METHOD 31

REF: Reg: 8-3   8-19   8-31   8-50
              8-4   8-20   8-32   8-51
              8-14   8-29   8-35
              8-16   8-30   8-45

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN PAINT STRIPPERS, SOLVENT CLEANERS AND LOW SOLIDS COATINGS

1)   PRINCIPLE

1.1   This method is applicable to the determination of volatile organic compounds **(VOC)** in paint strippers, solvent cleaners and low solids coatings. The non-volatile **(NV)** content is determined by heating an aliquot of the sample in an oven for 1 hour at 110°C ± 5°C.

1.2   Water, methylene chloride, 1,1,1-trichloroethane (**TCA**) and other exempt chlorinated solvents compounds are determined by gas chromatography, using ethanol as the internal standard.

1.3   This method does not exclude water and may or may not exclude exempt chlorinated solvents compounds when calculating the volatile organic compound content of in the sample.

1.4   If other exempts compounds such as acetone, parachlorobenzotriflouride, volatile methylsiloxanes or methyl acetate are present in the sample, the material must be analyzed by BAAQMD Methods 22, 41 or 43, or ASTM D6133-02.

2)   APPARATUS

2.1   Gas Chromatograph. This unit is fitted with a thermal conductivity detector (TCD), a glass sleeve injection port, a temperature programmer and a compatible integrator or data station. The suggested operating parameters are as follows:

	Initial	Final
Oven Temperature (°C)	110	220
Time Delay (min)	0	10
Program Rate (°C/Min)	10	
* Injector Temperature (°C)	250	
Detector Temperature (°C)	250	

Filament Current (ma)	150
Injection Sample Size (μl)	2
Carrier Gas	He
Carrier Gas Flow (cc/Min)	20

    * **Glass-sleeve insert is used in the injection port.**

2.2 **Analytical Column:** <u>Any analytical column capable of separating and resolving the compounds of interest is acceptable. The suggested analytical columns are;</u>

    2.2.1   A 6' x 1/8" O.D. SS Column packed with Porapak Q, 80 to 100 mesh.

    2.2.2   **Alternate Column to Confirm the Presence of Chlorinated Hydrocarbons (CLHC)**. Use only if interfering peaks are found.

                A 12' x 1/8" O.D. SS Column packed with 20% SP-2100 + 0.1% Carbowax 1500, 100 to 120 mesh supelcoport.

2.3 **10 μl Syringe.**

2.4 **Burrell Wrist Action Shaker.**

2.5 **Refrigerator.**

2.6 **Aluminum Foil Dish.** 57 mm diameter x 10 mm high with a flat bottom.

2.7 **Drying Oven, Forced Air.** Capable of maintaining a temperature of 110°C $\pm$ 5°C

2.8 **Analytical Balance.** Capable of weighing to $\pm$ 0.0001 g.

2.9 **Top Loading Analytical Balance.** Capable of weighing to $\pm$ 0.01 g.

2.10 **Disposable Beral Pipettes.** These are available from Curtin Matheson Company **(Catalog #376-970).**

2.11 **Spatula.**

2.12 **Gardner-Weight-per-Gallon Cup. (83 ml). These are available from Thomas Scientific (Catalog # 8353A01).**

2.13 **Vials with Screw Caps.** 2 dram size.

2.14 **Paper Clip.** Bent to a 90° angle.

3) REAGENTS

3.1 Toluene or other Suitable Solvents.

3.2 Ethyl Alcohol. 200 proof. <u>Other suitable internal standards. Reagent grade or highest available purity.</u>

3.3 Dimethylformamide (DMF). Spectroquality. Water content must not exceed 0.05% (w/w). <u>Other suitable solvents, Reagent Grade</u>.

3.4 Helium.

3.5 Methylene Chloride. Reagent grade or highest available purity.

3.6 Distilled Water.

3.7 1,1,1-Trichloroethane (TCA). Reagent grade or highest available purity.

