

STANDARD OPERATING PROCEDURE APPROVAL SHEET

SOP TITLE: Analysis of Volatile Organic Compounds in Ambient Air Using Polished Stainless Steel Can Passivated Canisters By EPA Method TO-14A/TO-15

DOCUMENT CONTROL NUMBER: TO-14A/TO-15-Analysis

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APPROVALS:

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STANDARD OPERATING PROCEDURE

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS FROM POLISHED STAINLESS STEEL PASSIVATED CANISTERS BY EPA METHOD TO-14A/TO-15

1.0 SCOPE AND APPLICATION

- 1.1 Method TO-14A/TO-15 is used to determine volatile organic compounds collected from ambient air using polished stainless steel passivated canisters.
- 1.2 Method TO-14A/TO-15 can be used to quantify most volatile organic compounds that have boiling points below 150°C. Volatile polar compounds can be included in this analytical technique, although they are not included in the method target analyte list.
- 1.3 The estimated quantitation limit (EQL) for an individual compound is approximately 1 ppb, with some exceptions.
- 1.4 Method TO-14A/TO-15 is based upon concentrating compounds obtained from a sample of air. The volatile organic compounds desorbed from the concentrator are analyzed by a gas chromatographic/mass spectrometric procedure.
- 1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra and their use as a quantitative tool.
- 1.6 Clients may choose to utilize Tedlar[®] Bags, or equivalent, for sampling for convenience or if samples are taken from a site that is known to be heavily contaminated.

2.0 SAFETY PRECAUTIONS

- 2.1 Treat samples as if they are hazardous.
- 2.2 Canisters may be under pressure, employ necessary safety considerations.

3.0 SAMPLE HANDLING

- 3.1 All samples should be analyzed within 14 days of sampling.
 - 3.1.1 Fortunately, under conditions of normal use for sampling ambient air, most VOCs can be recovered from canister near their original concentrations after storage times of up to 30 days.
- 3.2 Samples and standards will not be stored together.
- 3.3 Following analysis, canisters will be cleaned according to the current standard operation procedure.

4.0 ESTIMATED QUANTITATION LIMITS AND WORKING LINEAR RANGE

- 4.1 Routinely, the Estimated Quantitation Limits (EQLs) listed in Appendices 2 & 3 will be reported.
- 4.1.1 If specifically requested by the client, values may be reported between the current calculated MDL and the EQL. These values will be denoted with a "J" flag indicating estimation.
- 4.2 The reporting units will be ppb.
- 4.3 The working linear range is approximately 1-120 ppb.

5.0 INTERFERENCES

- 5.1 Interferences concentrated from the samples will vary considerably from source to source, depending upon the particular sample being tested. The analytical system, however, will be checked to ensure freedom from interferences, under the analysis conditions, by analyzing a method blank daily.
- 5.2 Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially. Whenever a high-level sample is analyzed, sample analysis will cease until the system has been proven free of contaminants. This proof may be the analysis of a system blank or a sample that is free of the contaminant being investigated. The concentrator system may require bake-out and purging with nitrogen following analysis of a high-level sample.

6.0 APPARATUS

- 6.1 Microsyringes - 10- μ L, 25- μ L, and 250 - μ L.
- 6.2 Syringes: 5-mL, 25-mL and 1-L gas-tight.
- 6.3 Entech Model 7000 concentrator or equivalent.
- 6.4 Gas chromatograph/mass spectrometer system.
- 6.4.1 Gas chromatograph - an analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.
- 6.4.2 Column - DB624, 60 meter, 0.32 millimeter internal diameter, 1.8 micron film thickness or equivalent column. An equivalent column is defined as a column that when used will pass all the QC criteria specified in the SOP (BFB, Initial Calibration. etc.).
- 6.4.3 Mass spectrometer - capable of scanning from 35-300 amu every 1.7 seconds or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass-spectrum that meets all the criteria in Appendix 1 (Section 15.0) when 50 ng of 4-bromofluorobenzene (BFB) are injected through the gas chromatograph inlet.
- 6.4.4 Data system - A Hewlett-Packard 486 Vectra DOS PC with Enviroquant software or equivalent. Included in the data system is the NIH/EPA/NIST Mass Spectral Library.

