Appendix K. Chemical Analytical Method
1,3-dichloropropene and methyl bromide - canisters
U.S. Environmental Protection Agency, Region 9 Laboratory

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE #310

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN AIR COLLECTED IN SPECIALLY PREPARED CANISTERS OR TEDLAR BAGS

Signature & Title

Prepared by: _____ _____
Barbara Bates, Senior Chemist Date

Reviewed by: _____ _____
Ken Hendrix, Chemist/Quality Assurance Officer Date

Approved by: _____ _____
Brenda Bettencourt, Lab. Director Date

Periodic Review:

Signature	Title	Date

TABLE OF CONTENTS

1.0 SCOPE AND APPLICATION

2.0 METHOD SUMMARY

3.0 DEFINITIONS

4.0 HEALTH AND SAFETY

5.0 SAMPLE HANDLING AND PRESERVATION

6.0 INTERFERENCES

7.0 APPARATUS AND MATERIALS

8.0 QUALITY CONTROL

9.0 ANALYTICAL PROCEDURES

10.0 DOCUMENTATION

11.0 REFERENCES

APPENDIX A
ATTACHMENT A
ATTACHMENT B
ATTACHMENT C
ATTACHMENT D
ATTACHMENT E
ATTACHMENT F

1.0 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) is applicable to analysis of air samples collected in specially prepared stainless steel canisters or Tedlar bags. Canisters included are SUMMA® polished interior canisters and SilcoSteel™ silica coated interior canisters. Air samples may originate from soil pores, the ambient environment, the indoor environment, or air pollution source emissions. This method is appropriate for a variety of applications including ambient air monitoring, soil vapor analysis, and indoor air analysis in support of EPA, Superfund, RCRA, Water, and Air programs. The target compounds for this analysis are found in Attachment A.

The Region 9 Air Analyses Laboratory is a located in Room 203. The laboratory is maintained at positive pressure to prevent intrusion of volatile contaminants from the surrounding laboratories.

2.0 METHOD SUMMARY

This Standard Operating Procedure (SOP) describes the procedures used at the Region 9 Laboratory for the analysis of volatile organic compounds in air samples collected in specially prepared stainless steel canisters or Tedlar bags. The procedures are based on EPA methodologies, specifically Compendium Method TO15, titled "The Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)". A known volume of sample is directed from the sample container to a three-stage preconcentration process called Microscale Purge and Trap. At the Region 9 Laboratory, a 400 ml sample size represents an undiluted sample (i.e. Dilution Factor = 1).

The first stage of preconcentration by Microscale Purge and Trap involves concentrating an aliquot of the air sample in a cryogenic glass-bead trap cooled to a temperature below the freezing point of the VOCs of interest. This first stage eliminates N_2 and O_2 from the air sample while retaining VOCs, water and CO_2. The glass-bead trap is then heated while slowly passing helium through the trap to transfer the sample to a second trap. The second trap in the process contains Tenax which has also been cooled. This second trap removes much of the water and CO_2 in the air sample with minimal loss of VOCs. The Tenax trap is then heated and the VOCs are swept to a third trap with a minimal volume of helium. The third and final trap is cooled and focuses the VOCs into a small volume. Upon heating, the VOCs are swept from the final trap with helium and rapidly injected

3.8 Gauge Pressure — Pressure measured with reference to the surrounding atmospheric pressure. Zero gauge pressure is equal to atmospheric pressure. Expressed as kPa or psig.

3.9 Absolute Pressure — Pressure measured with reference to absolute zero pressure. Expressed as kPa or psig.

4.0 HEALTH & SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals should be minimized through the use of personal protective equipment and laboratory engineering and design. A reference file of material safety data sheets (MSDS) is available to all personnel involved in the chemical analysis and can be found in the library (Room 118).

4.2 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, methylene chloride and vinyl chloride. Primary standards of these toxic compounds are prepared from commercially prepared gas reference standards that are available in various gas cylinder sizes. These standards must be prepared in a hood or if standards preparation is by dynamic dilution of the gaseous contents of a cylinder of stock gas calibration standards, the dilution system must be vented into a hood.

4.3 Due to the unknown and potentially hazardous characteristics of samples all sample handling and preparation must be performed in or vented into a laboratory fumehood.

4.4 All compressed gas cylinders must be securely chained to laboratory benches or walls and placed so that the label can be easily read.

4.5 Canisters should never be pressurized beyond 40 psig which is the maximum allowable pressure for specially-prepared canisters.

5.0 SAMPLE HANDLING AND PRESERVATION

5.1 Sample receipt is performed according to chain-of-custody procedures outlined in SOP #110; "Sample Receipt and Storage".

5.2 Prior to analysis, the air analysis laboratory staff shall assume custody of the air samples and transfer the samples to the storage cabinets in the air analysis laboratory.

5.3 The following information shall be checked by an analyst to ensure that the information on the sample containers corresponds to the information on the tracking sheets and the chain-of-custody record.

5.3.1 EPA sample number.

5.3.2 Region 9 Laboratory number.

5.3.3 Case number.

5.3.4 Sample Delivery Group number.

5.4 The analyst shall confirm that the integrity of the canister samples has not been compromised by checking the pressure of the canisters and comparing that with the canister pressure noted on the chain of custody record. Any problems should be noted in the run logbook and mentioned in the case narrative.

5.5 Samples shall be sorted according to date sampled, so that samples can be analyzed in order of date sampled to prevent missed holding times.

5.6 Samples in stainless steel canisters shall be analyzed within 30 days of the time of sampling. Samples in Tedlar bags shall be analyzed within 72 hours of the time of sampling.

5.8 Canisters and Tedlar bags with excess air samples shall be stored in the storage cabinets in the air analysis laboratory. Upon completion of the analysis for an SDG the excess samples for the entire SDG shall be stored, for a period of 14 days after the submission of the data deliverables associated with the sample delivery group (SDG). After 14 days, the canisters shall be opened in the fume hood and cleaned as specified in SOP #312, "Cleaning and Certification of Specially Prepared Canisters for Air Sampling". After 14 days, the Tedlar bags shall be opened in the fume hood and discarded or upon request returned to the client.

6.0 INTERFERENCES

6.1 Interferences in canister samples may result from contamination of canisters due to poor manufacturing practices. To minimize this possibility, new canisters should be filled with humified air and then analyzed, after aging for 24 hours, to determine cleanliness. The cleaning apparatus, sampling system, and analytical system should be assembled of clean, high quality components.

6.2 Contamination may occur if canisters are not properly cleaned. Before each use, canisters must be throughly cleaned and certified as outlined in SOP #312, "Cleaning and Certification of Specially Prepared Canisters for Air Sampling".

6.3 Canisters should be capped tightly during storage and shipping to prevent leakage and minimize any compromise of the sample.

6.4 Interferences in Tedlar bag samples may result from contamination of bags due to poor manufacturing practices or improper handling. To minimize this possibility, the lab encourages samplers to flush their Tedlar bags three times with high purity Nitrogen (99.998%) prior to use.

6.5 Impurities in the calibration dilution gas and carrier gas, organic compounds out-gassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks. Zero air should be humidified with organic free water that has been prepared according to SOP #205, "Preparation of Organic-Free Method Blank Water". The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with rubber components must be avoided.

6.6 Significant contamination of the analytical system can occur whenever samples containing high VOC concentrations are analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by analysis of humidified zero air to check for carry-over contamination.

6.7 Solvents and other compounds which are target analytes must never be introduced into the laboratory where volatiles analysis is performed. Methylene chloride and other common laboratory chemicals are target analytes under this SOP and must be excluded

from Room 203.

7.0 APPARATUS AND MATERIALS

7.1 The analytical system for the analysis of volatile organic compounds in air consists of an Entech 7016CA canister autosampler, an Entech 7000 proconcentrator, a Hewlett Packard HP5890 gas chromatograph and a Hewlett Packard HP5972 mass spectrometer. This system allows for the sequential analysis of up to 16 canisters and/or Tedlar bags. The gas chromatograph is equipped with a DB624 0.32 mm ID and 60 m length capillary column with 1.8 micron film. The data system used is Hewlett Packard Chemstation operated on a 386 or higher personal computer.