3.8 Sodium Sulfate (Na_2SO_4), Anhydrous powder.

4) ANALYTICAL PROCEDURE

4.1 Determination of Total Volatiles.

4.1.1 Mix the sample thoroughly using a spatula. It is essential that the samples be well mixed to obtain valid results. **(NOTE 1).**

> **NOTE 1: Due to the high pressure generated by the components of the stripper, the sample must be kept in the refrigerator at all times prior to analysis. Mixing must always be done under the hood, using a spatula and never with a shaker.**

4.1.2 Precondition the aluminum dish **(2.6)** containing a bent paper clip **(2.14)** in the oven for at least 30 minutes at 110°C ± 5°C. Cool and store in a desiccator. Weigh accurately the aluminum dish with the paper clip to ± 0.0001 g.

4.1.3 Using a disposable Beral pipette (**2.10**), weigh accurately 0.4 to 0.6 g **(± 0.0001 g)** of the thoroughly mixed sample **(4.1.1)** in a pre-weighed aluminum dish containing a paper clip. Disperse the sample by adding 2 ml of distilled water or any appropriate solvent and stirring with the paper clip until the sample is evenly distributed.

6.1.1 Dry the sample in the oven at 110°C ± 5°C for 1 hour. Cool the sample in the desiccator and weigh to ± 0.0001 g. Run samples in duplicate. Results should not vary by more than ± 1% of from the mean.

4.2   Calculations for the Determination of Total Volatile and Non-Volatile Content.

   4.2.1   Weight of Sample = (4.1.3) - (4.1.2)

   4.2.2   Weight of Non-Volatile (NV) = (4.1.4) - (4.1.2)

   4.2.3   % NV (W/W) = $\dfrac{(4.2.2) \text{ x } 100}{(4.2.1)}$

   4.2.4   % Total Volatiles in the sample = 100% - (4.2.3)

4.3   Determination of Density.

   4.3.1   Calibrate the volume of the Gardner weight per gallon cup as described in ASTM D 1475-85.

   4.3.2   Accurately weigh the cup **(4.3.1)** to ± 0.01 g.

   4.3.3   Transfer an aliquot of the thoroughly mixed sample **(4.1.1)** to the cup. Cap the container, leaving the overflow orifice open. Immediately remove excess overflow sample material by wiping dry with absorbent material. Avoid occluding air bubbles in the container.

   4.3.4   Accurately weigh the filled cup to ± 0.01 g.

   4.3.5   Calculate the density in grams per milliliter of the sample as follows:

$$D \text{ g/ml} = \frac{(4.3.4) - (4.3.2)}{(4.3.1)}$$

   Where: D g/ml = density, g/ml

   4.3.6   ~~Samples must be run in duplicate and agree within ± 1% of the mean~~. <u>Run samples in duplicate. Reanalyze the sample if the results vary by more than .006 g/ml.</u>

   4.3.7   Calculation for Compliance in the Absence of Exempt ~~Solvents~~ <u>Compounds</u> and Water.

      4.3.7.1   Wt of 1 liter of Sample = 1000 ml x (4.3.5)

      4.3.7.2   Gram VOC/l of Sample = (4.2.4) x (4.3.7.1) x 10^{-2}

4.3.7.3   Lb VOC/gal Sample = (4.3.7.2) x 8.34 x 10^{-3}

$$\text{Where:} \quad 8.34 \times 10^{-3} = \frac{3.785 \text{ l/gal}}{454 \text{ g/lb}}$$

4.4   Gas Chromatographic Determination of the Water and Chlorinated Hydrocarbon Content of the Sample. (NOTES 2 and 3).

> **NOTE 2: Screen each sample for interfering peaks prior to analysis. Phenolic compounds do not interfere with this determination. If the sample contains ethanol, use another appropriate internal standard.**

> **NOTE 3:   If the sample is not dispersible in DMF, use a more suitable solvent such as dimethylsulfoxide (DMSO).**

4.4.1   Set up the gas chromatograph as described in **Section 2.1.**

4.4.2   Determination of Relative Response Factors.

4.4.2.1   Ethanol **(3.2)** is used as an internal standard. The response factor of water, methylene chloride and 1,1,1-TCA relative to the internal standard is determined by means of the following procedure:

4.4.2.2   Prepare a blank, by weighing accurately 0.2 g **(± 0.0001 g)** ethanol into a vial containing 2 ml of dimethylformamide. Shake the vial for about 2 minutes and let stand for about 5 minutes prior to injection into the gas chromatograph. **(NOTE 4).**

> **NOTE 4: Dimethylformamide is harmful if inhaled or absorbed through the skin. It is suspected to be embryotoxic. Use only with adequate ventilation. Avoid contact with skin, eyes and clothing.**

4.4.2.3   Using a 10-µl syringe, inject 2 µl of the blank **(4.4.2.2)** into the gas chromatograph. If a water peak is observed, dry both the ethanol and dimethylformamide using anhydrous Na_2SO_4 powder.

