Designation: D2074 – 07 (Reapproved 2013)

Standard Test Methods for Total, Primary, Secondary, and Tertiary Amine Values of Fatty Amines by Alternative Indicator Method[1]

This standard is issued under the fixed designation D2074; 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 test methods were prepared jointly by ASTM and the American Oil Chemists' Society.

1. Scope

1.1 These alternative test methods cover the indicator procedure for determining the total, primary, secondary, and tertiary amine values of fatty amines. These procedures are not applicable to fatty amidoamines and fatty diamines.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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 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:*[2]
D1193 Specification for Reagent Water

3. Terminology

3.1 *Definitions:*

3.1.1 *primary amine value, n*—the number of milligrams of potassium hydroxide (KOH) equivalent to the primary amine basicity in 1 g of sample.

3.1.2 *secondary amine value, n*—the number of milligrams of potassium hydroxide (KOH) equivalent to the secondary amine basicity in 1 g of sample.

3.1.3 *tertiary amine value, n*—the number of milligrams of potassium hydroxide (KOH) equivalent to the tertiary amine basicity in 1 g of sample.

3.1.4 *total amine value, n*—the number of milligrams of potassium hydroxide (KOH) equivalent to the basicity in 1 g of sample.

4. Apparatus

4.1 *Erlenmeyer Flasks,* wide-mouth, alkali-resistant, borosilicate-glass, 250-mL capacity.

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

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.[3] 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 D1193.

5.3 *Bromphenol Blue Indicator Solution*—Dissolve 0.2 g of bromphenol blue in 100 mL of methanol, ethanol, or isopropanol.

5.4 *Bromcresol Green Indicator Solution*—Dissolve 0.1 g of bromcresol green sodium salt in 100 mL of water.

5.5 *Chloroform* ($CHCl_3$).

5.6 *Hydrochloric Acid, Standard Solution* (0.1 *N*)—Add 17 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 1000 mL of isopropyl alcohol in a 2-L volumetric flask. Make up to volume after cooling to room temperature. Standardize with sodium carbonate using bromcresol green as the indicator.

[1] These test methods are under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.33 on Polymers and Resins.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] *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.

5.7 *Hydrochloric Acid, Standard Solution* (0.2 *N*)—Add 34 mL of concentrated HCl (sp gr 1.19) to 1000 mL of isopropyl alcohol in a 2-L volumetric flask. Make up to volume after cooling to room temperature. Standardize with sodium carbonate using bromcresol green as the indicator.

5.8 *Isopropyl Alcohol (99 %).*

5.9 *Phenyl Isothiocyanate.*

5.10 *Salicylaldehyde.*

6. Procedure for Total Amine Value

6.1 Melt the sample, if it is not already liquid, in a water bath. Mix thoroughly, and accurately weigh 1 to 4 g to 0.1 mg into a 250 mL flask. Add 50 mL of alcohol and boil for 1 min to drive off any free ammonia that may be present. Cool to room temperature.

6.2 Add 5 drops of bromphenol blue indicator and titrate, while swirling, with 0.2 *N* HCl to the yellow end point.

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

7.1 Determine the specimen size as follows:

Amine Value	Specimen Weight, g
10 or less	5
Over 10	2

7.2 Melt the sample if it is not already liquid. Mix thoroughly and accurately weigh the designated specimen size into two 150-mL beakers or 250-mL flasks. Mark them *S* and *T*. Add 50 mL of $CHCl_3$ to each flask (or beaker) and boil for 1 min on a hot plate to drive off any free ammonia. Cool to room temperature.

7.3 To beaker *S* add 3 mL of salicylaldehyde and allow to stand for 30 min. Add 1 mL of bromphenol blue indicator solution and titrate while swirling (or by using the magnetic stirrer if beakers are used) with 0.2 *N* HCl to a yellow end point (Note 1). The yellow may fade back to green upon standing, but this is to be disregarded if the yellow color is bright and the addition of another millilitre of 0.2 *N* HCl does not change the yellow color.

NOTE 1—In the case of titrating the tertiary amine content of a primary amine, it is advisable to use a microburet as the titration will be extremely small. Errors in titration are greatly magnified because of the high molecular weights involved.

7.4 To flask *T* add 5 mL of phenyl isothiocyanate and allow to stand for 30 min. Add 1 mL of bromphenol blue indicator solution and titrate while swirling (or by using the magnetic stirrer if beakers are used) with 0.2 *N* HCl to the yellow end point (Note 1 and Note 2). The yellow may fade back to green upon standing, but this may be disregarded if the yellow color is bright and the addition of another millilitre of 0.2 *N* HCl does not change the yellow color.

NOTE 2—Instead of 0.2 *N* HCl, 0.1 *N* HCl may be used if the quantity of tertiary amine is very low.

8. Calculation

8.1 Calculate the total amine value as follows:

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

where:

V = HCl required for titration of the specimen (7.2), mL,
N = normality of the HCl solution, and
S = specimen weight used, g.

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

$$\text{Titration } S \text{ amine value of secondary and tertiary amine groups} = (V \times N \times 56.1)/S \quad (2)$$

where:

V = HCl required for titration of the specimen (7.3), mL,
N = normality of the HCl solution, and
S = specimen weight used, g.

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

$$\text{Titration } T \text{ amine value of tertiary amine groups} = (V \times N \times 56.1)/S \quad (3)$$

where:

V = HCl required for titration of the specimen (7.4), mL,
N = normality of the HCl solution, and
S = specimen weight used, g.

8.4 Primary amine value equals total amine value minus the amine value of the secondary and tertiary amine groups.

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

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

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 amine values; fatty amines; total amine values