Standard Test Methods for Rosin Acids Content of Pine Chemicals, Including Rosin, Tall Oil, and Related Products[1]

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 pine chemicals products.

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

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.4 *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:*[2]

D1585 Test Methods for Fatty Acids Content of Naval Stores, Including Rosin, Tall Oil, and Related Products

E70 Test Method for pH of Aqueous Solutions With the Glass Electrode

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Summary of Test Method

3.1 The rosin acids content is determined by one of two procedures; by selective esterification of fatty acids to form methyl esters followed by titration of the unreacted rosin acids, by selective esterification of fatty acids to form butyl esters followed by titration of the unreacted rosin acids.

4. Significance and Use

4.1 This is a revision of the method for measuring rosin acids content combines the three major ways of determining the rosin acids content of pine chemicals products into a single method.

4.1.1 For materials containing less than 15 % rosin, the modified Glidden procedure has gained acceptance. For materials containing more than 15 % rosin the modified Wolfe Method is preferred. The modified Wolfe and modified Glidden procedures differ only in their details. They have been combined here into a single procedure. This procedure can be run using either a potentiometer or an internal indicator to determine the end point of the titration. Use of a potentiometer is preferred and is the referee method. Use of an internal indicator is the principal alternative method. They will be referred to as the Potentiometric Method and the Internal Indicator Method.

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.[3] 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.

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[1] These test methods are under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.34 on Pine Chemicals and Hydrocarbon Resins.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] *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.

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, 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 pine chemicals 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 E70. 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, 500 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 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. Weigh the sample to the nearest 0.001 g in a 250-mL or 500-mL (<15 % rosin samples) flask.

11.2 Dissolve the sample in 100 mL of methanol in a 250-mL flask (or 150 mL methanol for 500-mL flask with 40 g sample). 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 more than 15 % rosin acid, that is, high in rosin, add 5 mL of methyl sulfuric acid, connect the flask assembly, and reflux the solution for 2 to 20 min. (Solid samples must be in solution before beginning reflux.) For materials believed to contain concentrations of rosin acid less than 15 %, that is, low in rosin, one may use a 250- or 500-mL flask, one must 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 E70; then rinse the electrodes thoroughly with water and then with alcohol.

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

11.4 Immerse the electrode in the sample solution. Start the stirrer and adjust its speed for vigorous stirring without splattering.

11.5 Titrate the sample solution with 0.5 *N* KOH to a fixed pH of 4.0, the first end point. If it appears that the buret does not contain sufficient KOH to continue the titration to the second end point, refill the buret at this point. Continue the titration to the fixed pH of 10.8, the second point. Record the amount of KOH required for the titration between the first and second end point. If an automatic titrator is used, the end points shall be taken at the inflection points or at the fixed pH of 4.0 and 10.8.

12. Calculation

12.1 Calculate the percentage of rosin acids as follows:

12.1.1 For materials containing less than 15 % rosin:

$$\text{Rosin acids, \%} = \left[\left(AN/B\right) \times 30.24\right] - 1.1 \qquad (1)$$

where:

A = KOH solution required for titration between the first and second end points, mL,
N = normality of the KOH solution,
B = sample used, g, and
30.24 = (mol weight of abietic acid × 100)/1000

12.1.2 For materials containing greater than 15 % rosin:

$$\text{Rosin acids, \%} = \left(AN/B\right) \times 30.24 \qquad (2)$$

where:

A = KOH solution required for titration between the first and second end points, mL,
N = normality of the KOH solution,
B = sample used, g, and
30.24 = (mol wt of abietic acid × 100)/1000

12.2 Report the percentage of rosin acids calculated by either 12.1.1 or 12.1.2 to the first decimal place.

ROSIN ACIDS CONTENT BY THE INTERNAL INDICATOR METHOD

(*Alternative Method*)

13. Scope

13.1 This test method covers the determination of rosin acids content of tall oil rosin, tall oil fatty acid, and other pine chemicals products, using an internal indicator for the determination of the end point. It gives good results when routinely applied by a skilled analyst. However, where the most reproducible results by different analysts and laboratories are desired, the referee method (Sections 6 to 11) should be used.

14. Summary of Test Method

14.1 A sample is refluxed with methyl sulfuric acid to esterify the fatty acids. The rosin acids and sulfuric acid are then titrated in the presence of thymol blue indicator. The rosin acids content is then calculated from the difference between the two color end points obtained.

15. Apparatus

15.1 The apparatus for the esterification and titration of the sample shall consist of the flask, condenser, and buret described in Section 9.

16. Reagents

16.1 *Alcoholic Alkali, Standard Solution*—See 10.1.

16.2 *Methanol*—See 10.3.

16.3 *Methyl Sulfuric Acid Solution*—See 10.4.

16.4 *Thymol Blue Indicator Solution (1 g/L)*—Dissolve 1 g of thymol blue in 1000 mL of methanol.

16.5 *Toluene.*

17. Procedure

17.1 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. Weigh the sample to the nearest 0.001 g in a 250-mL or 500-mL (<15 % rosin samples) flask.

17.2 Dissolve the sample in 100 mL of methanol in a 250-mL flask (or 150 mL methanol for 500 mL flask with 40 g sample). 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 more than 15 % rosin acid, that is, high in rosin, add 5 mL of methyl sulfuric acid, connect the flask assembly, and reflux the solution for 2 to 20 min. (Solid samples must be in solution before beginning reflux.) For materials believed to contain concentrations of rosin acid less than 15 %, that is, low in rosin, one may use a 250- or 500-mL flask, one must 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, add 1 mL of thymol blue indicator.

17.3 Titrate with the KOH solution to the first end point, about pH 4.0, when the solution changes color from red to yellow. Record the reading or refill the buret. Continue the titration to the second end point, about pH 10.8, when the solution changes color from yellow to blue. Record to the nearest 0.1 mL the millilitres of KOH solution required for titration between the two end points.

NOTE 2—These end points approximate the inflection points under the nonaqueous conditions employed.

18. Calculation

18.1 Calculate the percentage of rosin acids as described in 12.1.

18.2 Report the percentage of rosin acids to the first decimal place.

19. Precision and Bias[4]

19.1 *Interlaboratory Test Program*—An interlaboratory study of the rosin acid content of three substances, tall oil fatty acids, distilled tall oil, and rosin, was run in 1994. Each of 14 laboratories tested each of the three materials. The design of the experiment, similar to that of Practice E691 and a within-between analysis of the data are given in ASTM Research Report No. RR:D01-1087.

19.2 *Test Result*—The precision information given below for the rosin acid content of pine chemicals products is for the comparison of two test results, each of which is the average of three test determinations as follows:

19.2.1 *Repeatability Limit*—95 % (within laboratory) = 0.6 %.

19.2.2 *Reproducibility Limit*—95 % (between laboratories) = 1.4 %.

19.3 These terms (repeatability limit and reproducibility limit) are used as specified in Practice E177. The respective standard deviations among test results, related to the above numbers by the factor of 2.8, are as follows:

19.3.1 Repeatability standard deviation = 0.2 %.

19.3.2 Reproducibility standard deviation = 0.5 %.

19.4 *Bias*—These test methods have no bias because rosin acid content is defined only in terms of these test methods.

20. Keywords

20.1 fatty acids; Glidden method; pine chemicals; rosin; tall oil; tall oil fatty acid; tall oil rosin; Wolfe Method

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1087. Contact ASTM Customer Service at service@astm.org.

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