



Designation: D1067 – 16

## Standard Test Methods for Acidity or Alkalinity of Water<sup>1</sup>

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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

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

### 1. Scope\*

1.1 These test methods<sup>2</sup> 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

<sup>1</sup> 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.

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<sup>2</sup> 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.

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:<sup>3</sup>

- 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

<sup>3</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto: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. Terminology

#### 3.1 Definitions:

3.1.1 The terms in this standard are defined in accordance with Terminology **D1129**.

3.1.2 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.<sup>4</sup> 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<sub>2</sub>) 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

<sup>4</sup> *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 Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

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<sup>4</sup>

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 addition, mix the solution thoroughly. Determine the pH when the mixture has reached equilibrium as indicated by a constant reading (see **Note 3**). Mechanical stirring, preferably of the magnetic type, is required for this operation; mixing by means of a gas stream is not permitted. Continue the titration until the necessary data for the titration curve have been obtained.

**NOTE 2**—If the sample requires appreciably more than 25 mL of standard solution for its titration, use a smaller aliquot, or a 0.1 *N* solution, prepared and standardized in the same manner (see Practice **E200**).

**NOTE 3**—An electrometric titration curve is smooth, with the pH changing progressively in a single direction, if equilibrium is achieved after each incremental addition of titrant, and may contain one or more inflection points. Ragged or irregular curves may indicate that equilibrium was not attained before adding succeeding increments. The time required will vary with different waters as the reaction rate constants of different chemical equilibria vary. In some instances the reaction time may be an interval of a few seconds while other slower, more complex reactions may require much longer intervals. It is important, therefore, that the period be sufficient to allow for any significant pH changes, yet consistent with good laboratory practices.

12.5 To develop a titration curve, plot the cumulative millilitres of standard solution added to the sample aliquot against the observed pH values. The acidity or alkalinity relative to a particular pH may be determined from the curve.

### 13. Calculation

13.1 Calculate the acidity or alkalinity, in milliequivalents per litre, using **Eq 1**:

$$\text{Acidity (or alkalinity), meq/L (epm)} = AN/B \times 1000 \quad (1)$$

where:

1000 = 1000 mL / litre

A = standard acid or alkali required for the titration, mL,

*N* = normality of the standard solution, and

B = sample titrated, mL.

### 14. Report

14.1 Report the results of titrations to specific end points as follows: “The acidity (or alkalinity) to pH at °C = meq/L (epm).”

14.2 Appropriate factors for converting milliequivalents per litre (epm) to other units are given in Guide **D596**.

### 15. Precision and Bias<sup>5</sup>

15.1 The precision and bias data presented in **Table 1** for this test method meet the requirements of Practice **D2777**.

15.2 The collaborative test of this test method was performed in reagent waters by six laboratories using one operator each, using three levels of concentration for both the acidity and alkalinity.

**TABLE 1 Determination of Precision and Bias for Acidity and Alkalinity by Electrometric Titration (Test Method A)**

Amount Added, meq/L	Amount Found, meq/L	<i>S<sub>t</sub></i>	<i>S<sub>o</sub></i>	Bias, %
Acidity				
48.30	48.76	1.25	0.44	+0.94
23.00	22.61	0.68	0.27	-1.67
17.10	16.51	0.71	0.26	-3.47
Alkalinity				
4.90	5.00	0.39	0.12	+2.12
2.46	2.45	0.14	0.06	-0.00
0.51	0.56	0.15	0.05	+10.59

15.3 Precision and bias for this test method conforms to Practice **D2777 – 77**, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice **D2777 – 13**, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

## TEST METHOD B—ELECTROMETRIC OR COLOR-CHANGE TITRATION

### 16. Scope

16.1 This test method covers the rapid, routine control measurement of acidity or alkalinity to predesignated end points of waters that contain no materials that buffer at the end point or other materials that interfere with the titration by reasons that may include color or precipitation.

### 17. Summary of Test Method

17.1 The sample is titrated with standard acid or alkali to a designated pH, the end point being determined electrometrically or by the color change of an internal indicator.

### 18. Interferences

18.1 Natural color or the formation of a precipitate while titrating the sample may mask the color change of an internal indicator. Suspended solids may interfere in electrometric titrations by making the glass electrode sluggish. Waste materials present in some waters may interfere chemically with color titrations by destroying the indicator. Variable results may be experienced with waters containing oxidizing or reducing substances, depending on the equilibrium conditions and the manner in which the sample is handled.

### 19. Apparatus

19.1 *Electrometric pH Measurement Apparatus*—See **10.1**.

### 20. Reagents

20.1 *Bromcresol Green Indicator Solution* (1 g/L)—Dissolve 0.1 g of bromcresol green in 2.9 mL of 0.02 *N* sodium hydroxide (NaOH) solution. Dilute to 100 mL with water.

20.2 *Hydrochloric Acid, Standard* (0.02 *N*) (**Note 1**)—See **11.1**, except that the acid may be standardized by colorimetric titration as directed in Practice **E200** when an indicator is used for sample titration.

<sup>5</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1149. Contact ASTM Customer Service at service@astm.org.

