



Determination of Chloride in Water

(Standard methods for water 20th edition 4.51 4500D)

Introduction

As tap water or surface water contains chloride ions at low concentration levels, chloride determination should be performed by titration with silver nitrate (AgNO_3) as titrant. The Standard method for water uses a potentiometric determination with a silver rod as measuring electrode and a glass electrode as reference electrode. This application uses a potentiometric titration with glass and silver electrodes.

Principle

The silver nitrate reacts with chloride ion according to $(\text{Ag}^+, \text{NO}_3^-) + \text{Cl}^- \rightarrow \text{AgCl} + \text{NO}_3^-$

1 mole of AgNO_3 reacts with 1 mole of chloride

The titrant concentration should be 0.0141 M (standard methods)

The results are expressed in mg/l of chloride (Cl^- with a atomic weight of 35.45 g/mol)

Electrode and reagents

pHG301 Glass Electrode (part no. E11M001) connected to the measuring input of the Titration Manager with CL114 cable (part no. A94L114).

M291Ag Metal Electrode (part no. E34M002) connected to the reference input of the Titration Manager with CL114 cable.

Note that you can use a M295Ag (part no. E34M003) connected to the reference input with adapter part no. A94P807 instead of the M291Ag.

- HNO_3 1M

Dilute 78 ml of concentrated nitric acid in 1000 ml of distilled water. This operation is highly exothermic. Observe laboratory safety regulations.

- AgNO_3 0.0141 M

Dry the AgNO_3 for 2 hours at 105°C and leave it to cool to room temperature in a dessicator.

Using a volumetric flask, dissolve 2.395 g of AgNO_3 in 1000 ml of distilled water.

- Distilled water

Inflection Detection settings

CONTINUOUS ADDITION MODE

Stirring speed:	450 rpm
Stirring delay:	30 s
Burette volume:	10 ml
Maximum volume:	10 ml (see notes)
Stop point:	-50 mV (see notes)
Smoothing parameter:	6
Number of inflection points:	1
Minimum speed:	0.1 ml/min
Maximum speed:	2 ml/min
Direction:	Decreasing mV (see notes)

Inflection 1

Min. ordinate:	-20 mV (see notes)
Max. ordinate:	+140 mV (see notes)

Sample unit:	ml
Sample amount:	50 or 100

Results	
Unit:	mg/l
Coefficients:	1 sample and 1 Titrant
Molar weight:	35.45 g/mol

Procedure

For tap and surface water, pipette 50 or 100 ml of sample, add 10 ml of nitric acid 1M.

Dip electrodes and delivery tip in the beaker.

Run the titration.

For wastewater, the sample should be treated first as laid down in the regulations.

Results

Generally expressed as mg/l of chloride ion (AW = 35.453)

As 1 molecule of titrant reacts with 1 molecule of Cl^-

$$R = V(\text{titr}) * C(\text{titr}) * 35.453 * 1000 / V(\text{smp})$$

- $V(\text{titr})$ = total volume of titrant to reach the inflection point in ml

- $C(\text{titr})$ = Titrant concentration in mol/l (0.0141 for Standard method)

- $V(\text{smp})$ = sample volume in ml

35.453 = Atomic weight of chloride ion

The above inflection detection settings allow the Titration Manager to calculate the result directly in mg/l of chloride.

For 6 determinations on tap water

Mean: 9.52 mg/l
Standard deviation: 0.14 mg/l
Relative standard deviation: 1.47%
Potential value for inflection: close to 80 mV

Working Range

As this application note works with continuous addition of titrant, it is recommended to work with one burette capacity. It is also recommended to have around 1 ml of titrant before and after the inflection point.

For a 10 ml burette, the "experimental" titrant volume should be between 1 ml and 9 ml. These volumes correspond to 5 to 45 mg/l of chloride for a sample volume of 100 ml and 0.0141 M titrant.

Notes

If you need to treat the sample before titration, run a "blank" titration with distilled water instead of the sample. The Titration Manager takes into account a blank titration.

Use slow speeds for titrant delivery to avoid "over-titration". For low concentrations of chloride ions, the precipitation of AgCl is not a fast reaction.

Between titrations, just rinse the silver electrode with distilled water, do not use abrasive strips to clean the silver rod.

Maintenance of the glass electrode:

Follow the Radiometer Analytical procedures given in the operating instructions. You can also clean the electrode by immersion in diluted NH₄OH (1 vol. of concentrated NH₄OH for 20 vol. of distilled water) to dissolve the AgCl at the surface of the glass bulb.

Analytical grade silver nitrate can be considered as a standard, but you can also standardise the silver nitrate solution versus a NaCl solution with the same molar concentration.

Prepare using very pure NaCl a 0.0141 M solution.

Dry the pure NaCl at 140°C and leave it to cool to room temperature in a desiccator.

Dissolve 0.824 g of NaCl in 1000 ml of distilled water using a volumetric flask.

Pipette and weigh a volume of NaCl solution corresponding to half the capacity of the burette.

As the solution density can be taken as 1, enter the measured weight as a volume.

Dilute the NaCl standard with 70 ml of distilled water and add 10 ml of nitric acid.

Calibrate the titrant using the above-mentioned sample inflection detection settings and follow the titrant calibration procedure of the Titration Manager.

NOTE REGARDING MAXIMUM VOLUME

You can save time and titrant by choosing a maximum volume of 1 or 2 ml above the expected volume at the inflection point.

NOTE REGARDING MINIMUM AND MAXIMUM ORDINATE AND STOP POINT

Using the glass and metal electrodes as described above, initial and final potentials depend on the pH of the solution.

For tap water diluted with nitric acid experimental values are generally close to
-140 mV for initial potential -20 mV for final potential (or stop point)
-85 mV for equivalent point potential

For the same tap water diluted with a pH 4.0 buffer solution values are close to
-35 mV for initial potential
-180 mV for final potential
-103 mV for equivalent point potential

You can improve the indicated settings:

Minimum ordinate = E(IP)-50 mV

Maximum ordinate = E(IP)+50 mV

With E(IP) = Experimental measured potential at the inflection point

NOTE REGARDING TITRATION DIRECTION

Using the Titration Manager, it is necessary to connect glass and metal electrodes as indicated:

pHG301 Glass Electrode to the measuring input

M291Ag Metal Electrode to the reference input

The titration direction is therefore the opposite of the titration direction using a (Hg/HgSO₄) reference electrode and a silver electrode connected in the normal way.

NOTE REGARDING ELECTRODE CREATION

With the Titration Manager

First create the reference electrode

Function: Reference / ID from other / ID: M291Ag Cl- (for example)

Then create the measuring electrode

Function: mV (i=0) / ID from catalogue/ pHG301/ ID: Cl- / Reference / from user / M291AgCl-

DYNAMIC INCREMENTAL ADDITION OF THE TITRANT (Dynamic IP)

In this particular case corresponding to relatively low delivered volumes of titrant, running an incremental addition of titrant is not as easy as continuous addition.

The curve shape depends on a slight modification of the settings.

The number of stored points may be too low to ensure good reproducibility.

However you can work with the following settings tested with the sample used with continuous addition:

Dynamic dose: 12

Maximum dose: 1 ml

Burette speed: 5 ml/min

Stabilisation: 6 mV/min

Acceptation: 30 s

Filter: 1

I.P. reject: 15

Curve

