Designation: D 5768 – 95

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
Reprinted from the Annual Book of ASTM Standards. Copyright ASTM

Standard Test Method for Determination of Iodine Value of Tall Oil Fatty Acids[1]

This standard is issued under the fixed designation D 5768; 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 Wijs procedure for determination of unsaturation (iodine value) of tall oil fatty acids.

1.2 Iodine value is a measure of the unsaturation of oils and fatty acids and is expressed in terms of the number of centigrams of iodine per gram of sample (weight percent of absorbed iodine).

1.3 When this test method is used to determine the iodine value of fatty acids having conjugated systems, the result is not a measure of total unsaturated, but rather is an empirical value that affords a comparison of unsaturation. Total unsaturation of conjugated systems may be measured in accordance with Test Method D 1541.

1.4 The test method described here is not reliable for tall oil fatty acids containing an appreciable quantity of rosin.

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 1193 Specification for Reagent Water[2]

D 1541 Test Method for Total Iodine Value of Drying Oils and Their Derivatives[3]

D 1959 Test Method for Iodine Value of Drying Oils and Fatty Acids[3]

3. Significance and Use

3.1 The iodine value of a fatty acid product is a measure of the unsaturated fatty acid content of that product and consequently a measure of the ease of oxidation or drying capacity of that fatty acid product.

3.2 This test method measures the unsaturation as iodine value by addition of an iodine/chlorine reagent. The amount of reagent absorbed is determined by back titrating the excess reagent and comparing it to a blank determination.

3.3 In samples containing conjugated double bonds, the iodine value obtained is empirical since the reagent does not react stoichiometrically with conjugated unsaturation. Where no conjugation is present, the iodine value obtained is a measure of the total unsaturation. By using proper specimen weights, the empirical values obtained are useful for comparative purposes.

3.4 This test method was developed in order to replace the hazardous solvent, carbon tetrachloride, used in Test Method D 1959 with the less hazardous and more available solvent, isooctane. Other solvents, such as cyclohexane, may also be satisfactory replacements for carbon tetrachloride. As data on the satisfactory use of other solvents becomes available, this test method will be amended to include those solvents.

3.5 This test method should have applicability to fatty acids and oils other than tall oil fatty acid but that possibility has not been investigated.

4. Apparatus

4.1 *Bottles*—Glass-stoppered bottles or Erlenmeyer flasks of 250-mL capacity.

4.2 *Pipets*—20 and 25-mL capacity.

5. Reagents

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.[4] 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 I of Specification D 1193.

5.3 *Acetic Acid (Glacial) 17.4 M*—Verify the absence of substances reducing permanganate as follows: Dilute 2 mL of the acid with 10 mL of water and add 0.1 mL of 0.1 *N* potassium permanganate ($KMnO_4$) solution. The pink color

---

[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.

Current edition approved Sept. 15, 1995. Published November 1995.

[2] *Annual Book of ASTM Standards*, Vol 11.01.

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

[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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

should not be entirely discharged at the end of 2 h.[5]

5.4 *Isooctane*.

5.5 *Chlorine (99.8 % Cl)*—**Precaution:** See Note 1. Commercial grades of chlorine available in cylinders may be used, provided the gas is dried by passing through concentrated sulfuric acid (H_2SO_4, sp gr 1.84) before passing it into the iodine solution. Alternatively, the chlorine may be prepared by allowing concentrated hydrochloric acid (HCl, sp gr 1.19) to drop onto potassium permanganate ($KMnO_4$) or onto a mixture of $KMnO_4$ and manganese dioxide (MnO_2). Dry the gas thus generated by passing it through concentrated H_2SO_4.

NOTE 1—**Precaution:** Extremely hazardous. For specific hazard information and guidance, see supplier's Material Safety Data sheets.

5.6 *Potassium Iodide Solution (150 g/L)*—Dissolve 150 g of potassium iodide (KI) in water and dilute to 1 L.

5.7 *Sodium Thiosulfate, Standard Solution (0.1 N)*—Dissolve 24.8 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in water and dilute to 1 L. Standardize against potassium dichromate ($K_2Cr_2O_7$)[6] as follows: Weigh to 0.1 mg, by difference from a weighing bottle, 0.16 to 0.22 g of $K_2Cr_2O_7$ that has been finely ground and then dried to constant weight at 105 to 110°C prior to use. Place the $K_2Cr_2O_7$ in a 500-mL flask or bottle and dissolve in 25 mL of water. Add 5 mL of concentrated hydrochloric acid (11.6 *M*) and 20 mL of KI solution, and rotate to mix. Allow to stand for 5 min and then add 100 mL of water. Titrate with the $Na_2S_2O_3$ solution, while shaking constantly, until the yellow color has almost disappeared. Add 1 to 2 mL of starch indicator solution and continue the titration, adding the $Na_2S_2O_3$ solution slowly until the blue color has just disappeared. Calculate the normality, *N*, of the $Na_2S_2O_3$ as follows:

$$N = (A \times 20.39) / C \quad (1)$$

where:

A = $K_2Cr_2O_7$ used, g, and

C = $Na_2S_2O_3$ solution required for titration of the $K_2Cr_2O_7$, mL.

