



Environmental Analysis Program

Pomona College
Biogeochemistry Laboratory

SOP-L301

Alkalinity – Titration Method

Standard Operating Procedure

SOP Number	SOP-L301
Revision	0.1
Author(s)	Marc Los Huertos
Date	2026-06-26
Organization	EA Program, Pomona College

FOR INTERNAL USE ONLY

This document is the property of the Environmental Analysis Program at Pomona College.
Unauthorized distribution is not permitted.

Table of contents

1 Purpose	2
2 Scope	2
3 Responsibilities	2
4 Definitions	2
5 Safety and Hazards	3
5.1 Required PPE	3
5.2 Emergency Procedures	3
6 Equipment and Materials	3
6.1 Equipment	3
6.2 Reagents	4
6.3 Optional Indicator Solutions	4
7 Procedure	4
7.1 Standardizing the 0.1 N H ₂ SO ₄	4
7.2 Preparing the 0.02 N H ₂ SO ₄ Working Titrant	5
7.3 Sample Collection and Handling	5
7.4 Selecting Sample Size and Titrant	5
7.5 pH Meter Calibration	6
7.6 Potentiometric Titration	6
7.7 Low-Alkalinity Method (Below 20 mg/L as CaCO ₃)	6
8 Quality Control and Acceptance Criteria	7
8.1 Calculations	7
8.2 Alkalinity Species	7
8.3 QC Requirements	7
9 Waste Disposal	7
10 References	8
11 Training Record	8

12 Appendix A: Titrant Preparation Quick Reference	8
12.1 N H ₂ SO ₄ from Concentrated H ₂ SO ₄	8
12.2 N H ₂ SO ₄ from 0.1 N Stock	9
13 Appendix B: Example Calculation	9
14 Appendix C: Troubleshooting	9

1. Purpose

This procedure describes the determination of alkalinity in water samples by potentiometric titration with standardized sulfuric acid, following Standard Methods 2320 B (APHA et al., 2012). Alkalinity is the acid-neutralizing capacity of water and is primarily a function of carbonate, bicarbonate, and hydroxide content. It is a fundamental parameter for characterizing water chemistry, assessing buffering capacity, and interpreting corrosivity, hardness, and suitability for irrigation or aquatic life.

2. Scope

- **Applies to:** Surface water, groundwater, stormwater, and wastewater samples collected per [SOP-F300](#)
- **Does not apply to:** Soil alkalinity, industrial process water requiring specialized titration protocols, or samples with alkalinity above 500 mg/L as CaCO₃ (which require 0.1 N titrant; see note in Section 6.4)
- **Location:** EA Program laboratory, SGM 133

3. Responsibilities

Role	Responsibility
Lab PI	Approve SOP, ensure training compliance
Lab Manager	Prepare and standardize titrant, maintain pH meter
Trained Personnel	Perform titrations, record and report results
New Students	Complete training before independent use

4. Definitions

- **Acid-neutralizing capacity (ANC):** The capacity of a water to neutralize strong acid; for most natural waters, ANC is approximately equal to total alkalinity.
- **Alkalinity:** The capacity of water to resist acidification, expressed in mg/L as CaCO₃; in natural waters, primarily contributed by bicarbonate (HCO₃⁻), carbonate (CO₃²⁻), and hydroxide (OH⁻).

- **Bicarbonate alkalinity:** Alkalinity attributable to HCO_3^- ; the dominant form in most fresh waters at pH 6.3–10.3.
- **Endpoint pH:** The pH at which the titration is stopped to correspond to the equivalence point of the reaction between the alkalinity species and the standard acid; 4.5 for routine total alkalinity, 8.3 for phenolphthalein (P) alkalinity.
- **Normality (N):** The number of gram-equivalents of a substance per liter of solution; for H_2SO_4 used in alkalinity titrations, 1 N = 0.5 M because each H_2SO_4 donates 2 protons.
- **Phenolphthalein alkalinity (P alkalinity):** Alkalinity measured to the pH 8.3 endpoint; represents OH^- and half of CO_3^{2-} content; zero if the sample pH is initially below 8.3.
- **Potentiometric titration:** Titration in which the endpoint is determined by monitoring electrode potential (pH) rather than by a color indicator.
- **Standardization:** The process of determining the exact concentration of a titrant by titrating a primary standard of known purity and mass (e.g., anhydrous Na_2CO_3).
- **Total alkalinity (T alkalinity):** Alkalinity measured to the pH 4.3–4.5 endpoint; represents the sum of all alkalinity species.

