

Total alkalinity in water by automatic titration

Water Analysis Instruments,
Thermo Fisher Scientific

Key words

m-alkalinity, p-alkalinity, p and m alkalinity, carbonate, bicarbonate, hydroxyl, wastewater, Standard Methods 2320, ASTM D1067, ISO 9663, Orion 8172BNWP, Orion 8102BNUWP, Orion Star T910, Orion Star T940.

Introduction

Total alkalinity (or m-alkalinity) in a water sample is determined using the preprogrammed method T2 TotAlkalinity. This method is a direct titration to a preset endpoint at pH 4.5 using acidic titrant. The method may be edited to perform total alkalinity in other samples as well.

Recommended equipment

- Thermo Scientific™ Orion™ Star™ Titrator T910 pH, or T940 All-in-One, or equivalent with a 20 mL burette
- Thermo Scientific™ Orion™ ROSS™ SureFlow™ 8172BNWP pH electrode, 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 hydrochloric acid (HCl) standard titrant solution, 0.1 M (0.1N) or 0.02 M (0.02 N)
- Reagent grade water (RGW)
- pH buffers: pH 4 and 7



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

Titration setup

Connect the Orion pH electrode, ATC, and the stirrer probe to the titrator. If not previously done, import the T2 TotAlkalinity preprogrammed method into the titrator from the Methods screen¹. Rinse and fill the burette with 0.1M (0.1N) HCl 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 before titrating samples. See the following Titration section.

T2 TotAlkalinity Method: Preprogrammed Parameters

Electrode	Parameter
Electrode Type	pH
Electrode Name	Edit as desired
Resolution	0.01
Buffer Group	USA

Titrant	Parameter
Titrant Name	HCl
Titrant ID	Edit as desired
Conc Input Mode	Standardization
Nominal Concentration	0.1M
Standardize Tech	Equivalence Pt.
Number of Endpoints	1
Results Units	M
Standardize Reaction Ratio	1
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	Medium

Titration	Parameter
Titration Technique	Preset end pt.
Number of Endpoints	1
Endpoint Values	4.5
Titration Type	Direct
Blank Required	No
Result Units	mg/L
Reaction Ratio	0.5
Sample Mol. Wt.	100.09
Sample Amount	Fixed vol, 100 mL
Pre-dose Titrant Volume	0.05
Max total titrant volume	20 mL
Titration Process Control	Routine
Pre-stir Duration	5 sec
Stir Speed	Medium
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

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

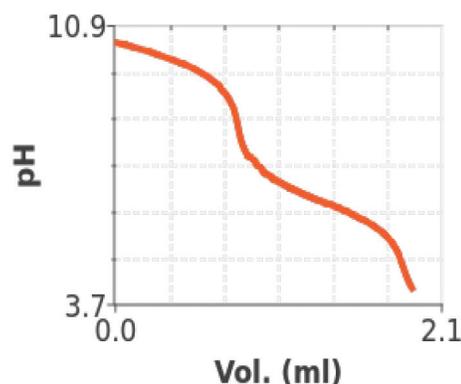
Sample titration

1. From the Home screen, select option to use a saved method, then select TotAlkalinity.

- At the pre-titration screen, select the Calibrate option and calibrate the electrode with pH 4 and 7 buffers.
- 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.
- Results are reported as mg/L as CaCO₃.

Results

Parameter	Sample	Average (n = 3)	RSD	Analysis Time
Total Alkalinity	Alkaline	98.7 mg/L as CaCO ₃ (1.97 mmol/l as H ⁺)	0.30%	02:39 minutes ²
Total Alkalinity	Tap Water	28.2 mg/L as CaCO ₃ (0.564 mmol/l as H ⁺)	0.42%	04:26 minutes



Range

This preprogrammed titration method covers a range from about 25 to 1000 mg/L total alkalinity as CaCO₃, when using 0.1M (0.1 N) acid titrant and 100 mL of sample. See below for method modifications to run other concentrations.

Method modifications

- For other concentrations:** For best accuracy with samples of lower alkalinity (e.g., <100 mg/L), switch to 0.02 M HCl titrant and titrate 200 mL of sample. Edit the Titrant section of the method to enter the correct titrant concentration. Edit the titration section of the method to enter a fixed volume of 200 mL.
- For other result units:** For units of mmol/l (per ISO 9963-1), edit the Titration section of the method as follows: choose the unit "mM" (which is mmol/l) and change the reaction ratio to "1".

