

METHOD 22

REF:	Regs:	8-3	8-14	8-29	8-45
		8-4	8-19	8-31	8-51
		8-11	8-20	8-32	
		8-12	8-23	8-38	
		8-13	8-26	8-43	

DETERMINATION OF COMPLIANCE OF VOLATILE ORGANIC COMPOUNDS FOR SOLVENT-BASED COATINGS, INKS AND OTHER RELATED PRODUCTS

1) PRINCIPLE

- 1.1 This method is applicable to the determination of volatile organic compounds (**VOC**) in solvent-based coatings, inks and other related products. The non-volatile contents are determined by heating an aliquot of the material in an oven for a specific time and temperature.
- 1.2 The concentrations of acetone, methylene chloride and 1,1,1-trichloroethane must be determined by gas chromatography.
- 1.3 For multicomponent systems, the components must first be mixed in the appropriate ratio. The exempt ~~solvents~~ compounds, density and total non-volatiles are determined from 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.
- 1.4 This method may or may not exclude chlorinated hydrocarbons (**CLCH**) when calculating the VOC content of the sample. If water is present in the sample, it must be analyzed by Method 21, **Section 4.4**.
- 1.5 If other exempt compounds such as parachlorobenzotrifluoride, volatile methyl siloxanes or methyl acetate are present in the sample, the material must also be analyzed by BAAQMD Method 41, BAAQMD Method 43 or ASTM D6133-02.
- 1.6 This method may not be applicable to all types of coatings, printing inks and other products. ~~Other procedures may be substituted with mutual agreement of the manufacturer, user and the Air Pollution Control Officer (APCO).~~

2) APPARATUS

2.1 Gas Chromatographs:

2.1.1 For Chlorinated Hydrocarbons: This unit is fitted with a thermal conductivity or flame ionization detector, a glass-sleeved injection port, a temperature programmer and a compatible integrator or data station. The suggested operating parameters are as follows:

Initial Oven Temperature (°C)	110
Initial Hold Time (Min)	0
Temperature Program Rate (°C/min)	10
Final Oven Temperature (°C)	220
Final Hold Time (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

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

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

2.1.1.1.2 Alternate column to confirm the presence of CHCL. 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.

2.1.2 For Acetone: This unit is fitted with a photoionization detector, a glass sleeved injection port, a temperature programmer and a compatible integrator or data station. The suggested operating parameters are as follows:

Initial Oven Temperature (°C)	40
Initial Hold Time (Min)	10
Temperature Program Rate (°C/min)	30
Final Oven Temperature (°C)	210
Final Hold time (min)	10
Injector Temperature (°C)	250
Detector Temperature (°C)	250

Carrier Gas	He
Carrier Gas Linear Velocity (cm/sec)	40
Injection Sample Size (μ l)	1

2.1.2.1 Analytical Column : Any analytical column capable of resolving the compounds of interest is acceptable. The suggested analytical column for this method is:

A 60 m x 0.53mm DB-WAX Column, 1.0 μ film thickness (J & W Scientific). This column is available from Curtin Matheson Scientific, Inc. P. O. Box 1546, Houston Texas 77251-1546 (**Catalog # 284-933**).

- 2.2 Disposable syringe.** 3-5 cc used for coatings with highly volatile solvents. These are available from Curtin Matheson, Company (**Catalog # 262-264**).
- 2.3 Needles, Stainless Steel.** 21 gauge x 1-1/2" length. These are available from Curtin Matheson, Company (**Catalog # 222-414**).
- 2.4 10 μ l Syringe.**
- 2.5 Burrell Wrist Action Shaker.**
- 2.6 Desiccator.**
- 2.7 Aluminum Foil Dish.** 57 mm diameter x 10 mm high with a flat bottom.
- 2.8 Forced Draft Oven.** Capable of maintaining a temperature of $110 \pm 5^{\circ}\text{C}$.
- 2.9 Analytical Balance.** Capable of weighing to ± 0.0001 g
- 2.10 Top Loading Analytical Balance.** Capable of weighing to ± 0.01 g.
- 2.11 Disposable Beral Pipettes.** These are available from Curtin Matheson, Company (**Catalog #376-970**).
- 2.12 Spatula.**
- 2.13 Gardner Weight Per Gallon Cup.** This cup is available from Thomas Scientific, P.O. Box 99, Swedesboro, NJ 08085 (**Catalog #8353A01**).
- 2.14 Vials** with screw caps, 2 dram size.
- 2.15 Eberbach Shaker** for quart and less size containers.