5. Safety and Hazards

Hazards

- **Chemical:** Sulfuric acid (0.02 N) is a dilute acid but can cause skin and eye irritation. Concentrated H_2SO_4 used to prepare stock solutions is severely corrosive.
- **Physical:** Glassware (burets, beakers) poses a breakage and laceration risk.

5.1. Required PPE

- ☐ Safety glasses
- ☐ Lab coat
- ☐ Nitrile gloves

5.2. Emergency Procedures

For acid splashes to skin or eyes, flush immediately with water at the eyewash station for at least 15 minutes. For concentrated acid spills, neutralize with sodium bicarbonate and refer to [SOP-L003 Hazardous Materials Handling](#).

6. Equipment and Materials

6.1. Equipment

Item	Notes
pH meter with combination electrode	Calibrated per SOP-L300

Item	Notes
Magnetic stir plate and stir bar	For continuous mixing during titration
Buret, 50 mL (Class A)	For samples with alkalinity above 20 mg/L as CaCO_3
Buret, 10 mL (Class A, microburet)	For low-alkalinity samples (below 20 mg/L)
Buret stand and clamp	–
Volumetric flasks (100 mL, 1 L)	For standard preparation
Graduated cylinder (100 mL)	For measuring sample volumes
Beakers (150 – 250 mL)	For titration
Analytical balance	0.1 mg readability; see SOP-L200

6.2. Reagents

Item	Notes
Standard H_2SO_4 , 0.1 N	Prepare from concentrated H_2SO_4 or purchase pre-made; standardize against Na_2CO_3 (see Section 6.1)
Standard H_2SO_4 , 0.02 N	Dilute from 0.1 N stock (see Section 6.2)
Sodium carbonate (Na_2CO_3), primary standard grade	For standardizing the acid titrant
pH buffer solutions (pH 4.01, 7.00, 10.01)	For pH meter calibration
Deionized water (Type I or II)	For reagent preparation, blanks, and rinsing

6.3. Optional Indicator Solutions

Color indicators may be used for preliminary or routine titrations when the sample is free of interfering color and turbidity. Potentiometric (pH meter) titration is preferred for accuracy.

Indicator	Endpoint pH	Application
Phenolphthalein	8.3	Phenolphthalein (P) alkalinity
Bromocresol green	4.5	Total (T) alkalinity
Mixed bromocresol green – methyl red	4.5	Total (T) alkalinity

7. Procedure

7.1. Standardizing the 0.1 N H_2SO_4

1. Dry 3–5 g of primary standard Na_2CO_3 at 250 °C for 4 hours and cool in a desiccator
2. Weigh 2.500 $\pm$ 0.020 g (to the nearest 0.001 g) into a 1 L volumetric flask. Dissolve in DI water and bring to volume. This produces an approximately 0.05 N Na_2CO_3 solution.
3. Pipette 40.00 mL of the Na_2CO_3 solution into a 250 mL beaker. Add approximately 60 mL of DI water.
4. Titrate potentiometrically with the approximately 0.1 N H_2SO_4 to a pH of about 5

5. Remove the electrodes, rinse into the beaker, and gently boil the solution for 3–5 minutes under a watch glass to expel CO_2
6. Cool to room temperature, rinse the watch glass into the beaker, and continue titrating to the pH inflection point
7. Calculate the normality of the acid:

$$N_{\text{acid}} = \frac{A \times B}{53.00 \times C}$$

where A = g Na_2CO_3 weighed into the 1 L flask, B = mL Na_2CO_3 solution taken for titration, and C = mL acid used.

8. Adjust to 0.1000 N or use the measured normality in all subsequent calculations. At 0.1000 N, 1.00 mL = 5.00 mg CaCO_3 .

