

Determination of Chloride in Water by Automatic Titration

Introduction

Chloride in water is determined using the preprogrammed method, Chloride Water. Chloride in the sample is titrated to the equivalence point by argentometric titration using a silver nitrate titrant.^{1,2,3} A silver billet electrode is used to follow the titration.

Recommended Equipment

Thermo Scientific™ Orion Star™ T930 Ion Selective Electrode (ISE) Titrator or T940 All-in-One Titrator or equivalent with a 20 mL burette.

Thermo Scientific™ Orion™ 9780SC Silver Billet Combination Electrode (or equivalent) with cable Orion 91CBNC.

Thermo Scientific Orion START-TB2 light blocking tubing kit

Thermo Scientific Orion 810017 electrode storage sleeve

Pipette: 10 mL graduated.

Graduated cylinders: 100 & 250 mL

Beakers: 100 and 250 mL.

Required Reagents and Solutions

Titrant: Purchased or prepared silver nitrate, 0.01M (0.01N).

Standardizing Solution (optional): Orion 941708 1000 ppm (mg/L) Chloride Standard (0.02821 M).

ISE Fill solution: Thermo Scientific™ Orion™ 900062 Optimum Results B Fill Solution. (Do not use the 900011 fill solution for low level chloride titrations).



Orion Star T930 ISE Titrator with 20 mL burette

Acid for pH & ionic strength adjustment: Purchased or prepared nitric acid, 0.4M (0.4N, ~1.75%)

Electrode Cleaning Solution C: Orion 900023

Reagent grade water (RGW).

Use suitable Personal Protective Equipment (PPE) as recommended by the Safety Data Sheets (SDS) for the chemicals utilized during this procedure.

Titration Setup

If desired, install the START-TB2 light blocking tubing kit to help protect the integrity of the silver nitrate titrant. Connect the electrode and the stirrer probe to the titrator. If not previously done, import the Chloride Water preprogrammed method into the titrator from the “Methods” screen. Rinse and fill the burette with titrant. See the titrator user manual for details on setting up the titrator.

If bubbles are visible in the tubing, dispense titrant (from the “Burette” screen) until the bubbles have been expelled. Tap the tubing to dislodge bubbles. If using the light blocking tubing kit, bubbles will not be visible in the tubing. Instead, place the dispenser tip into a beaker of water. While dispensing titrant manually (from the Burette screen), tap the tubing to dislodge bubbles. Continue until air bubbles are no longer seen coming from the dispenser tip. Consider standardizing the titrant before titrating samples. See the “Titrant” section on page 4.

Table 1

T8 Chloride Water Preprogrammed Parameters	
Electrode	Parameter
Electrode Type	ISE-Titration
ISE Type	Silver (Ag+)
Electrode Name	edit as desired
Titrant	Parameter
Titrant Name	AgNO ₃
Titrant ID	edit as desired
Conc Input Mode	Standardization
Nominal Concentration	0.01M
Standardize Tech	Equivalence Pt.
Number of Endpoints	1
Results Units	mM
Standardize Reaction Ratio	1
Standard Name	Chloride
Standard Amount	Fixed Volume, 1 mL
Standard Concentration	0.02821 M
Pre-dose Titrant Volume	1.0 mL

Max total titrant volume	5 mL
Stand. Process Control	User Defined
ΔE	10.0 mV
ΔV_{min}	0.05 mL
ΔV_{max}	0.30 mL
dE/dt	8 mV/min
Tmin	2 seconds
Tmax	8 seconds
Threshold	50
Pre-stir Duration	5 seconds
Stir Speed	Fast
Titration	Parameter
Titration Technique	Equivalence Pt
Number of Endpoints	1
Titration Type	Direct Titration
Blank Required	No
Result Units	mg/L
Reaction Ratio	1.000
Sample MW	35.45 g/mol
Sample Amount	Variable volume
Pre-dose Titrant Volume	1.0 mL
Max total titrant volume	5.0 mL
Titration Process Control	User Defined
ΔE	10.0 mV
ΔV_{min}	0.05 mL
ΔV_{max}	0.30 mL
dE/dt	8 mV/min
Tmin	2 seconds
Tmax	8 seconds
Threshold	50
Prestir	5 seconds
Stir Speed	Fast
Sample ID	Manual

Reagents and Solutions Preparation

- Acid for pH & ionic strength adjustment, 0.4M (~1.75%): Place 975 mL of RGW into a plastic or glass container. Carefully add 25 mL of concentrated nitric acid (HNO₃).
- Storage solution for silver billet electrode: Place 10 mL of Optimum Results B fill solution into the electrode storage sleeve.