2.16 **Red Devil Paint Shaker** for gallon size containers.

3) REAGENTS

3.1 **Toluene or other suitable solvent.** Reagent grade.

3.2 **Methanol Absolute.** Water content must not exceed 0.2% (w/w).

3.3 **Dimethylformamide (DMF).** Spectroquality. Water content must not exceed 0.05% (w/w). Other suitable solvent, Reagent Grade

3.4 **Helium or Nitrogen,** 99.995% Purity or Higher.

3.5 **Hydrogen.**

3.6 **Air**

3.7 **Methylene Chloride.** Reagent grade or highest available purity.

3.8 **1,1,1-Trichloroethane (TCA).** Reagent grade or highest available purity.

3.9 **Sodium Sulfate (Na₂SO₄).** Anhydrous Powder.

3.10 **Acetone.** Reagent grade or highest available purity.

3.11 **Tetrahydrofuran (THF).** Reagent grade or highest available purity

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 or 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 (2.7) 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 containing a paper clip.
- 4.1.4 Disperse the coating by adding 2 ml of toluene or any appropriate solvent 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 the analysis in duplicate. Reanalyze the sample if the results 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, acetone, CIHC, and other exempt compounds, if present.

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

4.2.1 Weight of Coating (g) = (4.1.3) - (4.1.2)

Where: (4.1.3) = Weight of the coating and aluminum pan (g)
(4.1.2) = Weight of the aluminum pan (g)

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

Where: (4.1.4) = Weight of the dried coating and aluminum pan

(g)

4.2.3 %NV (w/w) = [(4.2.2) X 100] / (4.2.1)

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 1475-90.

- 4.3.2 Accurately weigh the cup (4.3.1) to ± 0.01 g.
- 4.3.3 Completely fill the cup with the thoroughly mixed coating. 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 Run the analysis in duplicate. Reanalyze the sample if the results vary by more than 0.006 g/ml.
- 4.3.6 **Calculation of Density.**

$$D = [(4.3.4) - (4.3.2)] / V = (\text{g/ml})$$

Where: D = Density (g/ml.)
 V = Volume in ml of the calibrated cup (4.3.1).
 (4.3.4) = Weight of the cup filled with coating (g)
 (4.3.2) = Weight of the cup (g)

4.4 **Calculation for compliance in the absence of exempt solvents compounds or water.**

- 4.4.1 Wt of 1 liter of Coating (g) = 1000 ml x (4.3.6).
- 4.4.2 Gram VOC/liter of Coating = (4.2.4) x (4.4.1) x 10^{-2}
- Where:** (4.2.4) = % total volatiles in coating (W/W)
- 4.4.3 Lb VOC/gal Coating = (4.4.2) x 8.34 x 10^{-3}

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

4.5 **Determination of Methylene Chloride and 1,1,1 Trichloroethane content of the coating by Gas Chromatography (NOTES: 2 AND 3).**

- 4.5.1 Set up the gas chromatograph as described in Section 2.1.1.

NOTE 2: Screen each sample for the presence of exempt solvents compounds and other interfering peaks prior to analysis. If the sample contains methanol, use 2-propanol or any appropriate compound as the

internal standard. If no exempt solvent compound is found, no GC analysis is required, otherwise continue on to Section 4.5.2

NOTE 3: If the coating contains water, ~~and the VOC content corrected for chlorinated hydrocarbons exceeds the regulation limits,~~ the concentration of water in the coating must be determined per Lab BAAQMD Method 21.

4.5.2 Determination of Relative Response Factor, (R_{CIHC}) for the exempt solvents.

4.5.2.1 Determine the response factor of the chlorinated hydrocarbon (R_{CIHC}) relative to the internal standard, anhydrous methanol, as follows:

4.5.2.2 Inject 1 μ l of the solvent into the gas chromatograph to check for contamination. If the solvent is contaminated, open a fresh bottle and repeat the step. (**NOTE 4**)

4.5.2.3 Weigh accurately 0.2 g (± 0.0001 g) of the individual chlorinated hydrocarbon and 0.2 g of methanol (± 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: 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. If the material to be analyzed is not dispersible in DMF, use a suitable solvent.