7.2 Reagents

7.2.1 Helium and air -- Ultrahigh purity grade in gas cylinders.

7.2.2 Liquid nitrogen (22 psig or 50 psig).

7.2.3 Organic-free water (Region 9 SOP 205)

7.2.4 Nitrogen (headspace from liquid nitrogen, gas line equipped with a hydrocarbon trap)

7.3 Standard Gas Mixtures

7.3.1 Internal Standard Gas Mixture - commercially prepared certified custom gas mixture containing 100 ppbv of the following with Nitrogen making up the balance: Bromochloromethane, Chlorobenzene-d5, 1,4-Difluorobenzene.

7.3.2 Calibration Gas Standard - commercially prepared certified gas standards containing nominally 100 ppbv of each target compound.

7.3.3 4-Bromofluorobenzene Tuning Standard - commercially prepared certified gas standard containing nominally 100 ppbv of BFB which is equivalent to 0.78 ng BFB per ml of standard mix.

{175g SUB BFB} OVER {mole SUB BFB} TIMES {100 * 10 SUP {-9} moles SUB BFB} OVER {mole SUB Nitrogen} TIMES {1 * 10 SUP {9}ng SUB {BFB}} OVER g SUB {BFB} TIMES {mole SUB {nitrogen}} OVER {22,400 ml SUB {Nitrogen}} = .78 ng SUB BFB/ml

7.3.4 Laboratory Control Sample - commercially prepared certified custom gas standard containing 100 ppbv of the following with Nitrogen making up the balance: vinyl chloride, trichlorofluormethane, methylene chloride, carbon tetrachloride, trichloroethylene, toluene, 1,1,2,2-tetrachloroethane, 1,2-dichlorobenzene.

7.3.5 Certificates of Analysis for each gas mixture must be maintained in the Standard Preparation Log/Notebook. Expiration dates for gas mixtures should be noted on these certificates.

7.4 Working Standards

A description of the preparation of all working standards is kept in a Standard Preparation Log (see Attachment B). The description should include all relevant calculations.

Before use, working standards should be allowed to equilibrate for 2 hours after preparation.

7.4.1 Preparation of BFB Tuning Standard

A clean SUMMA canister is filled to approximately 30 psig with the commercially available BFB standard. Replace the BFB canister standard every 3 months, or sooner if analysis indicates that the tuning standard has

degraded.

7.4.2 Preparation of Calibration Standard

7.4.2.1 Calibration gas standards are prepared by diluting as necessary commercially prepared certified gas standards that typically contain 100 ppbv of each target compound. For an initial calibration, the five concentration points are typically 1ppbv, 2 ppbv, 5ppbv, 10ppbv and 25ppbv. Typically a single working standard at 20 ppbv is prepared from which the five concentrations can be derived by simply varying the sample sizes to be taken during the preconcentration step.

7.4.2.2 Preparation of 20 ppbv Working Calibration Standard

Working calibration standards are to be prepared in SilcoSteel silica coated canisters. In order to further reduce adsorption of VOCs onto the interior of canisters, ten microliters of VOC free water is added to a certified clean evacuated canister. The canister is then equipped with a Swagelock® cross union tube fitting. One branch of the cross union is connected to the zero air gas line, one branch is connected to the stock calibration gas cylinder and the other branch is connected to a pressure gauge. Based on the barometric pressure, the amount of stock calibration mix added to the canister can then be determined by pressure difference. Based on the barometric pressure, zero air is then added to the canister until a predetermined pressure is reached that will achieve the dilution desired.

The concentration of the working standard is calculated using the following equation:

$$C_{WS} = C_I/DF$$

Where: C_{WS} is the concentration of the working standard
C_I is the initial concentration of the calibration standard
DF is the dilution factor.

Using pressure difference, the dilution factor is calculated using the equation:

$$DF = P_F/P_{STD}$$

Where: P_F = Final Canister Pressure (psia)
P_{STD} = Pressure of Commercial Calibration Standard Added

Replace the working calibration standard every 30 days, or sooner if analysis indicates that the standard has degraded.

7.4.3 Preparation of Method Blank

The method blank working standard is prepared in SilcoSteel silica coated canisters. In order to further reduce adsorption of VOCs onto the interior of canisters, ten microliters of VOC free water is added to a certified clean evacuated canister. The canister is then equipped with a Swagelock® cross union tube fitting. One branch of the cross union is connected to the zero air gas cylinder, another branch is connected to a pressure gauge and the other branch is capped. The canister is filled with zero air to a final canister pressure of approximately 30 psig. Replace the method blank working standard every 30 days, or sooner if analysis indicates that the standard has degraded.

7.4.4 Preparation of LCS Working Standard

The LCS working standard is prepared in SilcoSteel silica coated canisters. In order to further reduce adsorption of VOCs onto the interior of canisters, ten microliters of VOC free water is added to a certified clean evacuated canister. The canister is then equipped with a Swagelock® cross union tube fitting. One branch of the cross union is connected to the stock LCS gas cylinder, another branch is connected to a pressure gauge and the other branch is capped. The canister is filled with the stock LCS mixture to a final canister pressure of 20 - 30 psig. Replace the LCS working standard every 30 days, or sooner if analysis indicates that the standard has degraded.

7.5 Stainless steel tubing and stainless steel fittings

7.6 Stainless steel cylinder pressure regulator -- standard two-stage cylinder regulators with pressure gauges.

7.7 Pressure gauge with stainless steel wetted parts with ±0.25% accuracy.

7.8 Vacuum gauge with monel process connection with ±0.25% accuracy.

7.9 Gas-tight syringes (5-mL, 10-ml, 25-mL, 100-ml).

8.0 QUALITY CONTROL

This section describes the QA/QC criteria which shall be followed in the analysis of air samples for volatile organic compounds. A summary of the QA/QC criteria can be found in Attachment C.

8.1 Mass calibration.

8.1.1 Mass calibration of the analytical system shall be performed whenever the mass spectrometer is shut down, or whenever there is a mass misassignment. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer. Perfluorotributylamine (PFTBA) is the compound which shall be used to perform the mass calibration of the instrument. The PFTBA spectrum must meet the following criteria:

Mass	Target % of Mass 69
69	100
219	>30
502	>1

Isotope Ratio	
Mass Ratio	Target %
70/69	0.54-1.6
220/219	3.2-5.4
503/502	7.9-12.3

8.1.2 If the PFTBA spectrum does not meet the criteria listed above, corrective action must be taken. The corrective action may be as simple as adjusting the voltages/retuning the MS. If retuning the MS does not produce adequate PFTBA spectra, further maintenance such as cleaning the ion source may be required.

8.2 GC/MS System Performance Check (BFB analysis.)

8.2.1 Prior to the analysis of any calibration standards, blanks, and samples, the GC/MS system must meet the mass spectral ion abundance criteria for bromofluorobenzene (BFB). Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target and non-target compounds.

8.2.2 Frequency of GC/MS Performance Check.

BFB must be injected once at the beginning of each 24-hour period during which standards, blanks and samples are to analyzed. The twelve-hour time period begins at the moment of injection of the BFB. The time period ends after twenty-four hours have elapsed. If a sample is analyzed after the 24-hour time period has elapsed it must be re-analyzed.

8.2.3 The analysis of the GC/MS performance check standard is performed by introducing 50 ng of BFB into the analytical system. The procedure for analysis are outlined in section 9 of this SOP.

The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is conducted using a single scan prior to the elution of BFB.

8.2.4 The ion abundance ratios must meet the following criteria.

Mass (m/z)	Relative Ion Abundance Criteria*
50	8.0 - 40.0 percent of mass 95

75	30.0 - 66.0 percent of mass 95
95	Base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of mass 95
173	less than 2.0 percent of mass 174
174	50.0 - 120.0 percent of mass 95
175	4.0 - 9.0 percent of mass 174
176	93.0 - 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

*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 percent that of m/z 95.

