

# METHOD 46

## DETERMINATION OF THE COMPOSITE PARTIAL PRESSURE OF VOLATILE ORGANIC COMPOUNDS IN CLEANING PRODUCTS

REF: Reg. 8-20-309

### 1. PRINCIPLE

- 1.1 The volatile organic compounds (VOC) in the cleaning product are identified and quantified using a gas chromatograph equipped with a photoionization-flame ionization detector system connected in series (PID/FID).
- 1.2 Identification of the compounds in the cleaning product are is based mainly on the retention times of the compounds.
- 1.3 The weight percent of each VOC component of the material is determined by the internal standard method. This percentage is converted to mole fraction, which is then used to determine the partial pressure of the individual VOC.
- 1.4 The VOC composite partial pressure of the cleaning product is calculated by taking the sum of the individual partial pressures of the VOC components.
- 1.5 The limit of detection of this method is ~~0.05% (weight)~~ 0.1 mm Hg VOC composite partial pressure at 20 °C.

### 2. APPARATUS

2.1 Gas Chromatograph. This unit is equipped with a liquid injection port lined with a glass sleeve, a flame ionization detector, a photoionization detector, a temperature programmer and a compatible integrator or data station.

2.1.1 For hydrocarbon based cleaning products, the recommended GC parameters are:

	Initial	Final
Oven Temperature (°C)	40	200
Iso Time (min)	5	10
Temperature Program Rate (°/min)	2	
Injector Temperature (°C)	250	
Detector Temperature (°C)	250	
Carrier Gas	N <sub>2</sub> or He	
Carrier Gas Flow (ml/min)	3	
Injection Sample Size (µl)	1	

2.1.1.1 Analytical Column: Any analytical column capable of separating and resolving the compounds of interest is acceptable. The recommended analytical columns for this method are:

2.1.1.1.1 Primary Column:

60m x 0.25 mm ID ZDB-Wax Column, 0.5  $\mu\text{m}$  Film Thickness. (Available from J & W Scientific)

2.1.1.1.2 Alternate Column:

60 m x 0.32 mm ID, DB-1 Column, 1.0  $\mu\text{m}$  Film Thickness. (Available from J&W Scientific)

2.1.2 For water based cleaning products, the recommended GC parameters are:

	Initial	Final
Oven Temperature ( $^{\circ}\text{C}$ )	60	200
Iso Time (min)	5	10
Temperature Program Rate ( $^{\circ}/\text{min}$ )	5	
Injector Temperature ( $^{\circ}\text{C}$ )	250	
Detector Temperature ( $^{\circ}\text{C}$ )	250	
Carrier Gas	N <sub>2</sub> or He	
Carrier Gas Flow (ml/min)	20	
Injection Sample Size ( $\mu\text{l}$ )	$\approx 1$	

2.1.2.1 Any analytical column capable of separating and resolving the compounds of interest is acceptable. The recommended column for this procedure is:

A 12" X 1/8" O.D. SS Column packed with 20% SP 2100/0.15% Carbowax 1500 on Supelcoport, 100/120 mesh.

- 2.2 Burrell Wrist Action Shaker or equivalent.
- 2.3 Analytical Balance, capable of weighing to 0.0001 g.
- 2.4 Syringes, various sizes as needed.
- 2.5 Micro Syringe, 10  $\mu\text{l}$  capacity.
- 2.6 Volumetric Flask, various sizes as needed.
- 2.7 Graduated Cylinder, various sizes as needed.
- 2.8 Pipette, various sizes as needed.

~~2.9 Vials with screw caps, 2 dram capacity.~~

2.9 Refrigerator.

2.10 Disposable Beral pipettes.

### 3. REAGENTS

3.1 Compressed Air. (Note 1)

3.2 Carrier Gas, helium or nitrogen, 99.99% or higher purity. (Note 1)

3.3 Fuel Gas, hydrogen, 99.9% or higher purity. (Note 1)

**Note 1:** The carrier and fuel gases are compressed under high pressure. Hydrogen is an extremely flammable gas. Compressed air supports combustion. Read the precautionary labels before handling these materials.

