



Standard Test Methods for Determination of Amine Acid Acceptance (Alkalinity) of Halogenated Organic Solvents¹

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This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods, where applicable, cover the determination of the acid acceptance of halogenated organic solvents due to the presence therein of an organic amine titratable by standard acid. These test methods are suitable for samples of 0.001 to 0.02 weight percent (10 – 200 ppm) alkalinity as NaOH. Two test methods are covered as follows:

- 1.1.1 *Test Method A*—pH Method, and
- 1.1.2 *Test Method B*—Indicator Method.
- 1.1.3 *Test Method C*—GC Method.

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*:²

- D6806 Practice for Analysis of Halogenated Organic Solvents and Their Admixtures by Gas Chromatography
- E70 Test Method for pH of Aqueous Solutions With the Glass Electrode
- E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

3. Terminology

3.1 *Definitions*:

3.1.1 *amine acid acceptance*—the degree to which an organic amine present in the halogenated organic solvent is capable of absorbing or neutralizing acid generated by the solvent or introduced into it from an external source.

¹ These test methods are under the jurisdiction of ASTM Committee D26 on Halogenated Organic Solvents and Fire Extinguishing Agents and are the direct responsibility of Subcommittee D26.04 on Test Methods.

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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.

4. Significance and Use

4.1 This test method is useful for the determination of the amount of acid acceptance contributed by amines or bases as compared to other acid-accepting compounds.

5. Purity of Reagents

5.1 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 distilled water or water of equal purity. Additional requirements are specified in 8.1 and 12.1.

TEST METHOD A—pH METHOD

6. Summary of Test Method

6.1 The amine acid acceptance of the halogenated organic solvent is determined, after extraction into a volume of water preadjusted to a pH of 3.9, by titrating with standard acid to a pH of 3.9. The extraction is performed either by stirring the immiscible liquids mechanically or by shaking the immiscible layers of liquids manually.

7. Apparatus

7.1 *pH Meter*, equipped with a pH indicating electrode and pH reference electrode or combination electrode.

7.2 *Stirrer*, electric stirring bar, air-driven or magnetic.

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.

8. Reagents

8.1 *Water*—Adjust the pH of 1 L (or any convenient quantity) of water to 3.9. Boil 1 L of distilled water for 5 min in a borosilicate glass or stainless steel container, then cover and cool to room temperature. Titrate a 50-mL aliquot to a pH of 3.8 to 4.0 with 0.01 *N* hydrochloric acid (HCl) (or 0.01 *N* NaOH if the pH is below 3.8). From this titer, calculate the volume of 0.01 *N* HCl (or NaOH) required to adjust the pH of the remaining 950 mL of boiled distilled water to a pH of 3.8 to 4.0. The calculation is as follows:

$$\frac{950}{50} \times \text{titer} \quad (1)$$

Add the calculated amount of 0.01 *N* HCl (or NaOH) together with the titrated 50 mL aliquot of water to the 950 mL stock and mix thoroughly. Determine the pH of a second aliquot. If further adjustment is necessary to obtain a pH of 3.8 to 4.0, repeat the preceding procedure.

8.2 *Hydrochloric Acid, Standard* (0.01 *N*)—Dilute 1.8 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 1 L with water and standardize in accordance with Practice E200, Sections 20 through 23. Certified reagent of 0.01 *N* HCl may be purchased from supply houses.

8.3 *pH 4.0 Buffer Solution*, available from most supply houses.

8.4 *pH 7.0 Buffer Solution*, available from most supply houses.

NOTE 1—Hydrochloric acid of about 0.01 to about 0.02 *N* can be used. It can be difficult to see the end point when using hydrochloric acid much below about 0.01 *N* and concentrations much above 0.02 *N* increase the likelihood of over-titrating the end point when titrating samples of low alkalinity. For alkalinity below about 0.00075 % (75 ppm), 0.01 *N* HCl is appropriate. For alkalinity above about 75 ppm, 0.02 *N* HCl is appropriate.

