Designation: D 2073 – 92 (Reapproved 1998)$^{\epsilon 1}$

Standard Test Methods for Total, Primary, Secondary, and Tertiary Amine Values of Fatty Amines, Amidoamines, and Diamines by Referee Potentiometric Method[1]

This standard is issued under the fixed designation D 2073; 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.

These methods were prepared jointly by ASTM and the American Oil Chemists' Society.

ϵ^1 Note—Former Footnote 6 was deleted editorially in May 1998.

1. Scope

1.1 These referee test methods cover the potentiometric determination of the total, primary, secondary, and tertiary amine values of fatty amines and diamines, and the total amine value of fatty amidoamines. Test methods for primary, secondary, and tertiary amine values are not applicable to fatty amidoamines.

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.* Specific hazard statements are given in Note 1 and Note 2 and Note 6.1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 2080 Test Method for Average Molecular Weight of Fatty Quaternary Ammonium Chlorides[3]

E 70 Test Method for pH of Aqueous Solutions with the Glass Electrode[4]

3. Terminology

3.1 *Definitions:*

3.1.1 *total amine value*—the number of milligrams of potassium hydroxide (KOH) equivalent to the basicity in 1 g of specimen.

3.1.2 *primary amine value*—the number of milligrams of potassium hydroxide (KOH) equivalent to the primary amine basicity in 1 g of specimen.

3.1.3 *secondary amine value*—the number of milligrams of potassium hydroxide (KOH) equivalent to the secondary amine basicity in 1 g of specimen.

3.1.4 *tertiary amine value*—the number of milligrams of potassium hydroxide (KOH) equivalent to the tertiary amine basicity in 1 g of specimen.

4. Apparatus

4.1 *Air Condenser*, minimum length 650 mm.

4.2 *Erlenmeyer Flask*, wide-mouth, alkali-resistant, borosilicate-glass, 250-mL capacity.

4.3 *Glass Electrode pH Meter*, conforming to the requirements of Test Method E 70 or similar potentiometric titrator.

4.4 *Hot Plate*, with variable heat control.

4.5 *Magnetic Stirrer*, with inert plastic-coated stirring bar.

4.6 *Microburet*, graduated to 0.02 mL and having a capacity of 10 mL.

5. Reagents

5.1 *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.[5] 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 II of Specification D 1193.

5.3 *Acetic Acid, Glacial* (CH_3COOH). (**Warning**—See Note 1).

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[1] These test methods are under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications, and are 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] *Annual Book of ASTM Standards*, Vol 15.05.

[5] *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.

5.4 *Acetic Anhydride*.

5.5 *Chloroform* ($CHCl_3$). (**Warning**—See Note 2).

5.6 *Hydrochloric Acid, Standard Solution* (0.5 *N)*—Add 85 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 1000 mL of isopropyl alcohol in a 2-L volumetric flask. Dilute to volume and mix. Standardize with sodium carbonate to a pH of 3.5.

5.7 *Isopropanol* (1 + 19)—Add 5 mL of water to 95 mL of isopropyl alcohol (99 %).

5.8 *Perchloric Acid, Standard Solution* (0.1 *N)*—Prepare and standardize in accordance with Test Method D 2080.

5.9 *Salicylaldehyde*.

6. Hazards

6.1 Fatty amines and diamines can sensitize and irritate. Wash from clothing and body surfaces immediately on contact.

Note 1—**Warning:** Glacial acetic acid, concentrated hydrochloric acid, 70 to 72 % perchloric acid, and acetic anhydride can cause burns of skin and eyes; the vapor of each is irritating to mucous membranes. Use care in handling these acidic substances. In case of contact flush skin or eyes with plenty of water. The perchloric acid may form explosive mixtures if allowed to come in contact with oxidizable materials (organic substances). Flush spills to drain with plenty of water.

Note 2—**Warning:** The U. S. Food and Drug Administration has declared that chloroform is injurious to health. Care should be used in handling chloroform as it can be absorbed through the skin.

7. Standardization of pH Meter

7.1 Carefully follow the manufacturer's instructions for the particular meter used and standardize at pH's of 4.0 and 7.0.

8. Procedure for Total Amine Value

8.1 Melt the sample, if it is not already liquid, in a water bath. Mix thoroughly, and weigh 0.5 g to the nearest 0.1 mg into a 250-mL low-form beaker. Add 90 mL of $CHCl_3$, 10 mL of isopropyl alcohol solution and boil for 1 min on a hot plate. Cool to room temperature.