8.2.4.1 If the BFB acceptance criteria are not met, the MS must be retuned. It may be necessary to clean the ion source or take other necessary actions to achieve the acceptance criteria.

8.2.4.2 Results of the BFB tuning are to be maintained in the BFB binder that is kept in the Air Lab.

8.3 Initial calibration.

8.3.1 Prior to analysis of samples and blanks but after the instrument performance check criteria has been met, each GC/MS system must be calibrated at five concentrations that span the monitoring range of interest. Each GC/MS system must be recalibrated whenever a corrective action which may change instrument response (e.g., ion source cleaning, column replacement, etc.) is performed. Recalibration is also required if the continuing calibration acceptance criteria can not be met.

8.3.2 Analyze the initial calibration standards according to section 9 of this SOP. Quantitation ions for the target compounds are listed in Attachment A.

8.3.3 Calculate the relative response factor (RRF) for each target compound for all five calibration standards using the following equation. The quantitation ions and internal standard assignments are listed in Attachment A.

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

where: Ax = Area of quantitation ion of compound x
Ais = Area of quantitation ion for associated internal standard
Cx = Concentration of compound x
Cis = Concentration of the associated internal standard

8.3.4 Calculate the mean RRF for each compound using the equation:

RRF SUB avg= SUM FROM { i=1 }
TO n(x SUB i/n)

where: RRF_{avg} = Mean relative response factor
x_i = RRF of the compound at concentration i
n = Number of concentration values (i.e. 5)

8.3.5 Calculate the percent relative standard deviation (%RSD) of the RRF values for each compound using the following equations.

$$\%RSD = (SD/RRF_{avg})*100$$

SD SUB RRF = SQRT { { { SUM
FROM { i=1} TO n (RRF SUB i- RRF
SUB avg) SUP 2} } OVER {n-1 } }

8.3.6 Calculate the relative retention time (RRT) for each target compound over the initial calibration range using the following equation:

$$RRT = RT_c/RT_{IS}$$

where: Rt_c = Retention time of target compound (seconds)
RT_{IS} = Retention time of the internal standard (seconds)

8.3.7 Calculate the mean of the relative retention times (RRT_{avg}) for each analyte target compound over the initial calibration range using the following equation.

RRT SUB avg = SUM FROM {i=1}
TO n (RRT SUB i/n)

where: RRT_{avg} = mean relative retention time for the target compound for each initial calibration standard.
RRT = relative retention time for the target compound at each calibration level.

8.3.8 Calculate the mean area response Y_{avg} for each internal standard over the initial calibration range using the following equation.

Y SUB avg = SUM FROM { i=1} TO n
(Y SUB i OVER n)

where: Y_{avg} = Mean area response
Y = Area response for the primary quantitation ion for the internal standard for each initial calibration standard.

8.3.9 Calculate the mean of the retention times (RT_{avg}) for each internal standard over the initial calibration range using the following equation.

RT SUB avg = SUM FROM { i=1} TO
n (RT SUB i OVER n)

where: RT_{avg} = Mean retention time (seconds)
RT = Retention time for the internal standard for each initial calibration standard (seconds)

8.3.10 Immediately after the initial calibration is performed, the data files shall be processed and checked to ensure that the following technical acceptance criteria have been satisfied.

8.3.10.1 The calculated %RSD for the RRF for each compound

must be less than 30% with at most two exceptions up to a limit of 40%.

8.3.10.2 The RRT for each target compound at each concentration level must be within 0.06 RRT units of the mean RRT for the compound.

8.3.10.3 The area response Y at each calibration level must be within 40% of the mean area response Y_{avg} over the initial calibration range for each internal standard.

8.3.10.4 The retention time shift for each of the internal standards at each calibration level must be within 20 seconds of the mean retention time over the initial calibration range for each internal standard.

8.3.11 If any of the criteria have not been met because of a single concentration point in the curve, then that single point can be reanalyzed, and the data checked against the criteria. The system must be repaired so that the criteria are satisfied before any samples are analyzed. If repairs are made to the system, then a new initial calibration must be performed. The initial calibration should be checked for misidentified peaks due to retention time shifts.

8.3.12 If the initial calibration meets all the specified criteria, the remainder of the analytical period may be used for the analysis of blanks and samples, using the calibration standard that is the same concentration as the continuing calibration to quantitate the blank and sample data.

8.4 Continuing Calibration

8.4.1 A continuing calibration standard at a mid-level concentration (i.e. 10 ppbv) must be analyzed once every 24 hours. The daily calibration sequence starts with the injection of BFB and is analyzed after the BFB analysis meets the ion abundance criteria.

8.4.2 Analyze the continuing calibration standard according to section 9 of this SOP.

8.4.3 Calculate the relative response factor (RRF) for each target compound using the equation in Section 8.3.3.

8.4.4 For each target compound, calculate the percent difference (%D) between the continuing calibration RRF and the mean RRF in the most recent initial calibration using the following equation.

%D ~ = ~ { { RRF SUB c ~ - ~ RRF
SUB avg } OVER RRF SUB avg } ~
TIMES ~ 100

where: RRF_c = RRF of the compound in the continuing calibration standard.
RRF_{avg} = Mean Rrf of the compound in the most recent initial calibration.

8.4.5 The %D for each target compound in the daily calibration must be within ± 30 percent with at most two exceptions up to a limit of 40%. If the continuing calibration meets all the specified criteria, the quantitation method file is saved as ***mmddyyCC***.m. If this criteria is not satisfied, rerun the continuing calibration standard, or run a new initial calibration. If the system undergoes corrective action (i.e. clean the ion source, change of column) then a new initial calibration must be performed. Check the continuing calibration for mis-identified peaks due to retention time shifts.

8.5 Method blank analysis.

8.5.1 A method blank must be analyzed immediately after the calibration standard(s), and before the samples are analyzed, in order to demonstrate that the instrument is free of contamination.

8.5.2 Analyze the method blank according to section 9 of this SOP.

8.5.3 The method blank RIC and quantitation report must be checked immediately after it is analyzed, or as soon as possible, to determine that the following criteria have been met:

The method blank should not contain any target analyte at a concentration

greater than the reporting limits (See Attachment A) and should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte. In addition, the area response for each internal standard (IS) in the blank must be within ±40 percent of the mean area response of the IS in the most recent valid calibration. Finally, the retention time for each of the internal standards must be within ±0.33 minutes between the blank and the most recent valid calibration.

8.5.4 If the method blank does not meet the technical acceptance criteria, a new blank shall be analyzed before any samples are analyzed. If the technical acceptance criteria is still not met, the Laboratory must ensure that method interferences caused by contaminants in solvents, reagents, canisters, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures need to be taken and documented before further sample analysis proceeds.

8.5.5 If an analyte in the blank is found to be out of control (i.e., contaminated) and the analyte is also found in associated samples, those sample results should be "flagged" as possibly contaminated.

8.6 Laboratory control sample analysis (LCS)

8.6.1 The LCS must be analyzed and reported once per 24-hour analytical sequence.

8.6.2 Analyze the LCS according to section 9 of this SOP.

8.6.3 Calculate individual compound recoveries of the LCS using the following equation:

% Recovery = Concentration SUB
Reported OVER Concentration SUB
Spiked * 100

8.6.4 The percent recovery for each of the compounds in the LCS must be within the recovery limits of 70 to 130 percent. In addition, the retention time shift between the LCS and the most recent valid calibration for each of the internal standards must be within ±0.33 minutes.

