

METHOD 21

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|------|-------|------|------|------|
| REF: | Regs: | 8- 3 | 8-19 | 8-32 |
| | | 8-4 | 8-20 | 8-35 |
| | | 8-11 | 8-23 | 8-38 |
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DETERMINATION OF COMPLIANCE OF VOLATILE ORGANIC COMPOUNDS FOR WATER REDUCIBLE COATINGS

1) PRINCIPLE

- 1.1 This method is applicable to the determination of total water content and volatile organic compounds (**VOC**) of water reducible coatings. Water is determined by gas chromatography using ethanol as an internal standard. The total non-volatiles (**NV**) are determined by heating an aliquot of the coating for a specified time and temperature in an oven. Methylene chloride and 1,1,1 trichloroethane concentrations must be determined by gas chromatography, ~~if the total VOC exceeds the regulatory limits, if considered as exempt compounds in the regulation.-~~
- 1.2 For a multicomponent system, the components should be first mixed in the appropriate ratio; then the water, exempt compounds, density and total non-volatiles are determined on this mixture. The total non-volatile content is determined by allowing the test specimens to have an induction period of 30 minutes in the aluminum dish prior to oven heating.-
- 1.3 This method may not be applicable to all types of coatings or printing inks. ~~Other procedures may be substituted with mutual agreement of the manufacturer, user and the Air Pollution Control Officer (APCO).~~
- 1.4 This method excludes water when calculating the VOC content of the coating. If exempt compounds such as acetone or methyl acetate are present in the coating, the material must also be analyzed by BAAQMD Method 22 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:-

| | <u>Initial</u> | <u>Final</u> |
|-----------------------------------|----------------|--------------|
| Oven Temperature (°C) | 110 | 220 |
| Time Delay (min) | 0 | 10 |
| Temperature Program Rate (°C/min) | 10 | |
| *Injector Temperature (°C) | 250 | |
| Detector Temperature (°C) | 250 | |
| Carrier Gas | He | |
| Carrier Gas Flow (cc/min) | 20 | |
| Filament Current (ma) | 150 | |
| Injection Sample Size (µl) | 2 | |

* Glass sleeve insert is used in the injection port.

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

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

2.2.2 Alternate column to confirm the presence of chlorinated hydrocarbons (CIHC). 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 - 120 Mesh Supelcoport.

2.3 10 µl Syringe.

2.4 Burrell Wrist Action Shaker.

2.5 Desiccator.

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

2.7 Forced Draft Oven. Capable of maintaining a temperature of 110 ± 5°C.

2.8 Analytical Balance. Capable of weighing to ± 0.0001 g

2.9 Top Loading Analytical Balance. Capable of weighing to ± 0.01 g.

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

2.11 Spatula.

- 2.12 **Gardner Weight Per Gallon Cup.** These are available from Thomas Scientific (Catalog #8353A01).
- 2.13 **Vials** with screw caps, 2 dram size.
- 2.14 **Eberbach Shaker.**
- 2.15 **Red Devil Paint Shaker** for gallon size containers.
- 2.16 **Disposable Syringe.** 3-5 cc used for coatings with highly volatile solvents.

3) REAGENTS

- 3.1 **Distilled Water**
- 3.2 **Ethyl Alcohol.** 200 proof.
- 3.3 **Dimethylformamide (DMF).** Spectroquality. Water content must not exceed 0.05% (w/w). Other suitable solvents, Reagent Grade.
- 3.4 **Helium.**
- 3.5 **Isopropyl Alcohol.** Reagent grade or highest available purity.
- 3.6 **1,1,1 Trichloroethane (TCA).** Reagent grade or highest available purity.
- 3.7 **Methylene Chloride.** Reagent grade or highest available purity.
- 3.8 **Sodium Sulfate (Na₂SO₄).** Anhydrous Powder.

4) ANALYTICAL PROCEDURE

- 4.1 **Determination of Total Volatiles. (NOTE: 1)**
 - 4.1.1 Mix the coating thoroughly for about 30 minutes, using an Eberbach shaker or 5 minutes with the Red Devil Paint Shaker. It is essential that the samples be well mixed to obtain valid results. Stirring with a spatula may also be required.
 - 4.1.2 Precondition the aluminum dish (2.6) containing a paper clip in the oven for at least 30 minutes at 110 ± 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, weigh accurately 0.4 to 0.6 g (± 0.0001 g) of the thoroughly mixed coating (**4.1.1**) in the pre-weighed aluminum dish (**4.1.2**) containing a paper clip.
- 4.1.4** Disperse the coating by adding 2 ml of distilled water and stir with the paper clip until the sample is evenly dispersed. Dry the sample in the oven at $110^\circ \pm 5^\circ\text{C}$ for 1 hour. Cool the sample in the desiccator and weigh.
- 4.1.5** Run samples in duplicate. Results should not vary by more than $\pm 1\%$ (absolute) of from the mean.

