P and M alkalinity, carbonate, and bicarbonate in water by automatic titration

Preprogrammed method
P_M alkalinity

Key words
p-alkalinity, m-alkalinity, p&m alkalinity, carbonate, bicarbonate, hydroxide, methyl orange, phenolphthalein, wastewater, Standard Methods 2320, ASTM D1067, ISO 9663, Orion 8172BNWP, Orion 8107BNUMD, Orion Star T910, Orion Star T940

Introduction
P and M alkalinity in a water sample are determined using the preprogrammed method P_M Alkalinity. Carbonate and bicarbonate concentrations may be calculated from the results of this titration based on some simplifying assumptions. P alkalinity is also known as phenolphthalein alkalinity and is determined by titrating to the phenolphthalein endpoint at pH 8.3. Total or M alkalinity is also known as methyl orange alkalinity and is determined by titrating to the methyl orange endpoint at pH 4.5. This application note describes the method using a direct titration to preset endpoints at pH 8.3 (P alkalinity) and pH 4.5 (M or total alkalinity) using sulfuric acid titrant. The calculations to determine carbonate and bicarbonate are also described.

Recommended equipment
- Thermo Scientific™ Orion Star™ Titrator T910 pH or T940 all-in-one or equivalent with a 20 mL burette
- Thermo Scientific™ Orion™ 8172BNWP ROSS™ Sure-Flow™ pH electrode or Orion 8107BNUMD ROSS™ Ultra™ Epoxy pH Triode, or equivalent
- Thermo Scientific™ Orion™ Automatic Temperature Compensation (ATC) probe
- Analytical balance (for standardization)
- Volumetric flask, 1L (for standardization)
- Graduated cylinders, 100 mL and 250 mL
- Beakers, 150 mL and 250 mL

Required reagents and solutions
Purchased or prepared sulfuric acid standard titrant solution, 0.1N (0.05 M); reagent-grade water (RGW); and pH buffers: 4, 7, and 10. Optional (for standardization): Tris(hydroxymethyl)aminomethane (known as Tris or THAM) primary base/alkalimetric standard, solid. Use suitable personal protective equipment (PPE) as recommended by the Safety Data Sheets (SDS) for the chemicals utilized during this procedure.

Titrator setup
Connect the Thermo Scientific™ Orion™ pH electrode, ATC, and the stirrer probe to the titrator. If not previously done, import or program the P_M Alkalinity method into the titrator from the Methods screen1. Rinse and fill the burette with 0.1N (0.05M) sulfuric acid titrant. See the titrator user manual for details. If bubbles are visible in the tubing, dispense titrant (from the Burette screen) until the bubbles have been expelled. Consider standardizing the titrant

Table 1: P_M alkalinity method: preprogrammed parameters

Specification	Parameter
Electrode	
Electrode type	pH
Electrode name	Edit as desired
Resolution	0.01
Buffer group	USA
Titrant	
Titrant name	H2SO4
Titrant ID	Edit as desired
Conc input mode	Standardization
Nominal concentration	0.05M (0.1N)
Standardize tech	Equivalence pt.
Number of endpoints	1
Results units	M
Standardize reaction ratio	2
Standard name	Tris (THAM)
Standard amount	Variable weight
Standard molecular wt	121.14
Standard purity	100%
Pre-dose titrant volume	0 ml
Max total titrant volume	15
Stand. process control	Routine
Pre-stir duration	5 sec
Stir speed	Fast
Titration	
Titration technique	Preset end pt.
Number of endpoints	2
Endpoint values	8.3, 4.5
Titration type	Direct
Result units	mg/L
Reaction ratio	1
Sample mol. wt.	100.0
Sample amount	Variable vol, 100 mL
Pre-dose titrant volume	0 mL
Max total titrant volume	20 ml
Titration process control	Quick
Pre-stir duration	5 sec
Stir speed	Fast
Sample ID	Manual

Electrode preparation

Remove electrode from storage solution. Add electrode fill solution to the bottom of the fill hole and leave the fill hole open during testing. Rinse thoroughly with RGW before and between titrations.

Sample preparation

Routine alkalinity: Measure 100 mL of sample into a graduated cylinder. Transfer the sample to a clean 150 mL beaker for titration.

Low-level alkalinity titrations (e.g. < 20 mg/L): Measure 200 mL of sample into a graduated cylinder. Transfer the sample to a clean 250 mL beaker for titration.

Sample titration

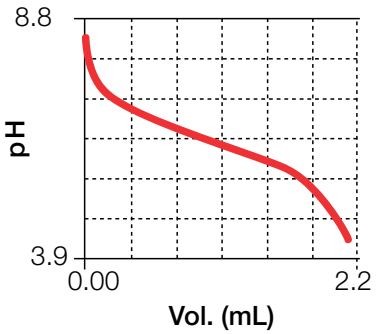
1. From the Home screen, select option to use a saved method, then select P_M Alkalinity.
2. At the pre-titration screen, select the Calibrate option and calibrate the electrode with pH 4, 7, and 10 buffers. Raise the dispenser so it does not touch the buffers during calibration.
3. After calibration, rinse well, and place the electrode, stirrer, ATC, and dispenser into the sample in the beaker. Ensure that the dispenser tip is inserted below the surface of the sample and start the titration.
4. Results are reported as mg/L as $CaCO_3$.