7.2. Preparing the 0.02 N H_2SO_4 Working Titrant

1. Dilute 200.00 mL of standardized 0.1000 N H_2SO_4 to 1000 mL with DI water in a volumetric flask
2. Mix thoroughly
3. Verify the normality by titrating 15.00 mL of 0.05 N Na_2CO_3 as described in Section 6.1
4. At 0.02 N, 1.00 mL = 1.00 mg CaCO_3
5. Store in a tightly capped borosilicate glass or polyethylene bottle. Do not keep for longer than 1 week without re-standardization.

7.3. Sample Collection and Handling

1. Collect samples in polyethylene or borosilicate glass bottles per [SOP-F300](#)
2. Fill sample bottles completely with no headspace; CO_2 exchange with air will alter the alkalinity
3. Analyze samples as soon as possible after collection, ideally within 24 hours. Refrigerate at 4 C if analysis must be delayed.
4. Do not filter, dilute, concentrate, or otherwise alter the sample before titration

7.4. Selecting Sample Size and Titrant

Choose the sample volume and titrant normality to use a reasonable volume of titrant (ideally 20 mL or more from a 50 mL buret) for good volumetric precision:

Expected Alkalinity (mg/L as CaCO_3)	Sample Volume	Titrant Normality
Less than 20	200 mL	0.02 N (10 mL microburet)
20 – 100	100 mL	0.02 N
100 – 500	100 mL	0.1 N

If the expected alkalinity is unknown, perform a preliminary titration with indicator to estimate the range before running the potentiometric titration.

7.5. pH Meter Calibration

Calibrate the pH meter with a three-point calibration (pH 4.01, 7.00, 10.01) per [SOP-L300](#) before each titration session. Verify that the calibration slope is between 90% and 102% of theoretical.

7.6. Potentiometric Titration

1. Measure the selected sample volume (e.g., 100 mL) into a clean beaker using a graduated cylinder
2. Place the beaker on the magnetic stir plate and add a clean stir bar. Set the stirrer to a speed that produces a gentle vortex without splashing or entraining air.
3. Immerse the pH electrode in the sample. Record the initial pH.
4. Fill the buret with standardized H_2SO_4 (0.02 N or 0.1 N as selected in Section 6.4). Record the initial buret reading.
5. **Phenolphthalein alkalinity (P):** If the initial pH is above 8.3, titrate to pH 8.3, recording the volume of acid used. This is the P alkalinity endpoint.
6. **Total alkalinity (T):** Continue titrating to the total alkalinity endpoint. Select the endpoint pH from the table below based on the expected alkalinity concentration:

Total Alkalinity (mg/L as CaCO_3)	Endpoint pH
Approximately 30	4.9
Approximately 150	4.6
Approximately 500	4.3
Routine or automated analyses	4.5

7. As the endpoint is approached, add acid in smaller increments (0.1–0.2 mL) and allow pH equilibrium to be reached before adding more titrant
8. Record the final buret reading

Tip

For best results, record the pH after each addition of acid and construct a full titration curve. The inflection point (steepest slope) on the curve confirms the endpoint pH. This is especially important for samples with unusual chemistry (e.g., high phosphate or silicate content) where the standard endpoint pH may not correspond to the true equivalence point.

7.7. Low-Alkalinity Method (Below 20 mg/L as CaCO_3)

For samples with alkalinity below 20 mg/L, use a 200 mL sample volume and titrate with 0.02 N H_2SO_4 from a 10 mL microburet. Record intermediate pH values to construct a titration curve and determine the endpoint from the inflection point. Report only low-alkalinity values determined by this method.

8. Quality Control and Acceptance Criteria

8.1. Calculations

Total alkalinity (mg/L as CaCO_3):

$$\text{Alkalinity} = \frac{A \times N \times 50,000}{V}$$

where A = mL of standard acid used, N = normality of the acid, and V = mL of sample.

Phenolphthalein alkalinity uses the same formula but substitutes the volume of acid titrated to pH 8.3.

8.2. Alkalinity Species

Once P and T alkalinity are determined, the individual carbonate species can be calculated:

Condition	Hydroxide (OH^-)	Carbonate (CO_3^{2-})	Bicarbonate (HCO_3^-)
$P = 0$	0	0	T
$P < T/2$	0	2P	$T - 2P$
$P = T/2$	0	2P	0
$P > T/2$	$2P - T$	$2(T - P)$	0
$P = T$	T	0	0

All values are expressed as mg/L CaCO_3 .

