Designation: D 2075 – 92 (Reapproved 1998)

Standard Test Method for Iodine Value of Fatty Amines, Amidoamines, and Diamines[1]

This standard is issued under the fixed designation D 2075; 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 method was prepared jointly by the American Society for Testing and Materials and the American Oil Chemists' Society.

1. Scope

1.1 This test method (Note 1) covers the determination of the iodine value of fatty amines, diamines, and amidoamines by the Wijs procedure.

NOTE 1—This test method is essentially equivalent to Test Methods D 2078 and D 1959. Use of mercuric acetate permits reduced reaction time compared to Test Methods D 2078 (30 min) and D 1959 (1 h).

1.2 *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]

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

3. Terminology

3.1 *Definition:*

3.1.1 *iodine value*—a measure of the unsaturation of the alkyl group or groups, expressed in terms of percent iodine absorbed.

4. Significance and Use

4.1 This test method measures the unsaturation of the alkyl groups as iodine value by addition of an iodine/chlorine reagent.

4.2 Where no conjugated double bonds are present, the iodine value obtained is a measure of the total unsaturation, and the values obtained are useful for comparative purposes.

4.3 If conjugated unsaturation is known to be present, use Test Method D 1541.

5. Apparatus

5.1 *Bottles*—Glass-stoppered bottles or wide-mouth Erlenmeyer flasks of 500-mL capacity.

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

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

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.[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.

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

6.3 *Acetic Acid* (*Glacial*)—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]

6.4 *Chlorine* (*99.8 % Cl*)—Commercial grades of chlorine available in cylinders may be used, provided the gas is dried by

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[1] This 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 D01.32 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.

[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, 1950.

passing through concentrated sulfuric acid (H_2SO_4, sp gr 1.84) before passing it into the iodine solution (see 6.10). 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 H_2SO_4 (sp gr 1.84).

6.5 *Chloroform*.

6.6 *Mercuric Acetate Solution*—Dissolve 2.5 g of mercuric acetate ($Hg(C_2H_3O_2)_2$) in glacial acetic acid (CH_3COOH) and make up to 100 mL.

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

6.8 *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 the nearest 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 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:

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

where:

A = weight of $K_2Cr_2O_7$ used, g, and

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

6.9 *Starch*—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.

6.10 *Starch Indicator Solution*—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, the solution shall be kept in a refrigerator at 4 to 10°C (40 to 50°F). Fresh indicator shall be prepared when the end point of the titration from blue to colorless fails to be sharp.

6.11 *Wijs Solution* (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 7.6 and 7.7.

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 Lopez Method,[7] as follows:

(1) *Iodine Content*—Pour 150 mL of saturated chlorine water into a 500-mL Erlenmeyer flask and add some glass beads. Pipet 5 mL of Wijs solution into the flask containing the saturated chlorine water. Shake and heat to boiling. Boil briskly for 10 min, cool, and add 30 mL of 2 % sulfuric acid (H_2SO_4) and 15 mL of KI solution. Mix well and titrate immediately with 0.1 *N* sodium thiosulfate ($Na_2S_2O_3$) solution to a starch end point.

(2) *Total Halogen Content*—Pour 150 mL of recently boiled water into a clean, dry 500-mL Erlenmeyer flask. Add 15 mL of KI solution. Pipet 20 mL of Wijs solution into the flask and mix well. Titrate immediately with 0.1 *N* $Na_2S_2O_3$ solution to a starch end point.

(3) *Calculation of Halogen Ratio:*

$$R = 2A/(3B - 2A) \quad (2)$$

where:

R = halogen ratio,

A = volume of $Na_2S_2O_3$ required for titration of the iodine, mL, and

B = volume of $Na_2S_2O_3$ required for titration of total halogens, mL

The halogen ratio, that is, the ratio of iodine to chlorine, should be 1.10 ± 0.10.

7. Procedure

7.1 Melt the sample, if it is not already liquid, in a water bath. Mix thoroughly, then weigh to 0.1 mg into two 500-mL flasks specimens of the size given in Table 1.

7.2 Add 20 mL of glacial acetic acid.

NOTE 4—If the specimen does not go into solution, the flask can be slightly warmed at this point until the specimen is dissolved, but the flask must be allowed to cool to room temperature before proceeding to the next step.

7.3 Pipet 25 mL of Wijs solution into each specimen flask and two flasks to be used as blanks, allowing the pipet to drain in the same manner for both specimens and blanks. Add 10 mL of $Hg(C_2H_3O_2)_2$ solution directly after adding the Wijs solution.

7.4 Stopper the flasks immediately and moisten the stopper with KI solution so as to prevent the loss of iodine or chlorine, but guard against the use of a quantity sufficient to run down the inside of the flask. Swirl the flask to obtain a good mixture.

[6] National Institute of Standards and Technology Standard Reference Material 136 (potassium dichromate) is recommended for this purpose and should be treated as directed in the certificate of analysis accompanying the standard sample.

[7] *Journal, American Oil Chemists' Society, September 1951, p. 390.*

TABLE 1 Specimen Weights

Iodine Value		Specimen Weight, g
Less than	10	1.5
	20	0.85 to 1.06
	40	0.64 to 0.79
	60	0.42 to 0.53
	80	0.32 to 0.40
	90	0.28 to 0.35
	100	0.25 to 0.32
	110	0.23 to 0.29
	120	0.21 to 0.27
	130	0.20 to 0.24
	140	0.18 to 0.23
	160	0.16 to 0.20
	180	0.14 to 0.18
	200	0.13 to 0.16

7.5 Store the flasks in a dark place for 3 min at a temperature of 25 ± 5°C. Swirl the flasks occasionally being careful not to allow the solution to crawl up the side of the flask over halfway.

7.6 Remove the flask from storage, and add 20 mL of KI solution, 50 mL of water, and 30 mL of chloroform.

7.7 Titrate with $Na_2S_2O_3$, adding it gradually and with constant vigorous shaking until the yellow color has almost disappeared.

NOTE 5—Mechanical stirring is very satisfactory for agitating during the addition of the $Na_2S_2O_3$.

7.8 Add 2 mL of starch indicator solution, rinsing the neck of the flask, and continue the titration until the blue to brown color begins to disappear. Near the end of the titration it is necessary to shake vigorously, with the stopper inserted, in order to free any iodine that dissolved so that it may be taken up with the KI solution. Only allow the stopper to come into contact with the liquid at this stage.

8. Calculation

8.1 Calculate the iodine value I of fatty amines as follows:

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

where:

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

9. Precision and Bias

9.1 Precision and bias were not established at the time this test method was written. An effort is being made to obtain the precision and, if obtainable, it will be published in future revisions. This test method has been in use for many years, and its usefulness has been well established.

10. Keywords

10.1 amidoamines; diamines; fatty amines; iodine value; Wijs solution