20.3 *Methyl Orange Indicator Solution* (0.5 g/L)—Dissolve 0.05 g of methyl orange in water and dilute to 100 mL.

20.4 *Methyl Purple Indicator Solution* (1 g/L)—Dissolve 0.45 g of dimethyl-aminoazobenzene-O-carboxylic acid, sodium salt, in approximately 300 mL of water. To this solution add 0.55 g of a water-soluble blue dye-stuff, Color Index No. 714,<sup>6,7</sup> and dissolve. Dilute to 1 L with water.

20.5 *Methyl Red Indicator Solution* (1 g/L)—Dissolve 0.1 g of water-soluble methyl red in water and dilute to 100 mL.

20.6 *Phenolphthalein Indicator Solution* (5 g/L)—Dissolve 0.5 g of phenolphthalein in 50 mL of ethyl alcohol (95 %) and dilute to 100 mL with water.

NOTE 4—Specially denatured ethyl alcohol conforming to Formula No. 3A or 30 of the U. S. Bureau of Internal Revenue may be substituted for ethyl alcohol (95 %).

NOTE 5—Indicators are available commercially in prepared form.

20.7 *Sodium Hydroxide, Standard* (0.02 N)—See 11.2, except that the alkali may be standardized by colorimetric titration as directed in Practice E200 when an indicator is used for sample titration.

## 21. Procedure

21.1 Depending on the method of titration to be used, pipette 100 mL of the sample, adjusted, if necessary, to room temperature, into a 300-mL, tall-form beaker or a 250-mL, narrow-mouth Erlenmeyer flask. Hold the tip of the pipette near the bottom of the container while discharging the sample.

21.2 Titrate the aliquot electrometrically to the pH corresponding to the desired end point (see Note 6). When using an indicator, add 0.2 mL (see Note 7) and titrate with 0.02 N acid (for alkalinity) or 0.02 N NaOH solution (for acidity) until a persistent color change is noted (see Note 8). Add the standard solution in small increments, swirling the flask vigorously after each addition. As the end point is approached, a momentary change in color will be noted in that portion of the sample with which the reagent first mixes. From that point on, make dropwise additions.

NOTE 6—The choice of end point will have been made to provide optimum data for the intended use or disposition of the water. When an indicator is used, those listed in 20.1 and 20.3 through 20.6 are used most frequently; others may be employed if it is to the user's advantage. Color change and endpoint data for indicators listed herein are presented in Appendix X2 and Table X2.1.

NOTE 7—After some practice, slightly more or less indicator may be preferred. The analyst must use the same quantity of phenolphthalein at all times, however, because at a given pH, the intensity of one-color indicators depends on the quantity.

NOTE 8—If the sample requires appreciably more than 25 mL of 0.02 N solution for its titration, use a smaller aliquot, or a 0.1 N reagent prepared and standardized in the same manner (see Practice E200).

<sup>6</sup> Refers to compounds, bearing such number, as described in "Color Index," Society of Dyers and Colourists, Yorkshire, England (1924).

<sup>7</sup> The sole source of supply of the dye (Calcocid Blue AX Double) known to the committee at this time is American Cyanamid Company, One Cyanamid Plaza, Wayne, NJ 07470. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.

## 22. Calculation

22.1 Calculate the acidity or alkalinity, in milliequivalents per litre, using Eq 2:

$$\text{Acidity (or alkalinity), meq/L (epm)} = (AN/B) \times 1000 \quad (2)$$

where:

1000 = 1000 mL / litre

A = standard acid or alkali required for the titration, mL,

N = normality of the standard solution, and

B = sample titrated, mL.

## 23. Report

23.1 Report the results of titration as follows: "The acidity (or alkalinity) to at °C = meq/L (epm)," indicating the pH and the temperature at which it was determined, or the name of the indicator used, for example, "The acidity to methyl orange at °C = meq/L (epm)."

## 24. Precision and Bias<sup>5</sup>

24.1 The precision and bias data presented in Table 2 for this test method meet the requirements of Practice D2777.

24.2 The collaborative test of this test method was performed in reagent waters by six laboratories using one operator each, using three levels of concentration for both the acidity and alkalinity.

24.3 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

## TEST METHOD C—COLOR-CHANGE TITRATION AFTER HYDROGEN PEROXIDE OXIDATION AND BOILING

## 25. Scope

25.1 This test method is intended specifically for mine drainage, surface streams receiving mine drainage, industrial waste waters containing waste acids and their salts, and similar waters bearing substantial amounts of ferrous iron or other polyvalent cations in a reduced state.

TABLE 2 Determination of Precision and Bias for Acidity and Alkalinity by Electrometric or Color-Change Titration (Test Method B)

Amount Added, meq/L	Amount Found, meq/L	$S_i$	$S_o$	Bias, %
Acidity				
48.30	49.06	0.802	0.589	+ 1.57
23.00	22.83	0.610	0.455	-0.74
17.10	16.84	0.334	0.146	-1.52
Alkalinity				
4.90	4.88	0.156	0.034	-0.41
1.92	1.80	0.080	0.014	-6.25
0.51	0.50	0.044	0.024	-1.96