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Yeoman Creek
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DETERMINATION OF VOLATILE ORGANIC COMPOUNDS
BY CARBON MOLECULAR SIEVE ADSORPTION AND GC/MS

Scope and Application: This method is applicable to ambient air or landfill gas collected on CMS cartridges.

Principle: TO2: A procedure for collection and determination of selected volatile organic compounds which can be captured on carbon molecular sieve (CMS) adsorbents and determined by thermal desorption GC/MS techniques. Compounds which can be determined by this method are selected nonpolar and nonreactive organics having boiling points in the range of -15 to 120°C.

Method: Modified EPA method TO2

Reference: EPA method TO2, April 1984, Rev. 1.0

Parameters to be Measured: See Table 1.

Apparatus: Sorbent Tube Desorber Conditions:

Injector Temp:	160°C
Sorbent Trap Temp:	<30 to 300°C
Bake Oven Temp:	350-400°C
Valve Oven Temp:	150°C
Transfer Line Temp:	150°C

Gas Chromatograph (GC) Conditions:

Injector Temp: 200°C
Aux-Temperature: 200°C
(transfer line)
Carrier Gas: Helium at 7 cc/min

GC Oven Program

Initial Temperature: -10°C for 1 minute
Initial Ramp Rate: 15°C/minute to 30°C
Final Ramp Rate: 6°C/minute to 150°C
Final Temperature: 150°C
Hold Time: 10 minutes

G.C. Column: 0.53 mm x 30 m DB-624 fused silica
capillary column (FSCC) or equivalent

Mass Spectrometer (MS) Conditions:

Mass Range: 35-300 amu
Scan Rate: 1 sec/scan
Electron Energy: 70 eV
Manifold Temperature: 100°C
Source Temperature: 240°C

Tekmar LSC 2000 Purge and Trap,

Heated Glass Sparge Vessel

Tekmar #8 trap

Purge Time : 10 minutes

Purge Temperature : ~~35°C~~ 35°C

Desorb Temperature : 260°C

Desorb Time : 4 minutes

Bake Temperature : 260°C

Bake Time : 20 minutes

Purge Flow : 30 mLs per minute UHP Helium

Working Linear Range: ~ 10-1000 ng/cartridge

Method Detection Limits: See Table 2.

Interference and Corrective Action:

When interference with the primary quantitation ion occurs, quantitation on a secondary ion is carried out. High level cartridge loadings may require thermal desorption into clean Tedlar bags.

Reagents and Calibration Standards:

Standards are prepared from EPA Certified Ultra Scientific and laboratory certified Aldrich neat materials. The Ultra Scientific mix was purchased certified to 200 ng/uL and blended down to cover a working range of 4 to 1000 ng spike. Standards prepared in neat form are first subject to capillary GC/FID analysis to determine purity. The percent purity must be greater than 96% or correction factors are used. Following the purity check, the standards are blended into the working range by taking known aliquotes and using density based calculations.

Table 1

<u>Internal Standards:</u>	<u>Primary Quan. Ion (m/z)</u>	<u>Secondary Quan. Ion(s) (m/z)</u>
bromochloromethane	128	49, 51
1,4-difluorobenzene	114	63, 88
chlorobenzene-D5	117	119, 82
 <u>Surrogates:</u>		
1,2-dichloroethane-D4	65	102
toluene-D8	98	70, 100
4-bromofluorobenzene	95	174, 176
 <u>Target Analytes:</u>		
chloromethane	50	52
1,1-dichloroethene	96	61, 98
* vinyl chloride	62	64
1,3-butadiene	39	54
bromomethane	94	96
trichlorofluoromethane	101	103
methylene chloride	49	84, 86
chloroform	83	85, 47
1,1,1-trichloroethane	97	99, 61
* carbon tetrachloride	117	119
* benzene	78	77
1,2-dichloroethane	62	64
trichloroethene	130	132, 95
1,2-dichloropropane	63	41, 62
toluene	91	92
* tetrachloroethene	164	129, 131, 166
1,2-dibromoethane	107	109
* chlorobenzene	112	77, 114
o-xylene	106	106
ethyl benzene	91	106

* continuing Calibration Check Compounds (CCC)

Note: All target analytes listed in Table 1 above have retention volumes in excess of 100 liters per cartridge at 37°C except vinyl chloride for which the value is 30 liters/cartridge and chloromethane (retention volume on CMS unknown).

