Designation: E 301 – 94

Standard Test Method for Total Acidity of Organic Acids[1]

This standard is issued under the fixed designation E 301; 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.

1. Scope

1.1 This test method covers the determination of assay of carboxylic acids by total acidity. The method is suitable for assaying acids which are soluble in water or isopropanol and have purities between 50 and 100 % calculated on the basis of the major component.

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 precautionary statements are given in Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[3]

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[3]

3. Terminology

3.1 There are no terms in this test method that require new or other than dictionary definitions.

4. Summary of Test Method

4.1 This test method employs the titration of the acid dissolved in water or isopropanol with standard aqueous sodium hydroxide solution. The color change of phenolphthalein is used as the end-point indicator.

5. Significance and Use

5.1 This test method provides a method of measurement of assay (relative purity) of single component organic acids that are soluble in water or isopropyl alcohol. Acids and acid solutions are used in many chemical processes. The relative concentration of acids affects the efficiency of these processes. This test method provides a test procedure for specification acceptance and manufacturing control.

6. Interferences

6.1 Carbon dioxide interferes quantitatively and should be excluded from the titration. Other materials acidic to phenolphthalein present as impurities in the sample also interfere quantitatively. Usually no correction for these is made.

7. Apparatus

7.1 *Buret*—A calibrated 100-mL buret with a 50 or 75-mL reservoir on top of a lower portion calibrated in 0.1-mL divisions and equipped with TFE-fluorocarbon stopcock plug is suitable.

8. Reagents and Materials

8.1 *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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean as defined by Type II or Type III of Specification D 1193.

8.3 *Isopropanol, Neutralized*—Add 2 mL of phenolphthalein indicator solution to 1 L of 99 % isopropanol and make faintly pink by the dropwise addition of NaOH solution.

8.4 *Phenolphthalein Indicator Solution* (10 g/L)—Prepare in accordance with Practice E 200.

8.5 *Sodium Hydroxide Standard Solution (0.5 N)*—Prepare and standardize a 0.5 N solution of sodium hydroxide (NaOH) in accordance with Practice E 200. Determine and record the temperature at which the standardization was performed. The normality of this solution shall be corrected to the temperature at which the determination is performed as follows:

$$N_2 = N_1 - 0.00014\,(t_2 - t_1) \qquad (1)$$

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[1] This test method is under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and is the direct responsibility of Subcommittee E15.01 on General Standards.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

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

[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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

where:
N_1 = normality when standardized,
N_2 = normality during analysis of sample,
t_1 = temperature of solution when standardized,
t_2 = temperature of solution during analysis of sample, and
0.00014 = factor to correct for thermal expansion of the solution.

8.6 *Water, Neutralized*—Add 2 mL of phenolphthalein indicator solution to 1 L of water and make faintly pink by the dropwise addition of NaOH solution.

9. Hazards

9.1 Consult current OSHA regulations and supplier's Material Safety Data Sheets for all materials used in this test method.

9.2 Many organic acids are corrosive and can be extremely hazardous if improperly handled.

10. Procedure

10.1 *Water-Soluble Acids*:

10.1.1 Into each of two 500-mL Erlenmeyer flasks, add 100 mL of neutralized water.

10.1.2 Weigh duplicate samples of the proper size (Note 1) to the nearest 0.1 mg into each flask and swirl to effect solution of the acid (Note 2).

10.1.3 Titrate with 0.5 *N* NaOH solution to the first pink end point persistent for 15 s (Note 3). Read and record the volume of titrant to the nearest 0.02 mL.

NOTE 1—The correct range of sample size shall be calculated as follows:

$$\text{Weight of sample, g} = \frac{[(4.5 \pm 0.2) \times M]}{B \times P} \tag{2}$$

where:
M = molecular weight of acid
B = number of reacting groups in acid, and
P = approximate expected percent assay of sample.

NOTE 2—If the sample is slow to dissolve, the titration may be started before solution is complete. The sample will dissolve more quickly as the sodium salt is formed. If this procedure is used, however, the sample must be completely dissolved before the end point is reached. For critical work, the flask should be swept with nitrogen to avoid contamination with atmospheric carbon dioxide.

NOTE 3—This color should match that of the original neutralized water. The pH 8.6 phenolphthalein end-point color standard suggested in Practice E 200 is helpful in determining the proper pink color.

10.2 *Water-Insoluble Acids*:

10.2.1 Replace the 100 mL of water with 100 mL of neutralized isopropanol and proceed as described in 10.1.2 and 10.1.3.

11. Calculation

11.1 Calculate the assay of the acid as follows (Note 4):

$$\text{Assay, wt. \%} = \frac{(A \times N_2 \times M)}{(10 \times W \times B)} \tag{3}$$

where:
A = NaOH, mL, required for titration of the sample,
N_2 = normality of the NaOH solution at temperature during analysis,
M = molecular weight of the acid,
B = number of reacting groups in the acid, and
W = sample used, g.

NOTE 4—If it is necessary to calculate the results as acid number, $M = 561$ and $B = 1$. The results will then be in terms of milligrams of potassium hydroxide (KOH) per gram.

12. Report

12.1 Report the assay of the acid to the nearest 0.01 %.

13. Precision and Bias

13.1 The following criteria should be used for judging the acceptability of results (Note 5):

13.1.1 *Repeatability* (*Single Analyst*)—The standard deviation for a single determination has been estimated to be 0.045 % absolute at 92 DF. The 95 % limit for the difference between two such runs is 0.13 % absolute.

13.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability, formerly called repeatability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days has been estimated to be 0.055 % absolute at 46 DF. The 95 % limit for the difference between two such averages is 0.15 % absolute.

13.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.194 % absolute at 7 DF. The 95 % limit for the difference between two such averages is 0.54 % absolute.

NOTE 5—The precision estimates are based on interlaboratory studies[5] performed in 1964 and 1966 on one sample each of acetic acid, 2-ethylhexanoic acid, adipic acid, fumaric acid, acrylic acid, and methacrylic acid. Nine laboratories analyzed the samples of acetic acid 2-ethylhexanoic acid, acrylic acid, and methacrylic acid in duplicate on each of 2 days and 7 laboratories analyzed the samples of adipic acid and fumaric acid in duplicate on each of 2 days of a total of 200 analyses. Practice E 180 was used in developing these precision estimates.

13.2 The bias of this test method has not been determined, due to the unavailability of suitable reference materials.

14. Keywords

14.1 assay; carboxylic acids; organic acids; titrimetric; total acidity

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[5] Supporting data giving results of cooperative tests are available from ASTM Headquarters. Request RR:E15-0070.

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