

SCAQMD METHOD 305-91
DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC)
IN AEROSOL APPLICATIONS

1. Principle

The amount of VOC in aerosol applications is determined by analysis of the propellant portion and the coating portion of an aerosol sample. The amount of propellant is determined gravimetrically. An aliquot of the propellant is analyzed for exempt compounds, if present, by gas chromatography (GC). The coating remaining in the can is analyzed for VOC by the procedure specified in SCAQMD Method 304.

2. Equipment

- 2.1 Laboratory exhaust hood
- 2.2 Freezer, capable of maintaining temperature at -15°C or lower
- 2.3 Balance, capable of weighing accurately to .01 g
- 2.4 Can piercer assembly (see Figure 1 for details). Available from Alltech Associates, Inc. 2051 Waukegan Road, Deerfield, IL 60015
- 2.5 Can opener
- 2.6 Gas chromatograph equipped with a thermal conductivity detector, and gas injector port with 1 mL sample loop and capable of temperature programming
- 2.7 Integrator, electronic
- 2.8 Column. 20' x 1/8" outside diameter, stainless steel, packed with 80/100 mesh Supelcoport^R coated with 10% Carbowax^R and substituted terephthalic acid packing material
- 2.9 Syringe, 50 mL, multifit glass with Luer-Lok^R tip equipped with stopcock
- 2.10 Other equipment. Refer to relevant individual methods in the SCAQMD method 304 manual for other equipment needed.

3. Reagents and Materials

- 3.1 Helium gas, 99.995% or higher purity
- 3.2 Nitrogen gas, 99.995% or higher purity
- 3.3 Exempt gas standards (Freon), 20% by weight in high purity nitrogen gas, certified
- 3.4 Refer to relevant individual methods in the SCAQMD Method 304 manual for reagents needed

4. Analytical Procedure

- 4.1 Preparation of Samples that Do Not Contain Exempt Compounds
 - 4.1.1 Remove cap, actuator, and all paper labels. Clean sample can with damp paper towel, wipe to dry.
 - 4.1.2 Write sample identification on the can using a marker.
 - 4.1.3 Let sample stand for 1/2 hour in the hood.
 - 4.1.4 Weigh sample can to the nearest 0.01 gram, (W1).
NOTE: All weights must be taken to the nearest 0.01 gram.
 - 4.1.5 Keep the sample can in the freezer overnight.
 - 4.1.6 Transfer sample can from the freezer to the hood and immediately attach can piercer to the top of the can (Figure 1). Tighten the screws to pierce the can.
 - 4.1.7 Slowly remove the can piercer. The can is pressurized and sudden removal of the can piercer may allow part of the liquid sample to be entrained with the propellant, which is not acceptable.
 - 4.1.8 Carefully enlarge the hole with the aid of a clean ice pick. Allow the propellant to be released for 12 - 15 hours.
 - 4.1.9 Swirl the sample can gently for 30 seconds to facilitate the removal of the remaining dissolved propellant. Allow to stand for 1/2 hour.

- 4.1.10 Check for the presence of residual propellant as follows: Plug the hole with a clean cork, swirl can gently for 30 seconds, remove the plug. If there is pressure buildup, swirl can gently for 15 seconds, let stand for one hour and check again for the presence of residual propellant. Repeat until there is no pressure buildup present.
 - 4.1.11 Wipe off the surface of the can, allow to stand for 1/2 hour, and weigh. This weight in grams is W2.
 - 4.1.12 Open the sample can with the aid of a can opener. Carefully pour the liquid contents to a clean, labeled 16-ounce sealable metal container. Be sure to keep the agitators in the original can. Tightly close the properly labeled container with samples. Proceed to step 4.2 for VOC analysis.
 - 4.1.13 Rinse original can and agitators several times with an appropriate solvent until clean. Dispose of the washings.
 - 4.1.14 Allow can and agitators to dry overnight, then weigh. Allow to stand for one hour and reweigh. Repeat until a constant weight is obtained. This weight in grams is W3.
- 4.2 Determination of Total Volatiles in the Liquid Portion
- 4.2.1 Analyze an appropriate aliquot of the sample from step 4.1.12 for total volatiles following the method specified in the SCAQMD Method 304.
 - 4.2.2 Determine the weight (in grams) of total volatiles in the liquid sample (Wv).
- 4.3 Determination of Water Content in the Liquid Portion
- 4.3.1 Analyze an appropriate aliquot of the sample from step 4.1.12 for water following the method specified in the SCAQMD Method 304.
 - 4.3.2 Determine the weight (in grams) of water in the liquid sample (Ww).
- 4.4 Preparation of Samples that Contain Exempt Compounds
- 4.4.1 Weigh the can without the plastic cap (W1).

- 4.4.2 Install a can piercer as close as possible to the bottom of the coating can. Weigh can and piercer assembly. Record weight for use in Section 4.5.11.
 - 4.4.3 Shake the can vigorously for 5 minutes, set the can in an upside down position for 10 minutes.
 - 4.4.4 Pierce the can by tightening clamps (See Figure 1).
- 4.5 Analysis of Exempt Compounds in the Propellant
- 4.5.1 Set the gas chromatograph (GC) to the parameters listed in Table 1.
 - 4.5.2 Condition column and instrument.
 - 4.5.3 Inject nitrogen gas as a blank.
 - 4.5.4 Flush out the 50 mL gas syringe several times with the exempt compound standard to be analyzed.
 - 4.5.5 Fill the syringe with standard and inject into the GC through the sample loop.
 - 4.5.6 Flush out the gas syringe several times with nitrogen.
 - 4.5.7 Inject nitrogen into the GC as a blank to check for any carryover of the standard.
 - 4.5.8 Flush out the syringe 3 times with headspace sample taken from the can (still under pressure in Section 4.4.4) through the septum. (See Figure 1).
 - 4.5.9 Fill the syringe with 10 mL of the sample, and dilute to 50 mL with nitrogen gas. Equilibrate the diluted sample for 2 minutes at room temperature. Inject the sample into the gas chromatograph.
 - 4.5.10 Repeat 4.5.8 to 4.5.9 for a duplicate injection. The results of the two injections must be within $\pm 10\%$ of each other.

