



# Standard Test Method for Alkalinity in Brackish Water, Seawater, and Brines<sup>1</sup>

This standard is issued under the fixed designation D3875; 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.

## 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 *Definitions*—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.

<sup>1</sup> 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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The pH values approximate the points where the hydroxide and bicarbonate ions are neutralized.

## 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.

NOTE 1—Automatic titrators with combined pH electrode are found

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

useful to increase reliability and save time. The use of an automatic titrator is recommended in the procedure.

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,<sup>2</sup> 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. (See Note 1.)

NOTE 2—Although most alkalinity methods titrate to a pH of 8.3, this method was proved out using a pH of 8.1.

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

<sup>2</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 *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.

## 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 3). Using Table 1, make the following calculations:

NOTE 3—The presence of interferences (see 6.1) may produce errors in these relationships.

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 Bias<sup>3</sup>

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<sub>T</sub>* = overall precision,  
*S<sub>O</sub>* = 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.

<sup>3</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1059. Contact ASTM Customer Service at service@astm.org.

TABLE 1 Volume Relationships for Alkalinity Calculations<sup>A</sup>

Results	Volume of Standard Acid Corresponding to		
	Bicarbonate, HCO <sub>3</sub> <sup>-</sup>	Carbonate, CO <sub>3</sub> <sup>=</sup>	Hydroxide, OH <sup>-</sup>
<i>P</i> = 0	<i>T</i>	0	0
<i>P</i> < ½ <i>T</i>	<i>T</i> -2 <i>P</i>	2 <i>P</i>	0
<i>P</i> = ½ <i>T</i>	0	2 <i>P</i>	0
<i>P</i> > ½ <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>

<sup>A</sup> "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

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

NOTE 4—The above bias estimate is based on an interlaboratory study on one artificial brine sample. Other samples used in the precision determination had been altered with acid after make-up to adjust the pH. Some alkalinity was lost in the process so these could not be used in the bias determination. The mean responses to the other two solutions were 176 mg/L and 537 mg/L.

12.3 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 **D2777** – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

### 13. Quality Control

13.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing alkalinity.

#### 13.2 Calibration and Calibration Verification:

13.2.1 Calibrate the pH meter using pH 4 and pH 7 solutions; or as recommended by the manufacturer.

13.2.2 For titration, standardize the titrant as directed above.

13.2.3 Verify titrant concentration after standardization by analyzing a standard at a mid-range concentration. The measured concentration of a mid-range standard should fall within  $\pm 15\%$  of the known concentration.

13.2.4 If calibration cannot be verified, recalibrate.

13.2.5 It is recommended to analyze continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or  $\pm 15\%$  of the known concentration.

#### 13.3 Initial Demonstration of Laboratory Capability:

13.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

13.3.2 Analyze seven replicates of a known solution prepared from an Independent Reference Material containing a known amount of alkalinity. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

13.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in **12.2**. This study should be repeated until the recoveries are within the limits given in **12.2**. If an amount other than the recommended amount is used, refer to Practice **D5847** for

information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

#### 13.4 Laboratory Control Sample (LCS):

13.4.1 To ensure that the test method is in control, analyze a LCS containing a known amount of alkalinity with each batch (laboratory defined in twenty samples). The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within  $\pm 15\%$  of the known amount.

13.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

#### 13.5 Method Blank:

13.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The amount of alkalinity found in the blank should be less than the analytical reporting limit. If the amount of alkalinity is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

#### 13.6 Matrix Spike (MS):

13.6.1 Alkalinity is not an analyte that can be feasibly spiked into samples.

#### 13.7 Duplicate:

13.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. The value obtained must fall within the control limits established by the laboratory.

13.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice **D5847** for information on applying the F test.

13.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

#### 13.8 Independent Reference Material (IRM):

13.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the analytical range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

## 14. Keywords

14.1 alkalinity; brackish; brine; seawater

## SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D3875 – 08) that may impact the use of this standard. (Approved Feb. 1, 2015.)

- (1) Sections 7 and 10 were modified to include a note about the use of an automatic titrator (Note 1). (3) 13.2.2, 13.2.3, and 13.2.5 were modified.
- (2) 10.3 had a note added about titrating to a pH of 8.1 and not 8.3 (Note 2).

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