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# Application Bulletin

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Of interest to: General analytical laboratories

A 1, 2, 4, 7, 10, 11, 12, 13

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## Chloride titrations with potentiometric indication

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### Summary

Besides acid/base titrations, the titrimetric determination of chloride is one of the most frequently used titrimetric methods of analysis. It is employed more or less frequently in practically every laboratory. This bulletin shows you how to determine chloride in a wide range of concentrations using automatic titrators.

Silver nitrate is normally used as titrant. (For environmental reasons one should refrain from using mercury nitrate.) The titrant concentration depends on the chloride content of the sample to be analyzed. It is especially important to choose the correct electrode for samples with low chloride contents.

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### Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or 726 or 796 Titroprocessor with 700 Dosino or 685 Dosimat
- 2.728.0040 Magnetic Stirrer
- 6.3014.XX3 Exchange Unit (with flat PCTFE/PTFE stopcock)
- Indicator electrode: A wide range of suitable electrodes is available from Metrohm. Here a selection of these:
  - 6.0430.100 Ag Titrode\*
  - 6.0450.100 combined Ag ring electrode\*
  - 6.0331.010 Ag rod electrode\*
  - 6.0350.100 Ag ring electrode\*
  - 6.0502.120 chloride ISE
  - 6.0502.180 silver/sulfate ISE

\* Bare or with AgCl or Ag<sub>2</sub>S coating, as desired.
- 6.0726.100 double-junction Ag/AgCl reference electrode (bridge electrolyte KNO<sub>3</sub>) with 6.2106.020 electrode cable (when using a separate Ag electrode without integrated reference system)

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### Reagents

- Titrant: c(AgNO<sub>3</sub>) = 0.001 ... 0.1 mol/L
- Chloride standard: c(KCl) = 0.1000 mol/L, e.g. Metrohm no. 6.2301.060, or dilutions from it
- Acid: c(HNO<sub>3</sub>) = 2 mol/L or c(H<sub>2</sub>SO<sub>4</sub>) = 1 mol/L

For special applications:

- Acetone, p.a., as free from chloride as possible
- Acetic acid  $w(\text{CH}_3\text{COOH}) = 80\%$ , containing 1.9 g/L amidosulfuric acid
- Protective colloid: polyvinyl alcohol, e.g. Merck no. 114266, as 0.2% aqueous solution (dissolve in hot dist. water)

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### **General remarks**

- Silver nitrate forms sparingly soluble precipitates with many anions. In mixtures containing different anions the obtained titration curve can therefore show several equivalence points. The anion forming the least soluble compound with  $\text{Ag}^+$  ions is determined first. Consequently, in a mixture of chloride, bromide and iodide the  $\text{Cl}^-$  ions will be titrated last. For the quantitative separation of anion mixtures the solubility products of the corresponding Ag compounds should differ as much as possible. In addition, as far as the anions to be analyzed are concerned, no great differences in concentration should exist. In certain cases, adding barium acetate and/or acetone can facilitate separation.
- Generally titration should be performed in an acidic solution (acidify with  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ ).
- Prior to the chloride titration, any cyanides, sulfides and thiosulfates present should be removed by means of oxidation, e.g. with  $\text{H}_2\text{O}_2$ .
- If the sample contains peroxides (e.g. after a digestion), these must be destroyed prior to the titration.
- Samples with high chloride contents (brines, salts) are not titrated directly, but an intermediate dilution is prepared first: A suitable amount of sample is weighed in and diluted with dist. water to a defined volume; a portion of this sample solution (aliquot) is then used for the titration.
- To prevent coagulation of the  $\text{AgCl}$  precipitate, a protective colloid can be added to the sample solution. 5 mL 0.2% polyvinyl alcohol solution per 100 mL sample solution prevents inclusions and keeps the electrode surface practically free from deposits.
- We favor the Ag Titrode. With this electrode there is no need to refill any electrolyte and there are no diaphragm problems.
- For the determination of small chloride concentrations or the titration of chloride in aggressive media, we recommend to use a Ag electrode with  $\text{Ag}_2\text{S}$  coating.

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### **Analysis**

#### **General procedure**

Place the sample or an aliquot of this in a glass beaker and add 0.5 mL  $c(\text{HNO}_3) = 2 \text{ mol/L}$  or  $c(\text{H}_2\text{SO}_4) = 1 \text{ mol/L}$ . In the case of higher chloride contents dilute with dist. water to 50 ... 100 mL. Immerse the electrode(s) and titrate in the mV measuring range using a  $\text{AgNO}_3$  solution of appropriate concentration.

