
Application Bulletin

Of interest to: General analytical laboratories

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

Chloride titrations with potentiometric end-point detection

Summary

Together with acid/base titrations, the titrimetric chloride determination is one of the most frequently used titrimetric methods of analysis. It is employed more or less frequently in practically every laboratory. The purpose of this Bulletin is to demonstrate the possibilities for determining chloride in a wide range of concentrations using automatic titrators.

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

Apparatus and accessories

- Titrino or Titrande with Dosino or Dosimate
- Magnetic Swing-out Stirrer
- Exchange unit
- 6.0726.100 Reference electrode (outer electrolyte KNO_3 , for use with separate Ag electrodes) with 6.2106.020 electrode cable
- Measuring electrodes; a wide range of suitable electrodes is available at Metrohm. Here a selection of these:
 - 6.0430.100 Ag-Titrode **
 - 6.0450.100 comb. Ag-ring electrode **
 - 6.0331.010 Ag-rod electrode **
 - 6.0350.100 Ag-ring electrode **
 - 6.0502.120 AgCl-ISE
 - 6.0502.180 Ag/S-ISE** if desired bare or with AgCl resp. Ag_2S coating.

Reagents

- Titrant: $c(\text{AgNO}_3) = 0.001 \dots 0.1 \text{ mol/L}$
- Standard: $c(\text{KCl}) = 0.1000 \text{ mol/L}$, e.g. Metrohm No. 6.2301.060, or dilutions from it

Acid: $c(\text{HNO}_3) = 2 \text{ mol/L}$ or $c(\text{H}_2\text{SO}_4) = 1 \text{ mol/L}$

and for special applications:

- Acetone, p.a. as free from chloride as possible
 - Acetic acid, $w = 80\%$, containing 1.9 g/L amidosulphamic 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 with many anions causes more or less soluble precipitations. Thus, in mixtures of several anions, also several end-points can appear in the titration curve. Here, the anion causing the most insoluble precipitation is recorded first. Consequently, in a mixture of chloride, bromide and iodide, chloride would be titrated last. For the quantitative separation of mixtures, the solubility products of the Ag compounds must be as far apart as possible. In addition, no great differences in concentration should exist. In some cases, adding barium acetate and/or acetone can facilitate separation.

Generally titration should take place in an acidic solution (acidify with HNO_3 or H_2SO_4).

Before the chloride determination, cyanide, sulphide and thiosulphate should be removed by means of oxidation, e.g. with H_2O_2 .

With samples containing peroxides (e.g. after digestions), these must first be destroyed before titration.

For the determination of high chloride concentrations (in brines, salts), the sample is weighed, diluted with dist. water to a certain volume and a portion of this (aliquot) is titrated.

To prevent an accumulation of the AgCl precipitation, protective colloid can be added to the sample solution. Polyvinyl alcohol (5 mL) 0.2 % per 100 mL sample solution prevents inclusions and keeps the electrode surface practically free from precipitation.

We prefer use of the Ag-Titrode. No electrolytes have to be replenished, nor will the diaphragms become blocked.

For the titration of samples with small contents of chloride or of chlorides in aggressive solutions, we recommend use of an electrode coated with Ag_2S .

General titration procedure

Place sample or an aliquot of this in a glass beaker and add 0.5 mL HNO_3 or H_2SO_4 . If content of chloride is high, dilute with dist. water 50 ... 100 mL. Immerse the electrode(s) and titrate on the mV measuring range with the selected AgNO_3 concentration.

Calculation

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

A few chosen 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 $c(\text{AgNO}_3) = 0.01 \text{ mol/L}$. Ag-Titrode with Ag_2S coating.

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

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. H_2O . Titrate with $c(\text{AgNO}_3) = 0.1 \text{ mol/L}$ using the Ag-Titrode.

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

3. Chloride in Cr(VI)-bath

In a glass beaker pipette 5.0 mL bath sample and 20 mL each dist. H_2O and ethanol. Add 0.5 mL conc. H_2SO_4 , heat and boil for 5 min to convert Cr(VI) entirely to Cr(III). After cooling, titrate with $c(\text{AgNO}_3) = 0.01 \text{ mol/L}$. Use Ag-Titrode with Ag_2S coating.

