Application Bulletin

Of interest to:	General analytical laboratories, Water; Food	A 1, 2, 7, 11

Potentiometric determination of trace bromide and iodide in chlorides

Summary

Bromide is removed from the sample as BrCN by distillation. The BrCN is absorbed in sodium hydroxide solution and decomposed with concentrated sulfuric acid, then the released bromide ions are determined by potentiometric titration with silver nitrate solution. Iodide does not interfere with the determination.

Iodide is oxidized to iodate by hypobromite. After destruction of the excess hypobromite, the potentiometric titration (of the iodine released from iodate) is carried out with sodium thiosulfate solution. Even in great excess, bromide does not interfere.

The described methods allow to determine bromide and iodide in the presence of a large excess of chloride (e.g. in brine, sea water, sodium chloride, etc.).

Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or
  726 or 796 Titroprocessor with 700 Dosino or 685 Dosimat
- 2.728.0040 Magnetic Stirrer
- 6.3014.153 (bromide) and 6.3014.213 (iodide) Exchange Units
- 6.0430.100 Ag Titrode with AgBr coating (bromide)
- 6.0431.100 Pt Titrode (iodide)
- 6.2104.020 Electrode cable

1. Determination of bromide

Reagents

- Chromic acid solution:
  Dissolve 750 g CrO_3 in dist. water and make up to 1 L.
- Sulfuric acid, w(H_2SO_4) = 96%, puriss. p.a.
- Sulfuric acid, c(H_2SO_4) = 2 mol/L
- Sodium hydroxide solution, c(NaOH) = 3 mol/L
- Potassium cyanide solution, c(KCN) = 1 mol/L
- Titrant: c($AgNO_3$) = 0.01 mol/L
- Nitrogen, from compressed gas cylinder with reducing valve

Sample preparation

The apparatus for sample preparation is shown in Figure 1.

Place 10 mL or 10 g sample into the distillation flask, then add 20 mL chromic acid solution and 20 mL c(H_2SO_4) = 2 mol/L. The absorption vessel 1 is filled with 30 mL dist. water and 20 mL c(NaOH) = 3 mol/L, the absorption vessel 2 with 10 mL c(NaOH) = 3 mol/L.

Immerse the distillation flask and the absorption vessel 1 in boiling water, then add 20 mL c(KCN) = 1 mol/L to the distillation flask using the dropping funnel. Distillation is performed immediately for 10 min with a vigorous stream of nitrogen. Afterwards the water baths are removed and nitrogen is passed through the system for a further 5 min.

The contents of the two absorption vessels, the adapters and the condenser are rinsed with dist. water into a beaker. 25 mL w(H_2SO_4) = 96% is carefully added and, after cooling down, the solution is transferred to a 200 mL volumetric flask, which is then filled to the mark with dist. water.

Since potassium cyanide is used, all work must be performed in a fume cupboard!

Analysis

100 mL of the prepared sample solution (from the 200 mL volumetric flask) is placed in a glass beaker and titrated with c($AgNO_3$) = 0.01 mol/L using the 6.0430.100 Ag Titrode with AgBr coating.

Calculation

1 mL c($AgNO_3$) = 0.01 mol/L corresponds to 0.79904 mg bromide

mg/L or mg/kg bromide = EP1 * C01 * C02 / C00

EP1 = titrant consumption in mL
C00 = 5 (quantity of sample used for the analysis in mL or g original sample)
C01 = 0.79904
C02 = 1000 (conversion factor in mL/L or g/kg)

2. Determination of iodide

Reagents

- Bromine solution:
  Approx. 3.6 g bromine per 100 mL dist. water.
- Sodium hydroxide solution, c(NaOH) = 1 mol/L
- Formaldehyde, w(HCHO) = 36%
- Acetic acid, w(CH_3COOH) = 96%
- Potassium iodide solution, w(KI) = 10%
- Titrant: c($Na_2S_2O_3$) = 0.002 mol/L

Sample preparation

Approx. 50 g sample is weighed exactly into a glass beaker and dissolved in 180 mL dist. water. Add 2 mL bromine solution as well as 10 mL c(NaOH) = 1 mol/L and allow to react for 2 min. Afterwards add 10 mL w(HCHO) = 36% and 10 mL w(CH_3COOH) = 96% and allow to react for a further 5 more min.

