Application Bulletin 91/2 e

Potentiometric analysis of brass and bronze plating baths

Of interest for:
Metals, Electroplating industries
A 10

Summary

Methods are described for the potentiometric analysis of the following bath components:

Brass plating bath: copper, zinc, free cyanide, ammonium, carbonate and sulfite

Bronze plating bath: copper, tin and free cyanide

Instruments and accessories

- Titrino or
  Titrando with Dosino or Dosimat
- Magnetic Stirrer
- Exchange Unit(s)
- 6.0502.140 ion-selective copper electrode (Cu ISE) with 6.2104.020 electrode cable
- 6.0726.107 double-junction Ag/AgCl reference electrode [filled with c(KCl) = 3 mol/L] with 6.2106.020 electrode cable
- 6.0430.100 Ag Titrode with Ag_2S coating
- 6.0255.100 combined LL double-junction pH glass electrode
- 6.0431.100 Pt Titrode

1. Brass plating baths

1.1. Copper and zinc

Reagents

- Acids for digestion:
  While cooling, carefully add 80 mL H_2SO_4 conc. to 150 mL HNO_3 conc.
- Titrant 1: c(Na_2EDTA) = 0.1 mol/L
- Titrant 2: c($Na_2S_2O_3$) = 0.1 mol/L
- Buffer solution pH = 10:
  Dissolve 54 g NH_4Cl and 350 mL w(NH_3) = 25% in dist. water and fill up to 1 L.
- Sulfuric acid, w(H_2SO_4) ≈ 25%
- Sodium hydroxide solution, c(NaOH) = 2 mol/L
- Potassium iodide, p.a.

Sample preparation

Work in fume cupboard. Toxic HCN and acid fumes are released!

Add approx. 20 mL dist. water to 10.0 mL bath sample in an Erlenmeyer flask. Carefully add 3 mL digestive acid, warm up the mixture, heating until white sulfuric acid fumes appear. After cooling, rinse with dist. water into a 100 mL graduated flask, fill up to the mark and mix.

Iodometric determination of copper

Pipet 10.0 mL of the prepared sample solution (corresponding to 1 mL of original sample) into a glass beaker and dilute with dist. water to approx. 50 mL. After adding 2 mL w(H_2SO_4) ≈ 25% and approx. 1 g KI, titrate the freed iodine with c($Na_2S_2O_3$) = 0.1 mol/L (Pt Titrode). Consumption of the titrant up to the equivalence point is stored in the titrator as common variable C31.

Calculation

1 mL c($Na_2S_2O_3$) = 0.1 mol/L corresponds to 6.3546 mg Cu^{2+}

g/L Cu^{2+} = EP1 * C01 / C00

EP1 = titrant consumption in mL

C00 = 1 (sample volume used in mL original sample)

C01 = 6.3546

Chelatometric (complexometric) determination of the sum of copper and zinc

Dilute 10.0 mL of the prepared sample solution (corresponding to 1 mL of original sample) in a glass beaker with dist. water to approx. 50 mL and pre-neutralize to pH ≈ 4 with c(NaOH) = 2 mol/L. After addition of 5 mL buffer solution pH = 10, titrate in MET mode with c(Na_2EDTA) = 0.1 mol/L (Cu ISE).

Calculation

1 mL $c(Na_2EDTA)$ = 0.1 mol/L corresponds to 6.538 mg Zn^{2+}

g/L Zn^{2+} = (EP1 – C31) * C01 / C00

EP1 = titrant consumption in mL

C00 = 1 (sample volume used in mL original sample)

C01 = 6.538

C31 = titrant consumption in mL during the iodometric titration of Cu^{2+} (common variable)

1.2. Free cyanide

Reagents

- Titrant: $c(AgNO_3)$ = 0.1 mol/L
- Potassium iodide solution, w(KI) = 10%
- Sodium hydroxide solution, c(NaOH) = 2 mol/L

Analysis

Add 2 mL c(NaOH) = 2 mol/L to approx. 50 mL dist. water in a glass beaker. Add 2.0 mL bath sample as well as 4 mL w(KI) = 10% and titrate with $c(AgNO_3)$ = 0.1 mol/L (Ag Titrode with Ag_2S coating).

