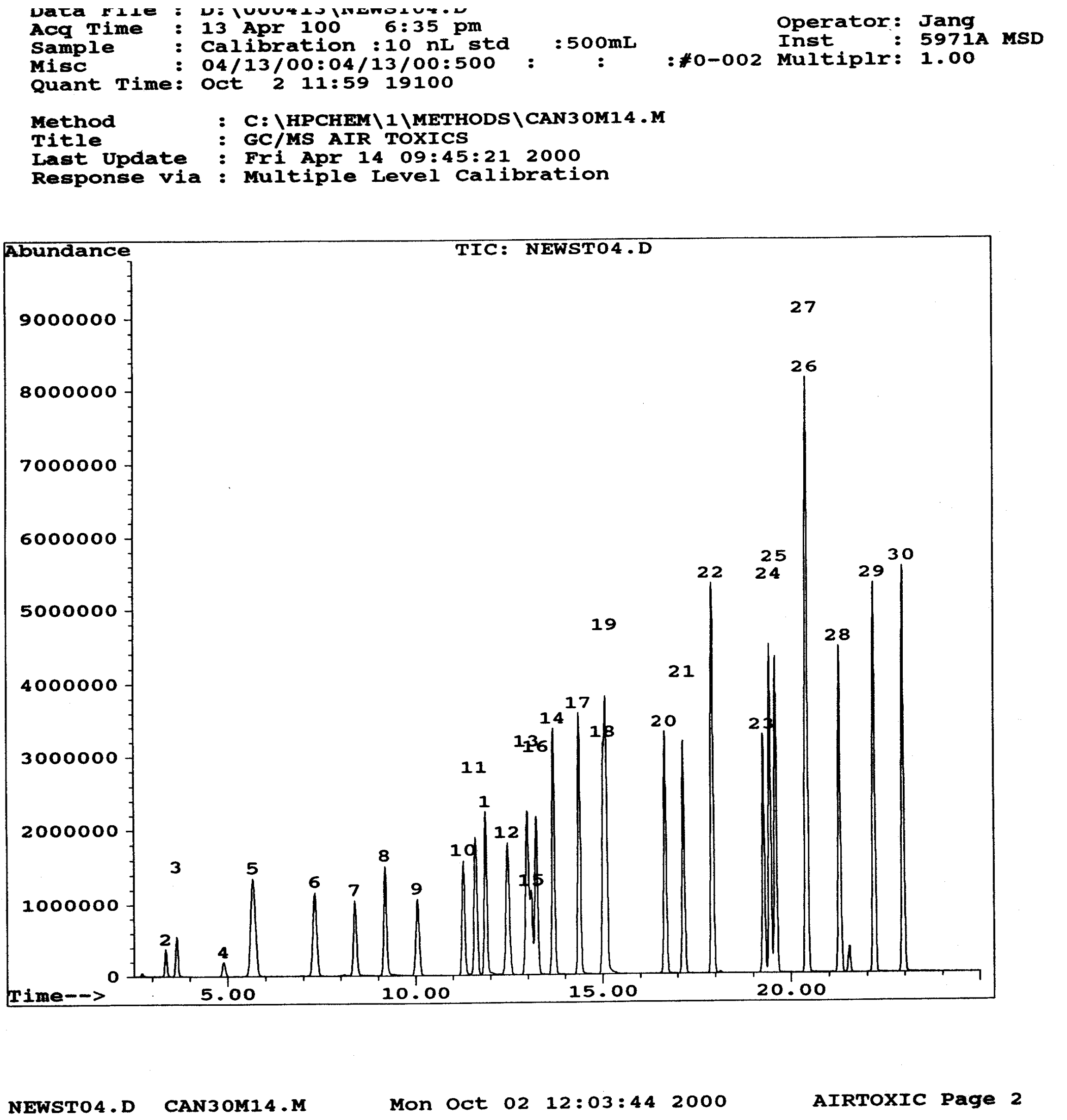


FIGURE 2. Quant Report

```
Data File   : D:\000413\NEWST04.D                                          Operator    : JANG
Injected at : 13 Apr 100 06:35 pm                                          Instrument : 5971A MSD
Name        : Calibration : 10nL STD    :500mL of 20ppb                    Dilution Factor: 1.00000
Quant time: Apr 13 19:01  19100
Misc: 04/13/00:04/13/00:500 :N/A :N/A :#2-002

Method         : C:\HPCHEM\1\METHODS\CAN30M14.M
Title          :  GC/MS AIR TOXICS
Last  Update  : Fri Jul 14 13:41:05 2000
Response via : Multiple Level Calibration

==============================================================================
Compound                                      R.T.      Area       Conc.      Units       q
------------------------------------------------------------------------------

1)  BROMOCHLOROMETHANE                        11.88     1602866    10.00      nL          49
14) 1,4-DIFLUOROBENZENE                       13.69     7793990    10.00      nL          114
23) CHLOROBENZENE                             19.27     5193141    10.00      nL          117
System Monitoring Compounds

Target Compounds
2)  CHLOROMETHANE                             3.36      891490     9.69       nL          50
3)  VINYL CHLORIDE                            3.65      1438004    9.74       nL          62
4)  CHLOROETHANE                              4.89      606711     7.02       nL          64
5)  TRICHLOROFLUOROMETHANE                    5.66      5582815    9.22       nL          101
6)  1,1-DICHLOROETHENE                        7.30      2625442    9.33       nL          61
7)  METHYLENE CHLRODE                         8.38      1417259    9.27       nL          49
8)  TRANS-1,2-DICHLOROETHENE                  9.19      2324718    9.47       nL          61
9)  1,1-DICHLOROETHANE                        10.05     3331249    9.45       nL          63
10) CIS-1,2-DICHLOROETHENE                    11.28     2241198    9.50       nL          61
11) TRICHLOROMETHANE                          11.61     4604304    9.35       nL          83