Table 2: Results

Sample	Parameter	Average (n=3)	RSD (%) & recovery (%R)	Titration time
Bicarbonate standard, 100 mg/L	P-Alkalinity	NA	NA	02:24 minutes
	M (T) -Alkalinity	101.1 mg/L as $CaCO_3$	0.12% (101% R)	
Buffered alkaline water	P-Alkalinity	12.17 mg/L as $CaCO_3$	3.1%	03:41 minutes
	M (T) - Alkalinity	38.16 mg/L as $CaCO_3$	0.12% (100%R)	
Tap water	P-Alkalinity	NA	NA	02:19 minutes
	M (T) - Alkalinity	26.03 mg/L as $CaCO_3$	1.4%	
Carbonate bicarbonate buffer	P-Alkalinity	120.6 mg/L as $CaCO_3$	0.51%	05:50 minutes*
	M (T) - Alkalinity	361.9 mg/L as $CaCO_3$	0.10% (96.5%R)	

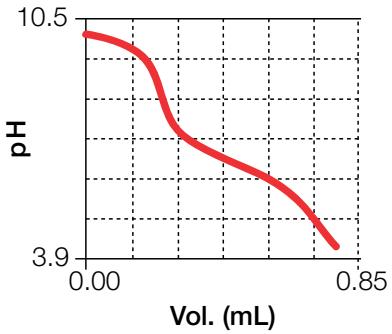
* For faster titration, titrate less sample

Biocarbonate standard



No P alkalinity; Initial pH < 8.3
M alkalinity endpoint at pH 4.5

Buffered alkaline water



P alkalinity endpoint at pH 8.3
M alkalinity endpoint at pH 4.5

Range

The P_M Alkalinity program titration method covers a range from about 20 to 1000 mg/L P&M alkalinity as $CaCO_3$, when using 0.05M (0.1 N) H2SO4 acid titrant and 100 mL of sample

Method modifications

- **For shorter titrations:** For samples >100 mg/L as $CaCO_3$, titrating less sample will result in a faster titration. For fast titrations, also ensure that the electrode is being maintained, stored, and cleaned according to the titrator and electrode user manuals. See hints and tips in the Titrator and Electrode Care section of this note.
- **For low-level alkalinity titrations (e.g. < 20 mg/L):** titrate 200 mL of sample. To titrate low alkalinity samples according to the modified method from Standard Methods SM2320 section 4.d, see our Tech Note on the subject.

Calculations for carbonate and bicarbonate

In most cases, the results of the alkalinity titration will show that P alkalinity (P, results to pH 8.3) is less than half the concentration of the M alkalinity (M, results to pH 4.5). M alkalinity is also known as total alkalinity (T). Carbonate and bicarbonate can be calculated from these results by assuming the alkalinity is due primarily to carbonate and bicarbonate.[2]

Carbonate and bicarbonate calculations

Result of the titration	Carbonate as $CaCO_3$	Bicarbonate as $CaCO_3$
P < ½ M	2P	M – 2P (M – Carbonate)

Carbonate (mg/L as CaCO3) = 2P = 2 × pH 8.3 result
*Bicarbonate (mg/L as CaCO3) = M - 2P = pH 4.5 result-Carbonate**

*Since 2P = Carbonate, we can simplify by calculating Bicarbonate as M - Carbonate

Example calculations

- **Example 1:** If pH 8.3 endpoint result (P) is 12.17 mg/L as $CaCO_3$ and pH 4.5 endpoint result (M) is 38.16 mg/L as $CaCO_3$, then calculate as follows:

  Carbonate = 2P = 2 × 12.17 = 24.34 mg/L as $CaCO_3$
  Bicarbonate = M - Carbonate = 38.16 – 24.34 = 13.82 mg/L as $CaCO_3$

- **Example 2:** If pH 8.3 endpoint result (P) is 0 and pH 4.5 endpoint result (M) is 101.1 mg/L as $CaCO_3$, then calculate as follows:

  Carbonate = 2P = 2 × 0 mg/L = 0 mg/L as $CaCO_3$ (No carbonate)

  Bicarbonate = M – Carbonate = 101.1 – 0 = 101.1 mg/L as $CaCO_3$

  Note that when the sample pH is < pH 8.3, P = 0, all the alkalinity (M) is present as bicarbonate and there is no carbonate.

Titrant

Over time, standard titrant solutions age and can change concentration. For higher accuracy, determine the exact concentration by standardizing the titrant. It is common to standardize on a weekly basis, but other standardization frequencies may be suitable.

