

SCAQMD METHOD 313-91**DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC)
BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)****1. Principle**

The headspace or liquid portion of a sample is injected directly into the gas chromatograph/mass spectrometer for quantitation of individual compounds. The total VOC is the sum of the concentrations of the individual compounds. A sample has VOC present if it contains components above ambient levels. Ambient levels is defined as less than 2 ppm total nonmethane hydrocarbons, as methane.

2. Equipment

2.1 GC/MS equipped with capillary open split interface

2.2 Column: DB-624^R, 30m X 0.53 mm, 3.0 um film

2.3 Syringes:

2.3.1 Glass, 1 mL with Luer tip syringe valve and 2-inch, 25 gauge needle

2.3.2 Gas-tight, 10 uL with needle

2.3.3 Gas-tight, 1.0 mL with needle

2.4 Volumetric Glassware

2.4.1 10 mL Volumetric Flask, Class A

2.4.2 1 mL Volumetric Pipets, Class A

2.5 Sample Containers

2.5.1 Jars, 250 mL, wide-mouth with Teflon^R faced septa

2.5.2 Vials, 40 mL, screw cap with Teflon^R faced septa

2.5.3 Cans, metal, 1 pint or 1 quart

2.6 Miscellaneous Supplies

- 2.6.1 Septa, Thermogreen™, 11 mm
- 2.6.2 Glass injection port liners
- 2.6.3 Vials, 5 mL, screw cap with Teflon^R faced septa

3. Reagents

- 3.1 Helium gas, chromatographic quality
- 3.2 VOC standards, >99% purity, as needed
- 3.3 Standard solutions, prepared by combining compounds with similar functional groups.
 - 3.3.1 Oxygenated organic compounds
 - 3.3.2 Hydrocarbon compounds
 - 3.3.3 Aromatic compounds
 - 3.3.4 Chlorinated compounds
- 3.4 4-Bromofluorobenzene (BFB), 25 mg/L in methanol

4. Procedure

- 4.1 Set up the GC oven program for the GC/MS. For a Hewlett-Packard 5970B, the following oven program is recommended:

Injector Temp:	200°C
Transfer line temp:	280°C
Detector Temp:	250°C
Oven Temp:	Hold at 50°C for 5 min. Ramp 15°C/min. to 200°C Hold at 200°C for 15 min Total Run Time: 30 min.

Scan start time: 0.0 min.
Scan Range: 5-250 amu

4.2 The system is checked for air leaks.

4.2.1 The system may be checked for air leaks either by running the program without any injection or by looking at the amount of air present during the optimization run using PFTBA. Air peak ions should meet the following criteria:

<u>m/z</u> <u>amu</u>	<u>Ion Abundance</u> <u>Criteria</u>	<u>Intensity</u> <u>(counts)</u>
18	ion of Water (<1% of 69 amu of PFTBA)	<200
28	ion of Nitrogen (<1% of 69 amu of PFTBA)	<500
32	ion of Oxygen (<1% of 69 amu of PFTBA)	<200

4.2.1.1 When the intensities of the water, nitrogen and oxygen ions are above their specified levels, it is an indication of a leak in the system.

4.2.1.2 Apply Freon 22 to fittings and tighten until no 51 amu signal is detected.

4.3 Check the tune by using perfluorotributylamine (PFTBA) prior to the start of an analysis or once a week if the instrument is not used daily.

4.3.1 The PFTBA ions should meet the following:

<u>m/z</u> <u>amu</u>	<u>Ion Abundance</u> <u>Criteria</u>	<u>Intensity</u> <u>(counts)</u>
69	Base Peak 100 %	75,000-200,000
219	30 - 60 % of 69 amu	22,500-120,000
502	1 - 10 % of 69 amu	750-20,000

4.3.1.1 The electron multiplier voltage is raised when the 69 amu intensity falls below 75,000 counts. Set the intensity count to about 150,000 when adjustment is needed.

