Standard Operating Procedure for the Determination of pH and Alkalinity

CCAL 10C.2

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Table of Contents

1.0 Scope and Application ... 3
2.0 Summary of Method ... 3
3.0 Definitions ... 3
4.0 Interferences ... 4
5.0 Safety ... 4
6.0 Equipment and Supplies ... 5
7.0 Reagents and Standards ... 5
  7.1 Preparation of Reagents ... 5
  7.2 Preparation of Standards ... 6
8.0 Sample Handling and Storage ... 6
9.0 Quality Control ... 6
10.0 Calibration and Standardization ... 6
11.0 Procedure ... 6
  11.1 Calibration of the pH Meter and Standardization of Titration Acid ... 6
  11.2 Sampling Procedures ... 7
  11.3 System Notes ... 7
12.0 Data Analysis and Calculations ... 8
13.0 Method Performance ... 9
14.0 Pollution Prevention ... 9
15.0 Waste Management ... 9
16.0 References ... 9
17.0 Tables, Diagrams, Flowcharts, and Validation Data ... 11
  17.1 pH, Alkalinity and Conductivity Data Sheet ... 11
18.0 Document Revision History ... 12

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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_2) at that point. The concentration of CO_2 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.*

6.1 ManTech AutoTitrator System

6.1.1 ManTech Burivar I/2 AutoTitrator
6.1.2 ManTech Automax73 Auto Sampler
6.1.3 Instrument Controller
6.1.4 Data Collection Software (PC-Titrate)

6.2 pH electrodes

6.3 Temperature probe

6.4 Mixing paddle with motor

6.5 125 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), or purchased as prepared solution. Standardize the acid by titrating standard 0.02 N Na_2CO_3 of two different dilute concentrations in 100 mL DI water. Calculate the acid normality at each concentration of Na_2CO_3 and average all values to determine the normality of the H_2SO_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 Na_2CO_3 in 1 L DI water. Store in a Pyrex bottle with a 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 Volume of standard pipetted is checked by weight at time of preparation.

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 1% of theoretical weight of aliquot volume.

11.0 Procedure

11.1 Calibration of the pH Meter and Standardization of Titration Acid

11.1.1 Prepare the auto-titrator system in accordance with operating procedures including electrode maintenance, clearing bubbles from the syringe and titrant flushing. Allow the instrument to warm up for at least 90 minutes to ensure complete electrode stabilization.

11.1.2 Prepare blanks and alkalinity standards according to operating procedures. Allow samples to stabilize two hours prior to analysis.

11.1.3 Calibrate the pH meter using three buffers: pH 4.0, pH 7.0, and pH 10.0. Evaluate results for validity and proceed with analysis.

11.1.4 Analyze blanks and standards for pH and alkalinity. Evaluate results for validity and proceed with analysis of samples.

11.2 Sampling Procedures

11.2.1 To each labelled 125 mL sample beaker add 100 mL of well mixed unfiltered sample. Allow samples to equilibrate to room temperature before analysis.

11.2.2 Enter the sample ID’s from the sample loading guide in the software sample table and analyze samples.

11.2.3 When analyses are complete and results evaluated, shut-down the auto-titrator and the computer. Place the electrodes into a clean beaker filled with electrode soaking solution.

11.3 System Notes

11.3.1 Blanks are 100 mL DI water (two per analysis run). Standards are 1.00 mL of 0.02 N Na_2CO_3 brought to 100 mL with DI water and 3.00 mL of 0.02 N Na_2CO_3 brought to 100 mL with DI water.

11.3.2 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.

11.3.3 The temperature compensator probe can mitigate temperature effects on sample pH, but sample temperature should be above 17ºC. The temperature of buffer solutions and samples should be approximately the same, and should be at or approaching room temperature.

11.3.4 For samples with conductivities greater than 100 µS/cm set-up and analyze 50 mL aliquots for alkalinity.

11.3.5 Electrode soaking solution is pH 4.0 buffer.

11.3.6 The pH program is a coupled method which contains a snippet designed to stir the sample for 10 seconds.

11.3.7 The H_2SO_4 titrant is entered into the alkalinity snippets as 0.020000N. However, the actual acid normality is calculated each day of analysis using the blanks and standards.

12.0 Data Analysis and Calculations

12.1 Determination of Total Alkalinity as $CaCO_3$

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

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

$$\text{Alkalinity as CaCO}_3\ \mu\text{eq/L} = \frac{N_a V_a * 50 * 1000}{Vsample} * 20$$

Where N= normality, N_a = final acid normality, V = volume, V_a = titrant volume. (Final acid normality is determined by averaging results for the 1 mL and 3 mL standards.)

12.2 Determination of Low Alkalinity as $CaCO_3$

For Alkalinity less than 20 mg/L, stop the titration at a pH of approximately 4.3. At a pH of approximately 4.6, record the volume and at a difference closest to 0.30 pH units less, record the volume.

$$\text{Low Alkalinity as CaCO}_3\ \mu\text{eq/L} = \frac{(2\text{ B - C}) * \text{N} * 50000}{\text{mL sample}}$$

Where N= normality of acid, B = mL titrant to first recorded pH, C = total mL titrant to reach pH 0.3 unit lower.

12.3 All raw data values are captured electronically, and results calculated within spreadsheet software. For samples with low alkalinity, volumes and pH are recorded on data sheet. Sample and instrument specific information is also recorded on the data sheet (see 17.1).

13.0 Method Performance

13.1 This method was validated through inter-laboratory studies. The CCAL Water Analysis Laboratory 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 16th 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 *Less is Better: Guide to Minimizing Waste in Laboratories*, available from the American Chemical Society at www.acs.org, and *Environmental Management Guide For Small Laboratories* (233B00001) from the US Environmental Protection Agency at https://nepis.epa.gov.

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. 21st 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.

16.5 Pellenberg, R.E. and T.M. Church. 1978. Analytical Chemica Acta 97.

16.6 Thomas J.F.J. & J.J. Lynch. 1963. J. Amer. Water Works Assoc.52:259.

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 ManTech Instrument, Software and Reference manuals. ManSci, Inc.; Tonawanda, New York. http://mansci.com.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

17.1 pH, Alkalinity Data Sheet

pH, Alkalinity

page _____ of ______

Project: __________ Alkalinity Volume (mL): _________ Filtered Unfiltered

Analyst: __________ Date: ____________________

Remarks: ____

____

Buffer Calibration:

Cup #	Sample #	Observations	Smplr #
	QPHB0		4
	QPHB1		5
	QPHB2		6
	QPHM1		7
	QPHM3		8
			9
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18.0 Document Revision History

Original Document: April 2006
Version: 10A.0

Edit Date: May 2008
New Version: 10B.0
Document updated for new instrumentation

Edit Date: February 2010
New Version: 10B.1
Address update
Section 13.1: add Environment Canada Proficiency Testing Program participation
Section 12.1: change reporting units for alkalinity to conform to current standards

Edit Date: February 2011
New Version: 10C.0
Document updated for new instrumentation
Add Jeffrey Wyant as Coauthor

Edit Date: February 2015
New Version 10C.1
Section 11.1: move operations information to system notes
Section 11.2: move operations information to system notes
Section 11.3: remove system programming tables
General editing

Edit Date: February 2026
New Version 10C.2
Section 12.0: Added sub-section for Determination of Low Alkalinity as $CaCO_3$.
*Low volume correction calculation started 4/16/20.
Section 17.1: Updated pH, Alkalinity Data Sheet
Section 13.0: Removed NWRI proficiency program participation
General editing