8.6.5 If the technical acceptance criteria for the LCS are not met, this must be documented in the case narrative.

8.7 Low standard quantitation limit (QL)

8.7.1 The QL at the 1 ppbv level must be analyzed and reported once per 24-hour analytical sequence.

8.7.2 Analyze the QL according to section 9 of this SOP.

8.7.3 The QL RIC and quantitation report must be checked immediately after it is analyzed, or as soon as possible, to determine that the following criteria have been met:

8.7.4 The concentration of each target compound in the QL must be within ± 50% of concentration of the low standard.

8.7.5 If the technical acceptance criteria for the QL are not met, this must be documented in the case narrative.

8.8 Instrument blanks

8.8.1 In the event that a sample is analyzed which exceeds the calibration range of the instrument, an instrument blank must be analyzed to demonstrate that the system is free of carryover contamination prior to the analysis of another sample.

8.8.2 Analyze the instrument blanks according to section 9 of this SOP.

8.8.3 The instrument blank should not contain any target analyte at a concentration greater than the reporting limits (see Attachment A) and should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte. In addition, the area response for each internal standard (IS) in the blank must be within ±40 percent of the mean area response of the IS in the most recent valid calibration. Finally, the retention time for each of the internal standards must be within ±0.33 minutes between the blank and the most recent valid calibration.

8.9 Internal standard recovery

8.9.1 Internal standard responses and retention times must be evaluated during or immediately after data acquisition.

8.9.2 If the retention time for any internal standard changes by more than 20 seconds from the latest daily (24-hour) calibration standard (or mid level standard if samples are analyzed in an inital calibration analytical sequence), the GC/MS system must be inspected for malfunctions, and corrections made as required.

8.9.3 If the area response for any internal standard changes by more than ±40 percent between the sample and the most recent valid calibration, the GC/MS system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

8.9.4 If after reanalysis, the total area for all internal standards are within the criteria, then the problem is considered to have been within the laboratory's control. Submit only the data from the reanalysis.

8.10 Sample dilution.

8.10.1 If the on-column concentration of any target compound in any sample exceeds the initial calibration range, a dilution of the sample must be analyzed. Dilution of the sample can be accomplished by reducing the sample size taken during the preconcentration step. However, a sample

size lower than 20 ml is not recommended.

8.10.2 If further dilution is necessary, an aliquot of the original sample must be taken and diluted into a certified clean canister with zero air. The diluted sample should be allowed to equilibrate for 2 hours after preparation before analysis.

8.10.2.1 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

8.10.2.2 The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

8.10.2.3 In the case of extremely contaminated samples several dilutions may be required.

8.10.3 After a sample is analyzed that contains one or more target compounds at a level exceeding the initial calibration range of the system, it must be demonstrated that there is no carryover to subsequent analyses. The laboratory must either:

8.10.3.1 Analyze an instrument blank immediately after the contaminated sample. The instrument blank must meet the acceptance criteria in Section 8.7.

8.10.3.2 Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the limits above. The maximum contamination criteria are as follows: the sample must not contain a concentration above the quantitation limit for the target compounds that exceeded the limits in the contaminated sample.

9.0 ANALYTICAL PROCEDURES

9.1 Analytical system preparation.

Mass calibration of the analytical system shall be performed according to the schedule prescribed in section 8.1. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer. Perfluorotributylamine (PFTBA) is the compound which shall be used to perform the mass calibration of the instrument.

9.1.1 Enter the control program of the instrument and enable the analyzer voltages.

9.1.2 Enter the tuning program of the instrument. Turn the filament and electron multiplier on and enable the scan function.

9.1.3 Open the calibration gas valve and allow the PFTBA to infuse into the analyzer.

9.1.4 Adjust the voltages according to the manufacturer's instruction manual and specifications to obtain the proper mass ratio, peak shape, and isotope peak resolution.

9.1.5 Calibrate the mass spectrometer as specified in the manufacturer's instruction manual.

9.1.6 The data system will automatically acquire a PFTBA spectrum, process the PFTBA spectrum data, and calibrate the mass spectrometer.

Check the mass spectrum/peak ratios with the specifications listed in section 8.1 The specifications shall be met or the instrument must be re tuned and recalibrated.

9.2 Mass Spectrometer Check

Analyzer temperatures and parameters indicative of a leak shall be checked on a daily basis, prior to the analysis of the 4-bromofluorobenzene (BFB) tuning standard.

9.2.1 Enter the control program (TuneMS Diagnostics/Vacuum Control Vacuum Vacuum Status) and check that the analyzer temperature

and foreline pressures are set to the following values:

9.2.1.1 MS temperature should be approximately 175°C.

9.2.1.2 The foreline pressure should be between 20 and 100 mTorr.

9.2.1.3 If the display indicates that the analyzer temperatures are not at the desired set points, corrective action must be performed according to the operator's manual.

9.2.2 Check the ionization gauge control for the mass spectrometer vacuum manifold pressure.

9.2.2.1 The vacuum manifold pressure should be between 5×10^{-6} to 2×10^{-4} Torr.

9.2.2.2 Values higher than indicated above are indicative of a leak and must corrected.

9.2.3 Using the GC panel ensure that the GC interface temperature is at 280°C.

9.2.4 Check the nitrogen (m/z 28) to water (m/z 18) ratio

Set the mass spectrometer to scan over a range of 10 to 50 m/z. Observe the ratio of the water peak (m/z 18) to the nitrogen peak (m/z 28). If a leak is present in the mass spectrometer the nitrogen peak will be greater than the water peak. Corrective action must be taken if a leak is detected.

9.3 GC/MS Performance Check

9.3.1 Prior to the analysis of any calibration standards, blanks, or samples (including MS/MSDs), the GC/MS system must meet the mass spectral ion abundance criteria for bromofluorobenzene (BFB) prescribed in section 8.2. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target and non-target compounds.

9.3.2 Set up the Preconcentrator with appropriate conditions. See Attachment D.

9.3.3 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment E.

9.3.4 Introduce 50 ng of BFB onto the analytical system. See Section 7.3.3 on calculating volume of BFB standard equivalent to 50 ng.

9.3.5 After the data acquisition is complete, locate th BFB peak, average three scans (the peak apex scan and the scans immediately preceding and following the apex) and perform a background subtraction. Execute the BFB evaluation procedure and print out a hard copy of the spectrum, the chromatogram, and the table of ion abundances.

9.3.6 The ion abundance ratios must meet the criteria listed in section 8.2.

9.3.7 The instrument must be retuned and recalibrated if any of the BFB relative ion abundance criteria are not met.

9.4 Analysis of air samples

The target compounds for this method are found in Attachment A.

9.4.1 Five-point initial calibration

A five-point initial calibration is performed in order to demonstrate that the GC/MS system provides a linear response over the desired concentration range. Based on a 400 ml sample size, the five concentration points are listed in the table below.

Calibration Standard Amounts

CALIBRATION POINT	Amount IS Standard 100 ppbv	Amount 20 ppbv Working Calibration Standard
25 ppbv	40 ml	500 ml
10 ppbv	40 ml	200 ml
5 ppbv	40 ml	100 ml
2 ppbv	40 ml	40 ml

1 ppbv	40 ml	20ml

9.4.1.1 Load closed canisters onto the autosampler. Prior to starting the analytical system, flush and evacuate the line to each autosampler port that is used. Flush & evacuation can be done automatically through the preconcentration control system. Alternatively flush and evacuation can be done manually by flushing the line for 5 seconds with N2 and then evacuating the line for 10 seconds. When done manually the flush/evacuation cycle should be repeated three times for each autosampler port. Prior to the flush/evacuation, ENSURE THAT CANISTER VALVES ARE CLOSED.

9.4.1.2 Set up the preconcentrator system with the appropriate parameters and open all loaded canisters that will be analyzed. See Attachment D.

9.4.1.3 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment E.

9.4.1.4 Analyze the standard and acquire the data.

9.4.1.5 Quantitate the data and print out a quantitation report and chromatogram.

9.4.1.6 Analyze the four other initial calibration standards following the procedures outlined above.

9.4.1.7 Update the initial calibration response factors in the method by associating the correct data file with each calibration level. Update the reference spectrum using the data file corresponding with the same concentration as the continuing calibration (10 ppbv). The quantitation method file is saved as ***mmddyyIC***.m where *mm* is the month and *dd* is the date and *yy* is the year.