Analysis

After addition of 10 mL w(KI) = 10%, the released iodine is titrated with c($Na_2S_2O_3$) = 0.002 mol/L using the 6.0431.100 Pt Titrode.

Calculation

mg/kg iodide = EP1 * C01 * C02 / (C00 * C03)

EP1 = titrant consumption in mL
C00 = approx. 50 (sample weight in g)
C01 = 2 (concentration of the titrant in mmol/L)
C02 = 126.905 [M(I^-) in g/mol]
C03 = 6 (6 IO_3^- correspond to 1 I^-)

Figures

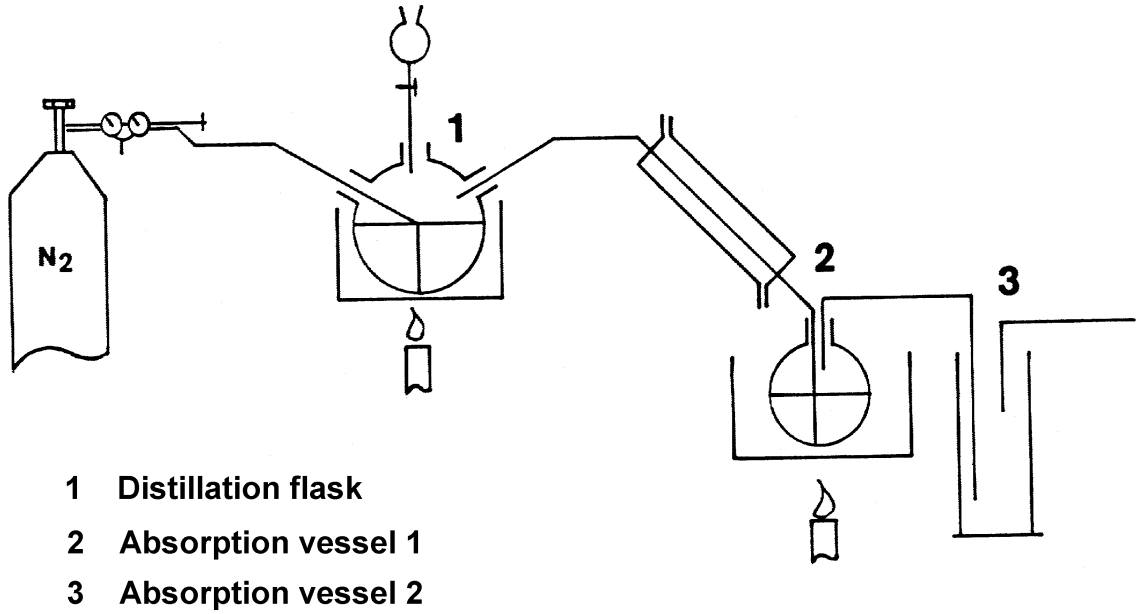

Fig. 1: *Apparatus for the separation of bromide by distillation.*

```
 'pa
736 GP Titrino          03222   736.0012
date  1999-06-29    time  18:25        6
DET  U              Bromide
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           25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                   20 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:          all
  activate pulse:         OFF
          ============


 'fm
736 GP Titrino          03222   736.0012
date  1999-06-29    time  18:25        6
DET  U              Bromide
>calculations
Bromide=EP1*C01*C02/C00;3;mg/kg
C00=              4.9875
C01=             0.79904
C02=                1000
          ============
```

