Application Bulletin 92/2 e

Potentiometric analysis of acidic lead and lead/tin plating baths

Of interest to:
Metals, electroplating
A 10

Summary

This Bulletin describes the potentiometric determination of lead, tin(II) and free fluoroboric acid.

Instruments and accessories

- Titrino or
  Titrando with Dosino or Dosimat
- Magnetic Stirrer
- Exchange Units (for NaOH possibly with 6.1608.040 PE reagent bottle)
- 6.0502.140 ion-selective copper electrode (Cu ISE)
- 6.0726.107 double-junction Ag/AgCl reference electrode [filled with *c*(KCl) = 3 mol/L]
- 6.0255.100 Profitrode, combined double-junction pH glass electrode with separable ground-joint diaphragm
- 6.0431.100 Pt Titrode
- 6.2104.020 and 6.2106.020 electrode cables

1. Determination of lead

Reagents

- *c*(Na_2EDTA) = 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.
- $Cu(NH_4)_2EDTA$, *c* = 0.1 mol/L (Merck no. 105217)

Analysis

Pipet a portion of the bath sample (should contain ca. 100 mg Pb) into a glass beaker and fill up to ca. 50 mL with dist. water. Add 5 mL each $Cu(NH_4)_2EDTA$ and buffer solution pH = 10 and, while stirring, allow to react for 30 s. Afterwards, titrate in the MET mode of the titrator with *c*(Na_2EDTA) = 0.1 mol/L against the Cu ISE. Work with a starting volume of 50% of the expected titrant consumption. The parameter «pause» is set at 30 s.

Calculation

1 mL *c*(Na_2EDTA) = 0.1 mol/L = 20.72 mg Pb

g/L Pb = EP1 * C01 / C00

C00 = sample size in mL

C01 = 20.72

2. Determination of tin(II)

Reagents

- Iodine solution, *c*(I_2) = 0.05 mol/L (0.1 N);
  Dissolve 25 g potassium iodide in 40 mL dist. water. Add 12.7 g iodine and while shaking, bring it into solution. Finally fill up to 1 L with dist. water. Titer determination e.g. against As(III).
- *w*(H_2SO_4) ≈ 30%

Analysis

Mix approx. 50 mL dist. water and 20 mL H_2SO_4 in a beaker and purge with nitrogen. After addition of 2.0 mL bath sample, titrate immediately (under nitrogen) with *c*(I_2) = 0.05 mol/L (Pt Titrode).

Calculation

1 mL *c*(I_2) = 0.05 mol/L = 5.9345 mg Sn(II)
g/L Sn(II) = EP1 * C01 / C00

C00 = 2.0 (sample size in mL)

C01 = 5.9345

3. Determination of free fluoroboric acid

Reagents

- Sodium hydroxide solution, *c*(NaOH) = 1 mol/L

Analysis

Dilute 10.0 mL bath sample with approx. 50 mL dist. water in a beaker and titrate (not too fast) with *c*(NaOH) = 1 mol/L. The flat potential jump at pH ≈ 3.2 is used for evaluation (combined pH glass electrode).

Calculation

1 mL *c*(NaOH) = 1 mol/L = 87.81 mg HBF_4
g/L free HBF_4 = EP1 * C01 / C00

C00 = 10.0 (sample size in mL)

C01 = 87.81

Literature

- Metrohm Application Bulletin No. 101
  Complexometric titrations with the Cu-ISE
  Metrohm Ltd., Herisau
- Metrohm Application Note T-21
  Sn(II) and sulfuric acid in tin plating bath
  Metrohm Ltd., Herisau
- Metrohm Application Note T-24
  Metal contents of alkaline plating baths for cadmium, copper, lead or zinc
  Metrohm Ltd., Herisau
- P. W. Wild
  Moderne Analysen für die Galvanotechnik
  Eugen G. Leuze Verlag, Saulgau, 1972
- T. W. Jelinek
  Prozessbegleitende Analytik in der Galvanotechnik
  Eugen G. Leuze Verlag, Saulgau, 1999
  ISBN 3-87-480-135-7