9. Procedure

9.1 Calibrate the pH meter in accordance with Test Method E70.

9.1.1 Prepare a blank using 100 mL of water previously adjusted to pH 3.9, and subject it to the same type and degree of agitation as the test samples. Titrate the blank to pH 3.9 and record the volume of titrant as *B*.

9.2 *Using Mechanical Agitation*—Transfer 50 mL of the halogenated organic solvent to a 150-mL beaker and add 50 mL of water previously adjusted to a pH of 3.9. Insert a stirrer, and stir as vigorously as possible for 10 s. Stop the stirrer and lift it out of the beaker. Allow the liquids to separate. Insert the pH meter electrodes into the separated aqueous upper layer, avoiding contact of the electrodes with the solvent layer, and titrate the water layer with 0.01 *N* HCl to a pH of 3.9. When the end point has been reached, remove the electrodes and reinsert the stirrer. Stir vigorously for 10 s again. Remove the stirrer, insert the electrodes, and again titrate to a pH of 3.9. Repeat the steps until additional stirring does not result in a change of pH (Note 2). Record the final titration and calculate the amine acid acceptance. When a magnetic stirring bar is used, it is not necessary to remove it between agitation periods.

NOTE 2—If the readings of the pH meter are erratic because the electrodes have been wet with halogenated solvent, it may be treated by

rinsing the electrode with acetone or alcohol, followed by thorough rinsing with water and soaking in water for a short time.

9.3 *Using Hand Agitation*—If no stirrer is available, the extraction and titration may be carried out as follows: Transfer 50 mL of the halogenated organic solvent to a 250-mL glass-stoppered Erlenmeyer flask, add 50 mL of water preadjusted to a pH of 3.9, and stopper the flask. Shake vigorously for 5 s. Pour the contents into a 150-mL beaker and allow the immiscible liquids to separate into layers. Insert the pH meter electrodes and titrate the water layer with 0.01 *N* HCl to a pH of 3.9. When the end point has been reached, remove the electrodes, return the liquids to the flask, and extract again for 5 s. Repeat the titration. Repeat the extraction and titration until no change in pH results from additional shaking (Note 2). Record the final titration and calculate the amine acid acceptance.

10. Calculation

10.1 Calculate the Amine Acid Acceptance (alkalinity) as NaOH, in weight percent as follows:

$$\text{Amine Acid Acceptance (alkalinity), as NaOH, Weight Percent} = (2)$$

$$\{[(V - (B/2)) \times N \times 0.040]/W\} \times 100$$

or as parts per million as follows:

$$\text{Amine Acid Acceptance (alkalinity), as NaOH, ppm} = (3)$$

$$\{[(V - (B/2)) \times N \times 0.040]/W\} \times 1000000$$

where:

- V* = millilitres HCl required for titration of the sample, mL,
- N* = normality of the HCl,
- B* = millilitres HCl required for titration of the blank, mL, and
- W* = weight sample used (or volume in millilitres times its specific gravity), g.

11. Precision and Bias

11.1 The precision limits of this test have been determined as 0.0005 % (equivalent NaOH, weight percent).

TEST METHOD B—INDICATOR METHOD

12. Summary of Test Method

12.1 The amine acid acceptance of the halogenated organic solvent is determined, after extraction into a volume of water preadjusted to the bromphenol blue end point yellow, by titrating with standard acid to the bromphenol blue end point, blue to yellow.

13. Reagents

13.1 *Water*—Add bromphenol blue indicator solution (1 drop for each 10 mL of water) to 1 L (or any convenient volume) of water and adjust to the bromphenol blue color change end point.

13.2 *Bromphenol Blue Indicator Solution* (10 g/L)—Dissolve 1 g of bromphenol blue in 100 mL of water.

13.3 *Hydrochloric Acid, Standard* (0.01 *N*)—See 8.2.