Fig. 2: *Parameter settings on the 736 GP Titino for the determination of bromide.*

```
 'fr
736 GP Titrino          03222   736.0012
date  1999-06-29    time  16:19        5
card label:Appl.736
U(init)          270 mV  DET U    Bromide
smpl size    4.9875 g
EP1           8.755 ml            178 mV
Bromide    1402.626 mg/kg
stop V reached
          ============


 'cu
736 GP Titrino          03222   736.0012
date  1999-06-29    time  16:19        5
start V      0.000 ml  DET  U    Bromide
1.0 ml/div      dU=20.0 mV/div
```

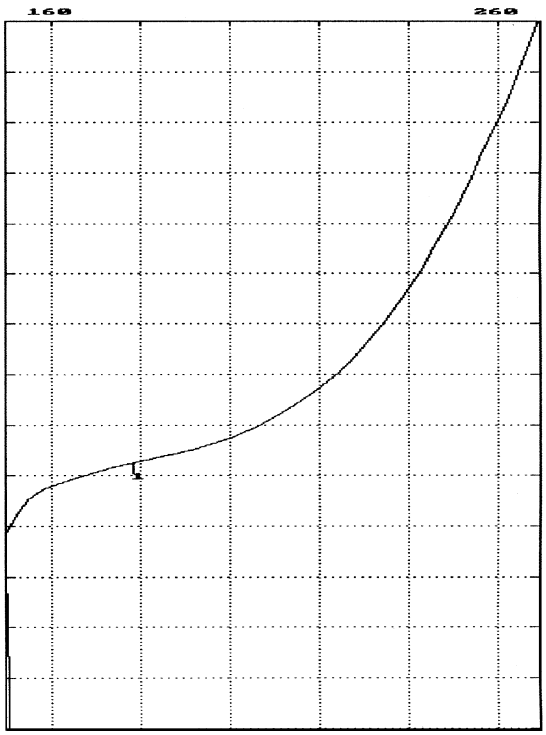

Fig. 3: *Result block and titration curve for the determination of bromide in brine.*

```
 'pa
736 GP Titrino          03222   736.0012
date  1999-06-28    time  16:01        4
DET  U                Iodid
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            25.0 °C
>stop conditions
  stop V:                abs.
  stop V                  2.5 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:          all
  activate pulse:         OFF
          ============

 'fm
736 GP Titrino          03222   736.0012
date  1999-06-28    time  16:02        4
DET  U                Iodid
>calculations
Iodid=EP1*C01*C02/C03/C00;3;mg/kg
C00=              50.029
C01=                   2
C02=             126.905
C03=                   6
          ============
```

Fig. 4: *Parameter settings on the 736 GP Titino for the determination of iodide.*

```
 'fr
736 GP Titrino          03222   736.0012
date  1999-06-28    time  14:22        1
card label:Appl.736
U(init)          -73 mV  DET U      Iodid
smpl size    50.031 g
EP1           0.467 ml              1 mV
Iodide         0.395 mg/kg
stop V reached
          ============


 'cu
736 GP Titrino          03222   736.0012
date  1999-06-28    time  14:22        1
start V      0.000 ml  DET  U      Iodid
1.0 ml/div      dU=50.0 mV/div
```

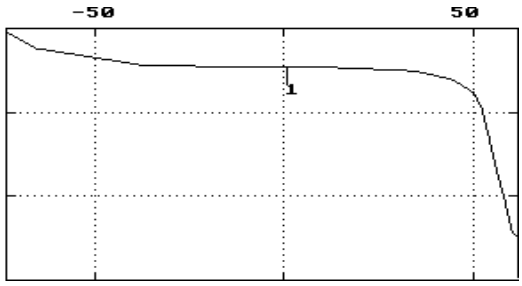

Fig. 5: *Result block and titration curve for the determination of iodide in sodium chloride.*

Literature

- J. D. Winefordner, M. Tim
  Separation of trace quantities of bromide from large amounts of chloride by a distillation method and measurement of the bromide by precision null-point potentiometry
  Anal. Chem. 35 (1963) 382–386.
- W. S. Wooster, P. S. Farrington, E. H. Swift
  Coulometric titration of iodide by electrolytically generated bromine and an amperometric endpoint
  Anal. Chem. 21 (1949) 1457–1460.