8.2 Insert the stirring bar into the beaker and adjust the beaker so that the lower half of each electrode of the pH meter is immersed in the sample. Start the stirrer and adjust the speed so that there is vigorous stirring without spattering.

8.3 Titrate with 0.5 *N* HCl using the millivolt scale. Record the millivolt readings every 1 mL, but in the vicinity of the end point record the millivolt readings every 0.1 mL. Plot a graph showing the millivolts against the millilitres required for titration. The end point is the mid-point of the inflection on the titration curve.

9. Procedure for Primary, Secondary, and Tertiary Amine Values

9.1 Determine the specimen size in accordance with Table 1.

9.2 Melt the sample, if it is not already liquid, in a water bath. Mix thoroughly and accurately weigh the designated specimen size into a 250-mL beaker for the secondary plus tertiary amine value, and into a 250-mL flask for the tertiary amine value. Mark the beaker *S* and the flask *T*.

9.3 To beaker *S* add 90 mL of $CHCl_3$ and boil for 1 min to drive off any free ammonia that may be present. Cool to room temperature. Add 5 to 6 mL of salicylaldehyde and allow to stand for 30 min. After 30 min add 10 mL of isopropanol solution. Insert the stirring bar into the beaker and adjust the beaker so that the lower half of each electrode of the pH meter is immersed in the sample. Start the stirrer and adjust the speed so that there is vigorous stirring without spattering. Titrate with 0.5 *N* HCl using the millivolt scale. Record the millivolt readings every 1 mL, but in the vicinity of the end point record the millivolt readings every 0.1 mL. Plot a graph showing the millivolts against the millilitres required for titration. The end point is the midpoint of the inflection on the titration curve.

TABLE 1 Specimen Weights

Type of Fatty Amine	Specimen Weight	
	Secondary plus Tertiary Amine Value, g	Tertiary Amine Value, g
Primary fatty amine	5	5
Secondary fatty amine	1	5
Tertiary fatty amine	1	1

9.4 To flask *T* add 25 mL of acetic anhydride, 2 mL of acetic acid, and 2 or 3 glass beads to the flask. Attach an air condenser, and reflux on a hot plate for 45 min allowing the condensate to rise only 2 in. (50 mm) in the condenser. Rinse down the condenser and quantitatively transfer the solution with 50 mL of glacial acetic acid into a 250-mL beaker. Cool to room temperature. Insert the stirring bar into the beaker and adjust the beaker so that the lower half of each electrode of the pH meter is immersed in the sample. Start the stirrer and adjust the speed so that there is vigorous stirring without spattering. Titrate with 0.1 *N* $HClO_4$ using the millivolt scale. Record the millivolt readings every 1 mL, but in the vicinity of the end point record the millivolt readings every 0.1 mL. Plot a graph showing the millivolts against millilitres required for titration. The end point is the mid-point of the inflection on the titration curve.

10. Calculations

10.1 Calculate the total amine value as follows:

$$\text{Total amine value} = (V \times N \times 56.1)/S \tag{1}$$

where:

V = HCl required for titration of the specimen 8.3), mL,
N = normality of the HCl solution, and
S = specimen weight used, g.

10.2 Calculate the value of the secondary and tertiary amine groups as follows:

$$\begin{aligned}&\text{Titration S amine value of secondary and}\\&\text{tertiary amine groups} = (V \times N \times 56.1)/S\end{aligned} \tag{2}$$

where:

V = HCl required for titration of the specimen (9.3), mL,
N = normality of HCl solution, and
S = specimen weight used, g.

10.3 Calculate the value of the tertiary amine groups as follows:

$$\text{Titration T amine value of tertiary} \tag{3}$$

$$\text{amine groups} = (V \times N \times 56.1)/S$$

where:

V = $HClO_4$ required for titration of the specimen (9.4), mL,
N = normality of the $HClO_4$ solution, and
S = specimen weight used, g.

10.4 Primary amine value equals total amine value minus the amine value of the secondary and tertiary amine group.

10.5 Secondary amine value equals amine value of the secondary and tertiary amine groups minus the amine value of the tertiary amine groups.

10.6 Tertiary amine value equals amine value of the tertiary amine groups.

11. Precision and Bias

11.1 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.

12. Keywords

12.1 amidoamines; amine values; diamines; fatty amines; potentiometry

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