

Standard Methods of Test for

ACIDITY AND ALKALINITY OF INDUSTRIAL WATER¹



ASTM Designation: D 1884 - 67

This Standard of the American Society for Testing and Materials is issued under the fixed designation D 1884; 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.

1. Scope

1.1 These methods cover the determination of acidity or alkalinity of industrial water. Four methods are given as follows:

	Sections
Referee Method (Electrometric Titration).....	5 to 13
Non-Referee Method A (Electrometric or Color-Change Titration).....	14 to 22
Non-Referee Method B (Color-Comparison Titration).....	23 to 30
Non-Referee Method C (Electrometric or Color-Change Titration after Boiling).....	31 to 39

1.2 In all the methods, hydrogen or hydroxide 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 standard acid (alkalinity). Of the four procedures, the Referee Method is the most precise and accurate. With it, a titration curve is developed which de-

¹ Under the standardization procedure of the Society, these methods are under the jurisdiction of the ASTM Committee D-19 on Water. A list of members may be found in the ASTM Year Book.

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finer inflection points and indicates buffering capacity; the acidity or alkalinity relative to a particular pH can be determined from the curve. The non-referee methods are used to determine acidity or alkalinity relative to a pre-designated end point based on the change in color of an internal indicator or the equivalent pH measured electrometrically. They are suitable for routine control purposes.

1.3 When titrating to selected datum points, the choice of end points will be determined primarily by the applicable process controls for the water; the choice must be such, however, that significant errors in titration due to inflection points on a typical titration curve are avoided. In some instances the titration end point may be at a pH beyond that at which the constituents of the water cease to react with the acid or alkali. Conversely, the desired end point may be such that only a part of the neutralizing capacity is measured.

2. Definitions

2.1 The terms "acidity" and "alkalinity" in these methods are defined in accordance with ASTM Definitions

D 1129, Terms Relating to Industrial Water and Industrial Waste Water,² as follows:

2.1.1 *Acidity*—The quantitative capacity of aqueous media to react with hydroxyl ions.

2.1.2 *Alkalinity*—The quantitative capacity of aqueous media to react with hydrogen ions.

2.2 For definitions of other terms used in these methods, refer to Definitions D 1129.

3. Purity of Reagents

3.1 Reagent grade chemicals, or equivalent, as defined in ASTM Methods E 200, Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis² shall be used in all tests.

3.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to ASTM Specifications D 1193, for Reagent Water,² referee grade. In addition, reagent water for this test shall be free of carbon dioxide (CO₂) and shall have a pH between 6.2 and 7.2 at 25 C (77 F). A procedure for the preparation of carbon dioxide-free water is given in Methods E 200.

4. Sampling

4.1 Collect the sample in accordance with the applicable method of the American Society for Testing and Materials, as follows:

- D 510—Sampling Industrial Water,²
- D 860—Sampling Water from Boilers,²
- D 1066—Sampling Steam,² and
- D 1192—Spec. for Equipment for Sampling Industrial Water and Steam.²

REFEREE METHOD

(Electrometric Titration)

5. Application

5.1 This method is applicable to the determination of acidity or alkalinity of

² Appears in this publication.

all industrial 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 relative to a particular pH is determined from the curve.

6. Summary of Method

6.1 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.

7. Interferences

7.1 Oily matter, soaps, suspended solids, and waste materials, sometimes found in industrial waters, may interfere with the pH measurement. Similarly, the development of a precipitate during titration may make the glass electrode sluggish and cause high results.

8. Apparatus

8.1 *Electrometric pH Measurement Apparatus*, conforming to the requirements given in ASTM Method D 1293, Test for pH of Industrial Water and Industrial Waste Water.²

9. Reagents

9.1 *Hydrochloric Acid, Standard Solution (0.02 N)* (Note 1)—Prepare and standardize as directed in Methods 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 having a normality of 0.02 N may be used instead of hydrochloric acid. Prepare and standardize in like manner.

9.2 *Sodium Hydroxide, Standard Solution (0.02 N)*—Prepare and standardize as directed in Methods 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.

10. Procedure

10.1 Mount the glass and reference electrodes in two of the holes of a clean, three-hole rubber stopper chosen to fit a 300-ml, tall-form Berzelius beaker without spout. Place the electrodes in the beaker and standardize the pH meter. Rinse the electrodes, first with reagent water, then with a portion of the sample. Following the final rinse, drain the beaker and electrodes completely.

10.2 Pipet 100 ml of the sample 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.

10.3 Measure the pH of the sample in accordance with Method D 1293.

10.4 Add either 0.02 *N* acid or alkali solution, as indicated, in increments of 0.5 ml or less (Note 2). After each addition, mix the solution thoroughly; determine the pH when the mixture has reached equilibrium as indicated by a constant reading (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 10 ml of standard solution for its titration, use a 0.1 *N* solution, prepared and standardized in the same manner (see Methods E 200).

NOTE 3—The equilibrium time will vary with different waters. In some instances, a waiting period of 30 sec may be required. When develop-

ing a titration curve, it is particularly important that equilibrium conditions be attained.

10.5 To develop a titration curve, plot the cumulative milliliters 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.

11. Calculation

11.1 Calculate the acidity or alkalinity, in equivalents per million as follows:

$$\text{Acidity (or alkalinity), epm} = AN \times 10$$

where:

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

N = normality of the standard solution.

12. Report

12.1 Report the results of titrations to specific end points as follows: "The acidity (or alkalinity) to pH at — C = — epm."

12.2 Appropriate factors for converting equivalents per million (epm) to other units are given in ASTM Method D 596, Reporting Results of Analysis of Industrial Water and Industrial Waste Water.²

13. Precision

13.1 No statement concerning the precision of this method can be made because of the transient nature of the equilibria involved and the pronounced variation in the characteristics of different waters.

NON-REFEREE METHOD A

(Electrometric or Color-Change Titration)

14. Application

14.1 This method covers the rapid, routine control measurement of acidity or alkalinity to predesignated end points