4.5.2.4 Inject separately 1 μ l of the mixture from (4.5.2.2) and (4.5.2.3) into the gas chromatograph, using a 10 μ l syringe. Integrate and record the peak areas of methanol and the chlorinated hydrocarbon. Retain the chromatogram. The order of elution is methanol, methylene chloride, 1,1,1-trichloroethane and dimethylformamide (**See Figure I**).

4.6 Calculation for the response factor, R_{CIHC} of Chlorinated Hydrocarbon.

- 4.6.1** Determine the response factor, R_{CIHC} for chlorinated hydrocarbon by means of the following equation: (**NOTE: 5**)

$$R_{\text{CIHC}} = \frac{W_i \times A_{\text{CIHC}}}{W_{\text{CIHC}} \times A_i}$$

Where:

- W_i = Weight of the internal standard.
- W_{CIHC} = Weight of the chlorinated hydrocarbon.
- A_{CIHC} = Peak area of the chlorinated hydrocarbon.
- A_i = Peak area of the internal standard

NOTE 5: It is necessary to determine the response factor for chlorinated hydrocarbon with each series of determinations.

4.7 Determination of the Chlorinated Hydrocarbon content of the coating

- 4.7.1** 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 methanol in a tared vial containing 2 ml of DMF. Immediately cap the vial.
- 4.7.2** 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.
- 4.7.3** Inject a 1 μ l aliquot of the supernatant liquid from (**4.7.2**) into the gas chromatograph. Integrate and record the area of the chlorinated hydrocarbon and the methanol peaks. Retain the chromatogram.
- 4.7.4** Confirm the presence of the chlorinated hydrocarbon, using the alternate column (**2.1.1.1.2**).

4.8 Calculation for % CIHC in the coating.

- 4.8.1** Use the data obtained in (**4.7.3**) to calculate the weight % of CIHC found in the sample, if the presence of chlorinated hydrocarbon (**CIHC**) is confirmed (**4.7.4**), as follows:

$$4.8.1.1 \quad \% \text{ CIHC (W/W)} = \frac{A_{\text{CIHC}} \times W_i}{A_i \times W_s \times R_{\text{CIHC}}} \times 100$$

Where:

- A_{CIHC} = Area of the individual CIHC peak
- A_i = Area of the internal standard peak.

W_i = Weight of the internal standard.

W_s = Weight of the coating.

R_{CIHC} = Response factor for CIHC.

- 4.8.2** Run the analysis in duplicate. Reanalyze the sample if the results vary by more than $\pm 1\%$ (absolute) of from the mean.

4.9 Determination of Acetone Content of the Coating by Gas Chromatography

- 4.9.1** Set up the gas chromatograph as described in **Section 2.1.2**.
- 4.9.2** Screen the sample for the presence of peaks interfering with the internal standard.
- 4.9.2.1** Prepare a solution of internal standard in DMF by weighing approximately 0.1 g of tetrahydrofuran into a vial containing 4 ml of DMF.
- 4.9.2.2** Inject a 1 μ l aliquot of the solution (**4.9.2.1**) into the gas chromatograph. Retain the chromatogram.
- 4.9.2.3** Weigh approximately 0.3 grams of the mixed sample into a vial containing 4 ml of DMF. Mix thoroughly and allow to stand for 5 minutes. Inject a 1 μ l aliquot of the mixture into the gas chromatograph. Compare the chromatogram to that obtained in **Section 4.9.2.2**. If there is no peak that interferes with tetrahydrofuran in the sample chromatogram, then proceed to **Section 4.9.3**. If an interfering peak is found, use methyl tertiary-butyl ether (MTBE) or any other appropriate solvent as internal standard. (NOTE 4)
- 4.9.3 Determination of Response Factor (R_{acetone}) for Acetone.**
- 4.9.3.1** Inject 1 μ l of the solvent into the gas chromatograph to check for contamination. If the solvent is contaminated, open a fresh bottle and repeat the step.
- 4.9.3.2** Weigh accurately 0.1g of tetrahydrofuran and 0.1 g of acetone (**± 0.0001 g**) in a pre-weighed sample vial containing 4 ml of dimethylformamide. Cap and shake the vial contents thoroughly for 15 minutes, using the Burrell Wrist Action Shaker. (**NOTE 4**)