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

4. Chloride in acidic copper bath

In a glass beaker pipette 20.0 mL bath sample, 2 mL $c(\text{HNO}_3) = 2 \text{ mol/L}$ and 50 mL dist. H_2O . Using the Ag-Titrode, titrate with $c(\text{AgNO}_3) = 0.01 \text{ mol/L}$.

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

5. Chloride in nickel (sulphate/sulphamate) bath

Depending on the expected chloride content, pipette 1.0 ... 5.0 mL sample into a glass beaker. Add approx. 50 mL dist. H_2O and 2 mL $c(\text{HNO}_3) = 2 \text{ mol/L}$ and titrate using the Ag-Titrode with $c(\text{AgNO}_3) = 0.1 \text{ mol/L}$.

$$\text{g/L chloride} = \underline{\text{EP1} \times 3.5453 / \text{C00}} \quad \text{C00} = \text{mL sample size}$$

6. Chloride traces in cement and clinker

Weigh exactly 2.500 g sample into a glass beaker and mix to a slurry with 30 mL dist. H_2O . Stirring, carefully add 6 mL conc. HNO_3 and place beaker for 1 - 2 min in an ultrasonic bath. Filter through a paper filter (free from chloride) into a 100 mL graduated flask, rinse filter well with dist. H_2O , fill up to mark and mix.

Pipette 50.0 mL (corresponding to 1.25 g original sample) into a glass beaker, add 20 mL glacial acetic acid and approx. 0.5 g sodium acetate and titrate with $c(\text{AgNO}_3) = 0.01 \text{ mol/L}$ using the MET-mode of the titrator.

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

7. Salt content in meats

(Dried meat, sausage, ham, smoked fish etc.)

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

Weigh 50 g of this homogeneous mixture into a glass beaker, then add 50 mL dist. H_2O and 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.

$$\% \text{ NaCl} = \text{EP1} \times 5.844 \times 0.1 / \text{C00} = \underline{\text{EP1} \times 0.5844 / \text{C00}}$$

C00 = g sample for titration (ca. 2.5)

8. Absorbable halogenated hydrocarbons (AOX)

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

Electrodes:

6.0331.010 with Ag_2S coating

6.0726.100 Ag/AgCl reference electrode. Outer electrolyte is $c(\text{NaOOCCH}_3) = 2 \text{ mol/L}$ in 80 % acetic acid

Figures

```
'fr
785 DMP Titrino      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 Titrino      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

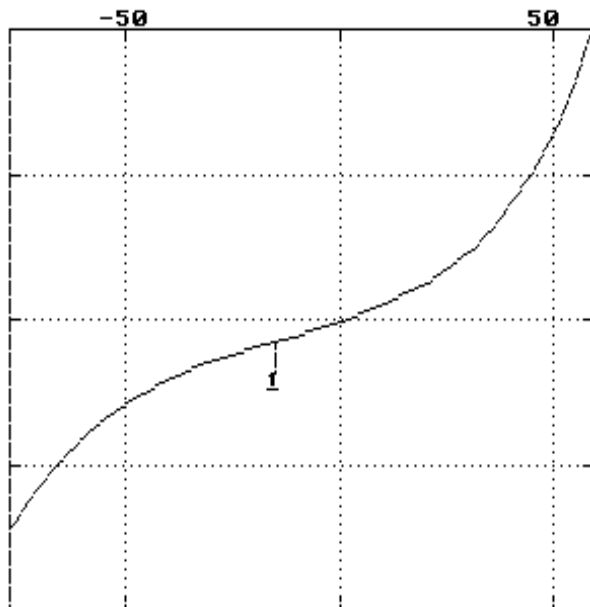


Fig. 1 Curve and result block for chloride determination in drinking water Herisau

```
'pa
785 DMP Titrino      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 xC
>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
```

Fig. 2 Parameters on Titrino for above determination

Literature

There are numerous standard methods for the potentiometric indicated chloride titration. 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, Teil 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, Kapitel 13** (1981)
Würzen, Suppen, Saucen. 05. Chlorid-Bestimmung
- **UOP 456-80** (1980)
Chloride in refinery waters