

SCAQMD METHOD 303-91
DETERMINATION OF EXEMPT COMPOUNDS

1. Principle

- 1.1 This method is based on the separation of components of a sample using a gas chromatograph (GC) and measurement of the response of separated components with a thermal conductivity (TC) detector. An internal standard is added to the sample and standards. The concentration of each component is determined by comparing the response of the component in the sample with the response of the component in the standard under the same conditions.
- 1.2 The identity and approximate concentrations of the organic components are confirmed by gas chromatography/mass spectrometry (GC/MS) before actual GC analysis is performed.

2. Apparatus and Equipment

- 2.1 Gas chromatograph. GC with thermal conductivity detector, temperature controlled injection port and oven
- 2.2 Recorder. Recorder with linear strip chart is acceptable. An integrator is recommended.
- 2.3 Regulators
- 2.4 Syringes. 1.0- and 10-microliter (uL) sizes
- 2.5 Teflon^R tubing. Diameter and length is determined by connection requirements of cylinder regulator and the GC.
- 2.6 Tubing fittings
- 2.7 Septum: Supelco Thermogreen^R LB-2
- 2.8 Soap film flow meters
- 2.9 Standard glass pipets and volumetric flasks, Class A

- 2.10 Autosampler (optional)
- 2.11 Column: 10% SP-1000 on Supelcoport^R (80 - 100 mesh)

3. Reagents

- 3.1 Helium, chromatographic quality
- 3.2 Isooctane (2,2,4-trimethylpentane), reagent grade
- 3.3 Trichlorotrifluoroethane, reagent grade
- 3.4 1,1,1-Trichloroethane, reagent grade
- 3.5 Methylene chloride (dichloromethane), reagent grade
- 3.6 Perchloroethylene (tetrachloroethene), reagent grade
- 3.7 Diluent: Ten mL perchloroethylene is diluted to 250 mL with isooctane.

4. Procedure

- 4.1 Preparation
 - 4.1.1 Distillation
Coatings and inks are distilled by following SCAQMD Method 302-91 (Distillation of Solvents from Paints, Coatings, and Inks).
 - 4.1.2 Samples
The distillate in vials from the distillation procedure is brought to ambient temperature before an aliquot is taken for analysis. Dilute 3 mL of the sample to 50 mL with diluent (See Section 3.7). The exempt compounds in the samples are identified by GC/MS.
 - 4.1.3 Standards
Standards are prepared by pipetting 3 mL of each of the identified exempt compounds into separate 50 mL volumetric flasks and bringing to volume with the diluent (See Section 3.7).

4.2 Analysis

4.2.1 Procedure

Quantitatively inject 3 uL aliquots of the prepared standard into the gas chromatograph. Duplicate analyses areas must be within 5% of their mean value. Repeat the above procedure for the prepared sample. Run a standard after every tenth sample injected (after twenty injections) or at the end of all sample runs if there are less than ten samples injected.

4.2.2 Instrument parameters

Typical operating conditions of the chromatograph are up as follows:

Analytical Column: 10% SP1000 on 80-100 mesh Supelcoport^R in grade 316 stainless steel, 1/8 inch O.D. x 20 feet.

Carrier Gas: Helium, 20-24 mL/min.

Reference Gas: He, 36 mL/min (approximately 1.5 times of carrier gas flow).

Injection Port Temperature: 200°C

Detector Temperature: 210°C

Temperature Program:

Hold at 80°C for 9 min

Ramp 20°C/min to 170°C

Hold at 170°C for 10 min

4.2.3 Automation

The method may be automated by use of an autoinjector.

5. Calculations

The following is used to calculate the weight percent exempt compound in the sample (Wt.% ExCmpd):

$$\text{Wt. \% ExCmpd} = \frac{A_{\text{pst}}}{A_{\text{est}}} \times \frac{A_{\text{es}}}{A_{\text{ps}}} \times \frac{(C)(V)(D)}{S}$$

In cases where perchloroethylene is known to be in the sample or when there are interfering compounds which co-elute with perchloroethylene, use the following equation:

$$\text{Wt. \% ExCmpd} = \frac{A_{\text{es}}}{A_{\text{est}}} \times \frac{(C)(V)(D)}{S}$$

Where:

- A_{pst} = Average area of perchloroethylene (perc) in the standard
- A_{est} = Average area of exempt compound in the standard
- A_{es} = Average area of exempt compound in the sample
- A_{ps} = Average area of perc in the sample
- C = Volume percent of exempt compound in standard (Section 3)
- V = Corrected volume of distillate, in mL
- D = Density of exempt compound, in g/mL
- S = Weight of sample distilled, in grams

6. Range

6.1 The range of this method is from about 0.5% v/v to upper limit governed by GC detector saturation or column overloading. The upper limit can be extended by diluting the sample with isooctane or injecting a smaller sample.

7. References

- 7.1 Code of Federal Regulations, Title 40, Part 60, Appendix A, Method 18, July 1, 1985.
- 7.2 American Society for Testing and Materials, Designation E-260, Standard Practice for Gas Chromatography, Philadelphia, 1985.

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This method applies to the qualitative and quantitative determination of exempt compounds in coatings, inks and solvents. This method, in conjunction with SCAQMD Method 302 (Distillation of Solvents from Paints, Coatings and Inks) provides data for the calculation of volatile organic content. This method is applicable to Rule 107 and to various Regulation XI rules.

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SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

APPLIED SCIENCE & TECHNOLOGY DIVISION

LABORATORY SERVICES BRANCH

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