METHOD 41

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN SOLVENT BASED COATINGS AND RELATED MATERIALS CONTAINING PARACHLOROBENZOTRIFLUORIDE

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

1.1 This method is applicable to the determination of parachlorobenzotrifluoride (PCBTF) in solvent based coatings and related products.

1.2 The concentration of PCBTF is determined by gas chromatography using ethanol, or any appropriate solvent, as the internal standard.

1.3 For multicomponent coating systems, the components must be mixed first in the appropriate ratio. The exempt solvents, density and total non-volatiles are determined from this mixture. The total non-volatile content is determined by allowing the test speciments to have an induction period of 30 minutes in the aluminum dish prior to oven heating.

1.4 Propylene glycol monomethyl ether acetate (PGMEA) interferes with the analysis of PCBTF. When this solvent is present in the sample, use the alternate column **(2.2.2).**

1.5 This method may not be applicable to all types of coatings or printing inks.

2) APPARATUS

2.1 **Gas Chromatograph.** This unit is fitted with a flame ionization detector (FID), a liquid injection port with glass insert, a temperature programmer and a compatible integrator or data station. The suggested operating parameters are as follows:

Initial Oven Temperature (°C)	**60**
Inital Hold time (min)	**5**
Temperature Program Rate (°C/min)	**5**
Final Oven Temperature (°C)	**200**
Final Hold time (°C)	**10**
Injector Temperature (°C)	**250**

Detector Temperature (°C)	**250**
Carrier Gas	**He**
Carrier Gas Flow (cc/min)	**20**
Injection Sample Size (µl)	**1**

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

2.2.1 Primary Column. A 12' x 1/8" O.D. SS column packed with 20% SP-2100/0.1% Carbowax 1500, 100/120 mesh Supelcoport. The packing material is available from Supelco.

2.2.2 Alternate column for the analysis of PCBTF. A 60M x 0.25mm ID DB-WAX Column, 0.5 µm film thickness (J&W Scientific).

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 Transfer Pipets. 3ml capacity with 1 and 2 ml graduations.

2.11 Spatula.

2.12 Gardner Weight Per Gallon Cup. 83 cc. This cup is available from Thomas Scientific.

2.13 Vials with screw caps. 2 dram size.

2.14 Eberbach Shaker for quart or less size containers.

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 Toluene or other suitable solvent. Reagent grade.

3.2 Ethanol, Absolute. 200 proof. **Other suitable anhydrous solvents.** Reagent grade.

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

3.4 Helium or Nitrogen, 99.995% or higher.

3.5 Hydrogen.

3.6 Air.

3.7 Parachlorobenzotrifluoride. Reagent grade or highest available quality.

3.8 Propylene Glycol Monomethyl Ether Acetate. Reagent grade.

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 after mixing is also 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 transfer 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. Record the total weight of the sample and dish in grams.

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 ± 5°C for 1 hour. Cool the sample in the desiccator and weigh.

4.1.5 Run the analysis in duplicate. Reanalyze the sample if results vary by more than ± 1% (absolute) 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 and PCBTF.

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) in g = (4.1.4) - (4.1.2)

Where: (4.1.4) = Weight of the non-volatile and aluminum pan, g.

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

4.2.4 % Total Volatiles in Coating = 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 1475-98 (2003).

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 **(4.1.1).** 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.

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

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

4.4 Determination of PCBTF Content of the Coating by Gas Chromatography.

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

4.4.2 Screen the sample for the presence of peaks interfering with the internal standard.

4.4.2.1 Prepare a solution of ethanol in DMF by weighing approximately 0.2 grams of ethanol into a vial containing 4 ml DMF. (NOTE 2).

NOTE 2: 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 compatible with DMF, then use a different solvent such as Carbon Disulfide. If Carbon Disulfide is used, change the internal standard to isopropanol or any other appropriate compound. Ethanol is not completely miscible with CS_2.

