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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Methods for Acidity or Alkalinity of Water [1]

This standard is issued under the fixed designation D 1067; 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. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by 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 *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:*

D 596 Practice for Reporting Results of Analysis of Water[3]
D 1129 Terminology Relating to Water[3]
D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[3]
D 1193 Specification for Reagent Water[3]
D 1293 Test Methods for pH of Water[3]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[3]
D 3370 Practices for Sampling Water from Closed Conduits[3]
E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[4]

3. Terminology

3.1 *Definitions*—The terms in these test methods are defined in accordance with Terminology D 1129.

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,

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[1] These test methods are under the jurisdiction of ASTM Committee D-19 on Water and are the responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[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 D-19.

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

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

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

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.[5] 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 D 1193, 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. A procedure for the preparation of carbon dioxide-free water is given in Practice E 200.

6. Sampling

6.1 Collect the sample in accordance with Specification D 1192 and Practices D 3370 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 D 1293.

11. Reagents [5]

11.1 *Hydrochloric Acid, Standard* (0.02 *N*) (see Note 1)—Prepare and standardize as directed in Practice E 200, 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 E 200, 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. 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 D 1293). 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 Pipet 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 pipet near the bottom of the beaker while discharging the sample.

12.3 Measure the pH of the sample in accordance with Test Methods D 1293.

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 0.1 *N* solution, prepared and standardized in the same manner (see Practice E 200).

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

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[5] *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.

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:

$$\text{Acidity (or alkalinity), meq/L (epm)} = AN \times 10 \qquad (1)$$

where:

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

N = normality of the standard solution.

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 Practice D 596.

15. Precision and Bias [6]

15.1 The precision and bias data presented in Table 1 for this test method meet the requirements of Practice D 2777.

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.

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.

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	S_t	S_o	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

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 E 200 when an indicator is used for sample titration.

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, [7] and dissolve. Dilute to 1 L with water. This indicator is available commercially in prepared form.

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 %).

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 E 200 when an indicator is used for sample titration.

21. Procedure

21.1 Depending on the method of titration to be used, pipet 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 pipet near the bottom of the container while discharging the sample.

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[6] Supporting data are available from ASTM Headquarters. Request RR:D19-1149.

[7] Refers to compounds, bearing such number, as described in "Color Index," Society of Dyers and Colourists, Yorkshire, England (1924). American Cyanamid Company's "Calcocid Blue AX Double" has been found satisfactory for this purpose.

21.2 Titrate the aliquot electrometrically to the pH corresponding to the desired end point (see Note 5). When using an indicator, add 0.2 mL (see Note 6) 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 7). 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 5—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 6—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 7—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 E 200).

22. Calculation

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

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

where:

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 [6]

24.1 The precision and bias data presented in Table 2 for this test method meet the requirements of Practice D 2777.

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.

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_t	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

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.

25.2 Because the oxidation and hydrolysis of ferrous iron generate acidity, a reliable measure of acidity or alkalinity is obtained only when complete oxidation is achieved and hydrolysis of ferric salts is completed (see Appendix X3). In many instances, the concentration of ferrous iron is such that a 2-min boiling period is not sufficient to assure complete oxidation. In this test method, hydrogen peroxide is added prior to boiling to accelerate the chemical reactions needed for equilibrium.

25.3 This test method may be used to determine approximate alkali requirements for neutralization and to assure comparability of results when both alkaline and acid flows are under consideration in mine drainage treatment.

26. Summary of Test Method

26.1 The pH of the sample is determined. Standard acid is added as needed to lower the pH to 4.0 or less. Hydrogen peroxide (H_2O_2) is added, the solution boiled, and finally either titrated while hot to the phenolphthalein end point, or cooled and titrated electrometrically with standard alkali to pH = 8.2, the desired end point.

27. Interferences

27.1 Natural color or the formation of a colored precipitate during boiling may mask the color change of the phenolphthalein end point, requiring a pH meter for the titration. Suspended solids may cause sluggishness in electrometric titrations; however, compensation is made by a 15-s pause between alkali additions or by dropwise addition of titrant when the designated pH is approached.

27.2 The standard acid added prior to boiling neutralizes volatile components, for example, bicarbonates which contribute to the alkalinity and, hence, minimizes this source of error.

28. Apparatus

28.1 *Electrometric pH Measurement Apparatus*—See 10.1.

29. Reagents

29.1 *Hydrogen Peroxide* (H_2O_2, 30 % Solution).

29.2 *Phenolphthalein Indicator Solution* (5 g/L)—See 20.6.

29.3 *Sodium Hydroxide, Standard* (0.02 *N*)—Prepare and standardize as directed in Practice E 200.

