Chlorides in Water

DOC316.52.93091

Based on the standard ISO 9297:2000

1. Introduction

As tap water, surface water or mineral water contain chloride ions at low concentration levels, chloride determination should be performed by titration with silver nitrate ($AgNO_3$) as titrant.

Standard NF ISO 9297 is based on the Mohr method. It uses a colorimetric determination of the equivalent point (with silver chromate). With the same titrant, it is possible to use a potentiometric determination of the equivalent point.

2. Principle

The silver nitrate reacts with chloride ion according to:

$$Ag^+ + Cl^- \rightarrow AgCl_{(precipitate)}$$

This application uses a potentiometric titration with a combined silver/reference electrode and the equivalence point is detected using the inflexion point mode.

The titration is performed in an acidic solution. The results are expressed in mg/L of chloride (Cl^- with a molar weight of 35.453 g/mol).

3. Electrode and reagents

- **MTC306** Intellical combined metal/reference ($Ag/AgNO_3$) electrode with integrated temperature sensor.
- **Titrant: $AgNO_3$ 0.02 mol/L**
  Dry $AgNO_3$ for 2 hours at 105 °C and leave it to cool to room temperature in a desiccator. Using a volumetric flask, dissolve an accurate weight of about 3.3974 g of $AgNO_3$ in 1000 mL of deionized water. Store the solution in a brown glass bottle.
- **Reagent: HNO_3 1 mol/L**
  Dilute 78 mL of concentrated nitric acid (65%) in 800 mL of deionized water and adjust the volume to 1000 mL with deionized water. This operation is highly exothermic. Observe laboratory safety regulations.
- **Standard for titrant calibration: NaCl 0.02 mol/L**
  Dry the pure NaCl at 105 °C and leave it to cool to room temperature in a desiccator. Dissolve an accurate weight of about 1.1688 g of NaCl in 1000 mL of deionized water using a volumetric flask.
- **Deionized water**

4. Ranges and settings

4.1. Default parameters

The working procedure is described using the following parameters:

- V sample = 100 mL
- Burette volume = 10 mL

4.2. Working ranges

The working range described in the norm NF ISO 9297 is 5 to 400 mg/L. It is possible to measure the sample with a higher concentration by using a smaller amount of sample and diluting it to 100 mL. With 0.02 M $AgNO_3$ as titrant, 1 mL of titrant corresponds to 7 mg/L of chloride.

For the equivalence point determination, it is recommended to have about 1 mL of titrant before and after the inflection point.

Sample amount/titrant volume	0.7 mL	5 mL	9 mL
100 mL	5 mg/L Cl^-	35 mg/L Cl^-	64 mg/L Cl^-
50 mL	10 mg/L Cl^-	71 mg/L Cl^-	127 mg/L Cl^-
15 mL	33 mg/L Cl^-	235 mg/L Cl^-	425 mg/L Cl^-

4.3. Settings

Name	Default parameter	Unit
Application		
Application name	Chlorides in water	
Advisable syringe	10mL (Hamilton)	
Sample		
Name	Water ? [1]	
Amount	100.0	[mL]
Minimum amount	15	[mL]
Maximum amount	110	[mL]
Probe		
Recommended probe	MTC 306	
Titrant		
Name	$AgNO_3$	
Titrant concentration	0.0200	[mol/L]
Leveling		
Active	No	
Automatic addition		
Active	Yes	
Reagent name	HNO_3 1M	
Pump	Pump 1	
Time	6	[s]
Stirring speed	25	[%]
Manual addition		
Active	No	
Stirring		
Active	Yes	
Time	10	[s]
Stirring speed	25	[%]
IP titration		
Stirring speed	25	[%]
Predose volume	0	[mL]
Delay	0	[s]
Max vol. stop point	10	[mL]
Stop on last EQP	Yes	
Result 1(R1) name	Chloride	
R1 hide	No	
R1 min	5.0	[mg/L]
R1 max	400	[mg/L]
R1 QC min	5.0	[mg/L]
R1 QC max	400	[mg/L]
R1 molar weight	35.453	

[1] "?" in the name, indicates that the sample name will be automatically incremented with a number for each analysis

4.4. Modification of the settings

4.4.1. Sample dilution

The final results are calculated based on the sample volume.

When a dilution of the sample is needed, **Enter the real sample amount** in the application edit window.

4.4.2. Addition of a predose volume

The parameters are defined in order to have the best compromise between accuracy and titration time.

For higher concentrations with a high titrant volume, the titration time can be reduced with an addition of titrant (predose) at the beginning of the titration. Enter the predose volume (in mL) and the stirring time after the addition, in the application edit window.

4.4.3. Reagent addition

It is possible to replace the automatic addition of nitric acid by a manual addition. This is done by deactivation and activation of the corresponding method in the application edit window.

4.4.4. Sample leveling

For a sample volume higher than 50 mL, it is possible to use a leveling method. It is deactivated by default.

To use this method, an external pump is required. All elements (probes, tubes from the titrator and the tube from the external pump) have to be well installed on the probe holder. The beaker has to contain a level of sample higher than the position of the tube of the external pump. When the beaker is attached to the probe holder, this method allows the system to automatically remove the excess sample by a defined pump working time, and always keep the same sample volume before launching the analysis.

In order to define this volume, the autoleveling calibration sequence has to be previously executed (see section **10 Appendix: Autoleveling calibration**).

When this option is active, the working time of the external pump must be set (default 30 s). The minimum working time must allow the pump to be removing air during the last few seconds of the external pump activation.

Note: *Do not forget to re-edit the sample amount with the expected value when deactivating the leveling method.*

5. Titration procedure

5.1. Sample preparation

For tap and surface water, pipette 100 mL of sample and put it in a 150 mL beaker.

For sparkling mineral water, it is necessary to degas the sample prior analysis.

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

5.2. Sample analysis

1. Dip the electrodes and titrant tip in the sample.
2. Verify that the porous tip of the reference electrode is located against the outside of the beaker and below the water level.
3. Adjust the tip from the peristaltic pump to above the sample surface.
4. Press **Start**. At the beginning of the analysis, 10 mL of nitric acid 1M will be automatically added with the peristaltic pump.

6. Results

6.1. Result calculation

The instrument calculates the result directly in mg/L of chloride.

As 1 mole of $AgNO_3$ reacts with 1 mole of chloride:

$$Result = V_{titr} \times C_{titr} \times 35.453 \times 1000 / V_{smp}$$

Where:

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 = Molar weight of the chloride ion

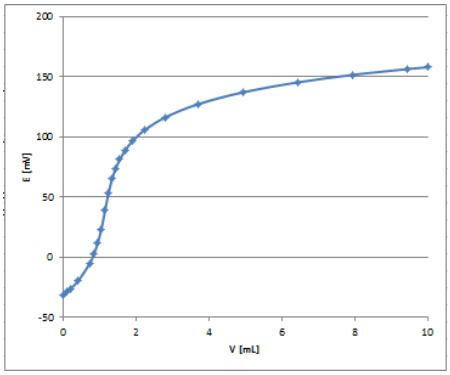
6.2. Experimental results

These results are indicative and have been obtained for a given sample of water for ten successive determinations.

Number of samples: 10
Mean value: 9.11 mg/L
Standard deviation: 0.066 mg/L
Relative standard deviation: 0.73%

6.3. Example of a titration curve

This curve has been obtained during the analysis of one of the 10 samples. Depending on the electrode used, minimum and maximum values of the potential can be different but should be between ±300 mV for a correct detection of the equivalent point.



7. Recommendations

Between titrations, rinse the silver electrode with distilled water. Do not use abrasive strips to clean the silver rod. If the potentials are not between -300 and +300mV, replace the electrolyte in the reference part of the electrode.

8. Bibliography

- *ISO 9297:2000 – Water quality – Determination of chloride — Silver nitrate titration with chromate indicator (Mohr's method)*

9. Appendix: Titrant calibration

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

1. Pipette and weigh 5 mL of NaCl solution (corresponding to half the capacity of the burette).
2. As the solution density can be taken as 1, if the weight is not exactly 5.000, enter the measured weight as a volume.
3. Dilute the NaCl standard to 100 mL with deionized water and add 10 mL of HNO_3 1M solution.
4. Calibrate the titrant using the titrant calibration module instead of the sample analysis.

Default settings for titrant calibration

Name	Setting	Unit
Automatic addition		
Active	Yes	
Reagent name	HNO_3 1M	
Pump	Pump 1	
Time	6	[s]
Stirring speed	25	[%]
Manual addition		
Active	No	
IP titration		
Stirring speed (%)	25	
Predose	3	[mL]
Delay	10	[s]
Stop on last EQP	Yes	
Max. vol. stop point	10	[mL]
Titer result		
Min titrant conc.	0.0120	
Max titrant conc.	0.0220	
Standard		
Standard name	NaCl	
Standard amount	5.000	[mL]
Min. amount	4	[mL]
Max. amount	6	[mL]
Concentration	0.0200	[mol/L]

10. Appendix: Autoleveling calibration

This option is **ONLY** available from the calibration menu if **Method Leveling** is set to Active (**Yes**). Refer to the documentation delivered with the external pump for a correct installation, paying particular attention to the suction tube from the pump.

1. Prepare a 0.001M NaCl solution in a 1000 mL volumetric flask, by diluting 50 mL of the standard solution NaCl 0.02M (used in the titrant calibration) with deionized water.
2. Pour a sufficient amount of the standard solution 0.01M into a beaker, allowing the external pump tube to be immersed in the liquid.
3. In the calibration menu, select **Autoleveling calibration** and then the application to use. The titration settings are the same as those used during a sample titration
4. At the end of the procedure, the result obtained is the volume remaining in the beaker after leveling. It is automatically written in the **Sample amount** field for the application editor and will be used in the next titration calculations of the application.
   This result is compared to the minimum and maximum sample amounts defined in the **Sample** section of the application editor. For this application, leveling can be used only for a sample volume higher than 50 mL (**Sample min. amount** has to be set to **50 mL**).

Settings for Autoleveling calibration

Name	Setting	Unit
Sample		
Min. amount	50	[mL]
Max. amount	110	[mL]
Method leveling		
Active	Yes	
Time	30	[s]
Autoleveling calibration		
Solution name	NaCl	
Concentration	0.01	[mol/L]