9.4.1.8 Generate the initial calibration summary report. Samples shall not be analyzed if the initial calibration does not meet the criteria

specified in Section 8.3.10 of this SOP.

9.4.1.9 If the initial calibration meets all the criteria specified in section 8.3.10 of this SOP, the remainder of the 24-hour analytical period may be used for the analysis of blanks and samples, using the 10 ppbv calibration standard to quantitate the blank and sample data files.

9.4.2 Continuing calibration

A continuing calibration standard shall be run once every 24-hour analytical time period, after BFB tuning and prior to a method blank analysis. The continuing calibration check is performed in order to determine if the GC/MS system is operating within the acceptable range as demonstrated by the percent difference and the minimum response factor criteria meeting the appropriate QA/QC criteria. The continuing calibration is analyzed at a level of 10 ppbv.

9.4.2.1 Load the closed canister containing the 20 ppbv working calibration standard and flush the line to its autosampler port as described in section 9.4.1.

9.4.2.2 Set up the preconcentrator system with the appropriate parameters (See Attachment D) and open the valve on the appropriate canisters that will be analyzed.

9.4.2.3 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment E.

9.4.2.4 Analyze the standard and acquire the data.

9.4.2.5 Quantitate the data and print out a quantitation report and chromatogram.

9.4.2.6 Generate the continuing calibration summary report. Samples shall not be analyzed if the continuing calibration does not meet the criteria specified in Section 8.4 of this SOP.

9.4.2.7 Update the response factors for the continuing calibration for each

analyte in the method. Save the method as mmddyycc where *mm* is the month, *dd* is the date and *yy* is the year.

9.4.2.8 If the continuing calibration meets all the criteria specified in section 8.4, the remainder of the 24-hour analytical period may be used for the analysis of blanks, laboratory control standards and samples, using the RRFs from the daily 10 ppbv continuing calibration file to quantitate the blank and sample data files.

9.4.3 Method blank analysis.

After the initial or continuing calibration is performed and before samples are analyzed, a method, or laboratory blank analysis shall be conducted.

9.4.3.1 Load the closed canister containing the humidified zero air and flush the line to its autosampler port as described in section 9.4.1.

9.4.3.2 Set up the preconcentrator system with the appropriate parameters (See Attachment D) and open the valve on the canister.

9.4.3.3 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions.See Attachment E.

9.4.3.4 Analyze the method blank and acquire the data.

9.4.3.5 Quantitate the data and print out a quantitation report and chromatogram.

9.4.3.6 Samples shall not be analyzed if the method blank does not meet the criteria specified in section 8.5 of this SOP.

9.4.3.7 If the method blank meets all the specified criteria, the remainder of the 24-hour analytical period may be used for the analysis of samples.

9.4.4 Laboratory Control Standard (LCS) analysis

After analysis of the method blank has been completely, analysis of the

LCS shall be conducted.

9.4.4.1 Load the closed canister containing the LCS working calibration standard and flush the line to its autosampler port as described in section 9.4.1.

9.4.4.2 Set up the preconcentrator system with the appropriate parameters (See Attachment D) and open the valve on the cylinder.

9.4.4.3 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment E.

9.4.4.4 Analyze the LCS and acquire the data.

9.4.4.5 Quantitate the data and print out a quantitation report and chromatogram.

9.4.5 Low standard quantation limit analysis.

After analysis of the laboratory control standard is performed and before samples are analyzed, a low standard quantitation limit analysis shall be conducted.

9.4.5.1 Load the closed canister containing the 20 ppbv working calibration standard and flush the line to its autosampler port as described in section 9.4.1.

9.4.5.2 Set up the preconcentrator system with the appropriate parameters (See Attachment D) and open the valve on the canister.

9.4.5.3 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment E.

9.4.5.4 Analyze the low standard quantitation limit and acquire the data.

9.4.5.5 Quantitate the data and print out a quantitation report and chromatogram.

9.4.6 Sample analysis.

Samples shall be analyzed only after the BFB tune, initial calibration, continuing calibration, and method blank analyses meet all of the appropriate criteria specified in Section 8 of this SOP. If time still remains in the 24-hour time period after meeting the initial calibration criteria, samples may be analyzed. It is not necessary to analyze a continuing calibration standard within this 24-hour time period, if the initial calibration standard that is at the same concentration as the continuing calibration standard meets the continuing calibration acceptance criteria.

9.4.6.1 Prior to analysis, samples should be allowed to equilibrate in the lab for at least 2 hours after collection.

9.4.6.2 The analyst shall check that the numbers on the canisters coincide with the numbers on the routing forms to ensure that the correct sample is being analyzed.

9.4.6.3 Break the chain of custody seal on the valve of the canister with a scalpel or other appropriate implement, and measure the canister pressure with an appropriate pressure gauge. Record the canister pressure on the chain of custody sheet.

9.4.6.4 Load the closed canisters onto the autosampler and record the canister ID number and the autosampler position for each sample in the runlog.

9.4.6.5 Set up the preconcentrator system with the appropriate parameters and enter the sequence of analysis. Add 40 ml of the internal standard. Set up the system to take a 400 ml aliquot of the sample. If very high concentrations are suspected, screen a 40 ml aliquot of the sample first. After the sequence has been entered, flush the appropriate autosampler lines as outlined in Section 9.4.1.

9.4.6.6 Setup the GC/MS system with the appropriate GC and mass spectrometer conditions. See Attachment E.

9.4.6.7 Set up a data acquisition. The sample description shall

include the EPA sample number, the laboratory sample number, the sample volume and the dilution factor (i.e. 1234, AB12345, 400, 1). Additional header information shall include instrument ID and the analyst's initials.

9.4.6.8 Quantitate the data and print out a quantitation report and chromatogram.

9.4.6.9 Check the sample's internal standard recoveries with the criteria in the QA/QC section of this SOP.

9.4.6.10 In addition to the full strength analysis, the sample must be diluted and reanalyzed if any of the target analytes exceed the calibration range of the instrument. The sample should be diluted so that the target compound(s) which was originally outside of the calibration range, will fall within the upper half of the initial calibration range of the instrument.

10.0 DOCUMENTATION

10.1 Data from the Region 9 Laboratory is presented to the client in one of two general reporting formats: a complete, validatible data package or a summary report. For the former the laboratory prepares summary forms of calibration, quality control, and sample results and provides this information along with the raw data, a case narrative, and an analytical report spreadsheet to the client. If a summary report is all that is required, the laboratory prepares a case narrative and the analytical spreadsheet for delivery to the client and collects the raw data which will be filed at the laboratory. Section 10.2 details the requirements of a complete data package and Section 10.3 lists the summary report requirements.

10.2 Data package assembly.

The analyst, or other chemist, shall assemble a discrete data package for each SDG in each case requiring the delivery of a validatible data package according to the following instructions, and in the following order. Each section of the data package shall have a cover sheet titled with the appropriate section name. The data package shall be sequentially numbered after assembly using a hand operated

numerator.

10.2.1 Case Narrative section

10.2.1.1 The Case Narrative section shall contain a text narrative describing, but not limited to, the following.

10.2.1.1.1 Site name.

10.2.1.1.2 Case number.

10.2.1.1.3 SDG number.

10.2.1.1.4 Date(s) the samples were received.

10.2.1.1.5 EPA sample number.

10.2.1.1.6 Region 9 laboratory sample number.

10.2.1.1.8 Summary of the analyses performed.

10.2.1.1.9 Problems with the analyses.

10.2.1.1.10 Summary of the QA/QC results.

10.2.2 Analytical report spreadsheet

10.2.2.1 A spreadsheet (Lotus 123, Version 5) containing a summary of the results for all target analytes for all samples and blanks will be included in the data package.

