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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Methods for Fatty and Rosin Acids in Tall Oil Fractionation Products by Capillary Gas Chromatography¹

This standard is issued under the fixed designation D 5974; 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 These test methods describe the determination of the amounts of the individual fatty acids and rosin acids in fractionated tall oil products using capillary gas chromatographic separation of the volatile methyl esters of these acids.

1.2 Three methods for forming the methyl esters and two methods for determining the amounts of the individual fatty acids and rosin acids are described.

1.3 The methods for forming the methyl esters are through the use of diazomethane, tetramethylammonium hydroxide (TMAH) or trimethylphenylammonium hydroxide (TMPAH).

1.4 The two methods for determining the amount of the individual fatty acids and rosin acids are the “internal standard” method, which yields absolute values and the “area percent” method, which yields relative values.

1.5 *This standard does not purport to address all of the safety concerns, if any, 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.*

2. Referenced Documents

2.1 ASTM Standards:

D 509 Test Methods of Sampling and Grading Rosin²

D 804 Terminology Relating to Naval Stores, Including Tall Oil and Related Products²

D 3008 Test Method for Resin Acids in Rosin by Gas Chromatography²

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method³

3. Significance and Use

3.1 Tall oil fractionated products derived from tall oil are important commercial materials primarily composed of fatty acids and rosin acids but also containing some neutral material (see Terminology D 804). For many applications, it is necessary to know the level of the individual fatty acids and rosin acids present in these products. Gas chromatography has

proven to be a useful tool for such determinations (see Test Methods D 3008, and D 508) and capillary chromatography, described in these test methods, is considered to be the most effective analytical technique currently available. Other techniques may be more suitable than gas chromatography where particular situations exist. For example, the presence of fatty acid esters in the sample would result in transesterification during the derivatization step that may affect the results.

3.2 Due to hydrogen bonding, unmodified tall oil fatty acids and rosin acids cannot be volatilized at atmospheric pressure without undergoing decomposition, and so it is necessary to convert the free acids to the more volatile and more stable derivative, such as the methyl ester, prior to chromatographic separation.

3.3 These test methods describe three ways to prepare methyl esters. Other methylating derivatizing agents (for example, *N,N*-dimethylformamide dimethylacetal), may be used providing it has been demonstrated that such agents yield equivalent results to those described herein.

3.3.1 The classic method is the use of diazomethane. However, diazomethane is a hazardous and toxic material. It should only be used by, or under the supervision of, technically qualified individuals.

3.3.2 TMAH causes the isomerization of a sample's di- and polyunsaturated fatty acids, when it is used in even a slight excess. This leads to inaccurate results for the individual fatty acid components. TMAH should be used for materials containing only rosin acids, or when the identification or quantitation of individual fatty acid components is not important.

3.3.3 TMPAH is the recommended methylating agent when the identification or quantitation of individual di- and polyunsaturated fatty acids is required. TMPAH produces results that are very similar to those of diazomethane, but without the hazards that are normally associated with diazomethane. A considerable excess of TMPAH may cause isomerization of conjugated compounds similar to that encountered with TMAH.

3.4 Two test methods for calculating the amounts of the individual fatty acids and rosin acids are included in this standard. When the actual weight percentage of a given compound is required, the “internal standard” method must be used. This method involves adding a known amount of an internal standard to a known amount of test material and comparing the area of the peak associated with the internal

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

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² Annual Book of ASTM Standards, Vol 06.03.

³ Annual Book of ASTM Standards, Vol 14.02.

standard with the area of the peak of the individual fatty acid or rosin acid. The "area percent" method will give the relative amount of each component by comparing the area of the appropriate peak to the total area of all peaks. Non-eluting compounds will lead to erroneous (absolute) results with this method.

PREPARATION OF METHYL ESTERS

NOTE 1—Any of these three methods can be used with the choice being dependent on the factors mentioned in 3.3.

4. Conversion By Means of Diazomethane

4.1 Apparatus:

4.1.1 *Test Tube*, four, 25 by 200 mm.

4.1.2 *Standard Laboratory Glassware*.