12) 1,1,1-TRICHLOROETHANE                     12.46     4023557    9.35       nL          97
13) CARBON TETRACHLORIDE                      12.98     4693237    9.33       nL          117
15) 1,2-DICHLOROETHANE                        13.09     2137725    9.45       nL          62
16) BENZENE                                   13.22     5817505    9.28       nL          78
17)  TRICHLOROETHYLENE                        14.37     2876781    9.25       nL          95
18)  BROMODICHLOROMETHANE                     15.02     5131057    9.47       nL          83
19) DIBROMOMETHANE                            15.09     2947758    9.50       nL          93
20)  TOLUENE                                  16.68     6713399    9.45       nL          91
21)  1,1,2-TRICHLOROETHANE                    17.16     2682132    9.40       nL          97
22)  TETRACHLOROETHYLENE                      17.93     4464981    9.43       nL          166
24)  ETHYLBENZENE                             19.46     9188848    9.48       nL          91
25)  META-XYLENE                              19.61     6942998    9.57       nL          91
26)  ORTHO-XYLENE                             20.41     7542470    9.68       nL          91
27)  STYRENE                                  20.43     5525639    9.72       nL          104
28)  1,1,2,2-TETRACHLOROETHANE                21.28     6773111    9.70       nL          83
29)  1,3,5-TRIMETHYLBENZENE                   22.19     4276016    9.71       nL          120
30)  1,2,4-TRIMETHYLBENZENE                   22.96     8468648    9.93       nL          105
```

FIGURE 3. Total Ion Chromatogram



```
Data File : D:\000413\NEWST04.D
Acq Time  : 13 Apr 100    6:35 pm                         Operator: Jang
Sample    : Calibration :10 nL std    :500mL              Inst    : 5971A MSD
Misc      : 04/13/00:04/13/00:500   :     :    :#0-002    Multiplr: 1.00
Quant Time: Oct  2 11:59 19100

Method          : C:\HPCHEM\1\METHODS\CAN30M14.M
Title           : GC/MS AIR TOXICS
Last Update     : Fri Apr 14 09:45:21 2000
Response via    : Multiple Level Calibration
```

```
NEWST04.D   CAN30M14.M          Mon Oct 02 12:03:44 2000          AIRTOXIC Page 2
```