7.0 REAGENTS

- 7.1 Nitrogen will be used for analysis of all method blanks.
- 7.2 Methanol, CH₃OH high purity purge-and-trap grade will be used.

8.0 CALIBRATIONS

- 8.1 Gas standards must be purchased.
 - 8.1.1 The amount of gas standard to be introduced to the canister must be determined using the ESP Software or equivalent. Please refer to the manufacturer's instructions for software operation.
 - 8.1.2 Inject 100.0 µL of reagent water into the top of the valve on the evacuated standard canister.
 - 8.1.3 Attach the standard canister to the static dilution apparatus.
 - 8.1.4 Begin to add ultra high purity nitrogen to the canister at a rate of 0.5 liters per minute. This will give an approximate time interval of 12 minutes to add the gas standard to the canister. Stop filling the canister with nitrogen at the pressure predetermined by the ESP software.
 - 8.1.5 Using a 1 liter syringe, inject the amount of gas standard as was determined by the software into the standard canister.
 - 8.1.6 Allow the standard canister to equilibrate for 4 hours prior to use.
- 8.2 Internal standards will be prepared by static dilution from neat standards. The internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d5.
 - 8.2.1 The amount of neat internal standard to be added to the cocktail mixture will be determined by using the ESP software.
 - 8.2.2 Using a 10 µL syringe, inject the amount of neat standard determined in step 8.2.1 into a GC vial. Repeat for all internal standards and mix thoroughly.
 - 8.2.3 Using a 10 µL syringe, inject the volume of internal standard cocktail mix determined in 8.2.1 into a 1 liter glass dilution flask. Heat to 50 °C.
 - 8.2.4 The amount of internal standard must be must be determined using the ESP software or equivalent. Please refer to the manufacturer's instructions for software operation.
 - 8.2.5 Inject 100.0 µL of reagent water into the top of the valve on the evacuated standard canister.
 - 8.2.6 Attach the standard canister to the static dilution apparatus.

- 8.2.7 Begin to add ultra high purity nitrogen to the canister at a rate of 0.5 liters per minute. This will give an approximate time interval of 12 minutes to add the internal standard to the canister. Stop filling the canister with nitrogen at the pressure predetermined by the ESP software.
- 8.2.8 Using a 10 μ L gastight syringe, transfer the volume of gaseous internal standard, as determined by the ESP software into the static dilution apparatus.
- 8.2.9 Allow the internal standard canister to equilibrate for 4 hours.
- 8.3 Polar and/or extra analytes.
 - 8.3.1 The amount of neat polar compound or extra analyte standard to be added to the cocktail mixture will be determined by the ESP software.
 - 8.3.2 Using a 10 μ L syringe, transfer the appropriate amount to neat polar or extra analyte solution to 25 mL of reagent water in a 25 mL volumetric flask.
 - 8.3.3 Using a 250 μ L syringe, transfer 100 μ L of solution into the valve of the standard canister and connect the canister to the static dilution apparatus.
 - 8.3.4 Add ultra high purity nitrogen to the canister to the predetermined pressure approximately (25psig).
- 8.4 Standards are routinely prepared by the DCL Salt Lake City laboratory, but may be purchased from a qualified provider (i.e. Entech, etc.).

