

Application Bulletin

Of interest to: General analytical laboratories

A 1, 3, 11

Potentiometric titration of chloride and bromide in the presence of each other

Summary

If chloride and bromide are present in approximately equal molar concentrations they can be titrated directly with silver nitrate solution after addition of barium acetate. If, however, the molar ratio $n(\text{Br}^-) : n(\text{Cl}^-)$ changes from 1 : 1 to 1 : 5, 1 : 10, 5 : 1 or 10 : 1 greater relative errors must be expected with this method. The bulletin describes an additional titration method that allows bromide to be determined besides a large excess of chloride. The determination of small chloride concentrations in the presence of a large excess of bromide is not possible by titration.

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(s)
- 6.0430.100 Ag Titrode with Ag_2S coating and 6.2104.020 electrode cable
- 6.0431.100 Pt Titrode

Reagents

A) For approximately equal molar concentrations of chloride and bromide

- Titrant: silver nitrate solution, $c(\text{AgNO}_3) = 0.1 \text{ mol/L}$
- Nitric acid, $c(\text{HNO}_3) = 2 \text{ mol/L}$
- Barium acetate, puriss. p.a.

B) For bromide in the presence of a large excess of chloride

- Titrant: sodium thiosulfate solution, $c(\text{Na}_2\text{S}_2\text{O}_3) = 0.1 \text{ mol/L}$
- Sodium formiate solution, $w(\text{HCOONa}) = 25\%$
- Sodium hypochlorite solution, $c(\text{NaClO}) = 1 \text{ mol/L}$
- Ammonium molybdate solution 0.5 mol/L
- Sulfuric acid, $c(\text{H}_2\text{SO}_4) = 3 \text{ mol/L}$

- Sodium chloride, puriss. p.a.
- Sodium dihydrogen phosphate, puriss. p.a.
- Potassium iodide, puriss. p.a.

Analysis

A) Simultaneous determination of bromide and chloride

To 50 mL sample solution (smaller sample volumes are made up to 50 mL with dist. water) add 0.5 mL $c(\text{HNO}_3) = 2 \text{ mol/L}$ and 1 ... 2 g barium acetate, then titrate with $c(\text{AgNO}_3) = 0.1 \text{ mol/L}$ using the Ag Titrode with Ag_2S coating.

Calculation

Two equivalence points are obtained, the first of which corresponds to the bromide content and the difference between the second and the first equivalence point to the chloride content.

1 mL $c(\text{AgNO}_3) = 0.1 \text{ mol/L}$ corresponds to 7.9904 mg Br^- or 3.5453 mg Cl^-

$$\text{mg/L Br}^- = \text{EP1} * \text{C01} * \text{C03} / \text{C00}$$

$$\text{mg/L Cl}^- = (\text{EP2} - \text{EP1}) * \text{C02} * \text{C03} / \text{C00}$$

EP1 = titrant consumption to reach the first EP in mL

EP2 = titrant consumption to reach the second EP in mL

C00 = sample volume in mL

C01 = 7.9904

C02 = 3.5453

C03 = 1000 (conversion factor in mL/L)

The following table lists the relative errors we have observed for the different molar ratios $n(\text{Br}^-) : n(\text{Cl}^-)$.

Analysis conditions:

0.25 ... 2.50 mL of the two standard solutions $c(\text{KBr}) = 0.1 \text{ mol/L}$ and $c(\text{KCl}) = 0.1 \text{ mol/L}$ are pipetted into a glass beaker and made up to 50 mL with dist. water; addition of 0.5 mL $c(\text{HNO}_3) = 2 \text{ mol/L}$ and approx. 1 g barium acetate; titration with $c(\text{AgNO}_3) = 0.1 \text{ mol/L}$.

$n(\text{Br}^-) : n(\text{Cl}^-)$	Relative error without Ba^{2+}		Relative error with Ba^{2+}	
5 : 1	$\text{Br}^- +1.28\%$	$\text{Cl}^- +9.7\%$	$\text{Br}^- -1.74\%$	$\text{Cl}^- +3.3\%$
10 : 1	$\text{Br}^- -1.57\%$	$\text{Cl}^- +6.2\%$	$\text{Br}^- +0.58\%$	$\text{Cl}^- +9.1\%$
1 : 5	$\text{Br}^- +12.2\%$	$\text{Cl}^- -1.24\%$	$\text{Br}^- +2.9\%$	$\text{Cl}^- \pm 0\%$
1 : 10	$\text{Br}^- +16.1\%$	$\text{Cl}^- -2.7\%$	$\text{Br}^- +5.4\%$	$\text{Cl}^- -2.0\%$

B) Determination of bromide in chloride

To 25 mL neutralized sample solution containing no more than 12 mg Br⁻ add 1 g NaH₂PO₄, 10 g NaCl and 5 mL c(NaClO) = 1 mol/L. Heat the mixture to boiling point, add 10 mL w(HCOONa) = 25% and boil for another 15 min. After cooling down, dilute the sample solution to approx. 150 mL with dist. water. Add approx. 1 g KI, 25 mL c(H₂SO₄) = 3 mol/L and 1 drop of ammonium molybdate solution, then titrate the released iodine with c(Na₂S₂O₃) = 0.1 mol/L using the Pt Titrode.

