

Standard Operating Procedure for the  
Determination of pH and Alkalinity  
CCAL 10B.0

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## Standard Operating Procedure for the Determination of pH and Alkalinity CCAL 10B.0

### 1.0 Scope and Application

- 1.1 The pH of most natural waters is usually in the 4 – 9 range. The majority are slightly basic because of the presence of carbonates and bicarbonates of the alkali and alkaline earth metals. The pH of a solution refers to its hydrogen ion activity and is expressed as the negative logarithm of the hydrogen ion activity in moles per liter at a given temperature. It is used in the calculation of carbonate, bicarbonate, carbon dioxide and other acid-base equilibria of importance to water analysis.
- 1.2 The alkalinity of water is its acid-neutralizing capacity, comprised of the total of all titratable bases. Alkalinity is a measure of the sum of properties of water, and can be interpreted in terms of specific substances only when the chemical composition of the sample is known. The alkalinity of most fresh waters is a function of concentration of carbonate, bicarbonate and hydroxide.

### 2.0 Summary of Method

- 2.1 The pH of a sample is determined electrometrically using a combination electrode.
- 2.2 Alkalinity of a sample is a measure of its quantitative capacity to neutralize an acid to a specific pH. When alkalinity is due predominately to carbonate or bicarbonate, as in fresh waters, the pH at the equivalence point is determined by the concentration of carbon dioxide (CO<sub>2</sub>) at that point. The concentration of CO<sub>2</sub> depends upon the total carbonate species originally present.

### 3.0 Definitions

- 3.1 DI water: Water that has been through a deionization system to produce water similar to ASTM Type I reagent with 16.7 Mohms resistivity (ASTM) (Reference 16.3).

- 3.2 Method Detection Limit (MDL): The minimum concentration of an analyte that can be measured and reported with 99% confidence, based on a one-sided 99% confidence interval ( $t$ -value at a significance level of 0.01 and  $n-1$  degrees of freedom) from at least seven repeated measurements of a low concentration standard measured within an analysis run.

$$\text{MDL} = ts$$

Where,

$t$  = Student's  $t$  value at a significance level of 0.01 and  $n-1$  degrees of freedom

$s$  = standard deviation of at least seven repeated measurements of a low level standard

## 4.0 Interferences

- 4.1 Surfactants, suspended solids or precipitates may coat the pH electrode and slow response. Allow the electrode to come to equilibrium between titrant additions. Do not filter, dilute or alter the sample.
- 4.2 Dissolved gases, such as inorganic carbon, may be lost during sampling, storage or titration. Minimize contact with air and sample hold times.
- 4.3 pH potential and ionization vary with temperature. Use temperature compensation adjustment and record the pH of the sample. Samples should be measured at ambient temperature.

## 5.0 Safety

- 5.1 The toxicity or carcinogenicity of each reagent has not been precisely determined; however, each chemical should be regarded as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Cautions are included for known extremely hazardous materials.
- 5.2 The following chemicals have the potential to be highly toxic or hazardous. For detailed explanations, consult the MSDS.
- 5.2.1 Sulfuric acid

## 6.0 Equipment and Supplies

**Note:** *Brand names, suppliers and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

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- 6.1 Radiometer AutoTitrator System
  - 6.1.1 Radiometer TIM840 AutoTitrator
  - 6.1.2 Radiometer SAC80 Auto Sampler
  - 6.1.3 Instrument Controller
  - 6.1.4 Data Collection Software (TitraMaster 85)
- 6.2 pH Electrodes
- 6.3 Temperature Probe
- 6.4 Mixing paddle with motor
- 6.5 150 mL beakers, dedicated to these two procedures.
- 6.6 Safety glasses
- 6.7 Nitrile gloves
- 6.8 Lab coat or apron
- 6.9 Laboratory Exhaust Fume Hood

## 7.0 Reagents and Standards

- 7.1 Preparation of Reagents
  - 7.1.1 *0.02 N Sulfuric acid solution:*  
Prepared from Dilut-it ampules of sulfuric acid (commercially available product). Standardize the acid by titrating standard 0.02 N  $\text{Na}_2\text{CO}_3$  of two different dilute concentrations in 100 mL DI water. Calculate the acid normality at each concentration of  $\text{Na}_2\text{CO}_3$  and average all values to determine the normality of the  $\text{H}_2\text{SO}_4$ .
- 7.2 Preparation of Standards
  - 7.2.1 *pH Buffers:*  
Commercially prepared buffer solutions of pH 4.0, 7.0 and 10.0.

### 7.2.2 *Sodium Carbonate Standard:*

Dissolve 1.06 g oven dried  $\text{Na}_2\text{CO}_3$  in 1 L DI water. Store in a pyrex bottle with ground glass stopper.

## 8.0 Sample Handling and Storage

- 8.1 Unfiltered samples are stored at 4°C in the dark. Samples are analyzed within 7 days to ensure sample integrity.