9.0 INSTRUMENT TUNING, INITIAL CALIBRATION, ROUTINE CALIBRATION, LABORATORY CONTROL SAMPLE AND METHOD BLANK

- 9.1 Hardware tune the instrument with an aliquot of \leq 50 ng of Bromofluorobenzene to meet the criteria listed in Appendix 15.1. Analysis of samples must not begin until the criteria of Appendix 15.1 are satisfied.
- 9.2 Initial calibration.
 - 9.2.1 For TO-14A initial calibration, a three point calibration is performed using standards in concentrations: 2.5, 10, and 30 ppb.
 - 9.2.2 For TO-15 initial calibration, a five point calibration is performed using standards in concentrations: 2.5, 5, 10, 20, 30 ppb.
 - 9.2.3 Using scan mode, analyze each standard once.
 - 9.2.4 The calculated response factors from the standard TO-14A target analyte list must have a percent RSD no greater than 30% with at most two exceptions up to a limit of 40% . If this condition is not met, reanalyze the appropriate standard concentrations or check the GC/MS system for malfunction.

- 9.3 Daily continuing calibration.
- 9.3.1 Daily continuing calibration verification is performed using a 10 ppb standard. The percent difference must be within ± 30 percent of the initial calibration curve for each TO-14A target analyte in order to proceed with the analysis of samples and blanks.
- 9.4 The internal standard responses and retention times in the continuing calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration (daily), the chromatographic system must be inspected for malfunctions and corrections must be made as required. If the extracted ion current profile area for any of the internal standards exceeds $\pm 50\%$ from the midpoint daily calibration standard, the analytical system must be inspected for malfunctions and corrections must be made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.
- 9.5 A second source Laboratory Control Sample is analyzed daily at 10 ppb and results should be within $\pm 30\%$ of the expected concentration for each analyte on the standard TO-14A target analyte list.
- 9.6 A method blank is analyzed for each daily tuning period. Before sample analysis may begin, a method blank must be analyzed and the acceptance criteria for the blank met to demonstrate that the method is free of interferences or contamination. The blank must contain < 0.2 ppb of standard TO-14A target analyte list (Appendix 15.2). Oxygenated compounds should be < 0.8 ppb.
- 9.6.1 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.

10.0 PROCEDURE

- 10.1 A new BFB tune, daily GC/MS calibration, laboratory control sample and method blank must be analyzed daily prior to sample analysis.
- 10.2 Connect the sample canister to the inlet.
- 10.3 Set the GC oven to a set point of 37 °C.
- 10.4 As soon as the cryogenic trap reaches its lower set point of -150 °C, initiate sample collection.
- 10.5 Collect the appropriate volume of sample. The standard volume is 200 mL.
- 10.5.1 A 4X dilution may be sampled using 50 ml directly from the canister.
- 10.5.2 Further dilution requires pumping of sample from the canister into a clean Tedlar[®] bag. From this bag further dilutions can be made by removing a volume of sample from this bag using a gas-tight syringe and adding the appropriate volume to a clean Tedlar[®] bag filled with nitrogen.
- 10.6 Thermally desorb the trapped analytes onto the head of a 60m x 0.32 mm SP capillary column. The GC oven temperature is held at 37°C for 3 minutes and then heated to 200 °C at 9 °C/minute and held for 3 minutes.

10.7 After desorbing the sample, the module trapping unit is baked out.

11.0 DATA INTERPRETATION

11.1 An analyte (*e.g.*, those listed in Appendices 15.2 & 15.3) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS on the same day. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

11.1.1 The sample component RRT must compare within +/- 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same day as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

11.1.2 (1) All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% must be present in the sample spectrum). (2) The relative intensities of ions specified in (1) must agree within +/- 20% between the standard and sample spectra.

11.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

11.2.1 Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

11.2.2 The relative intensities of the major ions should agree within +/- 20%.
(Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%)

11.2.3 Molecular ions, present in the reference spectrum should be present in the sample spectrum.

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

11.2.5 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 peaks. Data system library reduction programs can sometimes create these discrepancies.

11.2.6 Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of the sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

12.0 CALCULATIONS

- 12.1 Tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. The RF is calculated as follows:

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

Where:

A_x = Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the specific internal standard.