Calculation

1 mL $c(AgNO_3)$ = 0.1 mol/L corresponds to
5.204 mg CN^- or
9.802 mg NaCN or
13.024 mg KCN

g/L cyanide = EP1 * C01 / C00

EP1 = titrant consumption in mL

C00 = 2.0 (sample volume in mL)

C01 = 5.204 or 9.802 or 13.024

1.3. Ammonium

Reagents

- Titrant: c(HCl) = 0.1 mol/L
- Boric acid solution, $w(H_3BO_3)$ = 2%
- Sodium hydroxide solution, w(NaOH) = 20%
- Iron(II) sulfate solution, $w(FeSO_4 \times 7\ H_2O)$ = 25%

Analysis

A Kjeldahl distillation apparatus is used for this analysis. Add 5.0 mL bath sample, 4 mL $FeSO_4$ solution and 15 mL w(NaOH) = 20% to the distillation flask and begin distillation immediately. The cooling apparatus tube submerges in an initial solution of 50 mL $w(H_3BO_3)$ = 2%. After 15 min the ammonia is distilled over. Titrate the initial solution with c(HCl) = 0.1 mol/L (combined pH glass electrode). The equivalence point of the titration is at pH ≈ 4.5.

Calculation

1 mL c(HCl) = 0.1 mol/L corresponds to
1.8038 mg NH_4^+ or
1.4007 mg N

g/L NH_4^+ = EP1 * C01 / C00

g/L N = EP1 * C02 / C00

EP1 = titrant consumption in mL

C00 = 5.0 (sample volume in mL)

C01 = 1.8038

C02 = 1.4007

1.4. Carbonate

Reagents

- Titrant: c(HCl) = 1 mol/L
- Barium chloride solution, $w(BaCl_2)$ = 25%

Analysis

If the sample still contains free NaOH, two equivalence points are given. Because cyanide is also detected, the titration must be interrupted after this second EP, otherwise *toxic HCN* is released!

To a glass beaker with approx. 50 mL dist. water, add 2.0 bath sample. Add 5 mL $w(BaCl_2)$ = 25% and titrate with c(HCl) = 1 mol/L until shortly after the first (second) equivalence point is reached (combined pH glass electrode).

Calculation

1 mL c(HCl) = 1 mol/L corresponds to 106 mg Na_2CO_3

In *presence of free* NaOH:

g/L Na_2CO_3 = (EP2 – EP1) * C01 / C00

In *absence of free* NaOH:

g/L Na_2CO_3 = EP1 * C01 / C00

EP1 = titrant consumption up to the first EP in mL

EP2 = titrant consumption up to the second EP in mL

C00 = 2.0 (sample volume in mL)

C01 = 106

1.5. Sulfite

Reagents

- Titrant: $c(I_2)$ = 0.05 mol/L
- Barium chloride solution, $w(BaCl_2)$ = 25%
- Acetic acid, $w(CH_3COOH)$ = 96%
- Ammonia, $w(NH_3)$ = 25%

Analysis

Pipet 10.0 mL bath sample into an Erlenmeyer flask and dilute with dist. water to approx. 100 mL. Add 0.25 mL $w(NH_3)$ = 25%, warm up the mixture, then add 30 mL $w(BaCl_2)$ = 25% and heat to boiling point. Allow to settle, then pass through a folded filter. Rinse precipitation well with dist. water until rinse water reacts neutral. Penetrate the filter and rinse precipitation with dist. water into a glass beaker. While stirring, slowly and carefully add $w(CH_3COOH)$ = 96% to the mixture to acidify, then titrate immediately with $c(I_2)$ = 0.05 mol/L (Pt Titrode).

Calculation

1 mL $c(I_2)$ = 0.05 mol/L corresponds to 6.302 g Na_2SO_3

g/L Na_2SO_3 = EP1 * C01 / C00

EP1 = titrant consumption in mL

C00 = 10.0 (sample volume in mL)

C01 = 6.302

2. Bronze plating baths

Sample preparation for copper and tin

Work in fume cupboard. Toxic HCN and acid fumes are released!