Electrode Preparation

At the start of the day: Remove the electrode from storage solution. Add Orion 900062 Optimum Results B fill solution up to the bottom of the fill hole. Leave the fill hole open during testing. Gently wipe the sensor with a moistened lint-free wiper. Be careful not to bend the silver billet. Rinse thoroughly with RGW before and between titrations.

At the end of the day: Clean any foreign materials from the sensor by wiping gently with a moistened lint-free wiper. Thoroughly rinse the electrode with RGW and store in storage solution. Cover the fill hole when in storage.

Sample Preparation

Using a graduated cylinder or pipet, transfer an amount of the sample into a 100 or 250 mL beaker, according to the expected sample concentration. See Table 2 for guidance on recommended sample volumes. Record the volume used. If less than 60 mL of sample is placed in the beaker add RGW to the 60 mL mark on the beaker. For sample volumes up to 100 mL, add 1 mL of 0.4 M nitric acid. For samples between 100 to 200 mL, add 2 mL of 0.4M nitric acid. The sample is ready to titrate.

Sample Titration

1. From the “Home” screen or the “Methods” screen, select option to run the saved method “Chloride Water”.
2. Rinse the electrode, stirrer, and dispenser with RGW. Place the electrode, stirrer, and dispenser into the prepared sample in the beaker. Ensure that the dispenser tip is inserted below the surface of the sample. Ensure that the electrode junction is immersed.
3. Start the titration. Enter the sample volume and sample ID when prompted.
4. Results are reported as mg/L chloride.



Orion Star T930 ISE Titrator with 20 mL burette

Table 2

Recommended sample volumes				
Expected Sample Concentration (mg/L chloride)	Size beaker for use for titration (mL)	Measure this volume of sample into the beaker (mL)	Add this volume of RGW to the beaker (mL)	Add this volume of 0.4 M nitric acid to the beaker (mL)
5	250	200	---	2
10	250	100	---	1
25	100	40	To the 60 mL mark	1
50	100	20	To the 60 mL mark	1
100	100	10	To the 60 mL mark	1
200	100	5	To the 60 mL mark	1
500	100	2	To the 60 mL mark	1

Table 3

Sample Results			
Sample	Average	RSD	Average Analysis Time
Low-salt Water	4.300 mg/L	0.84 %	02:14 min
Tap Water	177.5 mg/L	0.39%	01:44 min
Salty Water	531.1 mg/L	0.58%	02:34 min

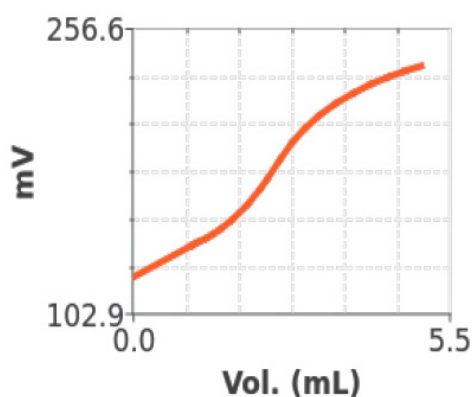


Figure 1. Low-salt Water

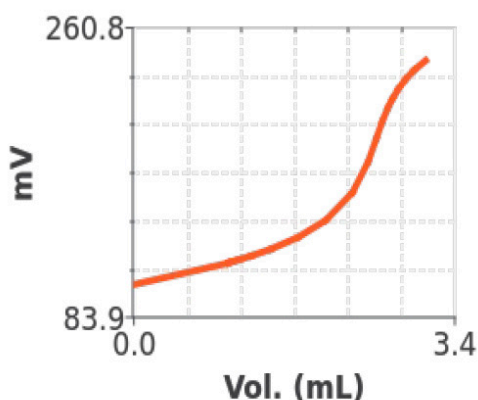


Figure 2. Tap Water

Range

This preprogrammed titration method covers a range of about 5 to 500 mg/L chloride, when using 0.01 M silver nitrate titrant and the prescribed volume of sample.

