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Standard Test Method for Resin Acids in Rosin by Gas-Liquid Chromatography¹

This standard is issued under the fixed designation D 3008; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the resin acids in tall oil, gum, or wood rosin after conversion to their methyl esters.

1.2 The composition is calculated from the ratio of each peak area to the total area of all peaks obtained. Rosins generally contain nonvolatile or polymeric materials for which no peaks are obtained under the conditions used. On the other hand, volatile neutral materials elute in the general region of resin acid methyl esters and can result in errors in the calculated composition. More reliable data is obtained by removal of neutral materials before gas chromatography.²

1.3 *This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific hazards are given in Note 2.*

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water³

D 3257 Test Method for Aromatics in Mineral Spirits by Gas Chromatography³

E 260 Practice for Packed Column Chromatography⁴

3. Summary of Test Method

3.1 A portion of the sample is prepared by either converting it to the tetramethylammonium salts or esterifying it with diazomethane. A specimen of the prepared sample is injected into a 275°C injection port to a 200°C column of ethylene glycol succinate silicone copolymer (EGSS-X) or diethylene glycol succinate on silanized diatomaceous earth solid support. If added as the tetramethylammonium salt, the sample is pyrolyzed to the methyl ester. The pyrolyzed esters or the prepared esters are carried through the column with nitrogen or helium carrier gas and the chromatogram is obtained using a flame ionization detector.

3.2 The peak areas are obtained by any of the conventional means and the percent of the respective resin in acids is calculated from the ratios of the areas of the individual peaks to the total area of all peaks.

4. Apparatus

4.1 *Gas Chromatograph*—Any gas-liquid chromatograph having a flame ionization detector that can be operated at the conditions given in Table 1.

4.2 *Column*—Six to 10 ft (1.8 to 3 m) of 1/8-in. (3.2-mm) outside diameter, 0.085-in. (2.15-mm) inside diameter, 0.020-in. (0.52-mm) wall-thickness stainless steel tubing specifically tempered for easy handling and packed with the material as described in 8.1.

4.3 *Recorder*—A recording potentiometer with a full-scale deflection of 0 to 1-mV full-scale response time of 1 s or less, chart speeds of 1/2 to 1 in. (12 to 25 mm)/min, and sufficient sensitivity and stability to meet the requirements of 4.1.

4.4 *Specimen Introduction System*—Any system capable of introducing a representative specimen into the column. Microsyringes, 10-μL capacity, with fixed needle have been found satisfactory.

4.5 *Integrating Equipment*—In order of preferences based on accuracy, electronic, disk, planimeter, or rule.

5. Reagents and Materials

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests unless otherwise specified. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

5.3 *Toluene.*

5.4 *N-Methyl-N-Nitroso-p-Toluenesulfonamide.*⁶

5.5 *Diethyl Ether, Anhydrous.*

5.6 *2-Ethoxyethanol.*

5.7 *Liquid Phase*—Diethylene glycol succinate (DEGS) or ethylene glycol succinate-silicone copolymer (EGSS-X, low-silicone content).

NOTE 1—EGSS-X is the preferred liquid phase because of its greater stability.

5.8 *Methanol.*

¹ This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials and is the direct responsibility of Subcommittee D01.34 on Naval Stores.

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² Zinkel, D. F., and Han, J., *Naval Stores Review*, Vol 96 (2), pp. 14–19 (1986).

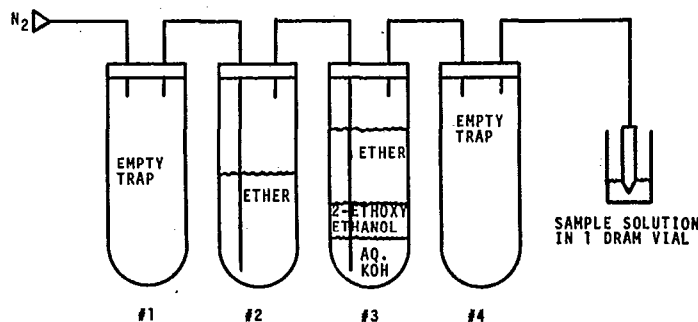
³ *Annual Book of ASTM Standards*, Vol 06.03.

⁴ *Annual Book of ASTM Standards*, Vol 14.01.

⁵ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

⁶ Available from Aldrich Chemical Co., Inc., Milwaukee, WI 53233 and Eastman Kodak, Rochester, NY 14650.

D 3008



NOTE—Connect four 25 by 200-mm test tubes in the hood as shown. Use rubber stoppers on Test Tubes 1 and 4; use cork stoppers on Test Tubes 2 and 3.

