Designation: D 1541 – 97

Standard Test Method for Total Iodine Value of Drying Oils and Their Derivatives[1]

This standard is issued under the fixed designation D 1541; 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[2] covers the determination of total iodine value.

1.2 This test method is applicable to oils, fatty acids, and bodied oils. While this test method is applicable to all oils and fatty acids and bodied oils, it is particularly useful for those drying oils or derivatives that have conjugated unsaturation.

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 whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Sections 6 and 7.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[3]

D 1959 Test Method for Iodine Value of Drying Oils and Fatty Acids[4]

3. Terminology

3.1 *Definitions:*

3.1.1 *total iodine value*—a measure of the total unsaturation present in fats and oils (Note 1), expressed as the number of centigrams of iodine equivalent to the unsaturation present in 1 g of sample (weight percent of absorbed iodine).

NOTE 1—When the total iodine value is determined on oils having conjugated systems, the result is a measure of the total unsaturation. This is in contrast to the iodine value method described in Test Method D 1959 which determines only part of the total unsaturation of conjugated systems.

4. Significance and Use

4.1 This test method measures the total amount of unsaturation including conjugated unsaturation by addition of bromine in a catalyzed bromine solution to the double bonds. The amount of bromine absorbed is determined by back titration of the excess bromine, and then compared to a blank determination. This test method is preferred over Test Method D 1959 for products containing conjugated unsaturation.

5. Apparatus

5.1 *Iodine Flasks*, glass-stoppered, of 250-mL capacity.

NOTE 2—The test may be run either in a photographic-type darkroom under red safelight illumination[5] or in a darkened laboratory in which the light intensity is adjusted to 0.5 footcandle (5.4 1x) or less. The darkroom with red safelights permits the use of clear flasks. If the test shall be run in a darkened laboratory, low-actinic (amber) flasks, or clear flasks protected from light by covering as described below, must be used. Alternative modes of using clear flasks in a darkened laboratory are described as follows. The type of covering is left to the discretion of the analyst:

(1) Place the clear iodine flask in a suitable metal can so that the neck of the flask is level with the can rim. Over the top of the can, place a piece of heavy cardboard, with a hole precut in the center to just fit over the neck of the flask; the top of the flask should just protrude out of the hole in the cardboard cover. Then run the analysis as usual in a darkened laboratory.

(2) Wrap heavy aluminum foil around the iodine flasks so as to cover all but the top rim. The foil can be then removed at the latter stage of titration. Run the analysis in a darkened laboratory.

(3) Place the flask in an opaque bag that has a drawstring neck. The rim of the iodine flask should just protrude from the bag to allow addition of reagent.

5.2 *Graduates*, 5, 25, and 50-mL capacity.

5.3 *Volumetric Pipets*, 10, 20, and 50-mL capacity.

NOTE 3—The bulb of the 50-mL pipet should be covered with aluminum foil.

5.4 *Buret*, 50-mL capacity graduated in 0.1-mL divisions.

5.5 *Weighing Device for Sample*—A small, wide-mouth vial, fitted with a cork stopper and medicine dropper, may be used to weigh the sample by difference. Alternatively, the sample may be weighed directly into a 1-mL microbeaker, and carefully dropped into the iodine flask.

5.6 *Photoelectric Light Meter*—Any suitable meter for measuring room illumination in footcandles. If a darkroom and red safelight illumination are to be used, a meter is not required.

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[1] This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materialsand is the direct responsibility of Subcommittee D01.32on Drying Oils.

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[2] This procedure is essentially identical with that of Planck, R. W., Pack, F. C., and Goldblatt, L. A., as published in the *Journal*, Am. Oil Chemists' Soc., Vol 30, 1953, p. 417, using the Rosenmund-Kuhnhenn reagent. Previously Benham, G. H., and Klee, L. J., published data on the use of this reagent for determining unsaturation in the *Journal*, Am. Oil Chemists' Soc., Vol 27, 1950, pp. 127–130.

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

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

[5] The sole source of supply of the red safelights Wratten No. 1 known to the committee at this time is Eastman Kodak Co., 343 State St. Rochester, NY 14650. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

5.7 *Erlenmeyer Flasks*, three, 250-mL.

5.8 *Volumetric Flasks*, four, 1-L, glass-stoppered.

5.9 *Bottle, Amber*, one, 4-L, glass-stoppered.

6. Reagents

6.1 *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.[6] 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.

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

6.3 Solvents: isooctane or fresh cyclohexane to replace long used carbon tetrachloride now banned as hazardous (**Precaution**—See 7.1).