4.4.2.2 Inject a 1 µl aliquot of the solution **(4.4.2.1)** into the gas chromatograph. Retain the chromatogram.

4.4.2.3 Weigh approximately 0.5 grams of the mixed sample into a vial containing 4 ml of DMF. Mix thoroughly and allow to stand for about 5 minutes. Inject a 1 µl aliquot of the mixture into the gas chromatograph. Compare the sample chromatogram to that obtained in **Section 4.4.2.2**. If there is no peak that interferes with ethanol in the sample chromatogram, then proceed to **Section 4.4.3**. If an interfering peak is found use 2-propanol or any other appropriate solvent as the internal standard.

4.4.3 Screen the sample for the presence of propylene glycol methyl ether acetate (PGMEA), (NOTE 3).

NOTE 3: It is necessary to screen the sample for PGMEA since this compound coelutes with PCBTF when using the primary column.

4.4.3.1 Prepare a PGMEA solution in DMF by weighing approximately 0.2 grams of the compound into a vial containing 4 ml DMF.

4.4.3.2 Inject a 1 µl aliquot of the solution **(4.4.3.1)** into a gas chromatograph fitted with the alternate column **(2.2.2) (NOTE 4).** Retain the chromatogram.

4.4.3.3 Inject a 1 µl aliquot of the sample prepared in **Section 4.4.2.3** and compare the chromatogram with the one obtained in **Section 4.4.3.2**. If PGMEA is present, use the alternate column **(2.2.2)** for quantifying the PCBTF in the sample **(NOTE 4).**

NOTE 4: If the alternate column (2.2.2) is preferred, use only one half of the weights required for the sample, standard and internal standard.

4.4.4 Determination of Response Factor (R_{PCBTF}) for PCBTF.

4.4.4.1 Inject 1 µl of the solvent into the gas chromatograph to check for contamination. If contaminated, open a fresh bottle and repeat the step.

4.4.4.2 Weigh accurately 0.2 g **(± 0.0001 g)** of the PCBTF and 0.2 g of ethanol **(± 0.0001 g)** in a pre-weighed sample vial containing 4 ml of DMF. Cap and shake the vial contents thoroughly for 15 minutes, using the Burrell Wrist Action Shaker. The mixture may be injected into the gas chromatograph immediately after shaking.

4.4.4.3 Using a 10 µl syringe, inject separately 1 µl of the mixture from **(4.4.4.2)** into the gas chromatograph. Integrate and record the peak areas of ethanol and PCBTF. Retain the chromatogram. The order of elution is ethanol, DMF and PCBTF.

4.5 Calculation for the Response Factor (R_{PCBTF}) of PCBTF

4.5.1 The response factor, R_{PCBTF} is determined by means of the following equation: **(NOTE: 5)**

4.5.1.1 $$R_{PCBTF} = \frac{W_i \times A_{PCBTE}}{W_{PCBTF} \times A_i}$$

Where:
W_i = Weight of the internal standard, g.
W_{PCBTF} = Weight of PCBTF, g.
A_{PCBTF} = Peak area of PCBTF.
A_i = Peak area of the internal standard.

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

4.6 Gas Chromatographic Determination of the PCBTF Content of the Coating.

4.6.1 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 4 ml of DMF. Immediately cap the vial **(NOTE 6).**

NOTE 6: If the amount of PCBTF in the sample is more than 60% by weight, rerun the analysis using a smaller sample weight (0.2 to 0.4 grams).

4.6.2 Shake the mixture on a Burrell Wrist Action Shaker for 15 minutes. It is essential that the sample be thoroughly mixed. Allow the sample to stand undisturbed 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 1 µl aliquot of the supernatant liquid from **(4.6.2)** into the gas chromatograph. The area of the PCBTF and the ethanol peaks are integrated and recorded. Retain the chromatogram **(See Figures I and II).**

4.6.4 It is a good practice to confirm the presence and concentration of the PCBTF using the alternate column **(2.2.2)**.

