Metrohm

Application Bulletin 61/3 e

Potentiometric determination of silver

Accurate determination according to EN ISO and GB/T standards

Branch

General analytical chemistry; metals, electroplating

Keywords

Titration; potentiometric titration; precipitation titration; silver; jewelry; fine silver; Ag Titrode; silver plating bath; EN ISO 11427; GB/T 17823; ISO 13756; GB/T 18996; 6.0430.100

Summary

Silver is an important metal not only in jewelry and silverware but also in electrical conductors and contacts. The knowledge of the exact silver content in fine silver and silver alloys ensures that quality standards for jewelry and silverware are met. As for the plating industry, the knowledge of the amount of silver in silver plating baths helps to run the bath efficiently.

While X-ray fluorescence (XRF) is a fast alternative to determine the silver content in fine silver and silver alloys, it can only determine the silver content of the outermost sections of the metal. In contrast, titration offers a more comprehensive solution considering the whole sample, thus preventing fraud by thick plating.

This application bulletin describes the potentiometric determination of silver in fine silver and silver alloys according to EN ISO 11427, ISO 13756, GB/T 17823, and GB/T 18996 as well as in silver plating baths by a titration with potassium bromide or potassium chloride, respectively.

Instruments

- Titrator with DET mode
- Stirrer
- 50 mL buret

Electrodes

Ag Titrode with silver bromide coating (EN ISO 11427, GB/T 17823)	6.00430.100Br
Ag Titrode with silver chloride coating (ISO 13756, GB/T 18996)	6.00430.100Cl

Reagents

- Potassium bromide, KBr, puriss p.a., >99.5%
- Nitric acid, w(HNO_3) = 33% (w/w)
  with low halide content, tested with the silver nitrate test
- Polyvinyl alcohol, PVA, p.a.
- Dimethylglyoxime disodium salt octahydrate, $Na_2C_4H_6N_2O_2 \cdot 8\ H_2O$, p.a.

Solutions

Titrant EN ISO 11427, GB/T 17823	c(KBr) = 0.1 mol/L 11.901 g dried KBr is weighed in a 1 L volumetric flask and dissolved in distilled water and the flask is filled up to the mark with distilled water.
Titrant ISO 13756 GB/T 18996	c(KCl) = 0.1 mol/L or c(NaCl) = 0.1 mol/L 7.455 g dried KCl or 5.844 g dried NaCl is weighed in a 1 L volumetric flask and dissolved in distilled water and the flask is filled up to the mark with distilled water.
Protective colloid solution	w(PVA) = 0.2% 2 g PVA is weighed into a volumetric flask and dissolved in hot distilled water. Afterwards the flask is filled up to the mark with distilled water.
Precipitation solution	10 g dimethylglyoxime disodium salt octahydrate is weighed into a 1000 mL volumetric flask. The flask is then filled up to the mark with distilled water.

Standard

Fine silver	Minimal purity of 999.9 per mil (‰) mass fraction.

Sample preparation

The sample preparation should be carried out in a fume hood as toxic nitrogen oxides and HCN (only silver plating bath) are released

Fine silver and silver alloys

A sample containing 300 – 500 mg silver is weighed to the nearest 0.01 mg into a beaker glass. 5 mL w(HNO_3) = 33% is added and the beaker glass is covered. The sample is heated to dissolve the silver. The heating can be stopped when nitrogen oxides are no longer produced. After cooling down to room temperature, 100 mL of distilled water is added.

Silver plating baths

Depending on the expected silver content, 1.0 – 10.0 mL of the plating bath sample is pipetted into a glass beaker and dilute to approx. 50 mL with distilled water. 5 – 10 mL w(HNO_3) = 33% is carefully added. The acid solution is then heated and boiled down, allowing about half to evaporate. After cooling down to room temperature, distilled water is added to obtain a sample volume of approx. 100 mL.

Analysis

Titer

The fine silver is prepared as described under Sample preparation. Afterwards, the prepared sample solution is titrated with the respective titrant until after the equivalence point using a coated Ag Titrode for the indication.

Sample

Fine silver and silver alloys

It the sample contains palladium, 50 mL precipitation solution per 100 mg palladium are added to the prepared sample solution prior to the titration.

The prepared sample solution is titrated with the respective titrant until after the equivalence point using a coated Ag Titrode for the indication.

