

METHOD 7356.1
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10 December 1993

SOLVENT CONTENT OF ENAMELS AND ENAMEL THINNERS
(GAS LIQUID CHROMATOGRAPHY)

1. SCOPE

1.1 This method provides for the qualitative and quantitative analysis of solvents for enamels by application of gas liquid chromatography. Two separate procedures are included in this method to include analysis for total aromatics specifically, and a separate procedure for toluene and ethylbenzene specifically. (In this form some of the tests may be omitted for some samples, depending on specification requirements.) A test for olefinic compounds is included.

2. MATERIALS

2.1 Gas chromatograph equipped with a suitable recorder and thermal conductivity detector. The operating conditions for the two procedures are as follows:

| | <u>6-ft. column</u> | <u>18-ft. column</u> |
|--------------------------------|---------------------|----------------------|
| Detector cell temperature, °C | 300 | 300 |
| Detector cell current, ma | 150 | 150 |
| Injection port temperature, °C | 300 | 300 |
| Helium flow at exit, cc/minute | 175 | 110 |
| Column temperature, °C | 125 | 100 |

2.2 Columns. Two lengths of 1/4-inch copper tubing, 6-feet and 18-feet long, both packed with 35 percent N, N-Bis (2-cyanoethyl) formamide on 60- to 80-mesh Chromosorb P.

2.3 Syringe, fixed needle, 10 microliter capacity.

3. REAGENTS

3.1 Benzene, A.C.S. reagent grade.

3.2 Acetone, A.C.S. reagent grade.

3.3 Phenylcyclohexane, high purity.

3.4 Potassium permanganate, 1 percent by solution in 95 mL of acetone and 5 mL of water.

3.5 Sulfuric acid. Mix concentrated sulfuric acid with 15 mL of water, cool, and dilute to 100 mL volume with concentrated acid.

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4. PROCEDURE

4.1 Total aromatic content - Procedure A. Transfer precisely 3 mL of distillate or thinner to a 25-mL glass-stoppered volumetric flask and add exactly 0.3 mL of high purity phenylcyclohexane. While cooling the graduate under tap water, add 15 mL of 85 percent sulfuric acid slowly. After all the acid has been added, shake vigorously for 2 minutes and allow the layers to separate. Add sufficient 85 percent acid to force the top layer into the neck of the flask and then transfer most of the top layer to a micro-separatory funnel. Wash the distillate with 5 mL portions of distilled water until all acid has been removed and reserve the washed solvent for chromatographic analysis. Install the 6-foot column and follow the operating conditions described above. Inject about 5 microliters of the acid-treated sample and allow the chromatogram to develop until the internal standard, phenylcyclo-hexane, emerges.

4.2 Calculate the percent of total aromatic solvents as follows:

$$\% \text{ total aromatic solvents, v/v} = \frac{A \times 1.07^* \times 10^{**}}{B}$$

where, A = area of aromatic solvent peaks.

B = area of internal standard peak.

* = correction factor for the detector response.

** = percentage of internal standard added.

4.3 Toluene and ethylbenzene - Procedure B (NOTE 1). Treat 3 mL of solvent in the same manner as described in procedure A except substitute benzene for phenylcyclohexane. Install the 18-foot column and follow the operating conditions described for that column. Inject about 3 microliters of sample and allow the chromatograph to develop until all of the xylene isomers appear. Purge the column by raising the column temperature to 120 °C. After the high boiling materials emerge, reset the column temperature to 100 °C. Calculate the percent of toluene and ethylbenzene as follows:

$$\% \text{ toluene, v/v} = \frac{(\text{area of toluene peak}) (1.017)^* (10)^{**}}{(\text{area of benzene peak})} \quad (\text{NOTE 2})$$

$$\% \text{ ethylbenzene, v/v} = \frac{(\text{area of ethylbenzene peak}) (1.054)^* (10)^{**}}{(\text{area of benzene peak})}$$

where, * = correction factor for the detector response.