29.4 *Sulfuric Acid, Standard* (0.02 *N*)—Prepare and standardize as directed in Practice E 200.

NOTE 8—Hydrochloric acid of similar normality may be used instead of sulfuric acid. Prepare and standardize in like manner.

30. Procedure

30.1 Pipet 50 mL of the sample into a 250-mL beaker.

30.2 Measure the pH of the sample (see Test Methods D 1293). If the pH is above 4.0, add 5-mL increments of standard H_2SO_4 to lower the pH to 4.0 or less (see Note 8).

30.3 Add only 5 drops of H_2O_2.

30.4 Heat the sample to boiling and continue to boil for 2 to 4 min.

30.5 If the sample is discolored, cool to room temperature and titrate electrometrically with standard NaOH solution to pH = 8.2, corresponding to the desired end point. If the sample is colorless, titrate to the phenolphthalein color change while hot.

31. Calculation

31.1 Calculate the acidity in milliequivalents per litre using Eq. 3 or Eq. 4:

31.1.1 Where no sulfuric acid is added:

$$\text{Acidity (boiled and oxidized), meq/L (epm)} = (BN_b/S) \times 1000$$

31.1.2 Where sulfuric acid is added:

$$\text{Acidity (boiled and oxidized), meq/L (epm)} = [(BN_b - AN_a)/S] \times 1000 \text{ (see Note 9)} \quad (3)$$

where:

A = H_2SO_4 added to sample, mL,
B = NaOH solution required for titration of sample, mL,
N_a = normality of the H_2SO_4,
N_b = normality of the NaOH solution, and
S = sample used, mL.

NOTE 9—Minus acidity represents excess alkalinity contributed by constituents such as bicarbonates.

32. Report

32.1 Report the results of titrations as follows: "The acidity (boiled and oxidized) to pH (or phenolphthalein) = meq/L (epm)."

33. Precision and Bias [6]

33.1 The precision and bias data presented in Table 3 for this test method meet the requirements of Practice D 2777.

33.2 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.

34. Keywords

34.1 acidity; alkalinity; titrations; water

TABLE 3 Determination of Precision and Bias for Acidity by Color-Change Titration After Hydrogen Peroxide Oxidation and Boiling (Test Method C)

Amount Added, meq/L	Amount Found, meq/L	S_t	S_o	Bias, %
		Acidity		
48.30	49.06	1.28	0.43	+1.57
23.00	23.00	0.46	0.37	0.00
0.07	0.15	0.12	0.69	+106.0

APPENDIXES

(Nonmandatory Information)

X1. DISCUSSION OF TERMS

X1.1 The terms, acidity and alkalinity, as used in water analysis may not be in accord with generally accepted terminology with a neutral point at pH 7. In water analysis, a pH of about 4.5 is frequently the end point for titration of alkalinity and a pH of about 8.2 for acidity.

X1.2 In addition to free hydroxide, alkalinity may be produced by anions that tend to hydrolyze; these include carbonate, bicarbonate, silicate, phosphate, borate, arsenate, aluminate, possibly fluoride, and certain organic anions in waste waters. All the effects due to these anions are lumped together in an alkalinity analysis.

X1.3 The factors causing acidity in water are also complex. Acidic materials encountered in water analysis include, in addition to free organic and mineral acids, uncombined dissolved gases, and acids formed on hydrolysis of salts of weak bases and strong acids. Hydrolyzable salts of aluminum and ferric and ferrous iron in mine drainage and certain industrial waste waters, are common causes of acidity. Acidity determinations on waters containing ferrous iron are further complicated by air oxidation of ferrous to the ferric state and subsequent hydrolysis to produce additional acidity.

X1.4 Since some water samples change on storage, analyses must be made without delay or results may be of little value. Interpretation of acidity and alkalinity data should be made cautiously. For a more thorough understanding of the subject, it is recommended that the analyst review the literature[8,9,10]. Then, the analyst may be able to develop an interpretation of his data better suited to his particular needs.

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[8] Hem, J. D., "Study and Interpretation of The Chemical Characteristics of Natural Water," *Geological Survey Water-Supply Paper 1473,* 1959, pp. 92–100.

[9] Rainwater, F. H., and Thatcher, L. L., "Methods for Collection and Analysis of Water Samples," *Geological Survey Water-Supply Paper 1454,* 1960, pp. 87–95.

[10] Sawyer, C. N., *Chemistry for Sanitary Engineers,* McGraw-Hill Book Co., Inc., New York, NY, 1960, pp. 211–227.