10.2.2.2 The header information for each sample will contain the station location, Sample ID, and date sampled.

10.2.2.3 The Region 9 Laboratory defines the quantitation limit as being equal to the lowest calibration standard. Values down to 1/2 the lowest standard are included in the Laboratory's analytical report. Reported values $\geq$ 1/2 and

less than the QL are flagged as estimated. Compounds that show up at < 1/2 the QL are included in the raw data section of the full data package but not reported in the analytical report. The results section will contain the results for each target analyte as follows:

If an analyte is not detected then the quantitation limit with a "U" qualifier will be reported

If an analyte is detected at a level > 1/2 the quantitation limit, then, the analytical report will include the value reported on the quantitation report along with any appropriate qualifier as defined here.

B This analyte was detected in the associated method blank or detected in the associated canister during certification.

E The amount detected exceeds the calibration range of the instrument.

J The amount detected is less than the reporting limit and is only an estimated value.

N The identification of this compound is based upon a mass spectral library search. This flag is used for tentatively identified compounds (TICs).

U This compound was analyzed for, but not detected.

10.2.3 Tracking Forms section

The Tracking Form section shall contain the following forms.

10.2.3.1 Region 9 sample cross reference form.

10.2.3.2 A copy of the chain of custody record received with each sample shipment.

10.2.3.3 A copy of the shipper's airbill, or bill of lading.

10.2.4 QA/QC Summary section

The QA/QC section shall contain the following summary forms for each day that samples for the specific sample delivery group were analyzed. All of the summaries shall be checked by the analyst to ensure that all of the filenames are correct, and that all of the appropriate standards, blanks, samples, spikes, and tune files have been included.

10.2.4.1 Laboratory Control Sample (LCS) recovery data in chronological order.

10.2.4.2 Blank summary data in chronological order.

10.2.4.4 Internal standard area recovery data in chronological order.

10.2.5 Sample section

The sample section shall contain the following forms and raw data for each sample in the sample delivery group, assembled in alphanumeric order.

10.2.5.1 Quantitation report generated by the analytical system listing all target compounds that were detected and the levels detected in the sample.

10.2.5.2 Tentatively identified compounds (TIC) non-target compound report form detailing the compound names, retention times and the estimated concentrations of up to ten tentatively identified compounds.

10.2.5.3 The reconstructed ion chromatogram (RIC) of the data file.

10.2.5.4 The raw spectra and enhanced spectra of the target compounds detected in the sample, as well as the enhanced spectra of the corresponding target compound in the calibration file, in order of elution.

10.2.5.5 Enhanced spectra of non-target compounds detected in the sample. Library search listing the three best fits of a forward library search of the non-target compounds.

10.2.6 Instrument QC Data section.

The Instrument QC Data section shall contain the following for each day that an initial calibration and/or analysis of samples in the SDG were performed, in chronological order.

10.2.6.1 Copies of all instrument run logbook pages in chronological order.

10.2.6.2 Data from the instrument tune file including, the background subtracted spectra, the mass listing, and the RIC labeled so as to indicate the BFB peak.

10.2.6.3 Form containing the response factors for each file, the average response factor for each compound, and the percent RSD for each compound in the initial calibration. Place the associated RIC and quantitation reports immediately following the form. All manual integration must be fully documented.

10.2.6.4 Form containing the average response factor for each compound in the initial calibration, and the response factor and %D for each compound in the continuing calibration. Place the associated RIC and quantitation reports after the form. All manual integration must be fully documented.

10.2.6.5 For each method blank file, the same data shall be submitted as that for each sample (section 10.2.5).

10.2.6.6 For each LCS, the quantitation report generated by the

analytical system listing all target compounds that were detected and the levels detected in the sample and the raw spectra and enhanced spectra of the target compounds detected in the sample, as well as the enhanced spectra of the corresponding target compound in the calibration file, in order of elution.

10.2.6.7 For each QL, the quantitation report generated by the analytical system listing all target compounds that were detected and the levels detected in the sample and the raw spectra and enhanced spectra of the target compounds detected in the sample, as well as the enhanced spectra of the corresponding target compound in the calibration file, in order of elution.

10.2.6.8 Copies of all applicable standards preparation logbook pages.

10.2.7 Miscellaneous Data.

10.2.7.1 Canister certification data should include raw data quantitation report, the reconstructed ion chromatogram (RIC) of the data file, the raw spectra and enhanced spectra of the target compounds detected in the sample, as well as the enhanced spectra of the corresponding target compound in the calibration file, in order of elution, and enhanced spectra of non-target compounds detected in the canister with a library search listing the three best fits of a forward library search of the non-target compounds.

10.2.7.2 Copies of all applicable sample dilution logbook pages.

10.3 Summary Report and Raw Data

When the client requirements stipulate a summary report the laboratory prepares the case narrative, analytical results spreadsheet, and organizes the raw data associated with each SDG for filing in the event that future data review or validation is required.

10.3.1 The case narrative is prepared according to the requirements listed in section 10.2.1.

10.3.2 The analytical results spreadsheet is prepared according to the specifications provided in section 10.2.2.

10.3.3 The raw data associated with the analysis of all the samples in the SDG must be organized for filing and presented for review along with the case narrative and the spreadsheet. No summary forms need be generated with the raw data but any forms which would normally be generated as part of the analysis must be included in the package. For example, the calibration summary reports generated by the data system and used by the analyst to assess the acceptability of the calibration should be filed with the raw data.

10.3.3.1 Sample tracking information as detailed in section 10.2.3 should be included as the analyst has a copy of the information readily available.

10.3.3.2 Sample raw data organized by EPA sample ID must include: the quantitation report; the RIC; the raw and enhanced spectra of the target compounds detected in the sample, as well as the enhanced spectra of the corresponding target compound in the calibration file; and enhanced spectra of non-target compounds detected in the sample along with the library search listing the three best matches for the non-target compounds. (Section 10.2.5.3 through 10.2.5.6)

10.3.3.3 Calibration data must include any available summary information and the quantitation reports and RICs for all initial calibrations and continuing calibrations associated with the SDG. This information must be organized by date. Additionally, any manual integration must be demonstrated by including the associated peak integration.

10.3.3.4 Raw data for QC samples must be included. Tuning data and the associated summary used by the analyst to determine acceptability, blanks (quant report, RIC and spectra and TICs), LCS data (quant report and RICs) should all be included in this order.

10.3.3.5 Runlogs and standard preparation logbooks need not be

included in the raw data as these are already filed in an accessible manner in the laboratory.

10.4 Technical review.

Each TO-15 data package shall be reviewed by the QA/QC Officer or a senior level chemist, other than the chemist who performed the analyses. After the peer review is performed, the case narrative and analytical report shall be submitted to the client with a cover letter signed by the Laboratory Director. If the client request third-party data review or validation of data, the data package shall be submitted to the Quality Assurance Office at Region 9.

10.5 Run logbook.

A run logbook shall be maintained for the air analytical system (See Attachment F). The data file name consists of a maximum of eight alphanumeric characters and are named according to the following convention.

DATA FILE	SYSTEM CHECK FILES	SAMPLE DATA FILE
Naming Convention	**Daily BFB: MMDDBFB** **Method Blank: MMDDBLK, MMDDBLK2** **Initial Calibration: MMDDICS1, MMDDICS2, MMDDICS3, MMDDICS4, MMDDICS5** **Daily Calibration: MMDDCCV** **Daily LCS: MMDDLCS** **Daily Quantitation Limit: MMDDQL**	**Sample: LABID# i.e. AB00000** **Dilutions: LABID#D, LABID#D2... i.e AB00000D, A00000D2**

11.0 REFERENCES

11.1 USEPA; Compendium Method TO-15; Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS); January, 1997.

11.2 USEPA; Compendium Method TO-14; Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA® Passivated Canister Sampling and Gas Chromatographic Analysis. May 1988.