NOTE 1: For multicomponent systems, premix the components in the correct proportions. Weigh accurately 0.2 - 0.4 g (± 0.0001 g) of mixture into a tared aluminum dish with paper clip. Disperse the sample in the aluminum dish using the paper clip, without adding any solvent. Allow an induction period of 30 minutes, prior to oven drying. Use the same mixture for the determination of density, exempt compounds and water content of the coating.

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

- 4.2.1** Weight of Coating = (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) = $\frac{(4.2.2)}{(4.2.1)} \times 100$
- 4.2.4** % Total Volatiles in Coating (w/w) = $100 - (4.2.3)$

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 coating (**4.1.1**) to the cup. Cap the container, leaving the overflow orifice open. Immediately remove excess sample 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 Run Samples in duplicate. Reanalyze the sample if the results vary by more than 0.006 g/ml.

4.3.6 Calculation of Density.

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

Where: D = Density, g/ml.

(4.3.1) = Volume in ml of the calibrated cup

(4.3.4) = Weight of the cup filled with coating (g)

(4.3.2) = Weight of the cup (g)

4.4 Determination of the Water Content of the Coating by Gas Chromatography

4.4.1 Set up the gas chromatograph as described in **Section 2.1 and 2.2.**

4.4.2 Determination of the Response Factor, (R_w), of Water. **(Notes 2 and 3)**

NOTE 2: Screen each sample for the presence of interfering peaks prior to analysis. If the sample contains ethanol, use 2-propanol as the internal standard. If the sample contains both ethanol and 2-propanol, use another appropriate internal standard.

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

4.4.2.1 Ethanol (**200 proof**) is used as an internal standard. The response factor of water relative to the internal standard is determined as follows:

4.4.2.2 Prepare a blank by weighing accurately 0.2 g of ethanol (**± 0.0001 g**) in a pre-weighed sample vial containing 2 ml of dimethylformamide. Cap and shake the vial vigorously for about 1 minute. Using a 10 μ l syringe inject 2 μ l of the mixture into the gas chromatograph. **(NOTES 2 and 3) (NOTES 4 and 5)**

NOTE 2 4: If a water peak is seen in the chromatogram of the blank, then treat the dimethylformamide and ethanol with anhydrous Na_2SO_4 powder, and reinject the blank into the gas chromatograph. Use the dried reagents to determine R_w , and also for sample analysis.

NOTE 3 5: 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** Weigh accurately 0.2 g of water and 0.2 g of ethanol (± 0.0001 g) in a pre-weighed sample vial containing 2 ml of dimethylformamide. Cap and shake the vial contents thoroughly for 15 minutes, using the Burrell Wrist Action Shaker. **(NOTE 5)**

~~**NOTE 3:** 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.~~

- 4.4.2.4** Using a 10 μ l syringe, inject 2.0 μ l of the mixture from **(4.4.2.3)** into the gas chromatograph. Integrate and record the peak areas of water and ethanol. The order of elution is water, ethanol, (methylene chloride, 1,1,1- trichloroethane, if present), and dimethylformamide. Retain the chromatogram.

4.4.3 Calculations.

- 4.4.3.1** The response factor (R_w) for water is determined by using the following equation: ~~(NOTE 4)~~ **(NOTE 6)**

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

Where:

- W_i = The weight of the internal standard.
- W_{H_2O} = The weight of water
- A_{H_2O} = The area of water peak
- A_i = Area of the internal standard

~~**NOTE 4**~~ **NOTE 6:** Peak height cannot be substituted for peak area in the equation. It is necessary to determine the response factor for water daily or with each series of determinations.

4.4.4 Determination of the Water Content of the Coating.

- 4.4.4.1 Weigh accurately 0.4 to 0.6 g (± 0.0001 g) of the mixed coating (4.1.1) and 0.2 g (± 0.0001 g) of ethanol in a tared vial containing 2 ml of DMF. If the concentration of water is greater than 65%, rerun the sample using 0.2 to 0.3 g (± 0.0001 g) of the coating. (NOTES 2 and 3).

~~NOTE 5: Screen each sample for the presence of interfering peaks prior to analysis. If the sample contains ethanol, use 2-propanol as the internal standard. If the sample contains both ethanol and 2-propanol, use another appropriate internal standard.~~

- 4.4.4.2 Shake the mixture on a Burrell Wrist Action Shaker for 15 minutes. It is essential that the sample be thoroughly mixed. The sample is allowed to stand for about 5 minutes after shaking and prior to injection. This is to allow the solids to settle at the bottom of the vial.
- 4.4.4.3 A 2 μ l aliquot of the supernatant liquid from (4.4.4.2) is injected into the gas chromatograph. The area of the water, ethanol and other peaks are integrated and recorded. Retain the chromatogram.
- 4.4.4.4 Samples must be run in duplicate and must agree within $\pm 1\%$ (absolute) ~~of~~ from the mean.