8.3. QC Requirements

- Standardize titrant before each batch and at least weekly
- Run a DI water blank at the start of each session; the blank should consume less than 0.2 mL of 0.02 N acid
- Prepare and titrate a laboratory fortified blank (LFB) using a known concentration of Na_2CO_3 at least once per batch of 20 samples. Recovery should be 90–110%.
- Run duplicate titrations on at least 10% of samples. Acceptable precision: $\pm 5\%$ relative percent difference for samples above 20 mg/L as CaCO_3 .
- Record all QC results in the laboratory notebook

9. Waste Disposal

Waste Type	Disposal Method
Titrated samples (no hazardous additions)	Drain with copious water

Waste Type	Disposal Method
Spent acid titrant	Neutralize with sodium bicarbonate to pH 6–8, then drain
Na ₂ CO ₃ standardization waste	Drain with copious water
Used pH buffer solutions	Collect in waste container per SOP-L300

10. References

- APHA, AWWA, WEF. (2012). Standard Methods 2320 B: Alkalinity – Titration Method. In: *Standard Methods for Examination of Water and Wastewater*. 22nd ed. American Public Health Association (Eds.). Washington. 1360 pp.
- USEPA Method 310.1: Alkalinity (Titrimetric, pH 4.5).

APHA, AWWA, & WEF. (2012). *Standard methods for the examination of water and wastewater* (22nd ed., p. 1360). American Public Health Association.

11. Training Record

Before performing alkalinity titrations independently, personnel must:

1. Read this SOP in full
2. Complete [SOP-L002 Laboratory Safety](#) and [SOP-L300 pH and Conductivity](#) training
3. Demonstrate pH meter calibration with acceptable slope
4. Prepare and standardize a batch of H₂SO₄ titrant under supervision with normality within 2% of the target value
5. Perform at least three practice titrations on known standards with acceptable recovery (90–110%)
6. Be signed off by the PI or lab manager

12. Appendix A: Titrant Preparation Quick Reference

12.1. N H₂SO₄ from Concentrated H₂SO₄

Concentrated H₂SO₄ is approximately 36 N.

1. Add approximately 900 mL of DI water to a 1 L volumetric flask
2. Slowly add 2.8 mL of concentrated H₂SO₄ to the water (**always add acid to water**)
3. Mix, cool to room temperature, and bring to volume with DI water
4. Standardize against primary standard Na₂CO₃ (Section 6.1)

12.2. N H₂SO₄ from 0.1 N Stock

1. Transfer 200.00 mL of standardized 0.1000 N H₂SO₄ to a 1 L volumetric flask
2. Bring to volume with DI water and mix thoroughly

13. Appendix B: Example Calculation

```
# Alkalinity calculation per Standard Methods 2320 B
acid_mL <- 24.5          # mL of standard acid used
acid_N <- 0.02           # Normality of acid (eq/L)
sample_mL <- 100         # mL of sample titrated

alkalinity_mg_L <- (acid_mL * acid_N * 50000) / sample_mL

cat(sprintf("Total alkalinity: %.1f mg/L as CaCO3\n", alkalinity_mg_L))
```

14. Appendix C: Troubleshooting

Symptom	Probable Cause	Corrective Action
Endpoint difficult to identify	Low alkalinity; flat titration curve	Use 200 mL sample, 0.02 N acid, microburet; construct full titration curve
Blank consumes excessive acid	CO ₂ absorbed into DI water; contaminated glassware	Use freshly boiled and cooled DI water; acid-wash glassware
Duplicate precision exceeds 5% RPD	Inconsistent titrant delivery; pH meter drift	Check buret for air bubbles; recalibrate pH meter; ensure pH equilibrium at endpoint
Alkalinity result seems too high	Sample exposed to air (CO ₂ loss raised pH)	Analyze samples promptly; fill bottles with no headspace
Alkalinity result seems too low	CO ₂ absorbed during storage or titration	Minimize exposure to air; do not stir vigorously enough to entrain air