METHOD 36

REF: Reg 8-49

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN WATER BASED AEROSOL PAINTS

1) PRINCIPLE

1.1 This method is applicable only to the determination of percent water content and volatile organic compounds(VOC) of a water based aerosol paint. The propellant is released from the can and the remaining contents tested for percent water and non-volatiles.The water content is determined by gas chromatography using ethanol as internal standard. The % non-volatile (NV) is determined by heating an aliquot of the aerosol paint for one hour at 110 ± 5°C.

2. APPARATUS

2.1 **Freezer.**

2.2 **Ice Pick.**

2.3 **Hammer.**

2.4 **Applicator Sticks.**

2.5 **Masking Tape.**

2.6 **Gas Chromatograph.** This unit is fitted with a thermal conductivity detector, a glass sleeve injection port, a temperature programmer and a compatible data station.

2.7 **Analytical column.** A 6' x 1/8" O.D. SS column packed with Poropak Q, 80 to 100 mesh.

2.8 **10 µl Syringe.**

2.9 **Burrell Wrist Action Shaker.**

2.10 **Desiccator.**

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

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

2.13 **Analytical Balance.** Capable of weighing to ± 0.0001 g.

2.14 **Spatula.**

2.15 Vials with screw caps, 2 dram size.

2.16 **Eberbach Shaker.**

2.17 **Disposable Beral Pipettes.**

2.18 **Disposable Syringes.** 3-5 cc used for paints with highly volatile solvents.

2.19 **Tin Snips or Metal Cutter.**

3. REAGENTS

3.1 **Distilled Water.**

3.2 **Ethyl Alcohol.** 200 Proof.

3.3 **Dimethylformamide (DMF). Spectroquality.** Water content must not exceed 0.05%.

3.4 **Helium.**

3.5 **Isopropyl Alcohol.** Reagent Grade or highest available purity.

3.5 **Sodium Sulfate (Na_2SO_4).** Anhydrous Powder.

3.6 **Acetone, Technical Grade.**

4. ANALYTICAL PROCEDURE

4.1 **Preparation of aerosol contents for analysis.**

4.1.1 Mix aerosol thoroughly for about 15 minutes, using an Eberbach shaker at the low speed setting **(Fig. 1).** It is essential that the samples be well mixed to obtain valid results.

4.1.2 Remove the cap and actuator from the can. Put the cap back and weigh the can to 0.01 g.

4.1.3 Place the can in a freezer where the temperature is held below 32°F. Keep the can in the freezer for 2 hours in an upside down position.

4.1.4 Put the can upside down in a fume hood. Puncture the bottom of the can near the edge with a very sharp ice pick. Slowly remove the ice pick from the hole. Leave the hole uncovered for about 12 hours. This will allow the propellant to escape completely.

4.1.5 Enlarge the hole slightly by tapping the ice pick further into the can. Swirl the can gently for 1 to 2 minutes to remove the remaining propellant.

4.1.6 Wipe off any condensate which may have accumulated on the can. Weigh the can to ± 0.01 g.

4.1.7 Plug the hole with a small applicator stick (about 1/2 cm long). Put a masking tape over the plugged hole.

4.1.8 Place the can in an Eberbach Shaker, making sure that the hole is at the highest possible position to prevent leakage of contents. Shake the sample for about 15 minutes at the low speed setting **(Fig. 1).**

4.1.9 Cut the bottom of the can using a metal cutter. Stir the contents with spatula, then transfer to a pint can with lid.

4.1.10 Rinse the can, agitators and bottom several times until clean using acetone as solvent. Allow the can agitators and bottom to dry. Weigh to ± 0.01 g.

4.2 Determination of Total Volatiles.

4.2.1 Precondition the aluminum dish **(2.1)** containing a paper clip 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.

4.2.2 Using a disposable Beral pipette or a syringe accurately weigh 0.4 to 0.6 g (± 0.0001 g) of the thoroughly mixed paint **(4.1.9)** in a pre-weighed aluminum dish containing a paper clip. Disperse the paint by adding 2ml of distilled water and stirring with the paper clip until the sample is evenly dispersed. Dry the sample in an oven at 110 ± 5°C for one hour. Cool the sample in a desiccator and weigh.