4.9.3.3 Inject separately 1 μl of the mixture from **(4.9.3.1)** and **(4.9.3.2)** into the gas chromatograph using a 10 μl syringe. Integrate and record the peak areas of tetrahydrofuran and acetone. Retain the chromatogram. The order of elution is acetone, tetrahydrofuran and dimethylformamide (**See Figure II**).

4.10 Calculation for the Response Factor, R_{acetone} , of Acetone.

4.10.1 Determine the response factor, R_{acetone} by means of the following equation: (**NOTE: 6**)

$$R_{\text{acetone}} = \frac{W_i \times A_{\text{acetone}}}{W_{\text{acetone}} \times A_i}$$

Where:

- W_i = Weight of the internal standard.
- W_{acetone} = Weight of acetone
- A_{acetone} = Peak area of acetone.
- A_i = Peak area of the internal standard

NOTE 6: It is necessary to determine the response factor for acetone with each series of determinations.

4.11 Gas Chromatographic Determination of the Acetone Content of the Coating.

4.11.1 Weigh accurately 0.2 to 0.4 g (± 0.0001 g) of the mixed coating **(4.1.1)** and 0.1 g (± 0.0001 g) of tetrahydrofuran in a tared vial containing 4 ml of DMF. Immediately cap the vial (**NOTE 7**).

4.11.2 Shake the mixture on a Burrell Wrist Action Shaker for 15 minutes. It is essential that the sample be thoroughly mixed. Let the sample stand undisturbed for about 5 minutes prior to injection to allow the solids to settle at the bottom of the vial.

4.11.3 Inject a 1 μl aliquot of the supernatant liquid from **(4.11.2)** into the gas chromatograph. The area of the acetone and the tetrahydrofuran peaks are integrated and recorded. Retain the chromatogram (**See Figure I**).

NOTE 7: If the sample contains more than 60% acetone, increase the volume of the solvent to 8 ml and 0.2 grams of the internal standard.

4.12 Calculation for % Acetone in the Coating.

4.12.1 Calculate the weight % of acetone in the sample, using the data obtained in (4.11.3), as follows:

$$4.12.1.1 \quad \% \text{ Acetone (W/W)} = \frac{A_{\text{acetone}} \times W_i}{A_i \times W_s \times R_{\text{acetone}}} \times 100$$

Where: A_{acetone} = Area of the acetone peak
 A_i = Area of the internal standard peak.
 W_i = Weight of the internal standard.
 W_s = Weight of the coating.
 R_{acetone} = Response factor for acetone.

4.13 Run the analysis in duplicate. Reanalyze the sample if the results vary by more than $\pm 1\%$ (absolute) of from the mean.

5) CALCULATION FOR COMPLIANCE OF COATING CONTAINING ACETONE AND CHLORINATED HYDROCARBONS

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

Where: (4.3.6) = Density of Coating (g/ml)
 (4.2.4) = % Total Volatiles in the Coating (W/W)

$$5.2 \quad \text{Weight of Acetone (g/l Coating)} = 1000 \text{ ml/l} \times (4.3.6) \times (4.12.1.1) \times 10^{-2}$$

Where: (4.12.1.1) = % Acetone in the Coating (W/W)

$$5.3 \quad \text{Weight of ClHC (g/l Coating)} = 1000 \text{ ml/l} \times (4.3.6) \times (4.8.1.1) \times 10^{-2}$$

Where: (4.8.1.1) = % ClHC in the Coating (W/W)

5.4 Total weight (g) of Acetone and ClHC per liter of coating = Sum of the individual weights (g) of Acetone and ClHC/l coating.

$$5.5 \quad \text{Volume (ml) of Acetone/l Coating} = (5.2) / D_{\text{ACETONE}}$$

Where: $D_{\text{ACETONE}} = 0.7905 \text{ g/ml}$

$$5.6 \quad \text{Volume (ml) of ClHC/l Coating} = (5.3) / D_{\text{ClHC}}$$

Where: $D_{\text{CIHC}} = 1.3227 \text{ g/ml}$ for MeCl
 $= 1.3293 \text{ g/ml}$ for 1.1.1-TCA

5.7 Total Volume (ml) of Acetone and Chlorinated Hydrocarbon per liter of coating = Sum of the individual volumes (ml) of acetone (5.5) and CIHC/l coating, (5.6).