X2. INTERNAL ACID-BASE INDICATORS

X2.1 Table X2.1 is provided as a guide in the selection of a titration indicator for determinations of acidity and alkalinity.

X3. USES OF THE HYDROGEN PEROXIDE TEST METHOD

X3.1 The hydrogen peroxide test method is particularly suitable for assessing the acidity of mine drainage waters that are discharged into public streams. Under such conditions, all ferrous iron is rapidly oxidized to the ferric state, resulting in the precipitation of $Fe(OH)_3$:

$$2\ Fe^{+2} + 1/2\ O_2 + 4OH^{-1} + H_2O \rightarrow 2\ Fe(OH)_3 \qquad (4)$$

X3.2 The presence of ferrous ion in waters creates a twofold problem. First, the solubility of ferrous ion at a pH of 8.2 (phenolphthalein end point) is appreciable and the full acidity potential of the water cannot be assessed by direct titration to this end point. Second, at a pH of 8.2, soluble ferrous iron is rapidly oxidized by atmospheric oxygen. Subsequent hydrolysis of the resultant ferric ion immediately decreases the pH, resulting in a fading end point.

X3.3 Both problems can be avoided by oxidizing the ferrous ion with hydrogen peroxide prior to titration:

$$2\ Fe^{+2} + H_2O_2 + 2H^{+1} \rightarrow 2\ Fe^{+3} + 2H_2O \qquad (5)$$

During the subsequent titration, the ferric ion is precipitated as ferric hydroxide:

$$Fe^{+3} + 3\ OH^{-1} \rightarrow Fe(OH)_3 \qquad (6)$$

Note that in Eq. 2 and Eq. 3, the net effect is that two hydroxyl ions are consumed for each ferrous ion originally present, although the end product in each case is ferric hydroxide.

TABLE X2.1 pH End Points Equivalent to Color Change of Indicators

Indicator	Range		End Point	
	pH	Color	pH	Color
Phenolphthalein	8.0 to 10	colorless-red	8.2	pink
Methyl orange	3.2 to 4.4	pink-yellow	4.2	pink-orange
Methyl purple [A]	4.8 to 5.5	purple-green	4.9	gray-purple
Methyl red	4.2 to 6.2	pink-yellow	5.5	orange
Bromcresol green	4.0 to 5.4	yellow-blue	4.5	green
Bromphenol blue	3.0 to 4.6	yellow-blue	3.7	green

[A] Available as a prepared reagent from most chemical supply houses.

X4. RATIONALE FOR DISCONTINUATION OF TEST METHODS

X4.1 *Color-Comparison Titration:*

X4.1.1 This test method was discontinued in 1988. The test method may be found in its entirety in the 1988 *Annual Book of ASTM Standards*, Vol 11.01.

X4.1.2 This test method is applicable to routine control used in determining the acidity or alkalinity to a particular end point of waters containing no materials that buffer at the end point or interfere with the titration due to color or precipitation, or other reasons.

X4.1.3 The sample is titrated with standard acid or alkali to a predesignated pH, the end point being determined by comparison of the color developed by an added indicator with the color of a standard buffer solution containing the same added indicator.

X4.1.4 This test method was discontinued because there were insufficient laboratories interested in participating in another collaborative study to obtain the necessary precision and bias as required by Practice D 2777.

X4.2 *Color-Change Titration After Boiling:*

X4.2.1 This test method was discontinued in 1988. The test method may be found in its entirety in the 1988 *Annual Book of ASTM Standards*, Vol 11.01.

X4.2.2 This test method is applicable to routine control measurement of acidity or alkalinity of waters containing concentrations of slowly hydrolyzable materials sufficient to significantly delay attainment of equilibrium conditions at a titration end point. It is particularly applicable to mine drainage, industrial waste waters carrying waste acids, and similar waters. Volatile components contributing to the acidity or alkalinity of the water may be lost during sample pretreatment.

X4.2.3 The sample aliquot (acidified if alkaline) is boiled to accelerate chemical reactions for attaining equilibrium conditions, cooled, and titrated with standard acid or alkali to a predesignated end point. Titration is carried out by means of an internal indicator using the color-change procedure described in Test Method B (Electrometric or Color-Change Titration).

X4.2.4 This test method was discontinued because there were insufficient laboratories interested in participating in another collaborative study to obtain the necessary precision and bias as required by Practice D 2777.

SUMMARY OF CHANGES

This section identifies the location of selected changes to these test methods that have been incorporated since the last issue. For the convenience of the user, Committee D-19 has highlighted those changes that may impact the use of these test methods. This section may also include descriptions of the changes or reasons for the changes, or both.

(1) Sections 15, 24, and 33 and Tables 1, 2, and 3 were added.