6.4 *Carbon Tetrachloride* (CCl_4)—(**Precaution**—See 7.1)

6.5 *Mercuric Acetate Solution*—Dissolve 25 g of mercuric acetate ($Hg(C_2H_3O_2)_2$) (**Precaution**—See 7.2) in glacial acetic acid (CH_3COOH) and dilute to 1 L with glacial acetic acid. (**Precaution**—See 7.3)

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

6.7 *Rosenmund-Kuhnhenn Reagent*—Place 40 mL of glacial acetic acid (CH_3COOH) in each of three 250-mL Erlenmeyer flasks. To the first, add slowly 28.4 ± 0.2 g of pyridine, (**Precaution**—See 7.4) with cooling in an ice bath. To the second flask, add slowly 35.5 ± 0.2 g of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) with cooling as above. When cool, add the contents of the second flask to the contents of the first flask, with further cooling. To the third flask, add the contents of a 1-oz (28.4-g) bottle (or ampule) of bromine. Add the bromine solution to the mixture of the first two solutions. Transfer to a 1-L volumetric flask with the aid of glacial acetic acid, and make up to 1 L with glacial acetic acid. Mix thoroughly and transfer to a 4-L, amber, glass-stoppered bottle. Add an additional 2.5 L of glacial acetic acid, making a total of 3.5 L of reagent. In this way, the weighing or measuring of bromine is eliminated. The reagent is approximately 0.1 *N* with respect to bromine. Fresh reagent should be prepared if the bromine concentration drops below 0.99 *N*. The normality of the reagent can be checked by running a reagent blank titration as described in 8.4, but eliminating the 1-h standing time.

NOTE 4—The stock bottle containing the Rosenmund-Kuhnhenn reagent should be kept stoppered when it is not in use to minimize loss of bromine.

6.8 *Sodium Thiosulfate, Standard Solution* (0.1 *N*) (**Precaution**—See 7.1-7.7)—Dissolve 24.8 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in water and dilute to 1 L. Add 0.5 g of sodium carbonate (Na_2CO_3) and a few drops of chloroform, as a preservative. Standardize against potassium iodate (KIO_3) primary standard as follows: Weigh, to the nearest 0.1 mg, into a 250-mL Erlenmeyer flask about 0.12 to 0.17 g of the KIO_3 and dissolve in 50 mL of water. Add 2 g of KI, and as soon as this is dissolved, 1 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) diluted to 10 mL. Titrate the liberated iodine immediately with the $Na_2S_2O_3$ solution, using starch indicator near the end point. Calculate the normality of the $Na_2S_2O_3$ solution as follows:

$$\text{Normality} = W/(0.03567 \times V) \quad (1)$$

where:

W = KIO_3 used, g, and

V = $Na_2S_2O_3$ solution required for titration of the KIO_3, mL.

NOTE 5—The $Na_2S_2O_3$ may be standardized against potassium dichromate ($K_2Cr_2O_7$), if desired, as described in Test Method D 1959.

6.9 *Starch Indicator Solution*—Make a paste with 10 g of 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 as a preservative. If long storage is required, keep the solution in a refrigerator at 40 to 50°F (4 to 10°C). Prepare fresh indicator when the end point of the titration from blue to colorless fails to be sharp.

7. Hazards

7.1 *Carbon Tetrachloride* is a very hazardous liquid. It is absorbed by the skin. Its vapor is hazardous through inhalation. It is an irritant to 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 supplier's Material Safety Data Sheet.

7.2 *Mercuric Acetate*—Mercuric acetate and other organic mercury compounds are poisonous by oral ingestion and can be absorbed by the skin. Overheating results in decomposition. Do not flush mercuric acetate and its solutions down a drain but disposed of as hazardous wastes. See supplier's Material Safety Data Sheet.

7.3 *Acetic Acid, Glacial*, is corrosive and may cause burns to the skin and eyes. See supplier's Material Safety Data Sheet.

7.4 *Pyridine* is a flammable liquid and hazardous by inhalation. It is an eye, skin and respiratory irritant (TLV-5 ppm). May cause liver and kidney damage. Use with adequate ventilation; perform all operations in a hood. See supplier's Material Safety Data Sheet.

7.5 *Sulfuric Acid* is corrosive to skin, eyes, and mucous membranes in form of liquid, mist or fumes. It causes severe burn. Take care to prevent the contact of the acid with eyes, skin, or on clothing. In making dilute solutions, always add the acid to water with care. See supplier's Material Safety Data Sheet.