3.4 Paraffin Hydrocarbon Standards, C<sub>7</sub> through C<sub>17</sub>, reagent grade, minimum purity of 99+ %.

3.5 Oxygenated Hydrocarbon Standards, reagent grade, minimum purity of 99+ %.

3.6 Aromatic Hydrocarbon Standards, reagent grade, minimum purity of 99+%.

3.7 Carbon Disulfide (CS<sub>2</sub>), low Benzene (<1 ppm) or other suitable solvent, Reagent Grade.

### 4. ANALYTICAL PROCEDURE

#### 4.1 Sample Preparation and Analysis:

4.1.1 Determination of Total Volatiles.

4.1.1.1 Determine the % Volatile (w/w) of the sample by following BAAQMD Method 21 or Method 22.

4.1.2 Determination of Water and Exempt Compounds.

4.1.2.1 Determine the exempt compounds and water in the cleaning product by ASTM D-6133-02, BAAQMD Method 21, BAAQMD Method 22 or any appropriate method in the BAAQMD Manual of Procedures. Express these concentrations in grams (W<sub>w</sub> or W<sub>e</sub>, respectively) per 100 grams of sample.

4.1.3 Set up the gas chromatograph as described in Section 2.1.

- 4.1.4 Depending on the type of cleaning product (solvent based or aqueous), use the appropriate analytical column as recommended in Sections 2.1.1 and 2.1.2.
- 4.1.5 Mix the sample thoroughly. It is essential that the sample is mixed well in order to get valid results.
- 4.1.6 Screen the sample in order to determine the internal standard to be used in the analysis and the types of compounds present for standard preparation. N-octane or any other compound can be used as internal standard if there are no interfering peaks present in the area where the compound elutes. (Note 2)

**Note 2:** The internal standard must be a compound which is not in the sample matrix and does not coelute with any other volatile component in the cleaning product. It must perform on the analytical systems in a manner similar to that of the compounds being measured.

- 4.1.7 Weigh and record approximately 2.5 g ( $W_s$ ) of the well mixed sample and 0.025 g ( $W_{is}$ ) of the internal standard (to 0.0001g) in a tared 25 ml volumetric flask.
- 4.1.8 Add diluent (3.7) to the mark. (Note 3)

**Note 3:** Carbon Disulfide is flammable. It is harmful if inhaled or absorbed through the skin. It is a possible mutagen/teratogen. Use only with adequate ventilation. Avoid contact with skin, eyes and clothing. If the material to be analyzed is not compatible with CS<sub>2</sub>, use a different solvent such as dimethylformamide, tetrahydrofuran or dimethyl sulfoxide. The diluent must be chosen such that the sample is miscible with it and the peak does not interfere with those of the analytes. The sample may be diluted further or made more concentrated to attain optimum peak areas.

- 4.1.9 Invert the flask (4.1.8) several times to mix its content thoroughly. Allow the vial to stand for ten to fifteen minutes undisturbed to allow the sample to reach equilibrium.
- 4.1.10 Inject 1  $\mu$ l of the sample (4.1.9) into the gas chromatograph. Record the peak areas and retention times of the compounds and retain the chromatogram.
- 4.1.11 Run the analysis in duplicate. ~~Reanalyze the sample if the results vary by more than 5% relative.~~ Calculate the relative difference between the two results by using the following equation:

$$\%RD = \frac{(PPc1 - PPc2) \times 100}{AVGPPc12}$$

Where: %RD = Relative Difference between twp results

PPc1 = VOC composite partial pressure result of run 1 (mm Hg at 20°C)

PPc2 = VOC composite partial pressure result of run 2 (mm Hg

$$\text{AVGPPc12} = \frac{\text{Average of PPc1 and PPc2} \text{ or } (\text{PPc1} + \text{PPc2})/2}{\text{at } 20 \text{ } ^\circ\text{C}}$$

4.1.12 Reanalyze the sample if the relative difference (%RD) between the two results is more than 5%.

## 4.2 Standard Preparation and Determination of the Response Factor (Rf)

4.2.1 In a 25 ml volumetric flask, weigh approximately 0.025 g ( $W_{\text{std}}$ ) of standard for each of the compounds present in the sample (to 0.0001g).