Calculation

1 mL c(Na₂S₂O₃) = 0.1 mol/L corresponds to 1.3317 mg Br⁻

$$\text{mg/L Br}^- = \text{EP1} * \text{C01} * \text{C02} / \text{C00}$$

EP1 = titrant consumption in mL

C00 = 25 (sample volume in mL)

C01 = 1.3317

C02 = 1000 (conversion factor in mL/L)

Literature

- Kolthoff, Belcher
Volumetric Analysis, volume II and III
Interscience Publishers, New York, London.

```
'pa
736 GP Titrino      10194  736.0012
date 1999-10-06   time 14:29    2
DET U              A
parameters
>titration parameters
  meas.pt.density  4
  min.incr.        10.0 ul
  titr.rate         max. ml/min
  signal drift     30 mV/min
  equilibr.time    32 s
  start V:         OFF
  pause            0 s
  dos.element:    internal D0
  meas.input:     1
  temperature      25.0 °C
>stop conditions
  stop V:          abs.
  stop V           10 ml
  stop U           OFF mV
  stop EP         OFF
  filling rate     max. ml/min
>statistics
  status:         OFF
>evaluation
  EPC             60
  EP recognition: all
  fix EP1 at U   OFF mV
  pK/HNP:        OFF
>preselections
  req.ident:      OFF
  req.spl size:  OFF
  activate pulse: OFF
=====
```

Fig. 1: Parameter settings on the 736 GP Titrino for the simultaneous determination of bromide and chloride.

```
'fr
736 GP Titrino      10194  736.0012
date 1999-10-06   time 14:29    2
U(init)           80 mV DET U      A
spl size          2.5 ml
EP1               2.531 ml         -43 mV
EP2               4.967 ml         -212 mV
Br                0.1012 mol/l
Cl                0.0974 mol/l
stop V reached
=====
```

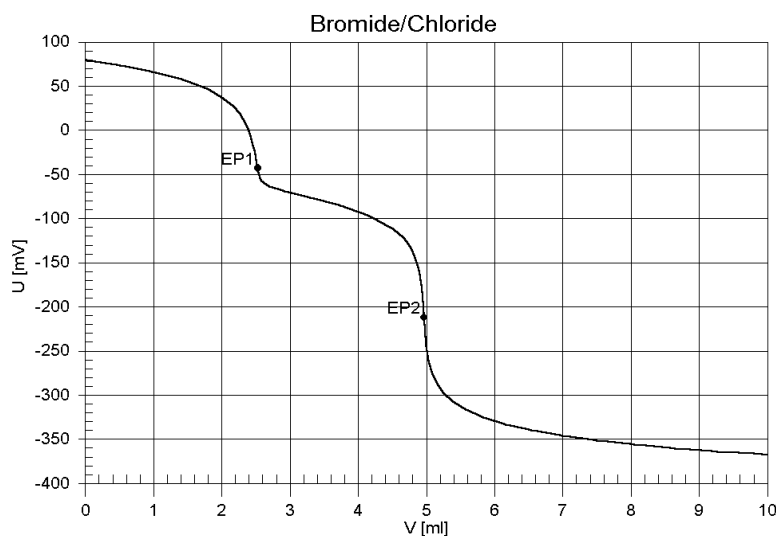


Fig. 2: Result block and titration curve for the simultaneous determination of bromide and chloride [2.50 mL c(KBr) = 0.1 mol/L + 2.50 mL c(KCl) = 0.1 mol/L; addition Ba²⁺].

```
'pa
736 GP Titrino      10194  736.0012
date 1999-10-07   time 15:10    4
DET U              B
parameters
>titration parameters
  meas.pt.density  4
  min.incr.        10.0 µl
  titr.rate        max. ml/min
  signal drift     50 mV/min
  equilibr.time    26 s
  start V:         OFF
  pause           0 s
  dos.element:    internal D0
  meas.input:     1
  temperature     26.1 °C
>stop conditions
  stop V:         abs.
  stop V         10 ml
  stop U         OFF mV
  stop EP       9
  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
  activate pulse: OFF
=====
```

Fig. 3: Parameter settings for the determination of bromide in chloride.

```
'fr
736 GP Titrino      10194  736.0012
date 1999-10-07   time 15:10    4
U(init)           389 mV DET U      B
smpl size         25 ml
EP1               4.290 ml          274 mV
Br                0.23 g/l
stop V reached
=====
```

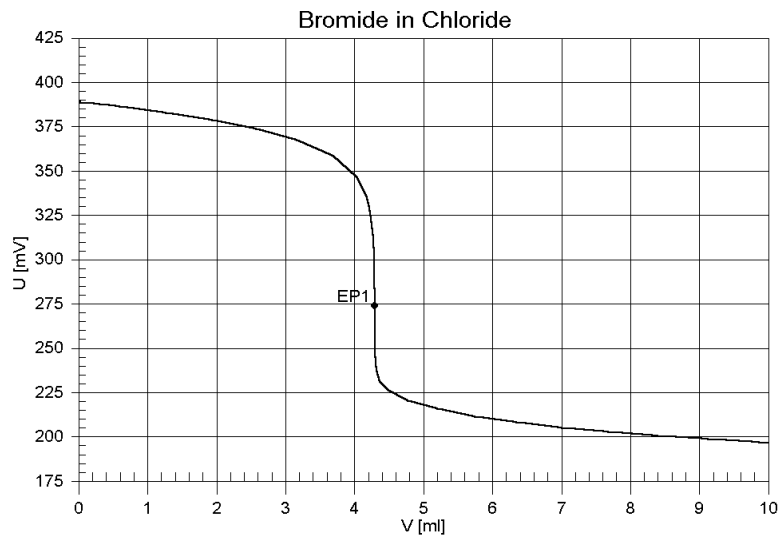


Fig. 4: Result block and titration curve for the determination of bromide in chloride.