5.8 If CIHC and Acetone are considered exempt solvents.

5.8.1

Grams VOC/l Coating (less CIHC, less Acetone) = $\frac{[(5.1) - (5.4) \times 1000 \text{ ml/l}]}{[1000 \text{ ml/l} - (5.7)]}$

5.8.2 lb VOC/gal Coating (less CIHC, less Acetone) = $(5.8.1) \times 8.34 \times 10^{-3}$

5.9 If only Acetone is considered an exempt solvent.

5.9.1 Grams VOC/Coating (less Acetone) = $\frac{[(5.1) - (5.2)] \times 1000 \text{ ml/l}}{[1000 \text{ ml/l} - (5.5)]}$

5.9.2 lb VOC/gal Coating (less Acetone) = $(5.9.1) \times 8.34 \times 10^{-3}$

5.10 For low solids materials, where acetone is considered part of the coating.

5.10.1 Grams VOC/l Coating = $[(5.1) - (5.2)]$

5.10.2 lb VOC/gal Coating = $(5.10.1) \times 8.34 \times 10^{-3}$

6) CALCULATION FOR COMPLIANCE OF COATING CONTAINING ACETONE AND OTHER EXEMPT SOLVENTS

6.1 Weight of total volatile (g/l Coating) = $1000 \text{ ml/l} \times (4.3.6) \times (4.2.4) \times 10^{-2}$

Where: $(4.3.6) = \text{Density of Coating (g/ml)}$
 $(4.2.4) = \% \text{ Total Volatiles in the Coating (W/W)}$

6.2 Weight of Acetone (g/l Coating) = $1000 \text{ ml/l} \times (4.3.6) \times (4.12.1.1) \times 10^{-2}$

Where: $(4.12.1.1) = \% \text{ Acetone in the Coating (W/W)}$

6.3 Total weight of Exempt Solvents (g/l of Coating) = Sum of the individual weights of the Exempt Solvents one liter of Coating (**Note 8**)

6.4 Total weight (g) of Acetone and Exempt Solvents/l of Coating = $(6.2) + (6.3)$

$$\underline{6.5 \text{ Volume (ml) of Acetone/l Coating} = (5.2) / D_{\text{ACETONE}}}$$

Where: $D_{\text{ACETONE}} = 0.7905 \text{ g/ml}$

$$\underline{6.6 \text{ Total Volume (ml) of Exempt Solvents/l Coating} = \text{Sum of the Individual Volumes of each Exempt Solvent in one liter of coating (Note 8)}}$$

$$\underline{6.7 \text{ Total Volume (ml) of Acetone and Exempt Solvents/ l of coating} = (6.5) + (6.6)}$$

$$\underline{6.8 \text{ Grams VOC/l Coating (less Acetone, less Exempt Solvents)} = [(6.1) - (6.4) \times 1000 \text{ ml/l}] [1000 \text{ ml/l} - (6.7)]}$$

$$\underline{6.9 \text{ lb VOC/gal Coating (less CIHC, less Exempt Solvents)} = (5.8.1) \times 8.34 \times 10^{-3}}$$

Note 8: Weights and volumes of exempt compounds from ASTM D-6133 and BAAQMD Methods 41 and 43.

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 D2369-93, Book of ASTM Standards.
- 6.3 "Density of Paint, Varnish, Lacquer and Related Products", ASTM Designation D1475-90, Book of ASTM Standards, Vol 6.01, 1990.
- 6.4 "Determination of Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph", ASTM Method D3792-91, Book of ASTM Standards
- 6.5 "Determination of Dichloromethane and 1,1,1 Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatography", ASTM Method D4457-85, Book of ASTM Standards.

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