4.7 Calculation for % PCBTF in the Coating.

4.7.1 Using the data obtained in **(4.6.3)**, calculate the weight % of PCBTF in the sample, as follows:

4.7.1.1 $$\% \text{ PCBTF (W/W)} = \frac{A_{PCBTF} \times W_i}{A_i \times W_s \times R_{PCBTF}} X100$$

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

4.8 Run the analysis in duplicate. Reanalyze the sample if the results vary by more than ±1% (absolute) from the mean.

5) CALCULATION FOR COMPLIANCE OF COATING CONTAINING PCBTF

5.1 Weight (g) of Total Volatiles /l of Coating = 1000 ml/l x (4.3.6) x (4.2.4) x 10^{-2}

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

5.2 Weight (g) of PCBTF /l of Coating = 1000 ml/l x (4.3.6) x (4.7.1.1) x 10^{-2}

Where: (4.7.1.1) = % PCBTF (W/W).

5.3 Volume (ml) of PCBTF /l of Coating = $\frac{(5.2)}{D_{PCBTF}}$

Where: D_{PCBTF} = 1.353 g/ml.

5.4 g VOC/l of Coating (less PCBTF) = $\frac{[(5.1) - (5.2) \times 1000 ml/l]}{[1000 ml/l - (5.3)]}$

5.5 lb VOC/gal of Coating (less PCBTF) = (5.4) x 8.34 x 10^{-3}

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

5.6 For low solids materials, where PCBTF is considered part of the coating:

5.6.1 g VOC/l of Coating = (5.1) - (5.2)

5.6.2 lb VOC/gal of Coating = (5.6.1) x 8.34 x 10^{-3}

6) REFERENCES

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

6.2 **"Standard Test Method for Volatile Content of Coatings",** ASTM D2369-04, Annual Book of ASTM Standards, Vol. 06.01, 2004.

6.3 **"Standard Test Method for Density of Liquid Coatings, Inks, and Related Products",** ASTM D1475-98 (2003), Annual Book of ASTM Standards, Vol. 06.01, 2004.

6.4 **"Standard Test Method for Water Content of Coatings by Direct Injection into a Gas Chromatograph"**, ASTM Method D3792-99, Annual Book of ASTM Standards, Vol. 06.01, 2004.

6.5 **"Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph",** ASTM D4457-02, Annual Book of ASTM Standards, Vol. 06.01, 2004.

6.6 **BAAQMD Manual of Procedures,"** Vol.3, Method 22.

Analytical Column: 12' x 1/8" O.D. SS Column packed with 20% SP2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport

GC parameters:

	Initial	Final
Oven Temperature (°C)	60	200
Time Delay (Min)	5	10
Temperature Program Rate (°C/min)	5	
*Injector Temperature (°C)	250	
Detector Temperature (°C)	250	
Carrier Gas	He	
Carrier Gas Flow (cc/min)	20	
Injection Sample Size (µl)	1	

*Glass Sleeve insert is used in the injection port.

C-R4A CHROMATOPAC Ch=2 REPORT No.=55 CHROMATOGRAM=2:LA9/12.C12 00/00/00 03:44:05

Analysis File : 2:SP21CA.R15

SHIMADZU GC -14-A FID
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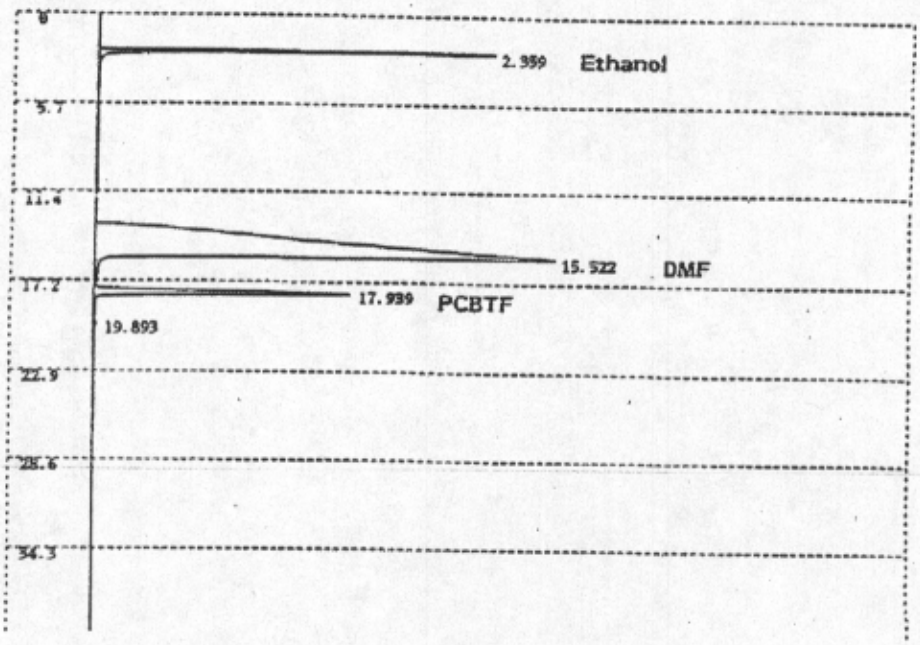