14. Procedure

14.1 Prepare a blank using 100 mL of water previously adjusted to the color change point of the indicator being used, and subject it to the same type and degree of agitation as the test samples. Titrate the blank to the color change point of the indicator and record the volume of titrant as *B*.

14.2 Transfer 50 mL of the halogenated organic solvent to a clean 250-mL glass-stoppered Erlenmeyer flask, and add 50 mL of water adjusted to the bromphenol blue end point (Note 3). Stopper the flask and shake for 10 s. Allow the immiscible liquids to separate, and titrate the aqueous upper layer with 0.01 *N* HCl to the bromphenol blue end point. Stopper the flask, and again shake for 5 s. If the end point has changed, titrate to the bromphenol blue end point again. Repeat until no change in indicator results when additional shaking is done. Record the titration and calculate the amine acid acceptance.

NOTE 3—Methyl orange indicator solution, modified methyl orange indicator solution, or bromothymol blue indicator solution may be substituted for bromphenol blue indicator solution where an operator has difficulty observing certain color changes.

14.3 Mechanical agitation may be used as described in 9.2.

15. Calculation

15.1 See Section 10.

16. Precision and Bias⁴

16.1 Precision determinations were performed at concentrations of 0.0009, 0.0018, and 0.0194 weight percent as NaOH.

16.2 The standard deviation of results (each the average of 5 replicates) obtained by different analysts on different days within the same laboratory has been estimated to be 0.0002 weight percent absolute at 12 degrees of freedom. The 95 % limit for the difference between two such averages is 0.0005 weight percent absolute.

16.3 The standard deviation of results (each the average of 5 replicates) obtained by analysts in different laboratories has been estimated to be 0.0003 weight percent absolute at 4 degrees of freedom. The 95 % limit for the difference between two such averages has been estimated to be 0.0008 weight percent absolute.

16.4 The bias of this test method was not determined.

TEST METHOD C—GAS CHROMATOGRAPHY METHOD

17. Procedure

17.1 Determine the weight ppm or weight percent of the amine or amines present using gas chromatography with a gas chromatographic method that is in compliance with Practice D6806.

17.2 It will be necessary to calibrate the gas chromatograph with a known standard of the amine or amines present. The known standard should be of approximately the same concentration as the amine to be measured.

17.3 If the amine is unknown it can be identified by GC mass spectroscopy.

17.4 Calculate the Amine Acid Acceptance (alkalinity) by the following formula:

$$\text{Amine Acid Acceptance (alkalinity), as NaOH} = \quad (4)$$

$$\frac{40 \times \text{ppm}}{\text{MW}} \text{ or } \frac{40 \times \text{wt } \%}{\text{MW}}$$

where:

- 40 = the molecular weight of NaOH,
- ppm = ppm of the amine as determined in 17.1,
- wt % = weight percent of the amine as determined in 17.1, and
- MW = the molecular weight of the amine.

17.5 If more than one amine is present the amine acid acceptance (alkalinity) will be the sum of the acid acceptance (alkalinity) of the individual amines.

18. Precision and Bias⁵

18.1 Precision and bias data was obtained with two different amines, *n*-methyl morpholine at about 20 ppm as NaOH in perchloroethylene, and diisopropyl amine, at about 3 ppm in trichloroethylene.

18.2 There was no statistically significant difference between alkalinity as determined between Methods B (titration with indicator) and Method C (determination of amine by GC). No bias is present.

18.3 The reproducibility of the method was found to average 2.1 % Relative Standard Deviation at 3 and 20 ppm.

18.4 Repeatability was calculated at 6.39 % RDS, that is two determinations should differ less than 6.39 % RSD (1.3 ppm at 20 ppm alkalinity).

19. Keywords

19.1 acid acceptance; alkalinity; amine acid acceptance; halogenated organic solvents

⁴ A Research Report is available from ASTM International Headquarters. Request RR:D26-1012.

⁵ A Research Report is available from ASTM International Headquarters. Request RR:D26-1019.

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