After the titration, the electrode and buret tips are rinsed with distilled water. To remove any adhering precipitate the electrode and buret tips can be dip-rinsed for 20 s in protective colloid solution.

Silver plating baths

5 mL protective colloid solution are added to the prepared sample solution, which is then titrated with c(KBr) = 0.1 mol/L until after the equivalence point using a silver bromide coated Ag Titrode for the indication.

Parameters

Titer

Mode	DET U
Stirring rate	8
Start volume	25 mL
Pause	10 s
Signal drift	20 mV/min
Min. waiting time	0 s
Max. waiting time	34 s
Meas. point density	4
Min. increment	10 µL
Stop EP	1
Volume after EP	1 mL
EP criterion	10
EP recognition	greatest

Sample

Mode	DET U
Stirring rate	8
Start volume	20 mL (fine silver and silver alloys) 0 mL (silver plating baths)
Pause	10 s
Signal drift	20 mV/min
Min. waiting time	0 s
Max. waiting time	34 s
Meas. point density	4
Min. increment	10 µL
Stop EP	1
Volume after EP	1 mL
EP criterion	10
EP recognition	greatest

Calculation

Titer

$$f = \frac{m_s}{V_{EP1}}$$

f:	Titer of the titrant in mg/mL
m_s:	Mass of fine silver used for the titer determination in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL

Sample

Fine silver and silver alloys

$$w_{Ag} = \frac{V_{EP1} \times f}{m_s} \times 1000$$

w_{Ag}:	Silver content in per mil (‰)
V_{EP1}:	Titrant consumption until the first equivalence point in mL
f:	Titer of the titrant in mg/mL
m_s:	Sample size in mg
1000:	Conversion factor to obtain per mil (‰)

Silver plating baths

$$\beta_{Ag} = \frac{V_{EP1} \times f}{V_s}$$

β_{Ag}:	Silver content g/L
V_{EP1}:	Titrant consumption until the first equivalence point in mL
f:	Titer of the titrant in mg/mL
V_s:	Sample volume in mL

Example determination

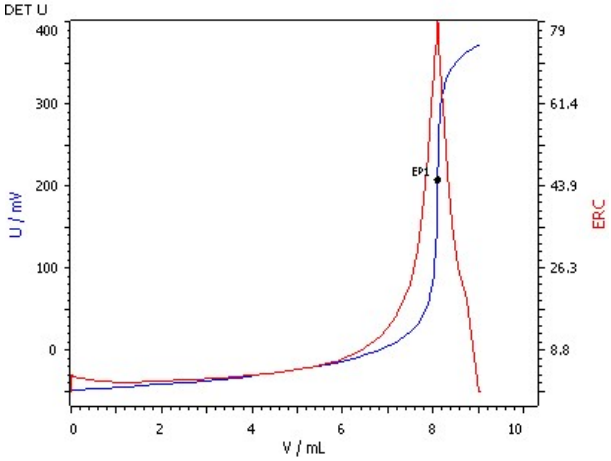

Fig. 1: Titration curve of fine silver according to EN ISO 11427

Comments

- To prevent coagulation of the AgBr or AgCl precipitate, the protective colloid is added to the sample solution. This addition prevents inclusions and keeps the electrode surface practically free from deposits.
- If necessary, the user himself can renew the AgBr or AgCl coating. For detailed instructions, see Application Bulletin No. 25.
- The determination of silver according to ISO 13756 and GB/T 18996 is very similar. The only differences are the use of a silver chloride coated Ag Titrode (6.0430.100Cl) as measuring electrode and the use of c(NaCl) = 0.1 mol/L or c(KCl) = 0.1 mol/L as titrant.

References

- EN ISO 11427
  Determination of silver in silver jewellery alloys – Volumetric (potentiometric) method using potassium bromide
- GB/T 17832
  Silver jewellery alloys – Determination of silver – Volumetric (potentiometric) method using potassium bromide
- ISO 13756
  Jewellery -- Determination of silver in silver jewellery alloys -- Volumetric (potentiometric) method using sodium chloride or potassium chloride
- GB/T 18996
  Determination of silver in silver jewellery alloys – Volumetric (potentiometric) method using sodium chloride or potassium chloride
- Application Bulletin AB-025
  Coatings of silver electrodes

Date

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