1. Standardizing the titrant
   – 0.1N (0.05M) H2SO4 acid titrant
   – i) Weigh 0.10 to 0.15 g of Tris (THAM) into a clean 100 or 150 mL beaker. Record the exact weight to a precision of 0.0001 g. Repeat twice more for a total of three beakers of Tris. Add RGW to the 60 mL mark on each beaker and stir for about 2 minutes or so until the Tris is completely dissolved.
   – ii) If the Tris purity is not 100%, edit the Titrant section of the method to enter the actual purity.
   – iii) Select the P_M Alkalinity preprogrammed method on the titrator.
   – iv) At the pre-titration screen, select the Standardize option and follow the prompts to standardize the titrant.
   – v) For best accuracy, run three cycles using the three prepared beakers of Tris.
   – vi) The new standardized titrant concentration will automatically be calculated, averaged, saved and used for subsequent P_M Alkalinity method titrations.
2. Certified standardized titrant solutions
   – Some customers may prefer not to standardize their titrant, instead choosing to purchase and use certified standardized titration solutions. In this case, edit the Titrant section of the method. Change Conc. Input Mode to Manual Entry and enter the certified concentration and titrant ID (i.e., lot number, if desired).

Titrator and electrode care

Refer to the titrator and electrode user manuals for details on cleaning, storage, and maintenance recommendations to keep the titrator and electrode performing well. For the quickest, most accurate, and repeatable titrations, the main points for care are summarized below.

Daily care

- Each day before the first titration, dispense a small amount of titrant (e.g. 5 mL) to clear the dispenser and expel air bubbles.
- If bubbles are still visible in the titrator tubing, dispense titrant until bubbles have been expelled.
- Add electrode fill solution to the bottom of the fill hole and leave the fill hole open during measurement.
- Rinse electrode well with RGW between titration cycles.
- Cover the fill hole and store electrode in storage solution overnight.

Weekly or biweekly care

- Drain and replace the fill solution of the electrode.
- Change the storage solution in the electrode storage bottle.
- Consider standardizing the titrant on a weekly basis.

As needed

- For slow or drifty electrode response, an acid cleaning is recommended. Use Orion pH cleaning solution D per instructions.
- For dirt, oil, or grease removal, soak 15 minutes in 1% laboratory detergent while stirring. Rinse well with RGW afterwards and change the fill solution.
- See the electrode and titrator user manuals for maintenance details.

Notes

1. Refer to the user manual for detailed instructions, if desired. To quickly program a method, select Start a New Titration on the Home screen and follow the simple instructions to set up the Electrode, Titrant, and Titration parameters. Enter the program parameters as shown in Table 1.
2. When P is not less than M, then slightly different calculations will apply. The basis of these calculations and the assumptions made are described in Standard Methods 2320B. See the References section for details of the method.

References

1. Eugene W. Rice, et al. 2012. Alkalinity (Method 2320 B). Standard Methods for the Examination of Water and Wastewater. Washington, DC: American Public Health Association. www.standardmethods.org.
2. ASTM International. Standard Test Methods for Acidity or Alkalinity of Water (D1067). West Conshohocken, PA. www.astm.org.
3. International Organization for Standardization (ISO). Water Quality – Determination of Alkalinity – Part 1 (ISO 9963-1). www.iso.org.

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Ordering information

Product	Description	Cat. No.
Titrator Kits	Orion Star T910 titrator standard kit with 8102BNUWP ROSS Ultra pH electrode and ATC probe	START9101
	Orion Star T910 pH titrator Sure-Flow kit with 8172BNWP ROSS Sure-Flow pH electrode and ATC probe	START9102
	Orion Star T940 all-in-one titrator standard kit with 8102BNUWP ROSS Ultra pH electrode and ATC probe	START9401
	Orion Star T940 all-in-one titrator Sure-Flow kit with 8172BNWP ROSS Sure-Flow pH electrode and ATC probe	START9402
Titrators	Orion Star T910 pH titrator without electrode	START9100
	Orion Star T940 all-in-one titrator without electrode	START9400
Electrodes	Automatic Temperature Compensation (ATC) probe	927007MD
	Thermo Scientific Orion ROSS Ultra Epoxy pH triode	8107BNUMD
Accessories	150 or 250 mL beakers	-
pH buffers	Orion pH 4.00 buffer, NIST traceable, 475 ml	910104
	Orion pH 7.00 buffer, NIST traceable, 475 ml	910107
	Orion pH 10.01 buffer, NIST traceable, 475 mL	910110
Reagents	0.1N (0.05M) sulfuric acid standard titrant	-
	0.02N (0.01M) sulfuric acid standard titrant	-
	Tris (hydroxymethyl)aminomethane (Tris), primary or alkalimetric standard grade	-
Reagent-grade water	Thermo Scientific™ Barnstead™ Smart2Pure™ 12 UV Water Purification system	50129890*

*Please contact your local Thermo Scientific representative for support on ordering the best water purification system for your application, and visit our website at thermofisher.com/labwater

Find out more at **thermofisher.com/titrator**

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