



Designation: D3875 – 08

Standard Test Method for Alkalinity in Brackish Water, Seawater, and Brines¹

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1. Scope

1.1 This test method covers the determination of alkalinity in brackish water, seawater, and brines.

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

1.3 *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:*

D1129 Terminology Relating to Water

D1193 Specification for Reagent 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 For definitions of terms used in this test method, refer to Terminology D1129.

4. Summary of Test Method

4.1 An electrotitrator or pH meter is used to determine the amount of acid necessary to reach pH 8.1 and 4.5, respectively. The pH values approximate the points where the hydroxide and bicarbonate ions are neutralized.

¹ This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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5. Significance and Use

5.1 Alkalinity as carbonate and bicarbonate of saline water is very important in chemical waterflooding or tertiary recovery processes for recovering petroleum. Alkaline waters offer better wetting to the formation rock and improve oil release. As an additional benefit, ions that provide alkalinity adsorb on rock surfaces occupying adsorption sites and decrease the loss of recovery chemical by adsorption. Determination of alkalinity in waters used in tertiary recovery processes is therefore very important.

5.2 An alkalinity value is necessary in the calculation of carbonate scaling tendencies of saline waters. It is also necessary to determine the alkalinity if the ionic balance of a water analysis is to be used as a check of the reliability of the analysis.

6. Interferences

6.1 Anions other than bicarbonate, carbonate, or hydroxide ions that form weakly dissociated acids that participate in hydrolysis reactions may also contribute to the alkalinity as may some organic materials. The user of this test method on determining the alkalinity is cautioned that all the effects of the anions entering into hydrolysis reactions are combined and reported as an equivalent amount of a single substance or two postulated ions. Included in the reported value is the alkalinity resulting from the presence of borate, silicate, sulfide, and phosphate. The effect of borate on the alkalinity value is considered negligible for waters with pH values of 7 or less.

7. Apparatus

7.1 *Electrotitrator or Standard pH Meter* with suitable electrodes. Maintenance and standardization of electrodes and pH meter should follow manufacturer's instructions because performance can be affected by improper treatment.

7.2 *Buret*, 10-mL micro.

8. Reagents

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,² where such specifications are available. 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, reference to water shall be understood to mean reagent water conforming to Specification D1193, Type I. 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 bias and precision of this test method. Type II water was specified at the time of round-robin testing of this test method.

8.3 *Sulfuric or Hydrochloric Acid, Standard Solution (not exceeding 0.1 N)*—See Practice E200 for preparation and standardization of acid.

8.4 *Buffer Solutions (pH 4, 7, and 10)*—These pH buffers are available from many chemical suppliers.

9. Sampling

9.1 Collect the sample in accordance with Practices D3370.

10. Procedure

10.1 Standardize the pH meter at a pH close to that of the samples. Normally this would be pH 7 for oilfield waters. However, depending on the source of the sample, it may be as low as pH 4 or as high as pH 10. Check the meter periodically with three buffers. Standardize the meter to 7 with pH 7 buffer and check its response at 4 and 10 with pH 4 and pH 10 buffers (within 0.1 pH unit). This is important. Serious errors can result if only one buffer is always used.

10.2 Make this analysis immediately after determining the pH in order to minimize errors due to decomposition of the bicarbonate of the sample. Transfer an undiluted sample, usually 50 to 100 mL, into a beaker.

10.3 Titrate with standard acid, while stirring, to pH 8.1 and record this volume as *P*. If water has a pH below 8.1, record *P* as zero and proceed to 10.4.

10.4 Continue the titration, with stirring, to pH 4.5 and record the total volume of acid used as *T*.

11. Calculation

11.1 Results of the titration offer a means for the stoichiometric classification of the three principal forms of alkalinity. The presence of the ions may be indicated by the relationships shown in Table 1 (Note). Using Table 1, make the following calculations:

NOTE 1—The presence of interferences (see 6.1) may produce errors in these relationships.

² *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 *Annual 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.

TABLE 1 Volume Relationships for Alkalinity Calculations^A

Results	Volume of Standard Acid Corresponding to		
	Bicarbonate, HCO ₃ ⁻	Carbonate, CO ₃ ⁼	Hydroxide, OH ⁻
<i>P</i> = 0	<i>T</i>	0	0
<i>P</i> < 1/2 <i>T</i>	<i>T</i> -2 <i>P</i>	2 <i>P</i>	0
<i>P</i> = 1/2 <i>T</i>	0	2 <i>P</i>	0
<i>P</i> > 1/2 <i>T</i>	0	2(<i>T</i> - <i>P</i>)	2 <i>P</i> - <i>T</i>
<i>P</i> = <i>T</i>	0	0	<i>T</i>

^A "Standard Methods for the Examination of Water and Wastewater," 13th edition, American Public Health Association, Washington, DC, 1975, p. 281.

T = total titration to pH 4.5, mL

P = titration to pH 8.1, mL

11.2 Bicarbonate:

$$HCO_3^-, \text{ mg/L} = (A \times N \times 61 \times 1000) / M$$

where:

- A* = millilitres of acid,
- N* = normality of acid, and
- M* = millilitres of sample.

11.3 Carbonate:

$$CO_3^-, \text{ mg/L} = (A \times N \times 30 \times 1000) / M$$

11.4 Hydroxyl:

$$OH^-, \text{ mg/L} = (A \times N \times 17 \times 1000) / M$$

11.5 Results of titrations to specific end points may alternatively be reported as follows: The alkalinity to pH ___ at ___, °C = ___ meq/L (epm).

12. Precision and Bias³

12.1 The precision of this test method within its designated range may be expressed as follows:

$$S_T = 0.005X + 2.8$$

$$S_O = 0.0076X + 0.375$$

where:

- S_T* = overall precision,
- S_O* = single-operator precision, and
- X* = concentration of alkalinity determined, mg/L.

Because of the instability of solutions prepared for alkalinity determinations, no statement of the accuracy of these measurements is practical. In determining the precision, six operators from five different laboratories analyzed three samples in duplicate on the same day.

12.2 The bias of this test method determined from recovery of a known amount of alkalinity in a prepared standard follows:

Amount Added mg/L	Amount Found mg/L	± Bias	± Bias	Statistically Significant (95 % Confidence Level)
975	973	-2	-0.2	no

³ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1059.