

Chloride titrations with potentiometric indication

Branch

General analytical chemistry; water, waste water, environmental protection; pharmaceutical industry; food, stimulants, beverages, flavors; metals, electroplating; fertilizers, base materials, explosives; detergents, surfactants, cosmetics; textiles, paper, ceramics

Keywords

Titration; potentiometric titration; chloride; water; food; branch 1; branch 2; branch 4; branch 7; branch 10; branch 11; branch 12; branch 13; 6.0430.100; 6.0430.100S; 6.0470.300; 6.0470.300S; 6.0450.100; 6.0450.100S; 6.0450.300; 6.0350.100; 6.0450.300S; 6.0726.100; Ag-Titrode, iAg-Titrode; Combined Ag-ring electrode; iAg-ring electrode combined; Separate Ag-ring electrode; Ag/AgCl DJ reference electrode

Summary

Beside acid/base titrations, the titrimetric determination of chloride is one of the most frequently used titrimetric methods of analysis. This bulletin describes 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.

Instruments

- Titrator with DET mode
- 10 mL buret or 20 mL buret (depends on concentration of titrant and chloride in sample)
- Stirrer

Electrodes

Ag-Titrode*	6.0430.100
iAg-Titrode*	6.0470.300
Combined Ag-ring electrode*	6.0450.100
iAg-ring electrode combined*	6.0450.300
Separate Ag-ring electrode	6.0350.100
Ag/AgCl DJ reference electrode	6.0726.100

* bare or with Ag₂S or AgBr coating, as desired

Reagents

- Dist. water

These reagents are for special applications only:

- Acetone, p.a. as free from chloride as possible
- Acetic acid, w(CH₃COOH) = 80%, containing 1.9 g/L amidosulfuric acid
- Protective colloid: polyvinyl alcohol (PVA), e.g., Merck no. 114266, as 0.2% aqueous solution (dissolve in hot dist. water)

Solutions

Titrant	c(AgNO ₃) = 0.001 ... 0.1 mol/L, if possible this solution should be bought from a supplier.
Acidifying solution	c(HNO ₃) = 2 mol/L or c(H ₂ SO ₄) = 1 mol/L

Standard

Potassium chloride	c(KCl) = 0.1 mol/L, e.g., Metrohm no. 6.2301.060 or dilutions from it
Sodium chloride	Sodium chloride is dried for 2 h in a drying oven at 120 °C and allowed to cool down in a desiccator.

Sample preparation

The sample preparation depends on the type of sample and its chloride content.

Analysis

Titer

Weigh, pipette or dispense with an appropriate buret the requested amount of NaCl or KCl standard (see table 1). Add the appropriate amount of $c(\text{HNO}_3) = 2 \text{ mol/L}$ or $c(\text{H}_2\text{SO}_4) = 1 \text{ mol/L}$ (see table 1) and approx. 60 mL dist. water. Immerse the electrode(s) and titrate in the mV measuring range using $c(\text{AgNO}_3)$ as titrant.

$c(\text{AgNO}_3)$	0.1 mol/L		0.01 mol/L	
Buret	10 mL	20 mL	10 mL	20 mL
Liquid KCl std. $c(\text{KCl}) = 0.1 \text{ mol/L}$	5 mL	10 mL	0.5 mL	1.0 mL
Solid NaCl std.	30 mg	60 mg	*	*
$c(\text{HNO}_3) = 2 \text{ mol/L}$	5 mL		0.5 mL	
$c(\text{H}_2\text{SO}_4) = 1 \text{ mol/L}$	5 mL		0.5 mL	

* It is not recommended using solid standard directly for low titrant concentrations

Table 1: Amount of standard and acid depending on the size of the used buret and the concentration of titrant

Sample

General procedure

Place the sample or an aliquot of it in a titration vessel and add the appropriate amount of $c(\text{HNO}_3) = 2 \text{ mol/L}$ or $c(\text{H}_2\text{SO}_4) = 1 \text{ mol/L}$ (see table 2). Dilute with 50 – 100 mL dist. water. In case of higher chloride contents add 2 mL PVA solution. Immerse the electrode(s) and titrate in the mV measuring range using an AgNO_3 solution of appropriate concentration as titrant.