11.3 USEPA; Statement of Work (SOW) for the Analysis of Air Toxics from Superfund Sites. Draft report, June 1990.

11.4 Region 9 SOP 312, Cleaning and Certification of Specially Prepared Canisters for Air Sampling.

11.5 EPA Method 0040, Sampling of Principal Organic Hazardous Constituents From Combustion Sources Using Tedlar Bags.

11.6 Entech Instruments, Inc.; 7000 Operators Manual; Version 1.1.

11.7 Entech Instruments Air Academy Course Manual.

11.8 Hewlett-Packard MS ChemStation User's Guide.

11.9 Hewlett-Packard HP5890 Operating and Reference Manuals.

11.10 Hewlett-Packard HP5972 Hardware Manual.

APPENDIX A

DEVIATIONS FROM EPA METHOD TO-15

1. The applicability of this SOP has been extended to include analysis of samples collected in Tedlar bags.

2. The working BFB standard is valid for a period of three months. Method TO-15 recommends a thirty day expiration period for all working standards prepared in canisters.

3. Method TO-15 does not require routine analysis and control of a Laboratory Control Standard or a Quantitation Limit Standard.

4. Method TO-15 does not implicitly include holding times for samples in canisters. A holding time of 30 days is included in this SOP based on studies referenced in Method TO-15 that indicate stable storage of up to 30 days for most VOCs. The holding time for Tedlar bags is based on information provided in EPA Method 0040; Sampling of Principal Organic Hazardous Constituents From Combustion Sources Using Tedlar Bags.

5. This SOP includes a requirement that freshly prepared working standards and field samples be allowed to equilibrate for at least 2 hours in the Air Lab prior to analysis. This is not a requirement of Method TO-15.

6. This SOP allows for two compounds in the daily calibration to exceed the %D limit of within $\pm$ 30 percent. However, the two compounds may not exceed a %D of 40%. Method TO-15 does not allow this exception.

7. Method TO-15 addresses sampling procedures. This SOP does not.

8. Method TO-15 addresses canister cleaning and certification. Canister cleaning and certification are not addressed in this SOP but are addressed in Region 9 Lab SOP #312.

9. Method TO-15 outlines typical Preconcentrator and GC operating conditions. This SOP included Preconcentrator and GC operating conditions that have been found to provide optimum results.

ATTACHMENT A

TARGET COMPOUND LIST FOR TO-15 AIR TOXICS ANALYSIS

The following is the Target Compound List for volatile organics, as well as the associated internal standards. Included are the internal standard reference for each target compound, as well as the quantitation mass for each analyte. The reporting limit for all compounds is 1 ppbv.

INTERNAL STANDARDS

COMPOUND	CAS NUMBER	ISTD #	QUAN m/z
Bromochloromethane	460-00-4	1	49
1,4-Difluorobenzene	540-36-3	2	114
Chlorobenzene-d5	3114-55-4	3	117

TARGET COMPOUNDS

COMPOUND	CAS NUMBER	ISTD	QUAN m/z	SECONDARY ION(S) amu/% base peak
Dichlorodifluoromethane (Halocarbon 12)	75-71-8	1	85	87/31
Dichlorotetrafluoroethane (Halocarbon 114)	374-07-2	1	85	135/56 87/33
Chloromethane	74-87-3	1	50	52/34
Vinyl Chloride	75-01-4	1	62	27/125 64/32
Bromomethane	74-83-9	1	94	96/85
Chloroethane	75-00-3	1	64	66/32
Trichlorofluoromethane (Halocarbon 11)	75-69-4	1	101	103/67
1,1-Dichloroethene	75-35-4	1	61	96/55 63/31
1,1,2-Trichloro-1,2,2-trifluoroethane (Halocarbon 113)	76-13-1	1	151	101/140 103/90
Methylene chloride	75-09-2	1	49	84/65 86/45
1,1-Dichloroethane	75-34-3	1	63	27/64 65/33
cis-1,2-Dichloroethene	156-59-2	1	61	96/60 98/44
Chloroform	67-66-3	1	83	85/65 47/35

1,1,1-Trichloroethane	71-55-6	1	97	99/64 61/61
Carbon Tetrachloride	56-23-5	1	117	119/97
Benzene	71-43-2	1	78	77/25 50/35
1,2-Dichloroethane	107-06-2	1	62	27/70 64/31
Trichloroethene	79-01-6	2	130	132/92 95/87
1,2-Dichloropropane	78-87-5	2	63	41/90 62/70
cis-1,3-Dichloropropene	10061-01-5	2	75	39/70 77/30
Toluene	108-88-3	2	91	92/57
trans-1,3-Dichloropropene	10061-02-6	2	75	39/70 77/30
1,1,2-Trichloroethane	79-00-5	2	97	83/90 61/82
Tetrachloroethene	127-18-4	2	166	164/74 131/60
1,2-Dibromoethane	106-93-4	2	107	109/96 27/115
Chlorobenzene	108-90-7	3	112	77/62 114/32
Ethylbenzene	100-41-4	3	91	106/28
p & m-Xylene	1330-20-7	3	91	106/40
o-Xylene	95-47-6	3	91	106/40
Styrene	100-42-5	3	104	78/60 103/49
1,1,2,2-Tetrachloroethane	79-34-5	3	83	85/64
1,3,5-Trimethylbenzene	108-67-8	3	105	120/42
1,2,4-Trimethylbenzene	95-63-6	3	105	120/42
1,3-Dichlorobenzene	541-73-1	3	146	148/65 111/40
1,4-Dichlorobenzene	106-46-7	3	146	148/65 111/40
1,2-Dichlorobenzene	95-50-1	3	146	148/65 111/40
1,2,4-Trichlorobenzene	120-82-1	3	180	182/98 184/30
Hexachloro-1,3-Butadiene	87-68-3	3	225	227/66 223/60

ATTACHMENT B

AIR LAB STANDARD PREPARATION LOG

STD ID:			CHEMIST:		PREP DATE:
CANISTER #	STD. MIX CONC.	SUPPLIER & LOT	FINAL CONC.	PREP. METH*	DESCRIPTION OF PREP.

STD ID:			CHEMIST:		PREP DATE:
CANISTER #	STD. MIX CONC.	SUPPLIER & LOT	FINAL CONC.	PREP. METH*	DESCRIPTION OF PREP.

STD ID:			CHEMIST:		PREP DATE:
CANISTER #	STD. MIX CONC.	SUPPLIER & LOT	FINAL CONC.	PREP. METH*	DESCRIPTION OF PREP.

* 1=Entech Dynamic Diluter (Description: include flowrates of standard mix and diluent; final canister pressure)
2= Dilution of Aliquot added by syringe (Description: include aliquot volume, initial, intermediate, and final canister
3= Dilution of Aliquot measured by pressure gauge (Description: include initial pressure, intermediate pressure, and final
4= Other (Description: include all relevant information needed to reproduce calculation)

ATTACHMENT C

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AIR
SUMMARY OF TECHNICAL ACCEPTANCE CRITERIA

ANALYSIS	TECHNICAL ACCEPTANCE CRITERIA
GC/MS System Performance Check (BFB analysis)	The ion abundance ratios must meet the following criteria. Mass (m/z) — Relative Ion Abundance Criteria* 50 — 8.0 - 40.0 percent of mass 95 75 — 30.0 - 66.0 percent of mass 95 95 — Base peak, 100 percent relative abundance 96 — 5.0 - 9.0 percent of mass 95 173 — less than 2 percent of mass 174 174 — 50.0 - 120.0 percent of mass 95 175 — 4.0 - 9.0 percent of mass 174 176 — 93.0 - 101.0 percent of mass 174 177 — 5.0 - 9.0 percent of mass 176 *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 percent that of m/z 95.
Initial calibration	•The calculated %RSD for the RRF for each compound must be less than 30% with at most two exceptions up to a limit of 40%. •The RRT for each target compound at each concentration level must be within 0.06 RRT units of the mean RRT for the compound. •The area response Y at each calibration level must be within 40% of the mean area response Y_{avg} over the initial calibration range for each internal standard. •The retention time shift for each of the internal standards at each calibration level must be within ±0.33 min (20 sec.) of the mean retention time over the initial calibration range for each internal standard.
Continuing Calibration	•The %D for each target compound in the daily calibration must be within ± 30 percent with at most two exceptions up to a limit of 40%.
Method blank	•Should not contain any target analyte at a concentration greater than the reporting limits for the compound and should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte. •The area response for each internal standard (IS) in the blank must be within ±40 percent of the mean area response of the IS in the most recent valid calibration. •The retention time for each of the internal standards must be within ±0.33 minutes (20 sec.) between the blank and the most recent valid calibration.
Laboratory control sample analysis (LCS)	•The percent recovery for each of the compounds in the LCS should be within the recovery limits of 70 to 130 percent. •The area response for each internal standard (IS) in the LCS must be within ±40 percent of the mean area response of the IS in the most recent valid calibration. •The retention time for each of the internal standards must be within ±0.33 minutes (20 sec.) between the blank and the most recent valid calibration.
Samples	•The area response for each internal standard (IS) must be within ±40 percent of the mean area response of the IS in the most recent valid calibration. •The retention time for each of the internal standards must be within ±0.33 minutes (20 sec.) between the blank and the most recent valid calibration.