## 9.0 Quality Control

- 9.1 Preparation of standards is recorded on worksheets and documented by weight of standard added to a given flask before dilution to volume with DI water. All records of certification are kept on file at CCAL Laboratory.
- 9.2 Blank: DI water twice each analysis batch.
- 9.3 Quality Control Check Sample: sample run once each analysis batch.
- 9.4 Method Detection Limit (MDL): Established for each analyte. Based on a one-sided 99% confidence interval (t-value) from at least seven repeated measurements of a low concentration standard. The t-distribution value is multiplied by the standard deviation of the population (n-1) to obtain the MDL.
- 9.5 Analytical Duplicate: Separate analysis from the same sample aliquot. Run a minimum of once each analysis set.

## 10.0 Calibration and Standardization

- 10.1 Balances: calibrated yearly by external vendor.
- 10.2 Pipette delivery checked by weight to within 2% of theoretical weight of aliquot volume.

## 11.0 Procedure

- 11.1 Calibration of the pH Meter and Standardization of Titration Acid

- 11.1.1 Before starting the pH and alkalinity determinations, uncover the hole on the side of the electrode by removing the rubber sleeve to allow the internal air pressure to equilibrate with atmospheric air pressure. If necessary, add 4 M KCl filling solution through the fill hole so that the fluid level is even with the hole. Ensure there are at least 1 cm of loose KCl crystals in the bottom of the electrode; if not, add. Turn on the TIM840 instrument, the SAC80 Autosampler, and the computer. Place the electrodes in a beaker of fresh DI water and set the TIM840 to display measurement to ensure the electrodes are working. Exit the display measurement, and allow the instrument to warm up for at least 90 minutes to ensure complete electrode stabilization.
- 11.1.2 Three buffers are used for initial calibration. Place the calibration beakers in the first three positions of the SAC80 Autosampler in the following order: pH 7.0, pH 4.0, pH 10.0. Place two rinse beakers with fresh DI water in the last two positions of the SAC80 Autosampler. On the TIM840, activate the pH probe calibration sequence and the method will automatically calibrate the pH probes. Remove the calibration beakers when finished.
- 11.1.3 As long as the calibration results are within the pre-set acceptance criteria, then the pH probe has been calibrated and is ready for the analysis of pH and alkalinity.
- 11.1.4 The temperature compensator probe can mitigate temperature effects on sample pH, but sample temperature should be above 17°C. The temperature of buffer solutions and samples should be approximately the same, and should be at or approaching room temperature.
- 11.1.5 Set up two 100 mL DI water blanks and one each of the following 0.02 N Na<sub>2</sub>CO<sub>3</sub> standards as follows:
  - a) 1.0 mL of 0.02 N Na<sub>2</sub>CO<sub>3</sub> brought to 100 mL with DI water.
  - b) 3.0 mL of 0.02 N Na<sub>2</sub>CO<sub>3</sub> brought to 100 mL with DI water.
- 11.1.6 Place the blanks and standards into the first four positions of the SAC80 Autosampler in the following order: Blank, Blank, 1 mL Std., 3 mL Std. Ensure there are two rinse beakers in the last two positions of the autosampler.
- 11.1.7 Using the TIM840 and the computer, enter the proper ID names and SAC80 positions of the samples to be analyzed, and activate a pH and alkalinity method on the blanks and standards.

11.1.8 After the analysis of the blanks and standards, evaluate the results. Compare pH values for blanks and standards to historic values to ensure that pH response is within analytical limits. Compare titration volumes for blanks and standards to historic values to ensure that the titrator is operating correctly, and that titrant concentration has not degraded.

## 11.2 Sampling Procedures

11.2.1 To each 150 mL sample beaker properly marked to identify sample, add 100 mL of the unfiltered and well mixed sample.

11.2.2 Analyze the samples for pH and alkalinity using the TIM840 analysis methods, ensuring to record the beaker number and SAC80 position number of each sample.

11.2.3 When analyses are complete, shut-down the TIM840, the SAC80, and the computer. Re-cover the electrode fill hole with the rubber sleeve, and place the electrodes into a clean beaker filled with electrode soaking solution.

## 11.3 System Notes

11.3.1 The following tables provide the programming parameters used in the TIM840 for the analysis of pH.

<b>pH Probe Parameters</b>	
Stability Criterion:	10 mpH/min
Acceptation:	8 min
Max Stab. Time:	8 min
ISO pH:	6.65 pH
Acceptance Criteria:	YES
Min pH0(25):	5.8 pH
Max pH0(25):	7.5 pH
Min Sensitivity:	95%
Max Sensitivity:	103%
Min Temp.:	0°C
Max Temp.:	60°C

<b>pH Program Parameters*</b>	
Mode:	Measurement
Measurement:	pH
Temperature:	Probe
number of tests:	1
Cell Grounding:	Reference
Auxiliary Output:	no
Stability:	10 mpH/min
Acceptation:	8 min
Max Stab. Time:	8 min
Stirring:	no