- **For P&M (phenolphthalein and total) alkalinity:** Edit the Titration section of the method to choose number of endpoints = 2. Then edit the endpoint values to enter pH 8.3 and pH 4.5.
- **For shorter titrations:** For routine titrations with well-established endpoint volumes, use a pre-dose to shorten the analysis time. Edit the pre-dose in the Titration section of the method. In general, set the pre-dose at a volume that is 0.5 mL less than the expected endpoint volume.
- **To use sulfuric acid (H₂SO₄) standard titrant solution instead of HCl:** For 0.1N H₂SO₄, edit the Titrant section of the T2 method to indicate the titrant is H₂SO₄. Change the concentration to 0.05M. Then edit the Titration section of the T2 method to change the Titrant Reaction Ratio to 1. Save the updated method. For 0.02N H₂SO₄, edit the Titrant section of the T2 method to indicate the titrant is H₂SO₄. Change the concentration to 0.01M. Then edit the Titration section of the T2 method to change the Titrant Reaction Ratio to 1. Save the updated method.

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

a. 0.1M (0.1N) acid titrant

- Use the analytical balance to weigh 0.10 to 0.15 g Tris (THAM) into a clean 100 or 150 mL beaker. Record the exact sample weight to the nearest 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.
- If the Tris purity is not 100%, edit the Titrant section of the method to enter the actual purity.
- Select the TotAlkalinity preprogrammed method on the titrator.
- At the pre-titration screen, select the Standardize option and follow the prompts to standardize the titrant.
- The new standardized titrant concentration will automatically be saved and used for subsequent T2 TotAlkalinity method titrations.

b. 0.02M (0.02N) acid titrant

- Prepare a 0.01M Tris (THAM) standard by weighing 1.211g into a 1L volumetric flask. Dilute with RGW and mix until dissolved.

- Pipet 5.0 mL of the 0.01M Tris standard into a 150 mL beaker. Add RGW to the 60 mL mark on the beaker. Repeat twice more for a total of three beakers of Tris.
- Edit the Titrant section of the TotAlkalinity preprogrammed method to enter the Standard Amount as “Fixed Volume”, “5 mL”. Save the method.
- At the pre-titration screen, select the Standardize option and follow the prompts to standardize the titrant.
- The new standardized titrant concentration will automatically be saved and used for subsequent T2 TotAlkalinity 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 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. Main points for care are summarized below.

Daily Care	Weekly or Biweekly Care	As Needed
<ul style="list-style-type: none"> • If bubbles are 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. 	<ul style="list-style-type: none"> • 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. 	<ul style="list-style-type: none"> • For slow or drift response, soak 15 minutes in 1% laboratory detergent while stirring. Rinse well with RGW afterwards. • If still slow or drift, use Orion pH cleaning solution D per instructions. • See the user manuals for maintenance details.

Notes

¹Refer to the user manual for detailed instructions.

²With a suitable pre-dose, as described in the Method Modifications section.

To purchase Thermo Scientific laboratory products, please contact your local equipment distributor and reference the part numbers listed below:

Product	Description	Cat. No.
Titrator kits	Thermo Scientific 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 SureFlow 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 SureFlow pH electrode and ATC probe	START9402
Titrators	Thermo Scientific Orion Star T910 pH Titrator without electrode	START9100
	Thermo Scientific Orion Star T9400 All-In-One titrator without electrode	START9400
Electrodes	Thermo Scientific Orion ROSS SureFlow pH Electrode	8172BNWP
	Thermo Scientific Orion ROSS Ultra pH Electrode	8102BNUWP
	Automatic Temperature Compensation (ATC) probe	927007MD
pH Buffers	Orion pH 4.00 buffer, NIST traceable, 475 ml	910104
	Orion pH 7.00 buffer, NIST traceable, 475 ml	910107
Reagent Grade Water	Thermo Scientific™ Barnstead™ Smart2Pure™ 12 UV Water Purification System	50129890*
Reagents	0.1M (0.1N) Hydrochloric acid standard titrant	
	0.02M (0.02N) Hydrochloric acid standard titrant	
	Tris (hydroxymethyl) aminomethane, primary or alkalimetric standard grade	

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

References

- 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.
- ASTM International. *Standard Test Methods for Acidity or Alkalinity of Water* (D1067). West Conshohocken, PA. www.astm.org.
- International Organization for Standardization (ISO). *Water Quality – Determination of Alkalinity – Part 1* (ISO 9963-1). www.iso.org.

Find out more at thermofisher.com/titrator