ATTACHMENT D

ENTECH 7000 PRECONCENTRATOR PARAMETERS

TO15 CONCENTRATION EVENTS

1. Wait for temperature to reach setpoints
2. Wait for GC Ready
3. Cool Module 1 to trapping temperature
4. Preflush with internal standard
5. Trap internal standard
6. Preflush with analytical standard (LCS)
7. Trap analytical standard (LCS)
8. Preflush with sample
9. Trap sample
10. Preflush with Helium sweep/purge Gas
11. Trap Helium sweep/purge gas
12. Preheat Module 1
13. Transfer VOCs from M1 M2
14. Wait for GC Ready
15. Cool focusing trap
16. M2 preheat
17. Transfer M2 M3
18. Heat M3, Inject, Start GC
19. Preflush with next sample
20. System Bakeout
21. Wait time after injection

BFB ANALYSIS

PARAMETER	SETTING
Sample:	
Preflush (sec)	5
Trap (cc/min)	150
Volume (cc)	200
Internal Standard:	
Preflush (sec)	2
Trap (cc/min)	100
Volume (cc)	40

Analytical Standard (LCS):	
Preflush (sec)	N/A (LCS is in a canister on the autosampler)
Trap (cc/min)	N/A
Volume (cc)	N/A
Sweep/Purge:	
Preflush (sec)	2
Trap (cc/min)	100
Volume (cc)	75

Attachment D (continued)

BFB ANALYSIS (continued)

PARAMETER	SETTING
M1 M2:	
Preflush (sec)	N/A
Trap (cc/min)	10
Volume (cc)	40
Module 1:	
Trap temp(°C)	-100
Preheat?	Y
Preheat temp (°C)	20
Desorb temp (°C)	20
Bake temp (°C)	130
Bake time (min)	5
Bulkhead 1:	
Trap temp (°C)	30
Desorb temp (°C)	30
Bake temp (°C)	N/A
Module 2:	
Trap temp(°C)	0
Preheat?	N
Preheat temp (°C)	
Desorb temp (°C)	180
Bake temp (°C)	190
Desorb (min)	3.5
Bulkhead 2:	
Trap temp (°C)	30
Desorb temp (°C)	100

Bake temp (°C)		
Module 3:		
Trap temp(°C)	-100	
Focus?	Y	
Inject temp (°C)		100
Inject time (min)		2
Bake temp (°C)		100
Bake time (min)		3
Bake on event #		3
Wait (min)		10
Sample Transfer temp (°C)		80
GC Transfer temp (°C)		100
MPOS Valve temp (°C)		100

Attachment D (continued)

AIR SAMPLE ANALYSIS

PARAMETER	SETTING
Sample:	
Preflush (sec)	10
Trap (cc/min)	150
Volume (cc)	400
Internal Standard:	
Preflush (sec)	2
Trap (cc/min)	100
Volume (cc)	40
Analytical Standard (LCS):	
Preflush (sec)	N/A (LCS is in a canister on the autosampler)
Trap (cc/min)	N/A
Volume (cc)	N/A
Sweep/Purge:	
Preflush (sec)	2
Trap (cc/min)	100
Volume (cc)	75

M1 M2:

Preflush (sec)		N/A
Trap (cc/min)		10
Volume (cc)		40

Module 1:

Trap temp(°C)	-160	
Preheat?		Y
Preheat temp (°C)		25
Desorb temp (°C)		25
Bake temp (°C)		130
Bake time (min)		5

Bulkhead 1:

Trap temp (°C)		30
Desorb temp (°C)		30
Bake temp (°C)		N/A

Module 2:

Trap temp(°C)	-30	
Preheat?		N
Preheat temp (°C)		
Desorb temp (°C)		180
Bake temp (°C)		190
Desorb (min)		3.5

Bulkhead 2:

Trap temp (°C)		30
Desorb temp (°C)		100
Bake temp (°C)		

Attachment D (continued)

AIR SAMPLE ANALYSIS (continued)

PARAMETER		**SETTING**
Module 3:		
Trap temp(°C)	-175	
Focus?	Y	
Inject temp (°C)		100
Inject time (min)		2.5
Bake temp (°C)		100
Bake time (min)		4

Bake on event #	13
Wait (min)	21
Sample Transfer temp (°C)	100
GC Transfer temp (°C)	100
MPOS Valve temp (°C)	100

OPTIONS

Wait for GC Before Final Focusing
Use Pressure Compensation
    Pressure Compensation Factor: 14
Additional Cryogenic Temperature Control
    Raise M2 Temperature Before He Sweep
        -M2 Helium Sweep Temperature (CTD): -10 deg C
    Max Temperature Below Setpoint Before Adding Heat
        -Ctrl Heaters During Trapping
            Cryo Module 1: 20 deg C
            Cryo Module 2: 20 deg C
Extra M2 M3 Transfer After Inject: .5 min

ATTACHMENT E

GC PARAMETERS

HP5890

The operating methods for the Gas Chromatograph which is interfaced with the HP5972 MS are as follows:

BFB analysis

PARAMETER	SETTING
Solvent Delay	5.0 minutes
Injector Temperature	250°C
Oven Equib. Time	0.5 minutes
Detector B	280°C
Initial Oven Temp	120°C
Initial Oven Time	1.0 minutes
Temperature Ramp	13°C/minute
Final Oven Temp	220°C
Final Hold Time	1.0 minutes
Column Flow rate	1.2 mL/min
EM Voltage	ABS 1850
Inlet B Pressure	19.1 psi

Air Sample Analysis

PARAMETER	SETTING
Solvent Delay	4.5 minutes
Injector Temperature	250°C
Oven Equib. Time	0.5 minutes
Detector B	280°C
Initial Oven Temp	40°C
Initial Oven Time	10.0 minutes
Temperature Ramp - level 1	8°C/minute
Final Temp - level 1	100°C
Final Hold Time - level 1	0.0 minutes
Temperature Ramp - level 2	10°C/minute

Final Temp - level 2	160°C
Final Hold Time - level 2	0.0 minutes
Temperature Ramp - level 3	12°C/minute
Final Temp - level 3	240°C
Final Hold Time - level 3	5.0 minutes
Column Flow rate	1.2 mL/min
EM Voltage	ABS 1850
Inlet B Pressure	19.1 psi

ATTACHMENT F

REGION 9 LABORATORY TO-15 RUN LOG

CASE: INT. STD. ID: LCS:
METHOD: TO-15
SDG: CAL. STD. ID: BFB STD ID
INSTR. ID: HP5972-TO-15

	FILE NAME	CAN #	Autosamp #	DATE	TIME	INIT	EPA ID	LAB ID	STD AMOUNTS	Volume	Dilution	EM VOLTS	COMM
1													
2													
3													
4													
5													
6													
7													
8													
9													
10													
11													
12													
13													
14													
15													
16													
17													
18													
19													
20													
21													
22													
23													

24														

Filename: TO-15.WK4 Reviewed by:_____ Date:_____ Lab Supervisor: