



Determination of Chloride in Water (ISO and NF ISO 9297)

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. Standard NF ISO 9297 uses a colorimetric determination (with silver chromate) of the equivalent point but it is possible with the same titrant to use a potentiometric determination of the equivalent point.

This application uses a potentiometric titration with a combined silver/reference electrode.

Principle

The silver nitrate reacts with chloride ion according to



1 mole of AgNO_3 reacts with 1 mole of chloride. The titrant concentration is generally 0.02 M (ISO and NF ISO standard). The results are expressed in mg/l of chloride (Cl^- with a molecular weight of 35.453 g/mol)

Electrode and reagents

MC6091Ag Combined metal/reference ($\text{Hg}/\text{Hg}_2\text{SO}_4$) electrode (part no. E34M002) with CL114 cable.

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 0.02M

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

Using a volumetric flask, dissolve 3.3974 g of AgNO_3 in 1000 ml of distilled water.

pH 4. Buffer solution

Dissolve 146 g of CH_3COONa (or 246 g of CH_3COONa , $3\text{H}_2\text{O}$) in 400 ml of distilled water, add 480 g of concentrated CH_3COOH and dilute to 1000 ml with 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:	0 mV
Smoothing parameter:	6
Inflexion points number:	1
Minimum speed:	0.1 ml/min
Maximum speed:	2 ml/min
Direction:	Increasing mV

Inflexion 1	
Min. ordinate:	-200 mV (see notes)
Max. ordinate:	-35 mV (see notes)

Sample unit:	ml
Sample amount:	50 or 100

Results	
Unit:	mg/l
Reaction:	1 sample + 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.

For tap and drinking water, it is possible to replace nitric acid 1M by the same volume of pH 4 buffer solution.

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(titr) = total volume of titrant to reach the inflection point in ml

-C(titr) = Titrant concentration in mol/l (currently 0.02)

-V(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: 9.48 mg/l

Standard deviation: 0.12 mg/l

Relative standard deviation: 1.28 %

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 7 to 63 mg/l of chloride for a sample volume of 100 ml and 0.02 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 kinetics 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.

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 a 0.02 M solution using very pure NaCl.

Dry the pure NaCl at 105°C and leave it to cool to room temperature in a dessicator.

Dissolve 1.1688 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 pH 4 buffer solution.

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

Using the combined metal/reference electrode described above, the starting potential is around -200 mV, the final potential close to 0 mV and the inflection point close to -130 mV. You can improve the indicated settings as

Minimum ordinate = E(IP)-50 mV in our case, -180 mV

Maximum ordinate = E(IP)+50 mV in our case, -80 mV

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

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