- 4.5.11 Spray out about 20% (~10% of the total weight of the sample determined in Section 4.4.2) of the propellant with the can in an upside down position. Reweigh the can and piercer assembly to determine if there has been an approximate 10% reduction in total weight of the sample.
 - 4.5.12 Repeat the analysis according to Section 4.5.8 to 4.5.11 until all propellant has been removed. To check for the presence of residual propellant, see Section 4.1.10.
 - 4.5.13 Remove can piercer.
 - 4.5.14 Weigh the can without plastic cap (W2).
 - 4.5.15 Follow Section 4.1.12 through 4.1.14 to prepare the liquid sample for VOC analysis and to determine the weight of the can and agitators.
 - 4.5.16 Test the VOC of liquid sample according to Sections 4.2, 4.3 and 4.6.
- 4.6 Determination of Exempt Compound Content of the Liquid Portion
- 4.6.1 Analyze an appropriate aliquot of the sample from step 4.1.12 for exempt compounds following SCAQMD Method 302 (Distillation of Solvents from Paints, Coatings and Inks) and SCAQMD Method 303 (Determination of Exempt Compounds).
 - 4.6.2 Determine the weight (in grams) of exempt compounds in the liquid sample (Wx).

5. Calculations

- 5.1 Weight percent of exempt in propellant at a given point in the analysis, E_n

$$E_n = \text{Est} \times \text{Df} \times \frac{A_{es}}{A_{est}}$$

- 5.2 Weight percent of exempt compound in propellant, E_p = Average the exempt compound amount at all points of analysis

$$E_p = \frac{1}{n} \sum_{i=1}^n E_i$$

Where:

n = Number of analyses

E_i = Weight percent exempt compound for the i th analysis.

5.3 Calculate the weight (in grams) of propellant (W_p) by:

$$W_p = W_1 - W_2$$

5.4 Weight in gram of exempt compounds in propellant, W_{exp}

$$W_{exp} = \frac{E_p}{100} \times W_p$$

5.5 Calculate the weight (in grams) of the total sample (W_s) by:

$$W_s = W_1 - W_3$$

5.6 Calculate the weight (in grams) of liquid sample (W_q) by:

$$W_q = W_s - W_p$$

5.7 Calculate the percent VOC (based on coating), $\%VOC_c$, by:

$$\% VOC_c = \frac{(W_v - W_w - W_x - W_{exp} + W_p)}{W_s - W_w - W_x - W_{exp}} \times 100$$

5.8 Calculate the percent VOC (based on material), $\%VOC_m$, by:

$$\% VOC_m = \frac{(W_v - W_w - W_x - W_{exp} + W_p)}{W_s} \times 100$$

5.9 Definition of variables

Est = Concentration of exempt compound in the standard, % (w/w)

Df = Inverse of dilution factor (Sample is diluted in Section 4.5.9)

Aes = Area of exempt compound in the sample

Aest = Area of exempt compound in the standard

W1 = Weight of sample can and contents, g (Sec. 4.1.4 or Sec. 4.4.1)

W₂ = Weight of sample can without propellant, g (Sec 4.1.11 or Sec. 4.5.14)

W₃ = Weight of the sample can, g (Sec. 4.1.14)

W_v = Weight of total volatiles in the liquid, g (Sec. 4.2.2)

W_w = Weight of water in the liquid, g (Sec. 4.3.2)

W_x = Weight of exempt compounds in the liquid, g (Sec. 4.6.2)

Table I
Typical GC Parameters

Column: 20' X 1/8" outside diameter. Stainless steel, packed with 80/100 mesh Supelcoport^R coated with 10% Carbowax^R and substituted terephthalic acid packing materials

Flow: 20 mL/min Nitrogen

Injector port temperature: 200°C

Detector temperature: 220°C

GC Program: Hold at 40°C for 10 min
 Ramp at 20°C/min to 170°C
 Hold at 170°C for 10 min

Injection volume: 1 mL

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

APPLIED SCIENCE & TECHNOLOGY DIVISION

LABORATORY SERVICES BRANCH

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This method is used to determine the volatile organic compounds (VOC) in samples contained in aerosol containers. The method is applicable to samples regulated under rules under Regulation XI.

CONTENTS

	<u>Page</u>
1. Principle	1
2. Equipment	1
3. Reagents and Materials	2
4. Analytical Procedure	2
4.1 Preparation of Samples that Do Not Contain Exempt Compounds	2
4.2 Determination of Total Volatiles in the Liquid Portions	3
4.3 Determination of Water Content in the Liquid Portion	3
4.4 Preparation of Samples that Contain Exempt Compounds	3
4.5 Analysis of Exempt Compounds in the Propellant	4
4.6 Determination of Exempt Compound Content of the Liquid Portion	5
5. Calculations	5
6. Figure 1: Aerosol Can and Piercer Assembly	9