In an Erlenmeyer flask, dilute 2.0 mL bath sample with approx. 20 mL dist. water. Carefully add 5 mL conc. H_2SO_4 as well as a few drops of $w(H_2O_2)$ = 30% and heat up until white sulfuric acid fumes appear. Cool, then rinse with dist. water into a 100 mL graduated flask, fill up to mark and mix.

2.1. Copper

Reagents

- Titrant: $c(Na_2S_2O_3)$ = 0.1 mol/L
- Sulfuric acid, $w(H_2SO_4)$ = 25%
- Potassium iodide, p.a.

Analysis

Add 5 mL $w(H_2SO_4)$ = 25% and approx. 1 g KI to 50 mL of the prepared sample solution (corresponding to 1 mL original sample) in a glass beaker and then titrate the freed iodine with $c(Na_2S_2O_3)$ = 0.1 mol/L (Pt Titrode).

Calculation

1 mL $c(Na_2S_2O_3)$ = 0.1 mol/L corresponds to 6.3546 mg de Cu^{2+}

g/L Cu^{2+} = EP1 * C01 / C00

EP1 = titrant consumption in mL

C00 = 1 (sample volume used in mL original sample)

C01 = 6.3546

2.2. Tin

Reagents

- $c(I_2)$ = 0.05 mol/L
- Hydrochloric acid, w(HCl) = 36%
- Iron powder, p.a.

Analysis

Add 20 mL w(HCl) = 36% to 50 mL of the prepared sample solution (corresponding to 1 mL original sample) in a glass beaker. While stirring, add approx. 1 g iron powder in small portions and heat shortly to boiling point. Cool the mixture, then pass it through a folded filter to enable the extraction of copper deposits and rinse well with hot dist. water. Add a further 10 mL w(HCl) = 36% as well as 0.5 g iron powder to the filtrate and boil until the iron is completely dissolved. Allow to cool, then titrate immediately with $c(I_2)$ = 0.05 mol/ (Pt Titrode).

Calculation

1 mL $c(I_2)$ = 0.05 mol/L corresponds to 5.9345 mg Sn^{2+}

g/L Sn^{2+} = EP1 * C01 / C00

EP1 = titrant consumption in mL

C00 = 1 (sample volume used in mL original sample)

C01 = 5.9345

2.3. Free cyanide

Reagents

- Titrant: $c(AgNO_3)$ = 0.1 mol/L
- Potassium iodide solution, w(KI) = 10%
- Sodium hydroxide solution, c(NaOH) = 2 mol/L

Analysis

Make an initial solution of approx. 50 mL dist. water and 2 mL c(NaOH) = 2 mol/L in a glass beaker. Add 2.0 mL bath sample and 4 mL w(KI) = 10%, then titrate with $c(AgNO_3)$ = 0.1 mol/L (Ag Titrode with Ag_2S coating).

Calculation

1 mL $c(AgNO_3)$ = 0.1 mol/L corresponds to
5.204 mg CN^- or
9.802 mg NaCN or
13.024 mg KCN

g/L cyanide = EP1 * C01 / C00

EP1 = titrant consumption in mL

C00 = 2.0 (sample volume in mL)

C01 = 5.204 or 9.802 or 13.024

Literature

- Metrohm Application Bulletin No. 101
  Complexometric titrations with the Cu ISE
  Metrohm Ltd., Herisau
- Metrohm Application Note T-23
  Hydroxide and carbonate in alkaline plating baths for cadmium, copper, lead or zinc
  Metrohm Ltd., Herisau
- Metrohm Application Note T-24
  Metal contents of alkaline plating baths for cadmium, copper, lead or zinc
  Metrohm Ltd., Herisau
- T. W. Jelinek
  Prozessbegleitende Analytik in der Galvanotechnik
  Eugen G. Leuze Verlag, Saulgau, 1999
  ISBN 3-87-480-135-7

Figures

```
 'pa
751 GP Titrino        05268   751.0011
date  10-01-01      time  15:50     0
DET  U              ********
Parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  titr.rate              max. ml/min
  signal drift             25 mV/min
  equilibr.time            34 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                   1
  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. 1: *Parameter settings for the iodometric determination of copper*