#### **Calculation**

1 mL  $c(\text{AgNO}_3) = 0.1 \text{ mol/L}$  corresponds to 3.5453 mg  $\text{Cl}^-$  or 5.8443 mg NaCl or 7.4555 mg KCl

## Examples

### 1. Chloride in drinking water

To 100 mL drinking water add 0.5 mL  $c(\text{HNO}_3) = 2 \text{ mol/L}$  and titrate with  $c(\text{AgNO}_3) = 0.01 \text{ mol/L}$ . Use the Ag Titrode with  $\text{Ag}_2\text{S}$  coating.

$$\text{mg/L chloride} = \text{EP1} * 0.3545 * 1000 / 100 = \text{EP1} * 3.545$$

### 2. Chloride in dialysis and/or infusion solutions

To 5.0 mL sample add 2 mL  $c(\text{HNO}_3) = 2 \text{ mol/L}$  and 30 ... 50 mL dist. water. Titrate with  $c(\text{AgNO}_3) = 0.1 \text{ mol/L}$  using the Ag Titrode.

$$\text{mmol/L chloride} = \text{EP1} * 0.1 * 1000 / 5 = \text{EP1} * 20$$

### 3. Chloride in Cr(VI) plating bath

Pipet 5.0 mL bath sample as well as 20 mL dist. water and 20 mL ethanol into a glass beaker. After addition of 0.5 mL conc.  $\text{H}_2\text{SO}_4$  heat the solution and boil for 5 min in order to convert all Cr(VI) to Cr(III). Allow to cool down, then titrate with  $c(\text{AgNO}_3) = 0.01 \text{ mol/L}$  using the Ag Titrode with  $\text{Ag}_2\text{S}$  coating.

$$\text{mg/L chloride} = \text{EP1} * 0.355 * 1000 / 5 = \text{EP1} * 71$$

### 4. Chloride in acidic copper plating bath

Pipet 20.0 mL bath sample, 2 mL  $c(\text{HNO}_3) = 2 \text{ mol/L}$  and 50 mL dist. water into a glass beaker. Using the Ag Titrode, titrate with  $c(\text{AgNO}_3) = 0.01 \text{ mol/L}$ .

$$\text{mg/L chloride} = \text{EP1} * 0.355 * 1000 / 20 = \text{EP1} * 17.75$$

### 5. Chloride in nickel plating bath (nickel sulfate/sulfamate)

Depending on the expected chloride content, pipet 1.0 ... 5.0 mL bath sample into a glass beaker. Add ca. 50 mL dist. water as well as 2 mL  $c(\text{HNO}_3) = 2 \text{ mol/L}$  and titrate with  $c(\text{AgNO}_3) = 0.1 \text{ mol/L}$  using the Ag Titrode.

$$\text{g/L chloride} = \text{EP1} * 3.5453 / \text{C00}$$

$$\text{C00} = 1.0 \dots 5.0 \text{ (sample volume in mL)}$$

### 6. Chloride traces in cement and clinker

Weigh exactly 2.500 g sample into a glass beaker and suspend with 30 mL dist. water. Carefully add 6 mL conc.  $\text{HNO}_3$  under stirring, then place the glass beaker for 1 ... 2 min in an ultrasonic bath. Filter through a paper filter (free from chloride!) into a 100 mL volumetric flask, thoroughly rinse the filter with dist. water, make up to the mark and mix.

Pipet 50.0 mL of the prepared sample solution (this corresponds to 1.25 g of the original sample) into a glass beaker, add 20 mL glacial acetic acid as well as ca. 0.5 g sodium acetate and titrate with  $c(\text{AgNO}_3) = 0.01 \text{ mol/L}$  using the MET mode of the titrator.

$$\% \text{ chloride} = \text{EP1} * 0.355 * 0.1 / 1.25 = \text{EP1} * 0.0284$$

**7. Salt content of meat (dried meat, sausage, ham, smoked fish, etc.)**

Cut the sample in tiny pieces with a knife. Weigh exactly ca. 10 g of this sample into a mixer, add 190 g dist. water and let run for 1 ... 2 min until the mixture is homogeneous.

Weigh 50 g of the homogenized mixture into a glass beaker and add 50 mL dist. water as well as 2 mL  $c(\text{HNO}_3) = 2 \text{ mol/L}$ . Titrate with  $c(\text{AgNO}_3) = 0.1 \text{ mol/L}$  using the Ag Titrode.

$$\% \text{ NaCl} = \text{EP1} * 5.844 * 0.1 / \text{C00} = \text{EP1} * \mathbf{0.5844} / \text{C00}$$

C00 = ca. 2.5 (sample mass used for the titration in g)

**8. Adsorbable halogenated hydrocarbons (AOX)**

The analysis of traces of adsorbable halogenated hydrocarbons represents a special case. After combustion of the sample the gases formed are absorbed in 80% acetic acid + 1.9 g/L amidosulfuric acid and titrated with  $c(\text{AgNO}_3) = 2 \text{ mmol/L}$  in 80% acetic acid.