** = percentage of internal standard added.

4.4 Test for olefinic or cyclo-olefinic compounds. Place 2-3 drops of the solvent or distillate into a small, clean test tube. Dissolve the sample in 1 mL of acetone and add 1 drop of 1 percent permanganate solution (see 3.4). Shake and allow to stand for 2 minutes. A positive test is indicated by the decolorization

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of the purple solution and the solvent is considered to contain olefinic or cyclo-olefinic compounds (NOTE 3).

5. NOTES

5.1 Note 1. If the total aromatic solvent content does not exceed the limitations of the specification for aromatics, procedure B may be omitted.

5.2 Note 2. Sensitivity of the instrument should be adjusted to keep peaks from running off the scale. Appropriate corrections must be made for changes in sensitivity when computing the peak areas.

5.3 Note 3. This test will not be positive for solvents containing less than 1 percent of these compounds.

6. PRECISION

6.1 No data.

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DETERMINATION OF PLASTICIZERS IN LACQUERS
(GAS-LIQUID CHROMATOGRAPHY)

1. SCOPE

1.1 This method describes a recommended practice for the qualitative and quantitative analysis of lacquers for plasticizer content by direct separation through the application of programmed temperature gas chromatography.

2. APPARATUS

2.1 Gas chromatograph equipped with a suitable recorder and a flow-control assembly to provide constant mass flow-rate of helium gas through the detector during programmed temperature operation, and separate controls for injection port, detector and column temperatures. The detector cell temperature should be maintained at 300 °C, injection port temperature 330 °C, detector cell current 160 ma, and the gas flow adjusted to 120 cc per minute at exit.

2.2 Column. Six feet of 1/4-inch diameter copper tubing packed with 20 percent by weight of silicone grease on acid and alkali washed chromosorb W, 60- to 80-mesh.

2.3 Syringe. Fixed needle, 50 microliter capacity.

2.4 Magnetic stirrer and bar.

3. REAGENTS

3.1 Acetone. A.C.S. reagent grade.

3.2 Hexanes. A.C.S. reagent grade.

3.3 Petroleum ether.

3.4 Butyl sebacate.

4. PROCEDURE

4.1 Weigh accurately about 100 mg of butyl sebacate or butyl adipate (preferably the former) as an internal standard into a 25-mL flask followed by 2 or 3 g of the lacquer vehicle which is also accurately weighed. Add 1 mL of

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acetone and insert a small magnetic stirring bar. With rapid stirring, add 3 mL of hexanes dropwise at the rate of 80-100 drops per minute, from a buret. Continue the stirring and add 3 mL of petroleum ether in the same manner. Filter through a rapid filter paper into a 25 mL beaker, add an antibumping stone and place in a 70 °C water bath. Remove the beaker as soon as boiling subsides.

4.2 Heat the chromatographic column to 210 °C, set the attenuation at a point of low sensitivity and inject 10 to 20 microliters of sample onto the column. Immediately engage the temperature programming mechanism for a column heating rate of 4 °C per minute. After the solvents have emerged, reset the sensitivity according to the type and amount of plasticizer anticipated. When the maximum temperature of 290 °C has been reached, maintain until the chromatogram has completely developed.

4.3 Identification.

4.3.1 Identify the peaks of the chromatogram by calculating their retention times, relative to the internal standard and compare to the calibration chart (table I).

TABLE I. Relative retention data for plasticizers.

| Plasticizer | Relative retention time (Dibutyl sebacate = 1) |
|-----------------------------------|---|
| Dimethyl phthalate | 0.16 |
| Diethyl phthalate | .26 |
| Dibutyl phthalate | .67 |
| Butyl benzyl phthalate | 1.32 |
| Di-(2-ethylhexyl) phthalate (DOP) | 1.65 |
| Tricresyl phosphate | 1/1.78-1.978 |
| Dioctyl sebacate | 2.20 |

1/ TCP is usually a mixture of isomers and will emerge as several peaks within the range indicated.

4.4 Calculation.

4.4.1 Determine the detector response correction factor for each plasticizer likely to be encountered in lacquer analysis by chromatographing known mixtures of each with the internal standard, and retain the data for future reference.

4.4.2 Measure the area of each peak obtained from chromatographing the unknown sample (see 4.2), correct for detector response, and calculate the amount of plasticizer by comparison to the internal standard.

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5. NOTES

5.1 None.

6. PRECISION

6.1 No data.