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 titrant

- a. Pipet 1.0 mL standardizing solution, 1000 ppm (0.02821M) chloride standard, into a clean 100 mL beaker. Add RGW to the beaker to the 60 mL mark. Add 1 mL of 0.4 M nitric acid.
- b. Select the “Chloride Water” method. At the titration pre-check screen, select the standardize option.
- c. Start the titration. Standardization results will be displayed at the end of the cycle.
- d. Run 3 or more cycles for the most accurate results. The average and relative standard deviation (RSD) of the cycles are automatically calculated when completed.
- e. The new standardized titrant concentration will automatically be saved and used for subsequent 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. Choose manual entry and enter the certified concentration and titrant ID (i.e., lot number, if desired).

Titration 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

- If bubbles are visible in the titrant tubing, dispense titrant until bubbles have been expelled. Tap tubing to dislodge bubbles that stick.
- Add Orion 900062 Optimum Results B electrode fill solution up to the bottom of the fill hole and leave the fill hole open during measurement.
- Wipe the silver billet sensor gently with a moistened lint-free wiper to keep the surface clean. Don't bend the silver billet.
- Rinse electrode well with RGW before and between titrations.
- Storage: Thoroughly rinse the electrode with RGW and store in storage solution. Cover the fill hole.

Weekly or biweekly care

- Drain and replace the fill solution of the electrode.
- Change the electrode storage solution.
- Consider standardizing the titrant on a weekly basis, or more frequently, as desired.

As needed

- For slow or drifty electrode response, soak the electrode in 1% laboratory detergent solution with vigorous stirring for 15 minutes. Rinse well with RGW. Drain and refill the electrode.
- For a more rigorous cleaning, use Orion 900023 pH electrode cleaning solution C. Follow instructions. Rinse well with RGW. Drain and refill the electrode.
- See the electrode user manuals for maintenance details.



Orion Star T930 ISE Titrator with 20 mL burette

Ordering Information

Product	Description	Cat. No.
Titration Kit	Orion Star T930 ion titrator salt/chloride content kit with 9780SC silver billet electrode and 91CBNC electrode cable	START9301
Titration	Orion Star T930 Ion Titrator without electrode Orion Star T940 All-in-One Titrator without electrode	START9300 START9400
Electrode Only	Orion Silver Billet Electrode Orion Electrode cable (for silver billet electrode)	9780SC 91CBNC
Orion Solutions	Orion Optimum Results B fill solution Orion Chloride standard solution, 1000 mg/L Orion pH Electrode cleaning solution C	900062 941708 900023
Accessories	<ul style="list-style-type: none"> • Orion Electrode storage sleeve • 100 & 250 mL beakers • 10 mL graduated pipet • 100 & 250 mL graduated cylinders 	810017
Reagents	<ul style="list-style-type: none"> • Silver Nitrate titrant, 0.01 M (0.01 N). • Nitric acid, concentrated (15.9 M or 70%). 	
Reagent Grade Water	Thermo Scientific™ Barnstead™ Smart2Pure™ Pro UV Water Purification System	50129890*

* Please contact a sales representative for support on ordering the best water purification system for your application, or find out more at thermofisher.com/purewater

1. Standard Methods 4500-Cl- D., Chloride, Potentiometric Method. Rice, Eugene W., Baird, Rodger B., Eaton, Andrew D., Lenore S. Clesceri. 2012. Standard methods for the examination of water and wastewater. Washington, DC: American Public Health Association.
2. ASTM D512-12, Standard Test Method for Chloride in Water. ASTM International, West Conshohocken, PA, USA, 2012. www.astm.org.
3. ISO 9297, Water Quality – Determination of Chloride – Silver nitrate titration with chromate indicator (Mohr's method). International Organization for Standardization, Geneva, Switzerland, 2017. www.iso.org.

Find out more at thermofisher.com/titrator