Mass Spectrometer Calibration: The mass spectrometer is calibrated with perfluorotributylamine (FC43).

Prior to the analysis of standards, blanks or samples, 50 ng of 4-bromofluorobenzene is injected into the GC and the following ion abundance criteria must be met:

m/z	BFB Ion Abundance Criteria
50	8.0 - 40.0 percent of mass 95
75	30.0 - 66.0 percent of mass 95
95	100 percent relative abundance
96	5.0 - 9.0 percent of mass 95
173	less than 2.0 percent of mass 95
174	50.0 - 120.0 percent of mass 95
175	4.0 - 9.0 percent of 174
176	93.0 - 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

A. Initial Calibration

Calibration is done at three different concentrations: 50, 200, and 800 ng. The percent relative standard deviation (%RSD) for each target analyte must be within 40% for the initial calibration.

Analysis of initial and continuing calibration standards requires several steps as described below:

1. Load a clean TO2 cartridge (or an investigative sample cartridge) onto the concentrator and leak check connections by placing a small amount of methanol on each fitting. The appearance of bubbles indicates a leak and fittings need to be tightened.
2. Load the internal standard and surrogates onto the CMS tube by injecting 2 uL of the mixture into the heated port on the tube desorber. The valve is in the LOAD position.
3. After 1 minute, switch the valve from LOAD to DESORB, turn on the heater control (the tube desorber is ballistically heated to 350°C) and place the front cover on the aluminum block. Step the Tekmar P&T to PURGE. The volatile compounds are swept from the CMS tube into the P&T for 10 minutes. During this time the trap of the P&T is at ambient temperature. Water and methanol pass thru the trap and out to vent while the VOC's remain trapped.

Note: Prior to starting the P&T DESORB, the GC should be at -10°C and the data system should be ready to acquire data.

4. After the initial 10 minute purge, the sorbent trap of the P&T is ballistically heated to 185°C and the volatile compounds are swept through the transfer line and onto the GC column.

B. Continuing Calibration

The daily standard (represented by the midpoint of the initial calibration, i.e., 200 ng) is required once every 12 hours before any blanks or samples are analyzed. The continuing calibration is validated using the five calibration check compounds (CCC) identified on page 4. The percent difference (%D) between the initial calibration and the continuing calibration check compounds cannot exceed 30 percent. If these criteria are met, analyses can proceed; otherwise, the standard is to be reanalyzed. If the %D criteria cannot be met, a new initial calibration is required.

C. Method Blank

The method blank (a clean TO2 cartridge analyzed in the same way a standard or sample is analyzed) is run before any samples are analyzed. Blank analysis is repeated until the trap and the system are shown to be clean. At this point the system is ready to analyze samples.

D. Sample Storage, Preparation and Analysis

CMS cartridges are prepared according to the attached SOP OP-TO2-PREP.

Investigative sample cartridges are stored in a refrigerator at 4°C upon receipt and are analyzed within 14 days of sample collection.

Investigative sample cartridges are allowed to reach room temperature and are purged with 2-3 liters of pure, dry nitrogen or helium to remove moisture prior to analysis. Purging is carried out at a flow rate of ~500 sccm in the same direction as sample flow.

Sample analysis is performed after all the above criteria have been met. Any analyses must be performed within a 12 hour period following BFB tune time.

Investigative samples are analyzed in an identical manner as calibration standards.

E. Data Validation

Qualitative identification of compounds determined by this method is based upon retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum (reverse library search). Relative retention times (RRT) of sample components must be within ± 0.06 RRT units of the RRT of the standard component. Relative intensities of the characteristic ions present in the sample spectrum must agree within 30% of the relative intensities of these ions in the reference spectrum.

Quantitative analysis of target compounds is based upon the integrated ion abundance from the extracted ion current profile of the primary characteristic ion for that compound. Quantitation is accomplished using the internal standard technique indicated in the section below. Backup cartridges should contain less than 10% of the amount of compounds of interest found in the primary cartridge.