C_x = Concentration of the compound being measured.

- 12.2 Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for standard TO-14A target analyte list.

$$\%RSD = (SD/Mean) * 100$$

Where:

RSD = Relative standard deviation.

Mean = Mean of initial calibration RFs for a compound.

SD = Standard deviation of average RFs for a compound.

- 12.3 Continuing Calibration Check: Calculate the percent difference using:

$$\% \text{ Difference} = ((RF_I - RF_C) / RF_I) * 100$$

Where:

RF_I = Average response factor from initial calibration.

RF_C = Response factor from current daily check standard.

- 12.4 Calculate the concentration of each identified analyte in the sample as follows:

$$\text{Concentration (ppb)} = ((A_x)(I_s)) / (A_{is})(RF)$$

Where:

A_x = Area of characteristic ion for compound being measured.

I_s = Amount of internal standard injected (50 ppb).

A_{is} = Area of characteristic ion for the internal standard.

RF = Average response factor from initial calibration curve.

- 12.5 Where applicable, an estimate of concentration for noncalibrated components in the sample will be made. The formulas given above will be used with the following modifications: the areas A_x and A_{is} will be from the total ion chromatograms, and the RF for the compounds will be assumed to be 1. The concentration obtained shall be reported indicating that the value is an estimate. Use the nearest internal standard free of interferences.

13.0 QUALITY CONTROL PROVISIONS

- 13.1 Before processing any samples, the analyst will demonstrate, through the analysis of a method blank, that interferences from the analytical system, and reagents are under control.
- 13.2 Required instrument QC is as follows:
- 13.2.1 The GC/MS system must be tuned to meet the BFB specifications in Section 9.1 daily.
- 13.2.2 There must be an initial calibration of the GC/MS system as specified in Section 9.2.
- 13.2.3 The GC/MS system must meet the routine calibration criteria and the internal standard criteria in Sections 9.3 and 9.4 daily.
- 13.2.4 The LCS criteria should meet the criteria found in Section 9.5.
- 13.2.4 The method blank must meet the criteria specified in Section 9.6 daily.
- 13.3 Method detection limit studies will be completed at least annually according to the current laboratory standard operating procedure and should result in MDL values ≤ 0.5 ppb for the standard TO-14A target analyte list.

14.0 REPORTING RESULTS

- 14.1 The results for the samples are reported in ppb.
- 14.2 Analytical methodology and any deviations and corrective actions taken for sample analysis will be stated in the data set comments.
- 14.3 A method blank will be reported daily.
- 14.4 Sample internal standard recoveries will be calculated and reported for each internal standard in each blank and sample. Internal standard recoveries are calculated based on the internal standard of the daily calibration verification standard.

15.0 APPENDICES

- 15.1 Appendix 1: BFB KEY ION ABUNDANCE CRITERIA
- 15.2 Appendix 2: STANDARD TO-14A ANALYTE LIST

15.3 Appendix 3: DATACHEM LABORATORIES ADDITIONAL ANALYTE LIST FOR
CANISTERS

16.0 REFERENCES

- 16.1 Compendium Method TO-14A, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - Second Edition, January 1999
- 16.2 Compendium Method TO-15, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - Second Edition, January 1999

APPENDIX 15.1:

**BFB TUNING
KEY ION ABUNDANCE CRITERIA**

<u>Mass</u>	<u>Ion Abundance Criteria</u>
50	8 to 40% of mass 95
75	30 to 66% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	50% to 120% of mass 95
175	4 to 9% of mass 174
176	greater than 93% but less than 101% of mass 174
177	5 to 9% of mass 176

APPENDIX 15.2:

STANDARD TO-14A ANALYTE LIST

Compound (Synonym)	CAS #	EQL (ppb)
Freon 12 (Dichlorodifluoromethane)	75-71-8	1
Methyl chloride (Chloromethane)	74-87-3	1
Freon 114 (1,2-Dichloro-1,1,2,2,-tetrafluoroethane)	76-14-2	1
Vinyl chloride (Chloroethylene)	75-01-4	1
Methyl bromide (Bromomethane)	74-83-9	1
Ethyl chloride (Chloroethane)	75-00-3	2
Freon 11 (Trichlorofluoromethane)	75-69-4	1
Vinylidene chloride (1,1-Dichloroethene)	75-35-4	1
Dichloromethane (Methylene chloride)	75-09-2	1
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	76-13-1	1
1,1-Dichloroethane (Ethylidene chloride)	74-34-3	1
cis-1,2-Dichloroethylene	156-59-2	1
Chloroform (Trichloromethane)	67-66-3	1
1,2-Dichloroethane (Ethylene dichloride)	107-06-2	1
Methyl chloroform (1,1,1-Trichloroethane)	71-55-6	1
Benzene	71-43-2	1
Carbon tetrachloride (Tetrachloromethane)	56-23-5	1
1,2-Dichloropropane (Propylene dichloride)	78-87-5	2
Trichloroethylene (Trichloroethene)	79-01-6	1
cis-1,3-Dichloropropene (cis-1,3-Dichloropropylene)	542-75-6	2
trans-1,3-Dichloropropene (cis-1,3-Dichloropropylene)	542-75-6	3
1,1,2-Trichloroethane	79-00-5	2
Toluene (Methyl benzene)	108-88-3	2
1,2-Dibromomethane (Ethylene dibromide)	106-93-4	2
Tetrachloroethylene (Perchloroethylene)	127-18-4	2
Chlorobenzene	108-90-7	1
Ethylbenzene	100-41-4	1
m-Xylene (1,3-Dimethylbenzene)	108-38-3	1
p-Xylene (1,4-Dimethylxylene)	106-42-3	1
Styrene (Vinyl benzene)	100-42-5	1
1,1,2,2-Tetrachloroethane	79-34-5	1
o-Xylene (1,2-Dimethylbenzene)	95-47-6	1
1,3,5-Trimethylbenzene (Mesitylene)	108-67-8	1
1,2,4-Trimethylbenzene (Pseudocumene)	95-63-6	2
m-Dichlorobenzene (1,3-Dichlorobenzene)	541-73-1	1
Benzyl chloride (α -Chlorotoluene)	100-44-7	1
o-Dichlorobenzene (1,2-Dichlorobenzene)	95-50-1	2
p-Dichlorobenzene (1,4-Dichlorobenzene)	106-46-7	2
1,2,4-Trichlorobenzene	120-82-1	1
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3-butadiene)	87-68-3	1

Note: Additional compounds analyzed by DataChem Laboratories are found in Appendix 15.3.

APPENDIX 15.3:

**DATA CHEM LABORATORIES
ADDITIONAL ANALYTE LIST**

Compound (Synonym)	CAS #	EQL (ppb)
Propene	115-07-1	2
1,3-Butadiene	106-99-0	2
2-Propanol	67-63-0	1
Acetone	67-64-1	8
Carbon Disulfide	75-15-0	1
Methyl-tert-butyl ether (MTBE)	1634-04-4	1
trans-1,2-Dichloroethene	156-60-5	1
Vinyl Acetate	108-05-4	1
Hexane	110-54-3	1
2-Butanone	78-93-3	1
Tetrahydrofuran	109-99-9	2
Cyclohexane	110-82-7	1
Heptane	142-82-5	1
Bromodichloromethane	75-27-4	2
4-Methyl-2-pentanone	108-10-1	2
2-Hexanone	591-78-6	2
Dibromochloromethane	124-48-1	2
Bromoform	75-25-2	1
4-Ethyl toluene	622-96-8	1

Datachem Laboratories is also analyzing all samples collected from the Hitchens School for acrylonitrile.