FI
G
U

RE 4. Summa Canister Sample Dilution Line System

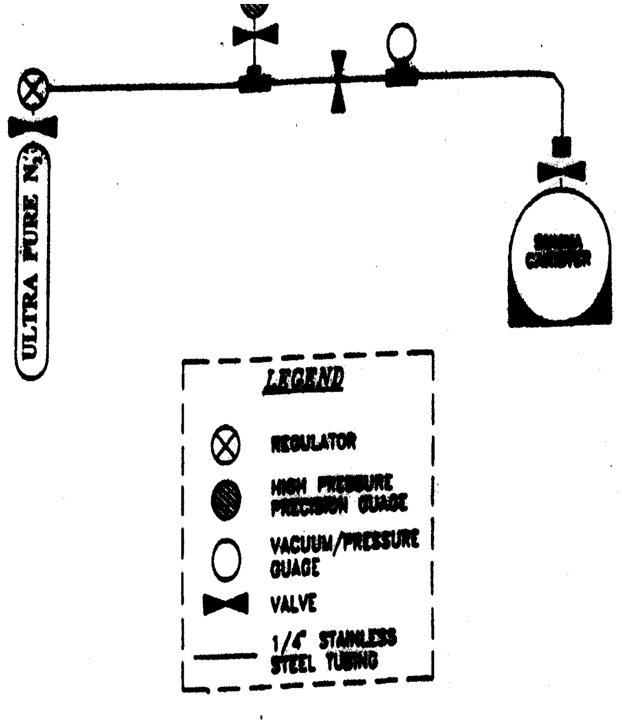


FIGURE 5. Summa Canister Analysis System

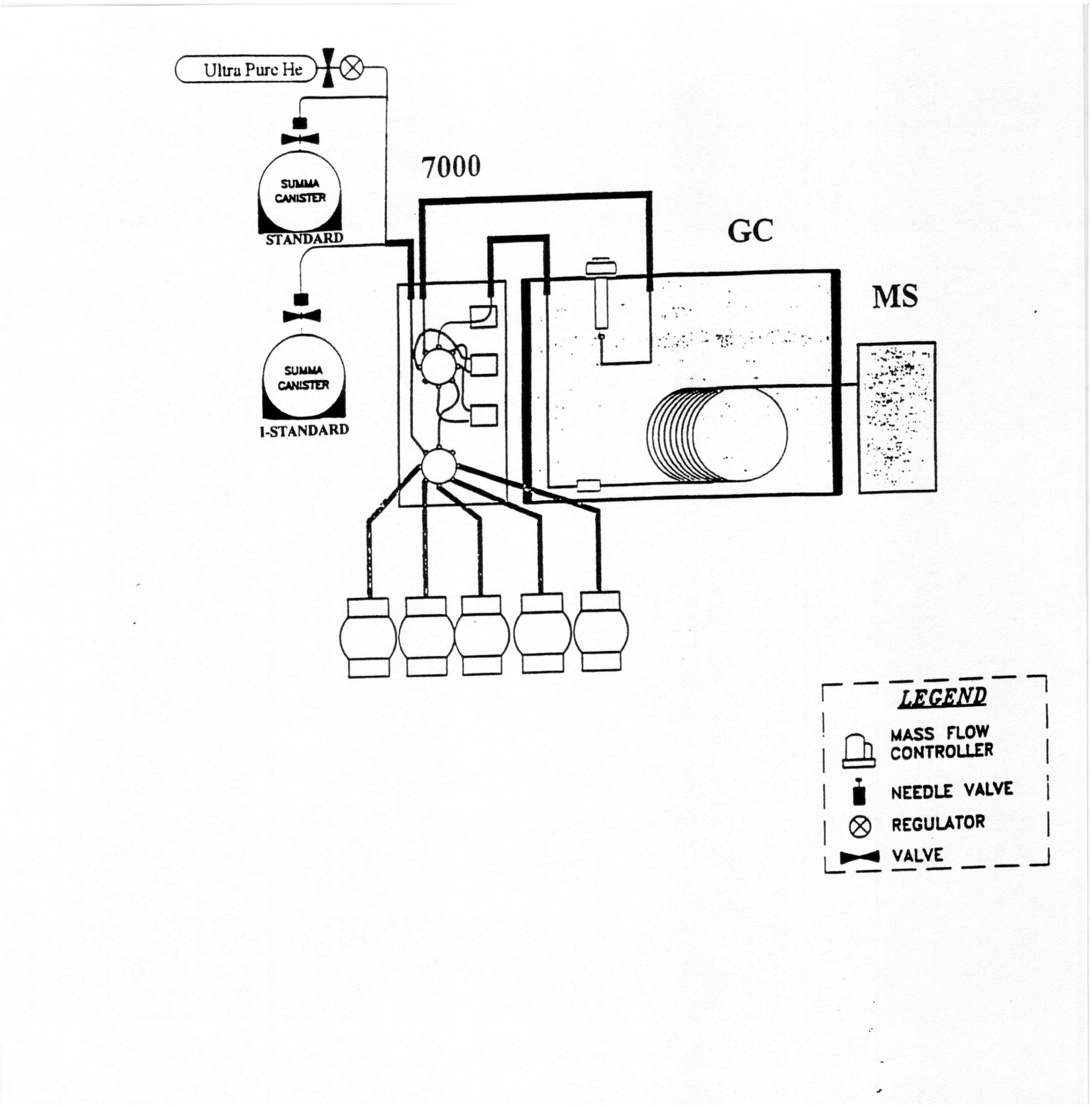


FIGURE 6.

Canister Sample Absorbed onto Absorbent Tube System

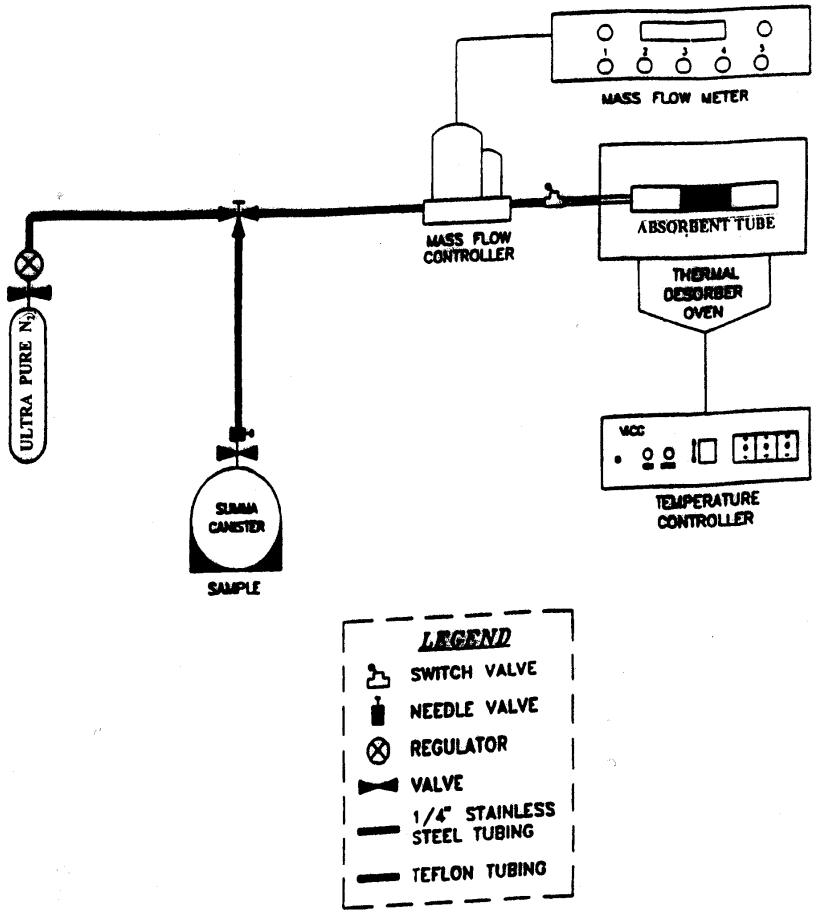

1
2
3
4
5
MASS FLOW METER
MASS FLOW CONTROLLER
ABSORBENT TUBE
THERMAL DESORBER OVEN
VICC
TEMPERATURE CONTROLLER
ULTRA PURE N_2
SUMMA CANISTER
SAMPLE
LEGEND
SWITCH VALVE
NEEDLE VALVE
REGULATOR
VALVE
1/4" STAINLESS STEEL TUBING
TEFLON TUBING

FIGURE 7. Single Tube Analysis System