4.4.2.4   Prepare a standard by weighing accurately 0.2 g of water, 0.2 g of ethanol, 0.2 g of 1,1,1-TCA and 0.2 g of methylene chloride **(± 0.0001 g)** in a pre-weighed sample vial containing 2 ml of dimethylformamide

(DMF). Cap and shake the vial contents thoroughly for about 15 minutes using the Burrell wrist action shaker.

    4.4.2.5   Using a 10-µl syringe, inject 2 µl of the standard **(4.4.2.4)** into the gas chromatograph. Record the peak areas of water, ethanol and the chlorinated hydrocarbons. The order of elution is water, ethanol, methylene chloride, TCA and DMF. Retain the chromatograms.

4.5   **Calculations.**

    4.5.1   The response factors (R_{ClHC}) for the individual ClHC compound are determined by means of the following equations.

$$R_{ClHC} = \frac{(W_i) \times (A_{ClHC})}{(W_{ClHC}) \times (A_i)}$$

Where:
W_i	=	Weight of the internal standard.
A_{ClHC}	=	Area of the individual ClHC peak
W_{ClHC}	=	Weight of the individual ClHC.
A_i	=	Area of the internal standard

    4.5.2   The response factor, (R_w) for water is determined by means of the following equation:

$$R_w = \frac{(W_i) \times (A_{H_2O})}{(W_{H_2O}) \times (A_i)}$$

Where:
W_i	=	Weight of the internal standard.
W_{H_2O}	=	Weight of water.
A_{H_2O}	=	Area of water peak.
A_i	=	Area of the internal standard.

4.6   **Gas Chromatographic Analysis of the Water and Chlorinated Hydrocarbon Content of the Sample. ~~(NOTE 4)~~ (NOTES 2 and 3)**

    ~~**NOTE 4: Screen each sample for interfering peaks prior to analysis. Phenolic compounds do not interfere with this determination. If ethanol is present in the sample, substitute with another internal standard.**~~

4.6.1 Weigh accurately 0.3 to 0.5 g **(± 0.0001 g)** of the thoroughly mixed sample **(4.1.1)** and 0.2 g **(± 0.0001 g)** of ethanol or any appropriate internal standard in a tared vial containing 2 ml of DMF. Immediately cap the vial. ~~**(NOTE 5)**~~.

> ~~**NOTE 5:** The use of an internal standard other than ethanol will be determined by the presence of interfering peaks in the sample.~~

4.6.2 Shake the vial on a Burrell wrist action shaker for about 15 minutes. It is essential that the sample be thoroughly mixed. Allow the sample to stand for about 5 minutes prior to injection. This is to allow the solids to settle at the bottom of the vial.

4.6.3 Inject a 2 µl aliquot of the supernatant liquid from **(4.6.2)** into the gas chromatograph. Record the areas of the water, chlorinated hydrocarbon and ethanol peaks. Retain the chromatogram.

4.7 **Calculations.**

4.7.1 The water concentration (% w/w) in the sample is determined by the following equation.

$$\% \ H_2O \ (w/w) \ = \ \frac{(A_{H_2O}) \ x \ (W_i) \ x \ 100}{(A_i) \ x \ (W_s) \ x \ (R_w)}$$

Where:
- A_{H_2O} = Area of water peak.
- A_i = Area of the internal standard
- W_i = Weight of internal standard
- W_s = Weight of the sample
- R_w = Response factor for water (4.5.2).