$c(\text{AgNO}_3)$	0.1 mol/L		0.01 mol/L	
$c(\text{HNO}_3) = 2 \text{ mol/L}$	2 mL		0.2 mL	
$c(\text{H}_2\text{SO}_4) = 1 \text{ mol/L}$	2 mL		0.2 mL	

Table 2: Amount of acid depending on the concentration of titrant

Parameters

Titer / Sample

Mode	DET U
Meas. point density	4
Min. increment	10 μL
Max. increment	off μL

Signal drift	50 mV/min
Max. waiting time	26 s
EP criterion (ERC)	5
EP recognition	all

Calculation

Titer with liquid KCl standard

$$\text{Titer} = \frac{c(\text{KCl}) \times V_{\text{KCl}}}{V_{\text{EP1}} \times c(\text{AgNO}_3)}$$

Titer:	Titer of the selected titrant
$c(\text{KCl})$:	Concentration of the KCl standard in mol/L; here $c(\text{KCl}) = 0.1 \text{ mol/L}$
V_{KCl} :	Volume of standard in mL
V_{EP1} :	Titration consumption until the first equivalence point in mL
$c(\text{AgNO}_3)$:	Concentration of the selected titrant in mol/L; here $c(\text{AgNO}_3) = 0.01 \text{ mol/L}$

Titer with solid NaCl standard

$$\text{Titer} = \frac{m_s}{V_{\text{EP1}} \times c(\text{AgNO}_3) \times M_A}$$

Titer:	Titer of the selected titrant
m_s :	Mass of standard in mg
V_{EP1} :	Titration consumption until the first equivalence point in mL
$c(\text{AgNO}_3)$:	Concentration of the selected titrant in mol/L; here $c(\text{AgNO}_3) = 0.1 \text{ mol/L}$
M_A :	Molecular weight of the analyte; here 58.443 g/mol

Sample

$$\beta(\text{Chloride}) = \frac{V_{\text{EP1}} \times c(\text{AgNO}_3) \times f \times M(\text{Cl}) \times 1000}{V_s}$$

$\beta(\text{Chloride})$:	Chloride content in mg/L
$V_{\text{last EP}}$:	Titration consumption until the first equivalence point in mL
$c(\text{AgNO}_3)$:	Concentration of titrant in mol/L; here $c(\text{AgNO}_3) = 0.1 \text{ mol/L}$
f:	Correction factor (titer) without unit
$M(\text{Cl})$:	Molar mass of Cl: 35.453 g/mol
1000:	Conversion factor g to mg
V_s :	Sample volume in mL

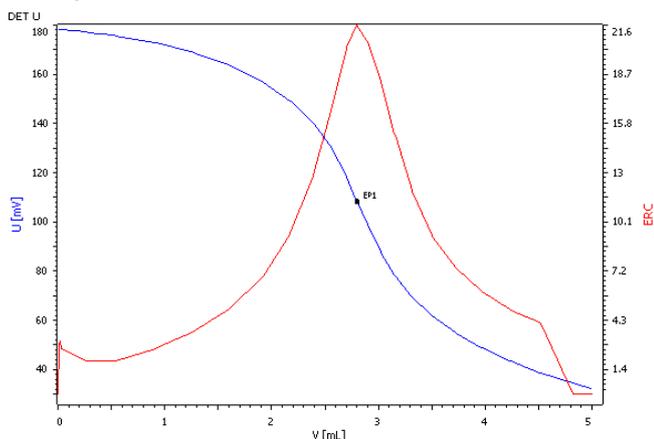
Example


Fig. 1: Potentiometric determination of chloride in acidic copper bath using the Ag Titrode (blue = measuring signal, red = ERC)

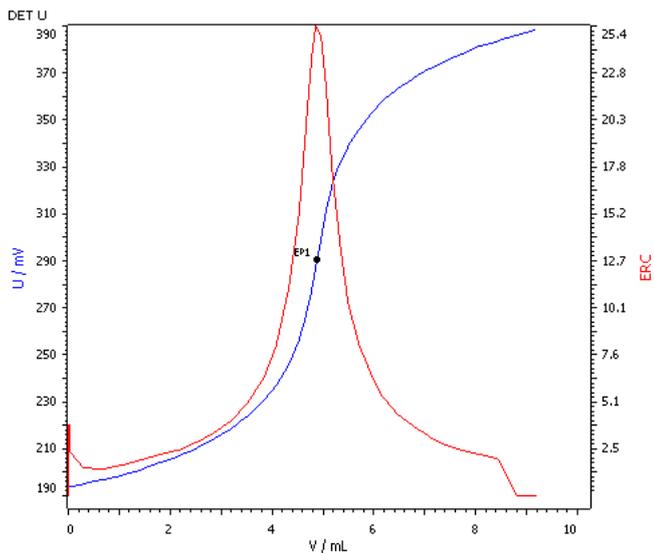


Fig. 2: Potentiometric determination of chloride in aqueous solution using the combined Ag-ring electrode (blue = measuring signal, red = ERC)

Comments

- Due to different reference systems for the Ag Titrode and the Ag-ring electrode the titration curves have the opposite direction compared to each other (see Fig. 1 and Fig 2).
- 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 Ag^+ ions is determined first.