Analytical Measurements:

$$RRF = \frac{\text{area of target cmpd. char. ion}}{\text{area of I.S. characteristic ion}} \times \frac{\text{amount of I.S.}}{\text{amount of target cmpd.}}$$

$$\text{Amount} = \frac{\text{area of target cmpd. char. ion}}{\text{area of I.S. characteristic ion}} \times \frac{\text{amount of I.S.}}{RRF}$$

IS = Internal Standard
RRF = Relative Response Factor

Calibration Standard Loading

Example using vinyl chloride @ 200 ppbv, 25°C, 1 atm., loaded onto TO2 cartridge for 10 minutes @ 50 sccm with a mass flow controller.

$$(\text{ng}) = \frac{200 \text{ nL}}{\text{L}} \times \frac{50 \text{ cc}}{\text{min}} \times \frac{10 \text{ min}}{1} \times \frac{\text{mole-}^\circ\text{K}}{.082 \text{ L-atm}} \times \frac{\text{atm}}{298^\circ\text{K}} \times \frac{62.5 \text{ g}}{\text{mole}}$$

vinyl chloride (ng) = 255.8

Data Deliverables:

Data deliverables will include at a minimum:

- case narrative;
- method code;
- results for investigative samples;
- dates of sample receipt, extraction, and analysis;
- lower limits of detection;
- summary of initial calibration and continuing

- calibration check results;
- surrogate recoveries;
- matrix spike/matrix spike duplicate summary;
- GC/MS tuning information summary; and
- chain-of-custody.

Quality Control Requirements:

4-BFB: must be analyzed every 12 hours and before the standard is run and must pass the above referenced criteria.

Method Blank: must be analyzed before any samples are determined, and no target analyte can exceed the reporting limit for that analyte with the exception of methylene chloride, a common laboratory contaminant, which may be present at levels up to 35 ng/cartridge.

Initial Calibration: must cover at least three points and result in a %RSD of less than 40% for all target compounds.

Continuing Calibration: The midpoint calibration standard must be analyzed once every 12 hour shift. The continuing calibration check compounds (see page 3) must not exceed 30% difference when compared with the mean RRFs obtained in the initial calibration else recalibration is required.

Internal Standard: Internal standard responses must be within a factor of two when compared with the responses obtained in the initial calibration.

Surrogate Control Limits:	<u>Lower</u>		<u>Upper</u>
1,2-dichloroethane-D4	70	-	120%
toluene-D8	75	-	120%
4-bromofluorobenzene	50	-	150%

Relative Retention Times: Target analytes must elute within ± 0.06 retention time units of the elution time of the standard analyzed each day.

Matrix spike and matrix spike duplicate analysis are carried out on a field sample collected in triplicate. Matrix spike compounds along with target recoveries are indicated directly below:

chloroform	50 - 150%
benzene	50 - 150%
trichloroethene	50 - 150%
toluene	50 - 150%
chlorobenzene	50 - 150%

The target relative percent difference for the MS and MSD is $\pm 25\%$. The matrix spike mixture is prepared from neat standards in a static dilution vessel at 60°C with nitrogen as the balance gas. The mixture is manually injected via Injection Port 1 during Counter 3 using a gas tight syringe fitted with a mininert valve.

Safety Precautions:

Safety glasses are required when handling compressed gas cylinders and when working in the laboratory.

Cylinders are strapped in a secure fashion.

TABLE 2
TARGET PARAMETERS
LANDFILL GAS

Target Analyte	CAS Registry Number	Minimum Reporting Limit, nG/tube
Vinyl Chloride	75-1-4	10
1,3-Butadiene	106-99-0	10
Bromomethane	74-83-9	10
Trichlorofluoromethane	75-69-4	10
Methylene Chloride	75-9-2	10
Chloroform	67-66-3	10
1,1,1-Trichloroethane	71-55-6	10
Carbon Tetrachloride	56-23-5	10
1,2-Dichloroethane	107-6-2	10
Trichloroethene	79-1-6	10
1,2-Dichloropropane	78-87-5	10
Toluene	108-88-3	10
Tetachloroethene	127-18-4	5
1,2-Dibromoethane	106-93-4	10
Chlorobenzene	108-90-7	5
o-Xylene	1330-20-7	5
Ethylbenzene	100-41-4	5
Benzene	71-43-2	5
Chloromethane	74-87-3	10
1,1-Dichloroethene	75-35-4	10

NOTES:

Study performed 4/2/92 in accordance with 40 CFR Part 136, Appedix B