



Designation: ~~D 3875-03~~ Designation: D 3875 - 08

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

This standard is issued under the fixed designation D 3875; 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 <sup>\*</sup>

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

~~1.2~~

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:*

D 1129 Terminology Relating to Water

~~D 1193 Specification for Reagent Water<sup>2</sup>~~ Specification for Reagent Water

D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D 3370 Practices for Sampling Water from Closed Conduits

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

E 200 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 D 1129.

### 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.

### 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

<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. Current edition approved Aug. 10, 2003. Published September 2003. Originally approved in 1980. Last previous edition approved in 1997 as D 3875-97. Current edition approved Oct. 1, 2008. Published November 2008. Originally approved in 1980. Last previous edition approved in 2003 as D 3875 - 03.

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

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,<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 D 1193, 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 E 200 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 D 3370.

## 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.

11.2 *Bicarbonate*:

$$\text{HCO}_3^-, \text{ mg/L} = (A \times N \times 61 \times 1000)/M$$

where:

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

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01-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<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

### 11.3 Carbonate:

$$CO_3^{2-}, \text{ mg/L} = (A \times N \times 30 \times 1000)/M$$

### 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:

$S_T$  = 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

NOTE 2—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 D 2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777—98, ~~– 06~~, 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 Verify instrument calibration by analyzing a sample with a known amount of alkalinity. The amount of the sample should fall within ±15% of the known concentration.

13.2.3 If calibration cannot be verified, recalibrate the instrument.

### 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. ~~The replicates may be interspersed with samples.~~

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 D 5847 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 or ten samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every ten samples. The LCS must be

<sup>2</sup> Annual Book of ASTM Standards, Vol 11.02.

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