- 4.3.1.2 Re-tune the gains and offsets if any of the PFTBA ion amu values specified in Section 4.3.1 are off by more than 0.2 amu.
 - 4.3.1.3 The "tilt" of the tune is changed by adjusting the repeller, ion focus and entrance lens voltages. This adjustment is performed when the intensities of the 219 and/or 502 ions are not within the recommended criteria specified in Section 4.3.1.
 - 4.3.1.4 Clean the source when the electron multiplier voltage must be increased to near 3000 V or tune criteria cannot be met. After cleaning the source the electron multiplier should be set to 1500 V or less.
 - 4.3.1.5 IMPORTANT: Whenever any of the tune parameters are changed it will be necessary to perform a new multi-level calibration and to verify the lower detection limit by analyzing the 0.1 g/L standard.
- 4.4 Check the system tune using 1.0 uL of 25mg/mL 4-bromofluorobenzene (BFB) in methanol every 6 months, after cleaning the source, or after retuning.
- 4.4.1. The BFB tune parameters should meet the following EPA criteria (intensity counts are not specified by EPA):

<u>m/z</u> <u>amu</u>	<u>Ion abundance</u> <u>Criteria</u>
50	15 - 40 % of 95 amu
75	30 - 60 % of 95 amu
95	Base peak 100 %
96	5 - 9 % of 95 amu
17	< 2 % of 174 amu
17	> 50 % of 95 amu
17	5 - 9 % of 174 amu
17	95 - 101 % of 174 amu
17	5 - 9 % of 176 amu

If the BFB criteria cannot be met, then re-tune the mass spectrometer by the following:

4.4.1.1 If the low intensity ions (96, 175 and 177) are not found, increase the electron multiplier voltage.

4.4.1.2 If the "tilt" is wrong (50, 75, 174 and 176 are too high or too low), then change the ion focus and entrance lens.

4.5 Preparation of Standards

4.5.1 Prepare four different 100 g/L standards (standards according to the groups in Section 3.3) in isooctane solvent. Prepare this standard at least every three months.

4.5.1.1 Starting with least volatile component, add 1.00 g of each component to a tared 10 mL volumetric flask and weigh to 0.1 mg.

4.5.1.2 Bring to mark with isooctane.

4.5.2 Prepare 10 g/L standard by adding 1.0 mL of each of the four 100 g/L standards to a 10 mL volumetric flask and diluting to the mark with isooctane.

4.5.3 Prepare the 1 g/L standard by adding 1.0 mL of the 10 g/L standard to a 10 mL volumetric flask and diluting to the mark with isooctane.

4.5.4 Prepare a 0.1 g/L standard by adding 1.0 mL of the 1 g/L standard to a 10 mL volumetric flask and diluting to mark with isooctane. This solution is used in Section 4.3.1.5 to verify the lower detection limit.

4.5.5 Prepare the 25 g/L standard by combining 1.0 mL each of the four 100 g/L standards in a 5 mL vial with a Teflon^R faced septum cap. Prepare this standard once a month.

4.6 Calibration

4.6.1 Inject a solvent blank to verify that the syringe and the system is clean.

- 4.6.2 Inject separately 1.0 uL of the 1 g/L standard, the 10 g/L, the 25 g/L and each of the four 100 g/L standards using solvent flush injection technique.

Solvent flush injection technique is described in Hewlett Packard GC Manual (HP 5890 Series II Reference Manual 6 - 22).

- 4.6.2.1 For each compound, create a multilevel calibration curve of counts vs. ug injected.
- 4.6.2.2 Calculate the response factor for each component. The response factor is defined as the counts divided by the ug injected.
- 4.6.2.3 Calculate the percent relative standard deviation (%RSD) of the average response factor of each component in the multi-level calibration. The values should be less than 25%.
- 4.6.3 Once a valid multi-level calibration exists, the GC/MS is checked by comparing the response factor of the 25g/L standard with those obtained from the valid multi-level calibration.
- 4.6.3.1 The percent difference (% Diff.) from the average response factor should be less than 25% for each component.
- 4.6.3.1.1 If the % Diff. is greater than 25% a recalibration is necessary if the the compounds found to be out of calibration are present in the sample.
- 4.6.3.2 Either prepare new standards (because standards have degraded over time) or prepare standards which are closer to the expected concentrations in the sample to create new calibration reponse factors.
- 4.6.4 For liquid samples, the linear range is 1 to 100 ug/uL, and the lower detection limit is 0.1 ug/uL.
- 4.6.5 For gas injections, a 10 ppm lower limit of detection has been demonstrated for BTX gases.