4.4.2 Determination of the Response Factor, (R_W) of water.

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 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 DMF. Cap and shake the vial contents thoroughly for about 15 minutes, using the Burrell Wrist Action Shaker. **(NOTE: 1).**

4.4.2.3 Prepare a blank as in **(4.4.2.2)**, using only ethanol and DMF.

4.4.2.4 Using a 10 μl syringe, inject separately 2.0 μl of the mixture from **(4.4.2.2)** and **(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 and DMF. Retain the chromatogram. **(NOTE: 2).**

4.4.3 Calculations. (NOTE: 3).

4.4.3.1 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 = **The weight of the internal standard**

${}^{W}H_2O$ = **The weight of water**

${}^{A}H_2O$ = **The area of water peak**

A_i = **The area of the internal standard**

NOTE 1: **Dimethylformamide is harmful if inhaled or absorbed through skin. It is pected to be embryotoxic. Use only with adequate ventilation. Avoid ontact with skin, eyes and clothing.**

NOTE 2: **If a water peak is seen in the chromatogram of the blank, then treat the DMF and ethanol with anhydrous Na_2SO_4 powder, and re-inject the blank into the gas chromatograph.**

4.3 Calculations for the determination of Total Volatile and Non-Volatile Contents.

4.3.1 Weight of Sample = (weight of aluminun dish with coating) - (weight of aluminum dish).

4.3.2 Weight of Non-volatile (NV) = (weight of aluminun dish with solids) - (weight of aluminun dish).

4.3.3 Weight of contents of can including the propellant = (4.1.2) - (4.1.10).

4.3.4 Weight of the contents of can excluding the propellant = (4.1.6) - (4.1.10).

4.3.5

$$\% \text{ NV (W/W)} = \frac{4.3.5100 \times (4.3.2) \times (4.3.4)}{(4.3.1) \times (4.3.3)}$$

4.3.6 %Total Volatiles = 100.0% - (4.3.5).

4.3.7 Run samples in duplicate. Results should not vary by more than ± 1% of the mean.

4.4 Determination of the water content of the coating by gas chromatography.

4.4.1 **Gas Chromatograph:** Column and operating parameters.

Column: 6' x 1/8" O.D. SS Column packed with Poropak Q 80/100 mesh.

	Initial	Final
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.

NOTE 3: Peak height cannot be substituted for peak area in the above equation. It is necessary to determine the response factor for water daily or with each series of determinations.

4.4.4 Gas Chromatographic Analysis of Water Content.

4.4.4.1 Weigh accurately 0.4 to 0.6 (± 0.0001 g) of the paint **(4.1.9)** and 0.2 g (± 0.0001 g) of ethanol in a tared vial containing 2 ml of DMF. When the concentration of water is greater than 65%, rerun the sample using 0.2 g of the paint. **(NOTE: 4).**

4.4.4.2 The mixture is then shaken in a Burrell Wrist Action Shaker for 15 minute. 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 μl 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 ± 2% of the mean.

NOTE 4: 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 must be utilized.

4.4.5 Calculation.

4.4.5.1 The water concentration (%W/W) in the coating is determined by the following equation:

$$\% H_2O\ (w/w) = \frac{(A_{H_2O}) \times (W_i) \times 100 \times (4.3.4)}{(A_i) \times (W_s) \times (R_W) \times (4.3.3)}$$

where:

A_{H_2O} = Area of water peak

A_i = Area of the internal standard

W_i = Weight of the internal standard in g

W_s = Weight of the paint in g

R_w = Response factor for water (4.4.3.1).

5) COMPLIANCE CALCULATIONS

5.1 % VOC(W/W) = (4.3.6) - (4.4.5.1)

5.2

$$\text{g VOC/g Solids} = \frac{(4.3.3) \times (5.1)}{(4.3.3) \times (4.3.5)}$$

5.3

$$\text{g VOC/g Solids} = \frac{(5.1)}{(4.3.5)}$$

6) REFERENCES

6.1 **"Determination of Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph".** ASTM Method D3792-86, Book of Standards.