```
 'fr
751 GPD Titrino       05268    751.0011
date 2001-01-10     time  16:10      16
U(init)         99 mV DET U     ********
Sampl size          1 ml
EP1           10.117 ml          153 mV
Cu            64.289 g/l
stop V reached
           ============
```

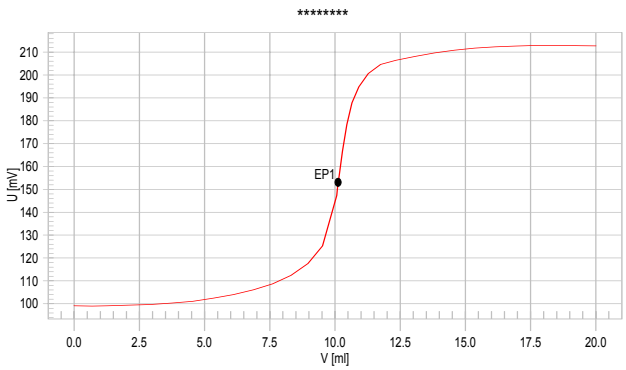

Fig. 2: *Titration curve for the iodometric determination of copper*

```
 'fr
751 GPD Titrino       05268    751.0011
date 2001-01-19     time 10:39        6
U(init)      -123 mV MET U     ********
sampl size          1 ml
EP1            4.155 ml         -205 mV
Sn            24.658 g/l
stop V reached
           ============
```

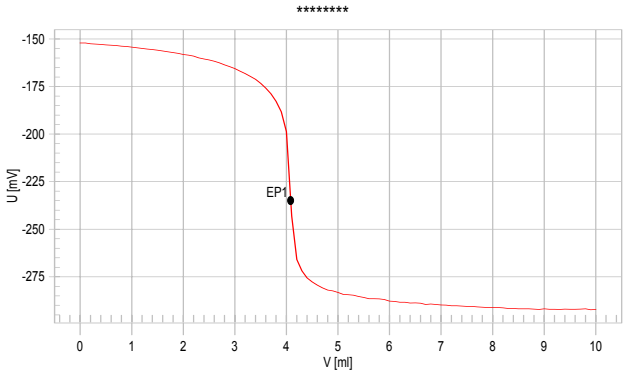

Fig. 3: *Titration curve for the iodometric determination of tin*

```
 'pa
751 GP Titrino        05268    751.0011
date  15-01-03      time  10:59      6
MET  U               ********
Parameters
>titration parameters
  V step                  0.05 ml
  titr.rate               max. ml/min
  signal drift              25 mV/min
  equilibr.time             34 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                   1
  filling rate            max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                      5.2 mV
  EP recognition:          all
  fix EP1 at U             OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
           ============
```

Fig. 4: *Parameter settings for the chelatometric determination of copper/zinc*

```
 'fr
751 GPD Titrino       05268    751.0011
date 2001-01-19     time  10:39       6
U(init)      -123 mV MET U     ********
sampl size          1 ml
EP1           41.552 ml         -205 mV
Zn            20.533 g/l
stop V reached
          ============
```

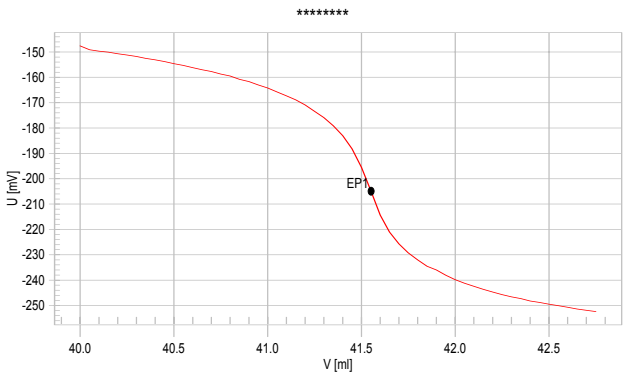

Fig. 5: *Titration curve for the chelatometric determination of copper/zinc*