5.8 *Starch Indicator Solution*:

5.8.1 Use soluble starch that will pass the following test for sensitivity: Make a paste with 1 g of starch and a small amount of cold water. Add, while stirring, 200 mL of boiling water. Dilute 5 mL of this solution with 100 mL of water and add 0.05 mL of 0.1 *N* iodine solution. The deep blue color produced must be discharged by 0.05 mL of 0.1 *N* $Na_2S_2O_3$ solution.

5.8.2 Make a homogeneous paste of 10 g of soluble starch in cold water. Add to this 1 L of boiling water. Stir rapidly and cool. Salicylic acid (1.25 g/L) may be added to preserve the indicator. If long storage is required, keep the solution in a refrigerator at 4 to 10°C (40 to 50°F). Prepare fresh indicator when the end point of the titration from blue to colorless fails to be sharp.

5.9 *Wijs Solution*—**Precaution:** See Note 1. Dissolve 13.0 g of iodine in 1 L of acetic acid. Gentle heat may be necessary to promote solution. Cool and remove a small quantity (100 to 200 mL) and set aside in a cool place for future use. Pass dry chlorine gas into the iodine solution until the original titration is not quite doubled. A characteristic color change takes place in the Wijs solution when the desired amount of chlorine has been added; this may be used to assist in judging the end point. A convenient procedure is to add a small excess of chlorine and bring back to the desired titration by addition of some of the original iodine solution that was taken out at the beginning. Determine the strength of the original iodine solution and the finished Wijs solution by titration against 0.1 *N* $Na_2S_2O_3$ solution as directed in 6.4.

TABLE 1 Specimen Weights

Iodine Value	Normal Fatty Acids, 100 to 150 % Excess of Reagent, g	Conjugated Fatty Acids, 115 to 135 % Excess of Reagent, g
Less than 3	10	
3	8.46 to 10.57	
5	5.08 to 6.35	
10	2.54 to 3.17	
20	0.85 to 1.59	
40	0.64 to 0.79	
60	0.42 to 0.53	
80	0.32 to 0.40	0.34 to 0.37
90	0.28 to 0.35	0.30 to 0.33
100	0.25 to 0.32	0.27 to 0.30
110	0.23 to 0.29	0.24 to 0.27
120	0.21 to 0.26	0.22 to 0.25
130	0.20 to 0.24	0.21 to 0.23
140	0.18 to 0.23	0.19 to 0.21
150	0.17 to 0.21	0.18 to 0.20
160	0.16 to 0.20	0.17 to 0.18
170	0.15 to 0.19	0.16 to 0.17
180	0.14 to 0.18	0.15 to 0.16

NOTE 2—Iodine monochloride (Wijs solution) can be purchased commercially from various laboratory supply houses. The halogen ratio should be checked prior to use.

The halogen ratio, that is, the ratio of iodine to chlorine, can be determined by the Graupner-Aluise method.[7]

6. Procedure

6.1 Melt the sample if it is not already liquid (do not exceed 10–15°C above the melting point of the sample) and filter, if necessary, to remove foreign materials.

6.1.1 All glassware used in this test must be completely clean and dry.

6.2 Place into a 250-mL flask or bottle an amount of the sample such that there will be an excess of Wijs solution of 125 ± 10 % for conjugated fatty acids and 125 ± 25 % for normal or nonconjugated fatty acids. Specimen weights meeting this requirement are shown in Table 1. Add 20 mL of isooctane and swirl to dissolve.

6.3 Pipet 25 mL of Wijs solution into the flask containing the specimen and also into each of at least two additional flasks to be carried through as blanks. Stopper the flasks and swirl the flask containing the specimen to ensure an intimate mixture. Store the flask in a dark place for 1 h at a temperature of 25 ± 5°C.

[5] "Analytical Reagents, ACS Specifications," American Chemical Society, Washington, DC, 1960.

[6] National Institute of Standards and Technology Standard Reference Material No. 136 of potassium dichromate is recommended for this purpose and should be treated as directed in the certificate of analysis accompanying the standard sample. Available from NIST, Gaithersburg, MD.

[7] Graupner, A. J., and Aluise, V. A., "A New Rapid Titration Method for Determining the Halogen Ratio of Wijs Solution and of Iodine Monochloride," *Journal*, American Oil Chemists' Soc., February 1966, p. 81.

6.4 Remove the flasks from storage and add 20 mL of KI solution and 100 mL of water. Titrate with $Na_2S_2O_3$ solution, adding it gradually and with constant and vigorous shaking (see Note 3). Continue the titration until the yellow color has almost disappeared. Add 1 to 2 mL of starch indicator solution and continue the titration until the blue color has just disappeared.

NOTE 3—Mechanical stirring is satisfactory for agitating during the addition of the $Na_2S_2O_3$ solution.

7. Calculation

7.1 Calculate the iodine value, *I*, as follows:

$$I = [(B - V)N \times 12.69] / S \quad (2)$$

where:

V = $Na_2S_2O_3$ solution required for titration of the specimen, mL,
B = $Na_2S_2O_3$ solution required for titration of the blank, mL,
N = normality of the $Na_2S_2O_3$ solution, and
S = sample used, g.

8. Precision and Bias

8.1 Precision and bias have not been determined, however, preliminary results indicate that the precision and bias of this test method are similar to that of Test Method D 1959.

9. Keywords

9.1 iodine value; tall oil fatty acids