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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Methods for Rosin Acids Content of Naval Stores, Including Rosin, Tall Oil, and Related Products[1]

This standard is issued under the fixed designation D 1240; 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 cover the determination of rosin acids in tall oil, tall oil fatty acid, tall oil rosin, and other naval stores products.

1.2 These test methods may not be applicable to adducts or derivatives of rosin, fatty acid, or other naval stores products.

1.3 *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 1585 Test Methods for Fatty Acids Content of Naval Stores, Including Rosin, Tall Oil, and Related Products[2]

E 70 Test Method for pH of Aqueous Solutions with the Glass Electrode[3]

E 177 Practice for the Use of the Terms Precision and Bias in ASTM Test Methods[4]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[4]

3. Summary of Test Method

3.1 The rosin acids content is determined using either the potentiometric method or the indicator method described in Sections 6 to 17. Rosin acids are calculated as abietic acid.

4. Significance and Use

4.1 This is a major revision of Test Methods D 1240. The old refereed version, the Herrlinger-Compeau Method, employed a sodium sulfate solution extraction. It is limited in application to materials containing less than 15 % rosin, principally fatty acids. It is used little in the industry, but since much early work is based on this test method, it is included here for reference.

4.1.1 For materials containing less than 15 % rosin, the modified Glidden procedure has gained acceptance as the method of choice over the Herrlinger-Compeau. For materials containing more than 15 % rosin the modified Wolfe Method, once part of Test Methods D 1585, is preferred. The modified Wolfe and modified Glidden procedures differ only in their details. Both methods have been combined here into a single procedure.

4.2 Rosin and tall oil are composed primarily of rosin acids and fatty acids, and, therefore, the measurement of these components is important in establishing the composition of these materials.

5. Reagents

5.1 *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 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 Unless otherwise indicated, references to water shall be understood to mean deionized or distilled water.

6. Preparation of Sample

6.1 Homogeneous liquid materials may be used without further preparation.

6.2 Nonhomogeneous liquid materials should be heated until they are homogeneous, then a portion taken for analysis.

6.3 Solid samples are subject to surface oxidation which may affect the results. Prepare the sample for analysis by chipping small pieces from a freshly exposed surface of a lump or lumps and crush to a coarse powder to facilitate weighing and solution. Prepare fresh on the same day, prior to weighing,

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[2] *Annual Book of ASTM Standards*, Vol 06.03.

[3] *Annual Book of ASTM Standards*, Vol 15.05.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

[5] *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

in order to avoid changes due to surface oxidation of crushed rosin on exposure to the air.

ROSIN ACIDS CONTENT BY THE POTENTIOMETRIC METHOD
(*Referee Method*)

7. Scope

7.1 This test method covers the determination of rosin acids content of tall oil rosin, tall oil fatty acid, and other naval stores products, where the most reproducible results are desired. By using the potentiometric inflection end points, the error due to colorimetric end points is avoided.

8. Summary of Test Method

8.1 A sample is refluxed with methyl sulfuric acid to esterify the fatty acids. The rosin acids and sulfuric acid are then titrated potentiometrically, and the rosin acids content calculated from the difference between the two inflection points obtained.

9. Apparatus

9.1 *pH Meter*—An indicating potentiometer having a limit of error not greater than ±0.1 pH over a range from pH 1 to pH 13, using an alkali-resistant glass electrode and a saturated calomel half-cell. The pH meter shall conform to the requirements of Test Method E 70. Alternatively, an automatic potentiometric titrator may be used.

9.2 *Stirrer*, magnetic, equipped with poly(tetrafluoroethylene)-coated stir bar.

9.3 *Buret*, 50-mL capacity, with 0.1-mL divisions. The so-called automatic buret is preferable as its use minimizes errors due to evaporation. The automatic buret should be guarded with soda-lime tubes against the absorption of CO_2 from the air.

9.4 *Erlenmeyer Flask*, 250-mL or larger of a chemically resistant glass with a standard-taper 24/40 joint.

9.5 *Condenser*, water-cooled, equipped with a joint fitting the flask described in accordance with 9.4.

