INTERNATIONAL

Designation: D 2106 – ~~95~~00

Standard Test Methods for ~~the Determination of~~ Determination of Amine Acid Acceptance (Alkalinity) of Halogenated Organic Solvents[1]

This standard is issued under the fixed designation D 2106; 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 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 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.

1.2 *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:*

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[1] These test methods are under the jurisdiction of ASTM Committee D~~-~~26 on Halogenated Organic Solvents and Fire Extinguishing Agents and are the direct responsibility of Subcommittee D26.04 on Test Methods.

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E 70 Test Method for pH of Aqueous Solutions With the Glass Electrode[2]

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[2]

3. Terminology

3.1 *Definition*:

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.

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.

8. Reagents

8.1 *Water*—Adjust the pH of 1 L (or any convenient qua~~l~~ntity) 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:

~~$\frac{950}{50} \times T\text{iter}$~~ (1)

$$\frac{950}{50} \times \text{titer} \tag{1}$$

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 ~~above~~ preceding procedure.

8.2 *Hydrochloric Acid, Standard* (0.02 *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 E 200, Sections 20 through 23. Certified reagent of 0.02 *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.

9. Procedure

9.1 Calibrate the pH meter in accordance with Test Method E 70.

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[2] *Annual Book of ASTM Standards*, Vol 15.05.

[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. Pharmacope~~utic~~al Convention, Inc. (USPC), Rockville, MD.

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 0.02 *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 1). 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 1—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 0.02 *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 1). Record the final titration and calculate the amine acid acceptance.

10. Calculation

10.1 Calculate the amine acid acceptance as equivalent sodium hydroxide in weight percent as follows:

~~Equivalent NaOH, weight percent = [~~
$(VN \times 0.040)/W] \times 100$ (2)

Equivalent NaOH, weight percent =
$\{(V - (B/2)) \times N \times 0.040]/W\} \times 100$ (2)

W

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

NOTE 2—*Example*~~—~~: Where the solvent is trichloroethylene, the equation becomes:

~~Equivalent NaOH, weight percent[4] = [(VN × 0.04)/(50 × 1.463)] × 100 = VN × 0.055~~ (3)

Equivalent NaOH, weight percent[4] $= [(VN \times 0.04)/(50 \times 1.463)] \times 100 = VN \times 0.055$ (3)

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* (0.02 ~~N)~~ *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

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[4] The appropriate specific gravity must be used for other solvents.

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 0.02 *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~~ or~~, 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.~~2~~3 Mechanical agitation may be used as described in 9.2.

15. Calculation

15.1 See Section 10.

16. Precision and Bias [5]

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.

17. Keywords

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

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[5] A Research Report is available from ASTM Headquarters. Request RR: D26-1012.