Total alkalinity in water by automatic titration

Water Analysis Instruments,
Thermo Fisher Scientific

Key words

m-alkalinity, 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™ T910 pH or T940 All-In-One Titrator, or equivalent with a 20 mL burrette
- Thermo Scientific™ Orion™ ROSS™ SureFlow™ 8172BNWP pH electrode, or equivalent
- Thermo Scientific™ Orion™ Automatic Temperature Compensation (ATC) probe
- Analytical balance (for standardization)
- Volumetric flask, 1 L (for standardization)
- Graduated cylinders: 100 mL and 250 mL
- Beakers: 150 mL and 250 mL

Required reagents and solutions

- Purchased or prepared sulfuric acid (H_2SO_4) standard titrant solution, 0.1 N (0.05 M)
- 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.

Titrator setup

Connect the Orion ROSS SureFlow 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 screen[1]. Rinse and fill the burette with 0.1 N (0.05 M) H_2SO_4 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 Titrant section.

Table 1. 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	H_2SO_4
Titrant ID	Edit as desired
Conc input mode	Standardization
Nominal concentration	0.05M
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	Quick
Pre-stir Duration	5 sec
Stir Speed	Fast

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	1
Sample mol. wt.	100.09
Sample amount	Variable volume
Pre-dose titrant volume	0.05
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

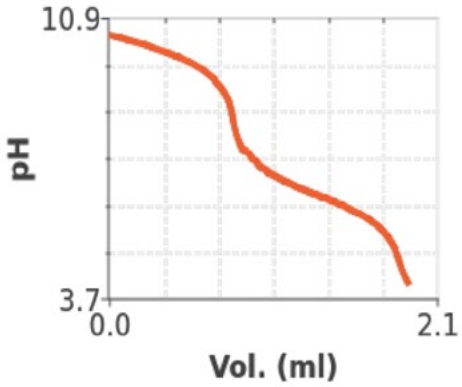
Measure 100 mL of sample into a graduated cylinder. Transfer the sample to a clean 150 mL beaker for titration.

Sample titration

1. From the Home screen, select option to use a saved method, then select TotAlkalinity.
2. At the titration pre-check screen, select the Calibrate option and calibrate the electrode with pH 4 and 7 buffers. Do not calibrate from the Measure mode. During calibration, raise the dispenser tip so that it is not immersed in the pH buffers.
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 immersed in the sample.
4. Results are reported as mg/L as $CaCO_3$.

Results

Parameter	Sample	Average (n = 3)	RSD	Analysis time
Total alkalinity	Alkalinity standard 100 mg/L as $CaCO_3$ (2mmol/L)	98.9 mg/L as $CaCO_3$ (1.97 mmol/l as H^+)	0.1% (98.9% Recovery)	02:57 minutes[2]
Total alkalinity	Tap water	33.9 mg/L as $CaCO_3$ (0.678 mmol/l as H^+)	0.5%	03:12 minutes



Range

This preprogrammed titration method covers a range from about 20 to 1,000 mg/L total alkalinity as $CaCO_3$, when using 0.1N (0.05M) sulfuric acid titrant. See below for method modifications to run other concentrations.

Method modifications

- **For other concentrations:** For best accuracy with samples of lower alkalinity (e.g., <50 mg/L), titrate 200 or 250 mL of sample or consider running a low level titration. Ask for our tech note on low level akalinity titrations according to Standard Methods 2320.
- **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 2.

- **For P&M (phenolphthalein and total) alkalinity:** See application note, "T012 P&M Alkalinity Carbonate Bicarbonate in Water by Automatic Titration."
- **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 to 1.0 mL less than the expected endpoint volume.

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. 0.1 N (0.05 M) sulfuric sulfuric acid titrant
      i. 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.
      ii. If the Tris purity is not 100%, edit the Titrant section of the method to enter the actual purity.
      iii. Select the TotAlkalinity preprogrammed method on the titrator.
      iv. At the pretitration screen, select the Standardize option and follow the prompts to standardize the titrant.
      v. The new standardized titrant concentration will automatically be saved and used for subsequent T2 TotAlkalinity method titrations.
2. Certified standardized titrant solutions
   a. 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
• 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 up 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.	• 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.	• For slow or drifty electrode response, soak 15 minutes in 1% laboratory detergent while stirring. Rinse well with RGW afterwards. • If still slow or drifty, use Thermo Scientific™ Orion™ pH cleaning solution D per instructions. • See the electrode and titrator user manuals for maintenance details.

1. Refer to the user manual for detailed instructions. 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 and Save the method.
2. With a suitable pre-dose, as described in the Method Modifications section.

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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	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	Orion Star T910 pH Titrator without Electrode	START9100
	Orion Star T9400 All-In-One Titrator without Electrode	START9400
Electrodes	Orion ROSS SureFlow pH Electrode	8172BNWP
	Orion ROSS Ultra pH Electrode	8102BNUWP
	Orion 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	Barnstead Smart2Pure 12 UV Water Purification System	50129890*
Reagents	0.1 N (0.05 M) Sulfuric Acid Standard Titrant	
	Tris (hydroxymethyl) Aminomethane, primary or alkalimetric standard grade	

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

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.

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

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