10. Reagents

10.1 *Alcoholic Alkali, Standard Solution (0.5 N)*—Dissolve 33 g of potassium hydroxide (KOH), preferably in pellet form, in methanol (CH_3OH) and dilute to 1 L with methanol. Standardize to ±0.001 *N* with potassium acid phthalate ($C_6H_4COOKCOOH$) in 60 mL of water followed by 40 mL of methanol; 2.553 g of potassium acid phthalate will be neutralized by 25.00 mL of 0.5 *N* KOH solution. Protect the standardized solution against evaporation and absorption of carbon dioxide (CO_2) from the air. Restandardize the solution frequently, either potentiometrically or colorimetrically, using phenolphthalein as the indicator.

10.1.1 For fatty acids containing low concentrations of rosin acids, 0.1 *N* alcoholic potassium hydroxide may give superior results.

10.2 *Ethanol (95 %)*—Denatured alcohol conforming to Formula No. 3A or No. 30 of the U.S. Bureau of Internal Revenue, neutralized by the addition of KOH.

10.3 *Methanol* (99.5 %).

10.4 *Methyl Sulfuric Acid Solution*—Slowly pour 100 g of concentrated sulfuric acid (H_2SO_4 sp gr 1.82 to 1.84), while stirring constantly, into 400 g of methanol. Extreme caution should be taken while preparing the methyl sulfuric acid. Adding sulfuric acid too rapidly may cause the methanol to flash out of its container. Store the methyl sulfuric acid in a glass-stoppered bottle.

10.5 *Toluene*.

11. Procedure

11.1 Weigh the sample to the nearest 0.001 g in a 250-mL flask. Choose the amount of sample so that the second titration will consume between 10 and 30 mL of KOH solution. For rosin acids, this will be about 5 g of material. For fatty acids containing less than 15 % rosin, this will be about 40 g of material. For fatty acids containing less than 3 % rosin acids titrating with 0.1 *N* KOH may give superior results. Table 1 gives suggested amounts of material to use.

11.2 Dissolve the sample in 100 mL of methanol in a 250-mL flask. If the sample has a high rosin content it may be helpful first to dissolve it in 25 mL of toluene before adding the methanol. For material believed to contain less than 15 % fatty acid, add 5 mL of methyl sulfuric acid, connect the flask assembly, and reflux the solution for 2 min. (Solid samples must be in solution before beginning reflux.) For materials believed to contain concentrations of fatty acid higher than 15 % use 10 mL of methyl sulfuric and reflux for 20 min. Measure reflux time from the moment the first drop of solvent returns to the flask from the condenser. Cool and transfer to a 400-mL beaker, using a total of 100 mL of methanol (Note 1) in three successive rinsings.

NOTE 1—Ethanol is preferable when an automatic titrator is used.

11.3 Turn the pH meter on and allow a few minutes for it to come to equilibrium. Balance the meter using a standard buffer solution as described in Test Method E 70; then rinse the electrodes thoroughly with water and then with alcohol.

11.4 Adjust the beaker containing the solution of the sample so that the buret tip is close to the surface of the solution. Adjust the electrodes so the lower half of each is immersed. Start the stirrer slowly; then adjust its speed for vigorous stirring without spattering. Record the initial pH if it is on the scale. Add suitable small portions of the KOH solution, and, waiting after each addition until an unchanging potential has been established, record the pH and buret readings. Add 5-mL portions of KOH solution until a pH solution until a pH of 1.0 to 1.5 is reached; then add 1-mL portions until the change in pH per portion added, exceeds 0.3 pH unit. Continue to add the KOH solution in 0.1-mL or smaller portions until the first end point has been passed, as indicated by a significant decrease in pH change per unit volume added. Thereafter, add 1 to 2-mL

TABLE 1 Sample Size and Titrant

Material	Sample Size, g	Reflux Time, min	KOH Normality, *N*
Rosin	5	2	0.5
Fatty acid, <15 % rosin	40	20	0.5
Fatty acid, <3 % rosin	40	20	0.1