4.7.2 The concentrations (% w/w) of the chlorinated hydrocarbons in the sample are determined by the following equation.

$$\% \ (w/w) \ ClHC \ = \ \frac{(A_{ClHC}) \ x \ (W_i) \ x \ 100}{(A_i) \ x \ (W_s) \ x \ (R_{ClHC})}$$

Where:
- A_{ClHC} = Area of individual ClHC
- W_i = Weight of the internal standard.
- A_i = Area of the internal standard.
- R_{ClHC} = Response factor for the individual ClHC (4.5.1),

$$W_s \quad = \quad \text{Weight of sample}$$

4.7.3 The total % concentration of the chlorinated hydrocarbons in the sample is the sum of the concentrations of each chlorinated hydrocarbon in the sample.

4.7.4 Samples must be run in duplicate and the results must agree within ± 1% (absolute) ~~of~~ from the mean.

5) COMPLIANCE CALCULATIONS FOR SAMPLES CONTAINING WATER AND CHLORINATED HYDROCARBONS

5.1 Weight (g) of 1 l sample = (1000 ml) x (4.3.5).

5.2 If ClHC **is considered** a part of the VOC content of the sample:

Grams VOC/l of Sample = $(5.1) - \left[(5.1) \times (4.2.3) \times 10^{-2} \right] - \left[(5.1) \times (4.7.1) \times 10^{-2} \right]$

5.3 If ClHC **is not considered** a part of the VOC content of the sample:

Grams VOC/l of Sample =
$(5.1) - \left[(5.1) \times (4.2.3) \times 10^{-2} \right] - \left[(5.1) \times (4.7.1) \times 10^{-2} \right] - \left[(5.1) \times (4.7.3) \times 10^{-2} \right]$ =

$\underline{(5.1) \left[1 - (4.2.3) \times 10^{-2} - (4.7.1) \times 10^{-2} - (4.7.3) \times 10^{-2} \right]}$

5.4 lb VOC/gal of Sample = (5.2) or (5.3) x (8.34×10^{-3})

$$\text{Where:} \qquad 8.34 \times 10^{-3} \quad = \quad \frac{3.785 \text{ l/gal}}{454 \text{ g/lb}}$$

5.5 For Regulation 8, Rule 35:

$$\% \text{ VOC (W/W)} = 100\% - (4.2.3) - (4.7.1)$$

6) COMPLIANCE CALCULATIONS FOR SAMPLES CONTAINING WATER AND OTHER EXEMPT COMPOUNDS:

6.1 Weight (g) of 1 l sample = (1000 ml) x (4.3.5)

6.2 Total Concentration (% w/w) of Exempt Compounds in the Sample = Sum of the Individual Concentrations (% w/w) of Exempt Compounds in the Sample **(Note 5)**

6.3 Grams VOC/l of Sample =

$$(5.1) - \left[(5.1) \times (4.2.3) \times 10^{-2}\right] - \left[(5.1) \times (4.7.1) \times 10^{-2}\right] - \left[(5.1) \times (6.2) \times 10^{-2}\right] =$$

$$(5.1) \left[1 - (4.2.3) \times 10^{-2} - (4.7.1) \times 10^{-2} - (6.2) \times 10^{-2}\right]$$

6.4   lb VOC/gal of Sample = (5.2) or (5.3) x (8.34 x 10^{-3})

Where: 8.34×10^{-3} = $\dfrac{3.785 \text{ l/gal}}{454 \text{ g/lb}}$

Note 5: Concentrations of exempt compounds from BAAQMD Method 22 and ASTM D-6133-02.

7)   REFERENCES

6.1   Hollis, O.L., **"Separation of Gaseous Mixtures Using Porous Aromatic Polymer Beads",** Anal. Chem. 38, 309 1966.

6.2   **"Volatile Content of Paint"**, ASTM Designation D 2369-87, Book of ASTM Standards.

6.3   **"Density of Paint, Varnish, Lacquer and Related Products"**, ASTM Designation D 1475-85, Book of ASTM Standards, Vol 06.01, 1986.

6.4   **"Determination of Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph"**, ASTM Designation D 3792-86, Book of ASTM Standards.

6.5   **"Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph",** ASTM Designation D 4457-85, Book of ASTM Standards, Vol 06.01, 1986.

H://tech2/eppie/method 31m1.doc