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AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
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Standard Test Method for
Iodine Value of Drying Oils and Fatty Acids[1]

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 Water[2]

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

D 2075 Test Method for Iodine Value of Fatty Amines, Amidoamines, and Diamines[3]

D 2078 Test Method for Iodine Value of Fatty Quarternary Ammonium Chlorides[3]

D 5768 Test Method for Iodine Value of Tall Oil Fatty Acids[3]

3. Terminology

3.1 *Definitions:*

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

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[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.

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 ($KMnO_4$) 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 (*CCl_4) (**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 (H_2SO_4, 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 ($KMnO_4$) 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.

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 ($Na_2S_2O_3{\cdot}5H_2O$) 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 (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 $Na_2S_2O_3$ 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:

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

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.

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* $Na_2S_2O_3$ 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* $Na_2S_2O_3$ 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 (KIO_3) 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 CCl_4 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 CCl_4 layer with the KIO_3 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 $Na_2S_2O_3$ solution to a starch end point.

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

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

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[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.

[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.

where:

V_1 = $Na_2S_2O_3$ solution required for total halogen, mL,
N_1 = normality of $Na_2S_2O_3$ solution,
V_2 = KIO_3 solution required for fre iodine, mL, and
N_2 = normality of the KIO_3 solution

8. Hazards

8.1 *Acetic Acid, Glacial* is corrosive and may cause burns to the skin and eyes. Wash clothing before reusing. See suppliers' Material Safety Data Sheet for further information.

8.2 *Carbon Tetrachloride* is a very hazardous liquid. It is absorbed by the skin. Its vapor is hazardous through inhalation. It is an irritant to the skin and eyes; avoid breathing (TLV-10 PPM). It causes liver and kidney damage and has cumulative effects. Use with adequate ventilation (in a hood) and wear rubber gloves. See suppliers' Material Safety Data Sheet.

8.3 *Chlorine* is a poisonous, strongly irritating gas. Exercise care in dispensing chlorine from a cylinder or in manufacture of chlorine by the action of hydrochloric acid on potassium permanganate. Wijs and other similar solutions should be prepared in a hood. For further information, see the Chlorine Manual of the Chlorine Institute[8] or suppliers' Material Safety Data Sheet.

8.4 *Wijs Solution*, iodine monochloride dissolved in glacial acetic acid, is corrosive and may cause burns to the skin and eyes. Wash clothing before reusing. Wijs solution should not be heated above 30°C as it may liberate chlorine, which is a strong, irritating gas. Wijs solution can be purchased commercially or prepared in a hood.

9. Procedure

9.1 Melt the sample if it is not already liquid (the temperature during melting and filtering should not exceed 10 to 15°C above the melting point of the sample) and filter (drying oils of high viscosity should not be filtered) through filter paper to remove any solid impurities and the last traces of moisture. The sample must be absolutely dry.

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

9.2 Place in a 500-mL flask or bottle, to which has been added 20 mL of solvent, an amount of sample such that there will be an excess of Wijs solution of 125 ± 10 % for conjugated oils or fatty acids and 125 ± 25 % for normal or nonconjugated oils or fatty acids. Specimen weights meeting this requirement are shown in Table 1.

NOTE 4—For dehydrated castor oil and fatty acids use a specimen weight between 0.11 to 0.13 g.

9.3 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. For conjugated oils or fatty acids such as tung, oiticica, and dehydrated castor, allow the absorption to proceed for 1 h at 25 ± 1°C.

TABLE 1 Specimen Weights

Iodine Value	Normal Oils and Fatty Acids, 100 to 150 % Excess of Reagent, g	Conjugated Oils and 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	0.245 to 0.27
120	0.21 to 0.26	0.225 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
190	0.13 to 0.17	0.14 to 0.16
200	0.12 to 0.16	0.135 to 0.15
210	0.12 to 0.15	0.13 to 0.14
220	0.12 to 0.14	0.12 to 0.135

9.4 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 (Note 5). 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 5—Mechanical stirring is very satisfactory for agitating during the addition of the $Na_2S_2O_3$ solution.

10. Calculation

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

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

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.

11. Precision and Bias

11.1 Precision and bias have not been determined.

12. Keywords

12.1 drying oils; fatty acids; iodine value

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[8] Available from Chlorine Institute, 342 Madison Ave., New York, NY 10173.