



Standard Test Method for Iodine Value of Drying Oils and Fatty Acids¹

This standard is issued under the fixed designation D 1959; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method covers the Wijs procedure for determination of unsaturation (iodine value) in drying oils. It is applicable to all natural and synthetic drying oils and their fatty acids.

1.2 When the iodine value is determined on oils or fatty acids having conjugated systems, the result is not a measure of total unsaturation, but rather is an empirical value that affords a comparison of total unsaturation.

1.3 To obtain the total iodine value on conjugated samples, use Test Method D 1541.

NOTE 1—This test method is essentially equivalent to Test Methods D 2075 and D 2078.

1.4 *This standard may involve hazardous materials, operations, and equipment. 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.* For specific hazard statements, see Section 8.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

D 1541 Test Method for Total Iodine Value of Drying Oils and Their Derivatives³

D 2075 Test Method for Iodine Value of Fatty Amines, Amidoamines, and Diamines³

D 2078 Test Method for Iodine Value of Fatty Quarternary Ammonium Chlorides³

D 5768 Test Method for Iodine Value of Tall Oil Fatty Acids³

3. Terminology

3.1 Definitions:

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 D 01.32 on Drying Oils.

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² Annual Book of ASTM Standards, Vol 11.01.

³ Annual Book of ASTM Standards, Vol 06.03.

3.1.1 *iodine value*—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).

3.1.1.1 *Discussion*—Total unsaturation of conjugated systems may be measured in accordance with Test Method D 1541. The Wijs iodine value method is not reliable for tall oil fatty acids containing an appreciable quantity of rosin acids.

4. Summary of Test Method

4.1 The determination of the iodine value of oils containing isolated double bonds is based on the absorption of halogen under conditions selected to promote stoichiometrical results.

5. Significance and Use

5.1 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.

5.2 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.

6. Apparatus

6.1 *Bottles*—Glass-stoppered bottles or wide-mouth (Note 2) Erlenmeyer flasks of 500-mL capacity.

NOTE 2—Wide-mouth bottles or flasks are essential if stirring is done by mechanical means.

6.2 *Pipets*, 20 and 25-mL capacity.

7. Reagents

7.1 *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.

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

7.3 Acetic Acid (Glacial) (Caution—see 8.1)—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 (KMnO₄) solution. The pink color should not be entirely discharged at the end of 2 h.⁵

7.4 Solvent: isooctane or fresh cyclohexane to replace long used carbon tetrachloride, now banned as too hazardous (**Caution—See 8.2**).

7.5 Carbon Tetrachloride (CCl₄) (Caution—See 8.2).

7.6 Chlorine (99.8% Cl) (Caution—see 8.3)—Commercial grades of chlorine available in cylinders may be used, provided the gas is dried by passing through concentrated sulfuric acid (H₂SO₄, sp gr 1.84) before passing it into the iodine solution (see 7.10). Alternatively, the chlorine may be prepared by allowing concentrated hydrochloric acid (HCl, sp gr 1.19) to drop onto potassium permanganate (KMnO₄) or onto a mixture of KMnO₄ and manganese dioxide (MnO₂). Dry the gas thus generated by passing it through concentrated H₂SO₄.

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

7.8 Sodium Thiosulfate, Standard Solution (0.1 *N*)—Dissolve 24.8 g of sodium thiosulfate (Na₂S₂O₃·5H₂O) in water and dilute to 1 L. Standardize against potassium dichromate (K₂Cr₂O₇)⁶ as follows: Weigh to 0.1 mg, by difference from a weighing bottle, 0.16 to 0.22 g of K₂Cr₂O₇ that has been finely ground and then dried to constant weight at 105 to 110°C prior to use. Place the K₂Cr₂O₇ in a 500-mL flask or bottle and dissolve in 25 mL of water. Add 5 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) 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 Na₂S₂O₃ 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 Na₂S₂O₃ solution slowly until the blue color has just disappeared. Calculate the normality, *N*, of the Na₂S₂O₃ as follows:

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

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.

⁵ "Analytical Reagents, ACS Specifications," Am. Chemical Soc., 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.

where:

A = K₂Cr₂O₇ used, g, and

C = Na₂S₂O₃ solution required for titration of the K₂Cr₂O₇, mL.

7.9 Starch Indicator Solution:

7.9.1 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* Na₂S₂O₃ solution.

7.9.2 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.

7.10 Wijs Solution (Caution—see 8.4) (Note 3)—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* Na₂S₂O₃ solution, as directed in .

NOTE 3—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 as follows:

Reagents:

(1) **Potassium Iodate Solution (0.04 *N*)**—Dry potassium iodate (KIO₃) for 1 h at 105 to 110°C. Weigh 2.1402 g of the dried salt, dissolve in water, dilute to 1 L in a volumetric flask, and mix.

(2) **Hydrochloric Acid (1+1)**—Dilute concentrated HCl (sp gr 1.19) with an equal volume of water.

(3) **Potassium Iodide Solution (150 g/L)** (See 7.6).

Procedure:

(1) Measure 50 mL of HCl (1+1) and 50 mL of CCl₄ into a 500-mL iodine flask. By means of a pipet, transfer 25.00 mL of the Wijs solution to the flask, and shake. Titrate the free iodine in the violet-colored CCl₄ layer with the KIO₃ solution to a colorless end point using vigorous shaking.

(2) On a second 25.00-mL portion of the Wijs solution, determine the total halogen by adding 150 mL of water, 15 mL of KI solution, and titrating with standard Na₂S₂O₃ solution to a starch end point.

Calculation—Calculate the iodine to chlorine ratio, *R*, as follows:

$$R = (V_1N_1 + V_2N_2)/(V_1N_1 - V_2N_2)$$

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, Am. Oil Chemists' Soc.*, February 1966, p. 81.