Indicator electrode: 6.0331.010 Ag rod electrode with  $\text{Ag}_2\text{S}$  coating

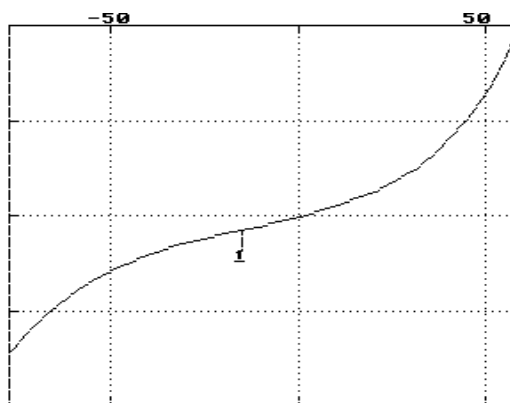
Reference electrode: 6.0726.100 double-junction Ag/AgCl reference electrode  
[bridge electrolyte  $c(\text{NaCH}_3\text{COO}) = 2 \text{ mol/L}$  in 80% acetic acid]

**Figures**

```
'pa
785 DMP Titrimo      02287  785.0010
user                 MEIER
date 1999-04-27     time 11:11      5
DET U               Chloride
parameters
>titration parameters
  meas.pt.density    4
  min.incr.          10.0 fl
  dos.rate           max. ml/min
  signal drift       50 mV/min
  equilibr.time      26 s
  start V:           OFF
  pause              0 s
  meas.input:        1
  temperature        17.2 °C
>stop conditions
  stop V:            abs.
  stop V             99.99 ml
  stop U             OFF mV
  stop EP            1
  filling rate       max. ml/min
>statistics
  status:            OFF
>evaluation
  EPC                5
  EP recognition:    all
  fix EP1 at U      OFF mV
  pK/HNP:            OFF
>preselections
  req.ident:         OFF
  req.smpl size:     OFF
  limit smpl size:  OFF
  activate pulse:    OFF
=====
```

```
'fr
785 DMP Titrimo      02287  785.0010
user                 MEIER
date 1999-04-27     time 11:01      5
U(init)             59 mV DET U      Chloride
smpl size           100 ml
EP1                 2.150 ml          -15 mV
Chloride            7.62 ppm
stop #EP reached
=====

'cu
785 DMP Titrimo      02287  785.0010
user                 MEIER
date 1999-04-27     time 11:01      5
start V             0.000 ml DET U      Chloride
1.0 ml/div          dU=50.0 mV/div
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**Fig. 1:** Parameter settings on the 785 DMP Titrimo for determining chloride in drinking water.

**Fig. 2:** Result block and titration curve.

**Literature**

There are numerous standard methods concerning chloride titrations with potentiometric indication. Here a few examples are listed:

- AOAC 963.05 (1990)  
Chlorides in tobacco. Potentiometric method.
- AOAC 971.25 (1990)  
Sodium chlorides in canned vegetables. Method III: Potentiometric method.
- AOAC 976.18 (1990)  
Salt (chlorine as sodium chloride) in seafood. Potentiometric method.
- AOAC 980.25 (1990)  
Chlorides in water-soluble color additives. Manual and automated potentiometric method.
- ASTM D 1570-95 (1995)  
Standard Test Methods for Sampling and Chemical Analysis of Fatty Alkyl Sulfates.
- ASTM D 1820-95 (1995)  
Standard Test Method for Hydrolyzable Chlorine Compounds in Chlorinated Aromatic Hydrocarbons (Askarels).
- ASTM D 1847-93 (1998)  
Standard Test Methods for Total Chlorine Content of Epoxy Resins.

- ASTM D 3673-89 (1995)  
Standard Test methods for Chemical Analysis of Alpha Olefin Sulfonates.
- ASTM D 4929-89 (1989)  
Standard Test Methods for Determination of Organic Chloride in Crude Oil.
- DIN EN 196, part 21 (1989)  
Prüfverfahren für Zement. Bestimmung des Chlorid-, Kohlenstoffdioxid- und Alkalianteils.
- ISO 457: 1983  
Soaps – Determination of chloride content – Titrimetric method.
- ISO 4573: 1978  
Plastics – Epoxide resins and glycidyl esters – Determination of inorganic chlorine.
- ISO 5810: 1982  
Starches and derived products – Determination of chloride content – Potentiometric method.
- ISO 5943: 1988  
Cheese and processed cheese products – Determination of chloride content – Potentiometric titration method.
- ISO 6227: 1982  
Chemical products for industrial use – General method for determination of chloride ions – Potentiometric method.
- ISO 9197-1: 1989  
Paper, board and pulps – Determination of water-soluble chlorides - Part 1: General method.
- Schweizerisches Lebensmittelbuch, chapter 13 (1981)  
Würzen, Suppen, Saucen. 05. Chlorid-Bestimmung.
- UOP 456-80 (1980)  
Chloride in refinery waters.