- 4.6.5.1 Samples that contain less than 10 ppm must be concentrated before being injected onto the column.

4.7 Analysis

4.7.1 Analysis of headspace gas

- 4.7.1.1 Inject 1 mL of ambient air taken from the vicinity of the GC/MS. There should only be a large air peak (18, 28, 32, and 40 amu). If other peaks are present, identify and quantitate each peak attributed to VOC. Do not quantitate the air peak.
- 4.7.1.2 If sample is in a container with a septum, take 1 mL aliquot of headspace through the septum using a syringe specified in Section 2.3.1. Do not allow the syringe tip to touch the surface of the liquid or solid portion of the sample. Close syringe valve before removing syringe assembly from the septum.
- 4.7.1.3 If sample is in a can, open lid slightly, take a 1mL aliquot of the headspace with a syringe specified in Section 2.3.1. Be careful not to touch the rag or the surface of the liquid while removing headspace gas. Close syringe valve before removing syringe assembly from the container. Immediately reclose the container.
- 4.7.1.4 Inject 1 mL headspace onto the GC/MS and identify and quantitate all peaks seen.
- 4.7.1.5 Subtract any VOC due to the ambient air.

4.7.2 Analysis of a liquid sample

- 4.7.2.1 With a syringe specified in Section 2.3.2, inject 1.0 uL isooctane using isooctane as solvent flush or other appropriate solvent if isooctane is known to interfere. Identify and quantitate all peaks except the solvent peak.

- 4.7.2.2 With a syringe specified in Section 2.3.2, inject 1.0 uL of sample using isooctane as solvent flush or other appropriate solvent if isooctane is known to interfere. Identify and quantitate all peaks except the solvent peak.
- 4.7.2.3 If any components are over the calibration range for that component (>100 g/L), dilute as needed.
- 4.7.2.4 If any components are observed but are not in the standard (See Section 3.2), prepare additional standards and calibrate.
- 4.7.3 If components are present which cannot be identified by matching to known spectra, provide spectra for possible future identification. Estimate the concentration of unknown peaks by area percent quantitation based on the Total Ion Chromatogram.

5. Calculations

5.1 Calculations

- 5.1.1 For headspace gas calculations, concentration of each compound in ppm by volume:

$$\text{Concentration, ppm (vol)} = [24.5(A) \cdot (10^3)] / [(B) \cdot (MW)]$$

where: A = quantified amount of a compound, ug

B = injection volume, mL

MW = molecular weight of the compound, g/mole

Note: 24.5 L/mole is the molar volume of an ideal gas at 25°C

- 5.1.2 For liquid sample calculations, concentration of each compound in percent by volume is:

$$\text{Concentration, \% by vol} = [(Y) \cdot (0.1)] / [(Z) \cdot (D)]$$

where: Y = quantified amount of a compound for one injection, ug

$Z =$ injection volume, μL

$D =$ density of the compound, g/mL

5.1.3 For liquid samples, concentration of each compound in g/L :

Concentration, $\text{g/L} = Y/Z$

where: $Y =$ quantified amount of a compound for one injection, μg

$Z =$ injection volume, μL

5.1.3.1 Total VOC, g/L is the sum of the concentrations of each compound.

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

APPLIED SCIENCE & TECHNOLOGY DIVISION

LABORATORY SERVICES BRANCH

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The method for the determination of volatile organic compounds (VOC) by Gas Chromatography/Mass Spectrometry (GC/MS) is for use in the analysis of samples regulated by Regulation XI.

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