
Application Bulletin

Of interest to: Control of precious metals, electroplating, mints

A 1, 10

Potentiometric determination of silver

Summary

This bulletin describes a potentiometric method for the determination of silver in fine silver, silver alloys and silver plating baths. After digestion of the sample with nitric acid, titration is performed with potassium bromide solution using the Ag Titrone with AgBr coating.

Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or 796 Titroprocessor with 700 Dosino or 685 Dosimat
- 2.728.0040 Magnetic Stirrer
- 6.3014.223 Exchange Unit
- 6.0430.100 Ag Titrone with AgBr coating and 6.2104.020 electrode cable

Reagents

- Titrant: potassium bromide solution, $c(\text{KBr}) = 0.1 \text{ mol/L}$
- Nitric acid, $w(\text{HNO}_3) = 65\%$, p.a.
- Protective colloid:
0.2% aqueous solution of polyvinyl alcohol, e.g. Merck no. 114266 (dissolved in hot dist. water)

Determination of the titer of the titrant

For the digestion, use the fume cupboard!

Approx. 500 mg fine silver is weighed into a glass beaker to the nearest 0.02 mg and dissolved in 20 mL $w(\text{HNO}_3) = 65\%$. Heat and boil the solution in order to evaporate the nitrogen oxides. After cooling down, dilute to approx. 250 mL with dist. water and, after addition of 5 mL protective colloid, titrate with $c(\text{KBr}) = 0.1 \text{ mol/L}$ (start volume: 40 mL).

Calculation

theoretical consumption = sample mass in mg / 10.7868

titer = theoretical consumption / practical consumption (EP1)

The titer is stored as the common variable C30 in the titrator.

Sample preparation**A) Fine silver and silver alloys**

Use the fume cupboard!

A quantity of sample containing approx. 500 mg Ag is weighed into a glass beaker to the nearest 0.02 mg. Add 20 mL $w(\text{HNO}_3) = 65\%$ and dissolve the sample, then heat and boil the solution in order to evaporate the nitrogen oxides. After cooling down, add approx. 250 mL dist. water.

B) Silver plating baths

Use the fume cupboard!

Depending on the expected silver content, pipet 1.0 ... 10.0 mL of the plating bath sample into a glass beaker and dilute to approx. 50 mL with dist. water, then carefully add 5 ... 10 mL $w(\text{HNO}_3) = 65\%$. Heat and boil down the acid solution, allowing about half to evaporate. After cooling down, make up to approx. 100 mL with dist. water.

Analysis

Add 5 mL protective colloid to the sample solution and titrate with $c(\text{KBr}) = 0.1$ mol/L. When analyzing digestion solutions of plating bath samples, titration is performed without a start volume. For digestions of fine silver or silver alloys, on the other hand, a start volume of 40 mL is used.

Calculation

1 mL $c(\text{KBr}) = 0.1$ mol/L corresponds to 10.7868 mg Ag

Analysis of fine silver/silver alloys:

$$\% \text{ Ag} = \text{EP1} * \text{C01} * \text{C02} * \text{C30} / \text{C00}$$

Analysis of silver plating baths:

$$\text{g/L Ag} = \text{EP1} * \text{C01} * \text{C30} / \text{C00}$$

EP1 = titrant consumption in mL

C00 = sample mass in mg or sample volume in mL

C01 = 10.7868

C02 = 1000 (conversion factor for ‰)

C30 = titer of the titrant (see above)

Remarks

- To prevent coagulation of the AgBr precipitate, the protective colloid is added to the sample solution. This addition prevents inclusions and keeps the electrode surface practically free from deposits.
- The Ag Titrode is available with AgBr coating. If necessary, the user himself can renew this coating (see Application Bulletin No. 25).
- The silver content of fine silver and silver alloys can be determined with a precision <1‰ (typical value: >0.5‰; in our investigations we reached a relative standard deviation of 0.4‰).

Figures

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'pa
785 DMP Titrino      01102  785.0011
user                str
date 1999-12-10    time 14:06      3
DET U               Ag
parameters
>titration parameters
  meas.pt.density    4
  min.incr.          10.0 µl
  dos.rate           max. ml/min
  signal drift       50 mV/min
  equilibr.time      26 s
  start V:           abs.
  start V            40 ml
  dos.rate           max. ml/min
  pause              20 s
  meas.input:        1
  temperature        25.0 °C
>stop conditions
  stop V:            abs.
  stop V             54 ml
  stop U             OFF mV
  stop EP            9
  filling rate       max. ml/min
>statistics
  status:            ON
  mean               n= 3
  res.tab:           original
>evaluation
  EPC                5
  EP recognition:    greatest
  fix EP1 at U      OFF mV
  pK/HNP:           OFF
>preselections
  req.ident:         OFF
  req.smpl size:     value
  limit smpl size:  OFF
  activate pulse:    OFF
  =====
    
```

Fig. 1: Parameter settings on the 785 DMP Titrino for the silver determination (with start volume).

```
'fr
785 DMP Titrimo      01102  785.0011
user                str
date 1999-12-10     time 14:18      3
card label:785 Lab1
U(init)            3 mV DET U      Ag
smp1 size          511.9 mg
EP1                47.322 ml      222 mV
w(Ag)              997.30 %
                  mean( 3)      +/-s      s/%
w(Ag)              997.70      0.390 %    0.04
stop V reached
=====
```

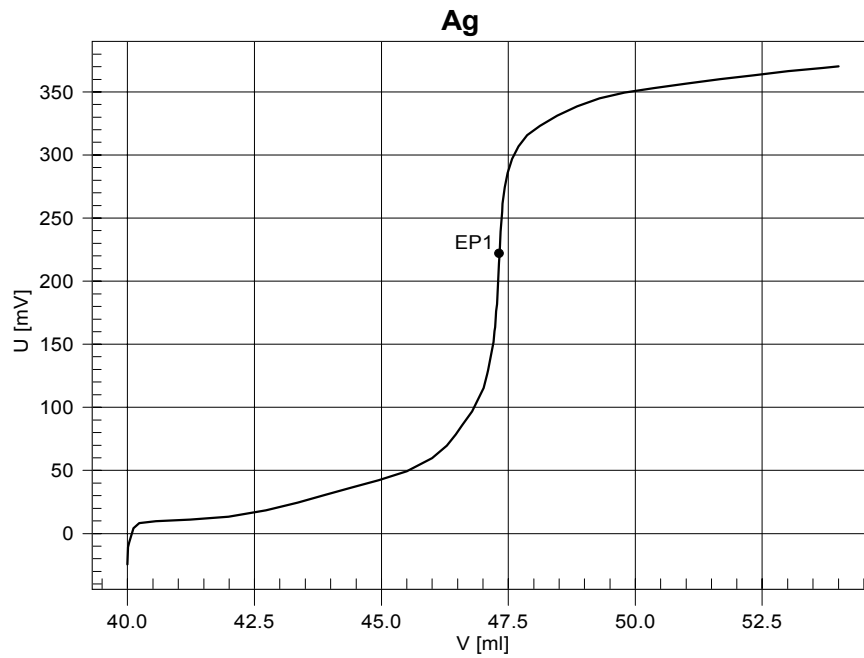


Fig. 2: Result block and titration curve for the determination of the silver content of fine silver.