*The pH program is a coupled method where the first method is a program designed to stir the sample for 10 sec. The second method is the pH program itself.*

11.3.2 The following tables provide the programming parameters used in the TIM840 for the analysis of alkalinity.

<b>Alkalinity Common Program Parameters</b>	
Mode:	End Point
Measurement:	pH
Temperature:	Probe
Number of Tests:	1
Cell Grounding:	Reference
Blank:	no
Titrant:	H <sub>2</sub> SO <sub>4</sub> (~0.02N)**
Predose:	0.00ml
Start Timer:	5sec
Max Volume:	30.00ml
Back Titration:	no
Direction:	decreasing pH
Number of Endpoints:	1
Auxiliary Output:	no
1-End Point:	4.500pH

*\*\* The H<sub>2</sub>SO<sub>4</sub> titrant is entered into the TIM840 as 0.02N. However, the actual acid normality is calculated each day of analysis using the blanks and standards.*

Alkalinity Program Differences***			
Parameters	Alk L	Alk M	Alk H
Minimum Speed:	0.01ml/min	0.02ml/min	0.08ml/min
Max Speed:	1.50ml/min	5.00ml/min	5.00ml/min
End Point Delay:	8sec	5sec	8sec
Proportional Band:	2.400pH	2.000pH	0.700pH

\*\*\* The different programs are used for various ranges of alkalinity. L for low level, M for mid range, and H for high level alkalinity. The use of a specific program is based on the measured conductivity, total alkalinity and ionic strength of each sample.

## 12.0 Data Analysis and Calculations

### 12.1 Determination of Total Alkalinity as HCO<sub>3</sub>-C

$$N_a = \frac{(N \text{ Na}_2\text{CO}_3) * (V \text{ Na}_2\text{CO}_3)}{(V \text{ H}_2\text{SO}_4 \text{ titrant} - V \text{ avg blank})}$$

$$\text{Total Alkalinity as HCO}_3\text{-C} = \frac{N_a V_a * 12 * 1000}{V_{\text{sample}}}$$

$$\text{Total Alkalinity as CaCO}_3 = \frac{N_a V_a * 50 * 1000}{V_{\text{sample}}}$$

$$\text{Total Alkalinity as CaCO}_3 \text{ ueq/L} = \frac{N_a V_a * 50 * 1000}{V_{\text{sample}}} * 83.256$$

Where N= normality, N<sub>a</sub> = final acid normality, V = volume, V<sub>a</sub> = titrant volume. (Final acid normality is determined by averaging results for the 1 mL and 3 mL standards.)

12.2 All raw data values are captured electronically, and results calculated within spreadsheet software. Sample and instrument specific information is recorded on the data sheet (see 17.1).

## 13.0 Method Performance

13.1 This method was validated through inter-laboratory studies. The CCAL participates in the USGS Standard Reference Water QA program.

## 14.0 Pollution Prevention

- 14.1 The chemicals used in this method pose little threat to the environment when properly managed.
- 14.2 All standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of disposable waste.
- 14.3 For further information on pollution prevention consult *Less is better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16<sup>th</sup> Street NW, Washington D.C. 20036, (202) 872-4477.

## 15.0 Waste Management

- 15.1 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, and to protect the environment by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required.
- 15.2 For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", and "Less is Better: Laboratory Chemical Management for Waste Reduction", both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16<sup>th</sup> Street NW, Washington DC, 20036.

## 16.0 References

- 16.1 Standard Methods For The Examination of Water and Wastewater, Method 2320-Alkalinity and 4500-H, pH Value. American Public Health Association. 21<sup>st</sup> Edition, 2005.
- 16.2 Code of Federal Regulations. Protection of Environment. Section 40, Appendix B to Part 136. Definition and procedure for the determination of the method detection limit. Revision 1.11. Revised July 1, 1990. Office of the Federal Register, National Archives and Records.
- 16.3 ASTM. American Society for Testing and Materials. Standard Specifications for Reagent Water. D1193-77 (Reapproved 1983). Annual Book of ASTM Standards, Vol. 11.01. ASTM: Philadelphia, PA, 1991.

- 16.4 Larson, T.E. and L.M. Henley. 1955. Determination of Low Alkalinity or Acidity in Water. *Anal. Chem.* 27:851.
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- 16.7 Winter, J.A. & M.R. Midgett. 1969. *Physical Analysis FWPCA*, Washington, D.C.
- 16.8 American Water Works Assoc. 1964. *Simplified procedures for water examinations manual. M12.* Amer. Water Works. Assoc. New York, New York.
- 16.9 Radiometer Instrument, Software and Reference manuals. Radiometer Analytical, Hach Company; Loveland, Colorado

## **17.0 Tables, Diagrams, Flowcharts, and Validation Data**

- 17.1 pH, Alkalinity and Conductivity Data Sheet



## **18.0 Document Revision History**

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Document updated for new instrumentation