```
 'fr
751 GPD Titrino       05268    751.0011
date 2001-01-15     time 16:41       15
U(init)       250 mV DET U     751.0011
sampl size          2 ml
EP1            8.351 ml          -68 mV
CN            21.729 g/l
stop V reached
          ============
```

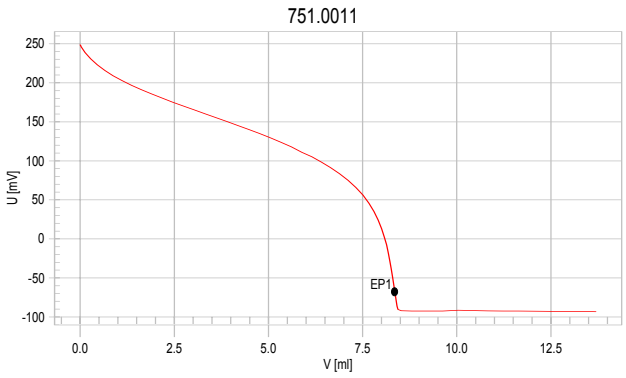

Fig. 6: *Titration curve for the determination of free cyanide*

```
 'fr
751 GPD Titrino       05268    751.0011
date 2001-01-10     time  11:09       6
U(init)         -5 mV DET U     751.0011
sampl size          5 ml
EP1            7.338 ml          151 mV
Ammonium       2.647 g/l
stop V reached
          ============
```

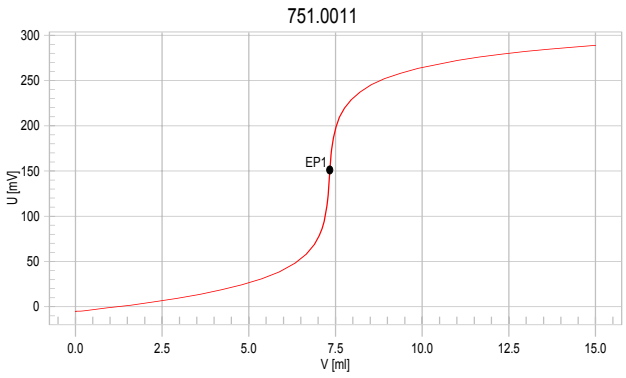

Fig. 7: *Titration curve for the determination of ammonium*

```
 'fr
751 GPD Titrino      05268   751.0011
date 2001-01-12    time  16:15      2
U(init)     -315 mV DET U    751.0011
sampl size         5 ml
EP1           4.545 ml        -109 mV
EP2           9.997 ml         213 mV
Na2CO3      115.582 g/l
stop V reached
           ============
```

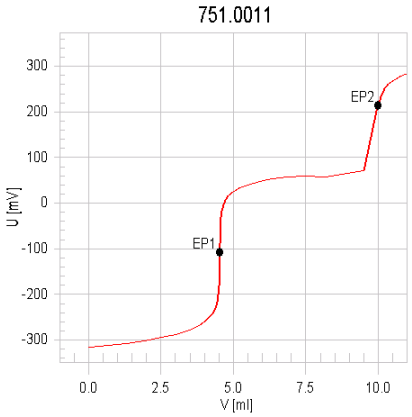

Fig. 8: *Titration curve for the determination of carbonate*

```
 'fr
751 GPD Titrino      05268   751.0011
date 2001-01-15    time  10:13      3
U(init)       78 mV DET U    751.0011
sampl size       10 ml
EP1           8.987 ml         -11 mV
Na2SO3        5.664 g/l
stop V reached
           ============
```

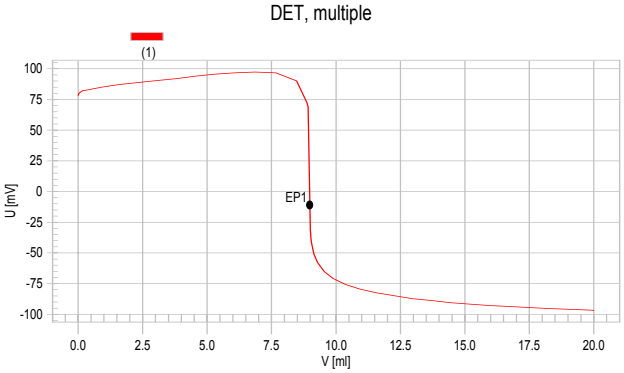

Fig. 9: *Titration curve for the iodometric determination of sulfite*