FIGURE I

A Typical Chromatogram Using the Primary Column (2.2.1)

Analytical Column: 60m x 0.25 mm ID, 0.5 µm FT DB-WAX

GC Parameters	Step 1	Step 2	Step 3
Oven Temperature (°C)	70	120	200
Time (Delay)	0	0	10
Temp Program Rate (°C/min)	3	30	
*Injector Temperature (°C)	250		
Detector Temperature (°C)	250		
Carrier Gas	He		
Carrier Gas Linear Velocity	25		
Injection Sample Size	1		

*Glass Sleeve insert is used in the injection port.

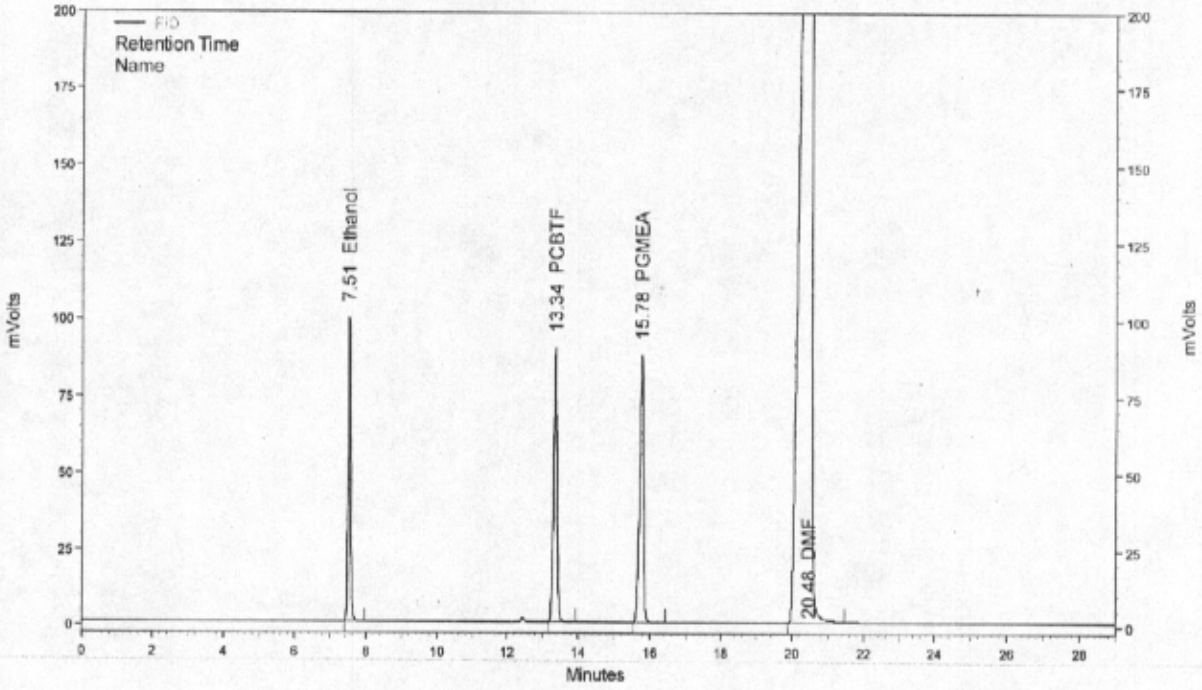

FIGURE II

A Typical Chromatogram Using the Alternate Column (2.2.2)