4.4.5 Calculation for % H₂O in the coating.

- 4.4.5.1 The percent of (W/W) in the coating is determined by the following equation:

$$\% \text{ H}_2\text{O (W/W)} = \frac{(A_{\text{H}_2\text{O}}) \times (W_i) \times 100}{(A_i) \times (W_s) \times (R_w)}$$

Where:

- $A_{\text{H}_2\text{O}}$ = Area of water peak.
- A_i = Area of the internal standard peak.
- W_i = Weight of the internal standard in g.
- W_s = Weight of the coating in g.
- R_w = Response factor for water (4.4.3.1).

5) COMPLIANCE CALCULATIONS FOR SAMPLES THAT CONTAIN WATER

$$5.1 \quad \text{Weight (g) of Total Volatile/ l of coating} = 1000 \text{ ml/l} \times (4.2.4) \times (4.3.6) \times 10^{-2}$$

Where: (4.2.4) = % Total Volatiles in the Coating (w/w)

(4.3.6) = Density, g/ml

$$5.2 \quad \text{Weight (g) of Water/l of coating} = 1000 \text{ ml/l} \times (4.3.6) \times (4.4.5.1) \times 10^{-2}$$

Where: (4.4.5.1) = % Water in the coating

$$5.3 \quad \text{Volume (ml) of Water /l of coating} = \text{Weight of water, g/l} \quad (5.2)$$

Assume density of water = 1 g/ml.

$$5.4 \quad \text{g VOC/l Coating (less H}_2\text{O)} = \left[\frac{(5.1) - (5.2)}{1000 \text{ ml/l} - (5.3)} \right] \times 1000 \text{ ml/l}$$

$$5.5 \quad \text{lb VOC/gal coating (less H}_2\text{O)} = (5.4) \times 8.34 \times 10^{-3}$$

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

6) COMPLIANCE CALCULATIONS FOR SAMPLES THAT CONTAIN WATER AND EXEMPT COMPOUNDS

$$6.1 \quad \underline{\text{Weight (g) of Total Volatile /l of coating}} = \underline{1000 \text{ ml/l} \times (4.2.4) \times (4.3.6) \times 10^{-2}}$$

Where: (4.2.4) = % Total Volatiles in the Coating (w/w)

(4.3.6) = Density, g/ml

$$6.2 \quad \underline{\text{Weight (g) of Water/l of coating}} = \underline{1000 \text{ ml/l} \times (4.3.6) \times (4.4.5.1) \times 10^{-2}}$$

Where: (4.4.5.1) = % Water in the coating

$$6.3 \quad \underline{\text{Total Weight (g) of Exempt Compounds/ l of coating}} = \underline{\text{Sum of the individual weights (g) of exempt compounds per liter of coating (Note 7)}}$$

$$6.4 \quad \underline{\text{Volume (ml) of Water /l of coating}} = \underline{\text{Weight (g) of water/l} \quad (5.2)}$$

Assume density of water = 1 g/ml.

$$6.5 \quad \underline{\text{Total Volume (ml) of Exempt Compounds /l of coating}} = \underline{\text{Sum of the individual volumes (ml) of exempt compounds per liter of coating (Note 7)}}$$

6.6 g VOC/l Coating (less H₂O, less exempt compounds) =

$$\frac{[(6.1) - (6.2) - (6.3)]}{[1000 \text{ ml/l} - ((6.4) + (6.5))]} \times 1000 \text{ ml/l}$$

6.7 lb VOC/gal coating (less H₂O, less exempt compounds) = (6.6) x 8.34 x 10⁻³

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

NOTE 7: Weights and volumes of exempt compounds from BAAQMD Method 22 and ASTM D-6133-02.

7) REFERENCES

- 7.1 Hollis, O.L., "Separation of Gaseous Mixtures using Porous Aromatic Polymer Beads", Anal, Chem. 38, 309, 1966.
- 7.2 "Volatile Content of Paint", ASTM Designation D2369-87, Book of ASTM Standards.
- 7.3 "Density of Paint, Varnish, Lacquer and Related Products", ASTM Designation D1475-85, Book of ASTM Standards, Vol 06.01, 1986.
- 7.4 "Determination of Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph", ASTM Method D3792-86, Book of ASTM Standards
- 7.5 "Determination of Dichloromethane and 1,1,1 Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph", ASTM Method D4457-85, Book of ASTM Standards.
- 7.6 "Standard Test Method for Acetone, p-Chlorobenzotrifluoride, Methyl Acetate, or t-Butyl Acetate Content of Solventborne and Waterborne Paints, Coatings, Resins, and Raw Materials by Direct Injection into a Gas Chromatograph", ASTM Method D6133-02, Book of ASTM Standards, Vol. 6.01.

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