Ag salt	$K_L / (\text{mol}^2/\text{L}^2)$ or $(\text{mol}^3/\text{L}^3)$
AgBr	7.7×10^{-13}
Ag ₂ CO ₃	6.15×10^{-12}
AgCl	1.56×10^{-10}
AgCN	2.2×10^{-12}
AgCNS	1.16×10^{-12}
AgI	1.5×10^{-16}
Ag ₂ S	1.6×10^{-49}

Table 3: Solubility product (K_L) of different Ag salts in water

Consequently, in a mixture of chloride, bromide and iodide the Cl^- ions will be titrated last. For the quantitative separation of anion mixtures, the solubility products of the corresponding Ag compounds should differ at least 5 orders of magnitude. 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. In the Application Bulletins 27 and 119 procedures to determine chloride, bromide and iodide in presence of each other are discussed.

- Generally titration should be performed in an acidic solution (acidify with HNO_3 or H_2SO_4).
- Prior to the chloride titration, any cyanides, sulfides and thiosulfates present should be removed by means of oxidation, e.g., with H_2O_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 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.
- The Ag Titrode is to favor as 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, it is recommended using a Ag electrode with Ag_2S coating
- It is also possible to determine chloride by thermometric titration (see AN-H-033)

References

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

- Metrohm Application Bulletin 27
Potentiometric titration of chloride and bromide in the presence of each other
- Metrohm Application Bulletin 119
Potentiometric determination of trace bromide and iodide in chlorides
- AOAC 963.05 (2005)
Chlorides in tobacco.
- AOAC 971.27 (2005)
Sodium chlorides in canned vegetables.
- AOAC 976.18 (2005)
Salt (chlorine as sodium chloride) in seafood.
- AOAC 980.25 (2005)
Chlorides in water-soluble color additives. Manual and automated potentiometric methods.
- 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 4929-07 (2007)
Standard Test Methods for Determination of Organic Chloride in Crude Oil.
- DIN EN 196 - 2 (2005)
Methods of testing cement – Part 2: Chemical analysis of cement.
- ISO 457: 1983
Soaps – Determination of chloride content.
- ISO:4573: 1978
Plastics – Epoxide resins and glycidyl esters – Determination of inorganic chlorine.
- ISO 5810: 1982
Starches and derived products – Determination of chloride content.
- ISO 5943: 1988
Cheese and processed cheese products – determination of chloride content.
- ISO 6227: 1982
Chemical products for industrial use – General method for determination of chloride ions.
- ISO 9197-1: 1989
Paper, board and pulps – determination of water soluble chlorides. Part 1. General method.
- Schweizerisches Lebensmittelbuch, chapter 13 (1981)
Determination of chloride in seasonings, soups, sauces
- Schweizerisches Lebensmittelbuch 322.1 (1999)
Determination of chloride in meat and meat products
- UOP 456-80 (1980)
Chlorides in Refinery Waters

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Appendix

Sample preparations for further application examples

1. Chloride in drinking water

To 100 mL drinking water add 2 mL $c(\text{HNO}_3) = 2 \text{ mol/L}$ and titrate with $c(\text{AgNO}_3) = 0.01 \text{ mol/L}$ using Ag Titrode with Ag_2S coating.

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.

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. H_2SO_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 Ag_2S coating.

4. Chloride in acidic copper plating bath

Pipet 20 mL bath sample, 2 mL $c(\text{HNO}_3) = 2 \text{ mol/L}$ and 50 mL dist. water into a glass beaker. Titrate with $c(\text{AgNO}_3) = 0.01 \text{ mol/L}$ using the Ag Titrode with Ag_2S coating.

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 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.

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. 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, fill 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.

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 50.0 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 Ag Titrode.

When using an automated system only cut the sample in tiny pieces with a knife and weigh an appropriate amount of meat into a sample beaker. Afterwards, the automated system equipped with a Polytron will undertake the whole sample preparation and titration for you.

8. Absorbable halogenated hydrocarbons (AOX)

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

Indicator electrode: 6.0331.010S Ag rod electrode with Ag_2S 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]