6.2 **"Volatile Content of Paint".** ASTM Method D2369-87, Book of Standards.

6.3 **"Method for Determining %VOC in Aerosol Paint, which May or May Not Contain Water".** National Paints and Coatings Association Method.

6.4 **"BAAQMD Manual of Procedures"**, Vol. 3, Method 21.

6.5 "Determination of Weight Percent Volatile Content of Water-Borne Aerosol Paints", ASTM Method D5325-92 1993 Annual Book of ASTM STANDARDS, Vol. 6.01

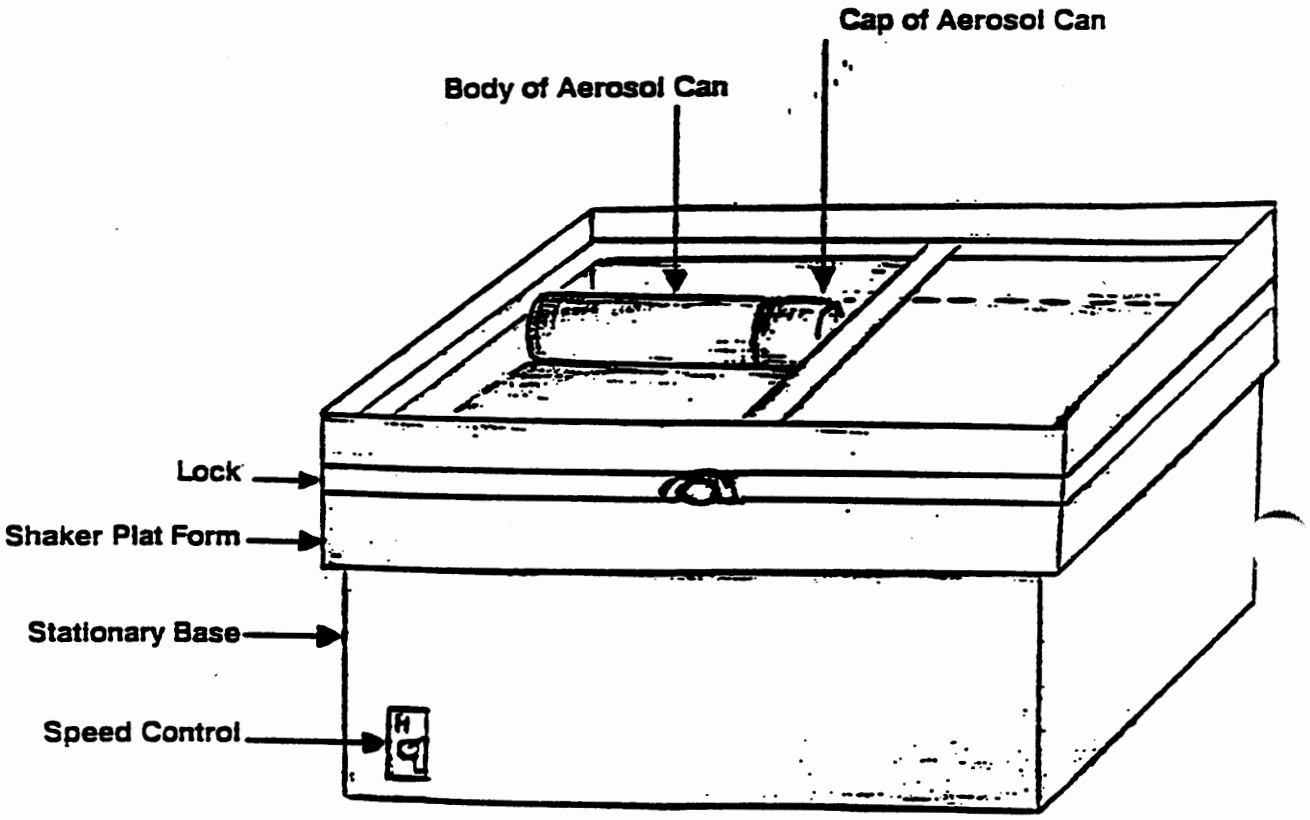

Figure 1 - Aerosol Can On Eberbach Shaker