Designation: D1067 – 06

An American National Standard

# Standard Test Methods for Acidity or Alkalinity of Water[1]

This standard is issued under the fixed designation D1067; 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[2] cover the determination of acidity or alkalinity of all types of water. Three test methods are given as follows:

| | Sections |
|---|---|
| Test Method A (Electrometric Titration) | 7 to 15 |
| Test Method B (Electrometric or Color-Change Titration) | 16 to 24 |
| Test Method C (Color-Change Titration After Hydrogen Peroxide Oxidation and Boiling) | 25 to 33 |

1.2 In all of these test methods the hydrogen or hydroxyl ions present in water by virtue of the dissociation or hydrolysis of its solutes, or both, are neutralized by titration with standard alkali (acidity) or acid (alkalinity). Of the three procedures, Test Method A is the most precise and accurate. It is used to develop an electrometric titration curve (sometimes referred to as a pH curve), which defines the acidity or alkalinity of the sample and indicates inflection points and buffering capacity, if any. In addition, the acidity or alkalinity can be determined with respect to any pH of particular interest. The other two methods are used to determine acidity or alkalinity relative to a predesignated end point based on the change in color of an internal indicator or the equivalent end point measured by a pH meter. They are suitable for routine control purposes.

1.3 When titrating to a specific end point, the choice of end point will require a careful analysis of the titration curve, the effects of any anticipated changes in composition on the titration curve, knowledge of the intended uses or disposition of the water, and a knowledge of the characteristics of the process controls involved. While inflection points (rapid changes in pH) are usually preferred for accurate analysis of sample composition and obtaining the best precision, the use of an inflection point for process control may result in significant errors in chemical treatment or process control in some applications. When titrating to a selected end point dictated by practical considerations, (*1*) only a part of the actual neutralizing capacity of the water may be measured, or (*2*) this capacity may actually be exceeded in arriving at optimum acidity or alkalinity conditions.

1.4 A scope section is provided in each test method as a guide. It is the responsibility of the analyst to determine the acceptability of these test methods for each matrix.

1.5 Former Test Methods C (Color-Comparison Titration) and D (Color-Change Titration After Boiling) were discontinued. Refer to Appendix X4 for historical information.

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

1.7 *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:*[3]

D596 Guide for Reporting Results of Analysis of Water
D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D1293 Test Methods for pH of Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

## 3. Terminology

3.1 *Definitions*—The terms in these test methods are defined in accordance with Terminology D1129.

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[1] These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

Current edition approved Dec. 15, 2006. Published January 2007. Originally approved in 1949. Last previous edition approved in 2002 as D1067 – 02. DOI: 10.1520/D1067-06.

[2] The basic procedures used in these test methods have appeared widespread in the technical literature for many years. Only the particular adaptation of the electrometric titration appearing as the Referee Method is believed to be largely the work of Committee D19.

[3] 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.

***A Summary of Changes section appears at the end of this standard.**

3.1.1 Certain uses of terminology exist in the water treatment industry which may differ from these definitions. A discussion of terms is presented in Appendix X1.

## 4. Significance and Use

4.1 Acidity and alkalinity measurements are used to assist in establishing levels of chemical treatment to control scale, corrosion, and other adverse chemical equilibria.

4.2 Levels of acidity or alkalinity are critical in establishing solubilities of some metals, toxicity of some metals, and the buffering capacity of some waters.

## 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.[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.

5.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type I. In addition, reagent water for this test shall be free of carbon dioxide ($CO_2$) and shall have a pH between 6.2 and 7.2 at 25°C. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the precision and bias of the test method. Type III water was specified at the time of round robin testing of this test method. A procedure for the preparation of carbon dioxide-free water is given in Practice E200.

## 6. Sampling

6.1 Collect the sample in accordance with Practice D1066 and Practices D3370 as applicable.

6.2 The time interval between sampling and analysis shall be as short as practically possible in all cases. It is mandatory that analyses by Test Method A be carried out the same day the samples are taken; essentially immediate analysis is desirable for those waste waters containing hydrolyzable salts that contain cations in several oxidation states.

## TEST METHOD A—ELECTROMETRIC TITRATION

## 7. Scope

7.1 This test method is applicable to the determination of acidity or alkalinity of all waters that are free of constituents that interfere with electrometric pH measurements. It is used for the development of a titration curve that will define inflection points and indicate buffering capacity, if any. The acidity or alkalinity of the water or that relative to a particular pH is determined from the curve.

## 8. Summary of Test Method

8.1 To develop a titration curve that will properly identify the inflection points, standard acid or alkali is added to the sample in small increments and a pH reading is taken after each addition. The cumulative volume of solution added is plotted against the observed pH values. All pH measurements are made electrometrically.

## 9. Interferences

9.1 Although oily matter, soaps, suspended solids, and other waste materials may interfere with the pH measurement, these materials may not be removed to increase precision, because some are an important component of the acid- or alkali-consuming property of the sample. Similarly, the development of a precipitate during titration may make the glass electrode sluggish and cause high results.

## 10. Apparatus

10.1 *Electrometric pH Measurement Apparatus*, conforming to the requirements given in Test Methods D1293.

## 11. Reagents [4]

11.1 *Hydrochloric Acid, Standard* (0.02 *N*) (see Note 1)—Prepare and standardize as directed in Practice E200, except that the titration shall be made electrometrically. The inflection point corresponding to the complete titration of carbonic acid salts will be very close to pH 3.9.

NOTE 1—Sulfuric acid of similar normality may be used instead of hydrochloric acid. Prepare and standardize in like manner.

11.2 *Sodium Hydroxide, Standard* (0.02 *N*)—Prepare and standardize as directed in Practice E200, except that the titration shall be made electrometrically. The inflection point corresponding to the complete titration of the phthalic acid salt will be very close to pH 8.6.

## 12. Procedure

12.1 Mount the glass and reference electrodes in two of the holes of a clean, threehole rubber stopper chosen to fit a 300-mL, tall-form Berzelius beaker without spout, or equivalent apparatus. Alternatively, a combination pH electrode can be used that has both a glass and a reference electrode in an integral unit. Place the electrodes in the beaker and standardize the pH meter, using a reference buffer having a pH approximating that expected for the sample (see Test Methods D1293). Rinse the electrodes, first with reagent water, then with a portion of the sample. Following the final rinse, drain the beaker and electrodes completely.

12.2 Pipette 100 mL of the sample, adjusted, if necessary, to room temperature, into the beaker through the third hole in the stopper. Hold the tip of the pipette near the bottom of the beaker while discharging the sample.

12.3 Measure the pH of the sample in accordance with Test Methods D1293.

12.4 Add either 0.02 *N* acid or alkali solution, as indicated, in increments of 0.5 mL or less (see Note 2). After each

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