4.2.2 Add diluent (3.7) to the mark. (Note 3) (Note 4)

**Note4:** The standard can alternatively be prepared by initially mixing a stock solution of the compounds of interest and the internal standard. A working standard is prepared by diluting the stock in the chosen solvent such that optimum areas are attained.

4.2.3 Invert the flask (4.2.2) several times to mix its contents thoroughly. Allow the vial to stand for ten to fifteen minutes undisturbed to allow the sample to reach equilibrium.

4.2.4 Inject 1  $\mu\text{l}$  of the sample (4.2.3) into the gas chromatograph. Record the peak areas and retention times of the compounds and retain the chromatogram.

4.2.5 Calculate the response factor of each of the compounds in the Standard. (Note 4 5)

$$R_f = \frac{W_{\text{is}} \times A_{\text{std}}}{W_{\text{std}} \times A_{\text{is}}}$$

Where:

- $R_f$  = Response factor of the standard
- $W_{\text{is}}$  = Weight of the internal standard, in grams
- $A_{\text{is}}$  = Area of the internal standard
- $W_{\text{std}}$  = Weight of the standard, in grams
- $A_{\text{std}}$  = Area of the standard

**Note 4 5:** It is necessary to determine the response factor for each of the standards with each series of determinations.

## 5. CALCULATIONS

- 5.1 Calculate the concentration of the "i"th VOC component of the cleaning product using the following equation:

$$5.1.1 \quad \% \text{ "i"th VOC (w/w)} = \frac{(A_{i\text{th}}) \times (W_{\text{is}}) \times 100}{(A_{\text{is}}) \times (W_{\text{s}}) \times R_{\text{f}}}$$

Where:

- $A_{i\text{th}}$  = Peak Area of the "i"th VOC component of the cleaning product
- $W_{\text{is}}$  = Weight of the internal standard, in grams
- $A_{\text{is}}$  = Peak Area of the internal standard
- $W_{\text{s}}$  = Weight of the sample, in grams
- $R_{\text{f}}$  = Response factor of the internal standard to "i"th component of the cleaning product (from 4.2.5)
- 100 = Factor to express the weight of the "i"th VOC component of the product as % (w/w).

- 5.2 Calculate the composite partial pressure of the VOC in the cleaning product using the following equation:

$$PP_{\text{c}} = \frac{\sum_{i=1}^n [(W_i) (VP_i) / (MW_i)]}{(W_{\text{w}}/MW_{\text{w}}) + (W_{\text{e}}/MW_{\text{e}}) + \sum_{i=1}^n (W_i/MW_i)}$$

Where:

- $PP_{\text{c}}$  = VOC composite partial pressure at 20°C, in mm Hg
- $VP_i$  = Vapor pressure of the "i"th VOC compound at 20 °C, in mm Hg
- $W_i$  = Weight of the "i"th VOC compound, in grams per 100 grams cleaning product (% "i"th VOC)
- $W_{\text{w}}$  = Weight of water, in grams per 100 grams cleaning product (from Method 21)
- $W_{\text{e}}$  = Weight of exempt compounds, in grams per 100 grams cleaning product (from Method 22)
- $MW_{\text{w}}$  = Molecular weight of water, in grams per gram-mole
- $MW_{\text{e}}$  = Molecular weight of exempt compound, in grams per gram-mole
- $MW_i$  = Molecular weight of the "i"th VOC compound, in grams per gram-mole

## 6. REFERENCES

- 6.1 "Volatile Content of Paint," ASTM Designation D2369-92, Book of ASTM Standards, Vol. 6.01, 1993.
- 6.2 "Determination of Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph," ASTM Designation D3792-91, Book of ASTM Standards, Vol. 6.01, 1993.
- 6.3 "BAAQMD Manual of Procedures," Vol.3, Method 22.
- 6.3 "BAAQMD Manual of Procedures," Vol.3, Method 21.

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