4.2 Reagents and Materials:

4.2.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. 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,⁴ where such specifications are available. 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.

4.2.2 *Diazald, N-Methyl-N-Nitroso-p-Toluenesulfonamide*, Chemical Abstracts Service (CAS) No. 80-11-5.

4.2.3 *Diethyl Ether*, anhydrous.

4.2.4 *2-Ethoxyethanol*.

4.2.5 *Methanol*, anhydrous.

4.2.6 *Potassium Hydroxide Solution*, aqueous, 40 % weight/volume (w/v).

4.2.7 *Toluene*.

4.3 Procedure:

4.3.1 **Precaution**—Diazomethane is explosive and an insidious poison. Use extreme care in using the following esterification procedure. The procedure must be performed in a fume hood.

4.3.2 Dissolve the sample from 9.2.2 or 17.1 in 0.5 mL of 10 % (v/v) methanol/diethyl ether.

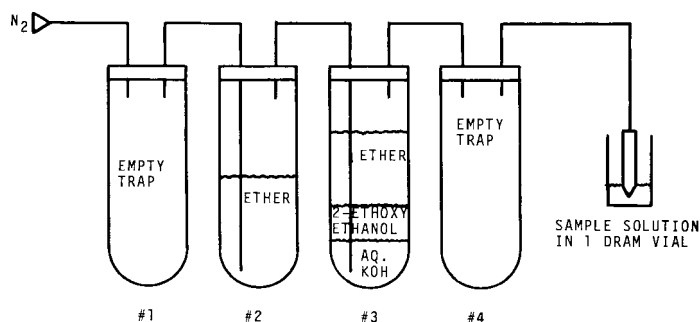
NOTE 2—With solid rosin or other samples that are difficult to dissolve, 2 to 3 drops of toluene may be added to the vial prior to derivatization to assist in dissolving the sample.

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

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

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

4.3.6 Place the vial with the methanol/ether solution of the



NOTE 1—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 Test Method D 3008)

sample under the delivery tube from Test Tube 4 so that the end of the tube dips beneath the surface of the liquid.

4.3.7 Add about 1 g of diazald 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.

4.3.8 The esterification is complete when the yellow color of excess diazomethane is apparent in the sample vial.

4.3.9 Evaporate the solution almost to dryness under a very gentle stream of nitrogen on a steam bath in a hood. Dilute with ether or other suitable solvent to about 0.5 to 0.6 mL.

NOTE 3—An alternate procedure would be to use a heat block at 50°C to evaporate the solvent. Regardless of the method, care must be taken not to lose the more volatile esters.

5. Conversion By Means of Tetramethylammonium Hydroxide (TMAH)

5.1 Apparatus:

5.1.1 *Standard Laboratory Equipment*.

5.2 Reagents and Materials:

5.2.1 *Purity of Reagents*, see 4.2.1.

5.2.2 *Tetramethylammonium Hydroxide Solution*, 24 % in methanol, CAS No. 75-59-2.

5.2.3 *Tetramethylammonium Hydroxide Solution*, 6 % (v/v) in methanol. Dilute 25 mL of the reagent described in 5.2.2 with 75 mL of methanol.

5.2.4 *Phenolphthalein Solution*, 1 % (w/v) in methanol.

5.2.5 *Diethyl Ether*, anhydrous.

5.2.6 *Methanol*, anhydrous.

5.2.7 *Acetic Acid*, 5 % volume/volume (v/v) in methanol.

5.2.8 *Toluene*.

5.3 Procedure:

5.3.1 Dissolve the sample from 9.2.2 or 17.1 in about 0.5 to 3.0 mL of a 50:50 ether/methanol mixture, add 2 to 3 drops of phenolphthalein indicator solution, and titrate to a pH of 7.8 to 8.1 or to the very first permanent pink color with a 6 % solution of TMAH in methanol. If the solution is overtitrated it can be back titrated with the acetic acid in methanol solution to the end point. Later, when the solution is injected into the heated injection port of the chromatograph, the tetramethylammonium salts are pyrolyzed to methyl esters.

NOTE 4—With solid rosin or other samples that are difficult to dissolve,

⁴ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.