FIG. 1 Apparatus for Diazomethane Methylation (see 7.3.2)

TABLE 1 Typical Instrument Operating Conditions (See Test Method D 3257)

Column temperature, °C	200 to 210
Injection port temperature, °C	275 to 300
Detector temperature, °C	285
Carrier gas:	prepurified nitrogen or helium
Pressure, psig	60
Flow rate, mL/min	25 to 30
Detector gas (hydrogen)	prepurified hydrogen
Pressure, psig	13
Flow rate, mL/min	30
Detector gas (air)	dried air
Pressure, psig	30
Flow rate, mL/min	400
Resin Acid Methyl Ester	Relative Retention ^A
	DEGS EGSS-X
Pimarate	1.00 1.00
Sandaracopimarate	1.13 1.12
Communate	1.28 1.27
Levopimarate	1.33 1.34
Palustrate	1.35 1.36
Isopimarate	1.49 1.46
Abletate	2.14 2.10
Dehydroabletate	2.33 2.32
Neoabletate	2.47 2.46

^A See Zinkel and Han.²

5.9 *Potassium Hydroxide Solutions, Aqueous*—Dissolve 300 g of potassium hydroxide (KOH) in 500 mL of water.

5.10 *Solid Support*—Acid-washed diatomaceous earth,⁷ 80 to 100 mesh, specially treated to minimum adsorption and tailing of polar compounds.

5.11 *Tetramethylammonium Hydroxide Solution (24 %)* in methanol.

5.12 *Tetramethylammonium Hydroxide Solution (6 %)* in methanol. Dilute 25 mL of the reagent described in 5.11 with 75 mL of methanol.

6. Reference Standards

6.1 *Abietic Acid*.⁸

6.2 *Dehydroabietic Acid*.⁸

7. Preparation of Methyl Esters

7.1 Diterpene resin acids are more effectively chromatographed as the methyl esters. Either of the two

following methods may be used.

7.2 *Conversion by Means of Tetramethylammonium Salts*—Weigh to 0.1 mg a 50-mg portion of the sample and dissolve in about 0.5 mL of toluene. Add phenolphthalein indicator solution and titrate to the first permanent pink color with the 6 % solution of tetramethylammonium hydroxide in methanol. A portion of the resulting solution is injected into the chromatographic column as described. The tetramethylammonium salts are pyrolyzed to methyl esters in the injection port.

7.3 Esterification with Diazomethane:

NOTE 2—Diazomethane is explosive and an insidious poison. Use extreme care with the following esterification procedure, carrying out the reaction in a hood.

7.3.1 Weigh to 0.1 mg 50 to 60 mg of the sample into a 1-dram (4-mL) vial and dissolve in 1.0 mL of diethyl ether-methanol (9/1).

7.3.2 Connect four 25 by 200-mm test tubes as shown in Fig. 1. Use rubber stoppers in Test Tubes 1 and 4 and cork stoppers in Test Tubes 2 and 3. Connect the tubes with glass tubing as shown. Draw down the outlet end or the glass tube from Test Tube 4 to about a 1 to 2-mm diameter opening.

7.3.3 Leave Test Tubes 1 and 4 empty to serve as traps. Fill Test Tube 2 about one-half full with diethyl ether.

7.3.4 Add about 10 mL of the KOH solution, 10 mL of 2-ethoxyethanol, and 20 mL of diethyl ester to Test Tube 3.

7.3.5 Place the vial with the specimen solution under the delivery tube from Test Tube 4 so that the end of the tube dips beneath the surface of the liquid. Figure 2 shows an assembly of the esterification apparatus.

7.3.6 Add about 1 g of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide to Test Tube 3. Apply nitrogen gas to the inlet of Test Tube 1 at such a rate as to sweep the generated diazomethane through the solution of the sample at a moderate rate.

7.3.7 The esterification is complete when the yellow color of excess diazomethane is just apparent throughout the vial.

7.3.8 Evaporate the solution just to dryness under nitrogen on a steam bath in a hood. Dilute with toluene or methyl *t*-butyl ether to approximately 1 to 2 mL.

8. Preparation of Apparatus

8.1 Prepare a 10 % mixture of DEGS or EGSS-X on the acid-washed, diatomaceous earth and pack the column as discussed in Practice E 260.

8.2 Install the column in the chromatograph and establish

⁷ Chromosorb W-AW, manufactured by Manville Sales Corp., Filtration and Minerals, P.O. Box 5108, Denver, CO 80217-5108, has been found satisfactory for this purpose. Available from chromatography supply houses.

⁸ These and most other resin acids are available from Helix Biotech Ltd., 217-7080 River Rd., Richmond, B. C., Canada V6X 1X5.