7.6 *Bromine* is a powerful oxidizer and may cause fire on contact with organic matter. Liquid and vapor may cause severe burns. The gas is toxic (TLV-0.1 ppm) and, as such, is a serious respiratory irritant. Use with adequate ventilation (in a hood); avoid contact with skin and eyes. Handle bromine with rubber gloves. See supplier's Material Safety Data Sheet.

[6] *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.

7.7 *Chloroform* is a hazardous liquid that can be absorbed through the skin. Its vapor is hazardous through inhalation. It is a narcotic. Use only with adequate ventilation (in a hood). It is also extremely flammable. See supplier's Material Safety Data Sheet.

8. Procedure

8.1 To a 250-mL glass-stoppered iodine flask (Note 2), add 5 mL of solvent. In this dissolve the specimen, weighed to 0.1 mg, using the weight of specimen prescribed in Table 1.

NOTE 6—The specimen weight is so chosen as to result in a 200 to 250 % excess of reagent of the amount absorbed. After running the analysis, use the following calculation to determine whether the proper specimen size has been used:

$$E, \% = [V_1/(B - V)] \times 100 \quad (2)$$

where:

E = excess reagent,
V_1 = $Na_2S_2O_3$ solution required for titration of the specimen, mL, and
B = $Na_2S_2O_3$ solution required for titration of the blank, mL.

If the reagent excess falls outside these limits, the analysis must be repeated using the proper specimen size.

8.2 Make sure that the specimen is completely dissolved, and then in a darkened room of light intensity preferably less than 0.5 footcandle (5.4 lx), as measured with a light meter, or in a darkroom under red safelight illumination, pipet into the flask 10.0 mL of the $Hg(C_2H_3O_2)_2$ solution. Swirl the flask two or three times, add 50.0 mL of the Rosenmund-Kuhnhenn reagent, and note the time. Stopper the flask, add a small amount of KI solution to the well of the flask to seal it, swirl until the contents are well mixed (2 or 3 s), and place the flask in a dark place at a temperature of 23 to 27°C.

8.3 Exactly 1 h after the addition of the Rosenmund-Kuhnhenn reagent to the specimen, bring the flask out into the darkened laboratory (or darkroom under red safelight), add 20.0 mL of KI solution by pipet, swirl two or three times, add 20 mL of water, swirl again, stopper the flask, and allow it to stand for 1 min. Then, using normal illumination, rinse the stopper and neck of the flask with about 10 mL of water.

8.4 Titrate the released iodine with $Na_2S_2O_3$ solution by adding rapidly from the 50-mL buret, with continuous agitation, about 25 to 30 mL (all but 5 to 10 mL) of the required $Na_2S_2O_3$ solution. Then, if low-actinic flasks are being used, transfer the contents to a colorless flask, rinsing three times with a total of about 30 mL of water, and complete the titration in the usual manner using starch indicator when near the end point. If clear flasks are used, there is no need to transfer. Simply add 30 mL of water and complete the titration as described, using starch indicator solution when near the end point.

8.5 With each group of samples, conduct at least two blank determinations following the same procedure as described in 8.1-8.4, except that no sample is added. In the titration, run into the flask about 40 to 45 mL of $Na_2S_2O_3$ solution before completing the titration as described.

TABLE 1 Iodine Value in Relation to Weight of Specimen

Total Iodine Value	Weight of Specimen, g	
	200 % Excess	250 % Excess
100	0.212	0.182
125	0.169	0.145
150	0.141	0.121
175	0.121	0.104
200	0.106	0.091
225	0.094	0.081
250	0.085	0.073
275	0.073	0.066
300	0.071	0.061

9. Calculation and Report

9.1 Calculate the total iodine value, T, as follows:

$$T = [(B - V) \times N \times 12.69]/S \quad (3)$$

where:

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

9.2 Report the total iodine value to the first decimal place.

10. Precision and Bias

10.1 *Repeatability*—Two results obtained by the same operator should be considered suspect, at the 95 % confidence level, if they differ by more than 3.6 in iodine level (3.6 % absolute).

10.2 *Reproducibility*—Two results, each the mean of two determinations, obtained by operators in different laboratories should be considered suspect, at the 95 % confidence level, if they differ by more than 6.1 in iodine value (6.1 % absolute).

10.3 *Bias*—Bias has not been determined.

11. Keywords

11.1 drying oils; iodine value; iodine value—drying oils