Figures

```
'pa
736 GP Titrino          04268   736.0011
date  15-01-09      time  08:30        7
MET  U                  Pb++
parameters
>titration parameters
  V step                 0.10 ml
  titr.rate              max. ml/min
  signal drift             50 mV/min
  equilibr.time            26 s
  start V:               abs.
  start V                   3 ml
  dos.rate               max. ml/min
  pause                    30 s
  dos.element:    internal D0
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                abs.
  stop V                    6 ml
  stop U                  OFF mV
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                       5 mV
  EP recognition:    greatest
  fix EP1 at U           OFF mV
  pK/HNP:                OFF
>preselections
  req.ident:             OFF
  req.smpl size:         OFF
  activate pulse:         ON
         ============
```

Fig. 1: Parameter report Titrino for the Pb determination.

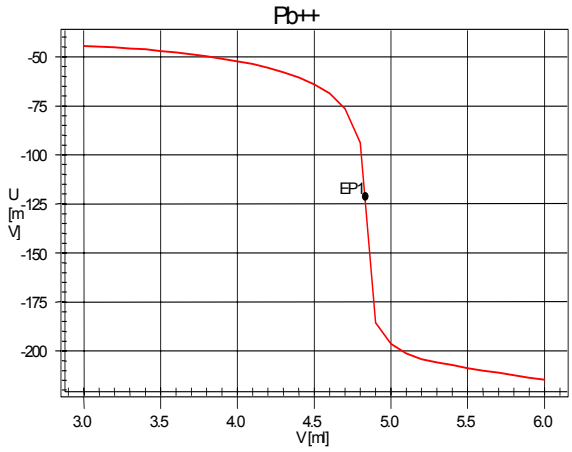

Fig. 2: Titration curve Pb.

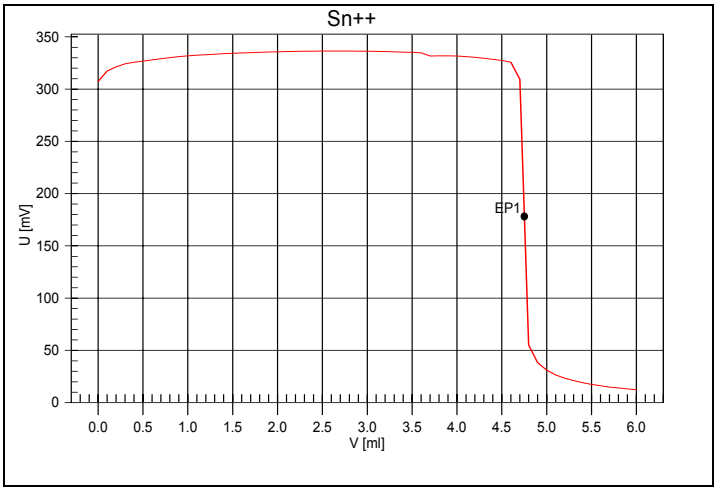

Fig. 3: *Titration curve Sn(II).*

```
'pa
736 GP Titrino           04268   736.0011
date  15-01-18      time  09:53       10
DET  pH                 HBF4
parameters
>titration parameters
  meas.pt.density          4
  min.incr.             10.0 µl
  titr.rate             max. ml/min
  signal drift            50 mV/min
  equilibr.time           20 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                   8 ml
  stop pH                OFF
  stop EP                  9
  filling rate          max. ml/min
>statistics
  status:                OFF
>evaluation
  EPC                      5
  EP recognition:        all
  fix EP1 at pH          3.2
  fix EP2 at pH          OFF
  pK/HNP:                OFF
>preselections
  req.ident:             OFF
  req.smpl size:         OFF
  activate pulse:        OFF
         ============
```

Fig. 4: *Parameter report Titrino for the determination of free HBF_4.*

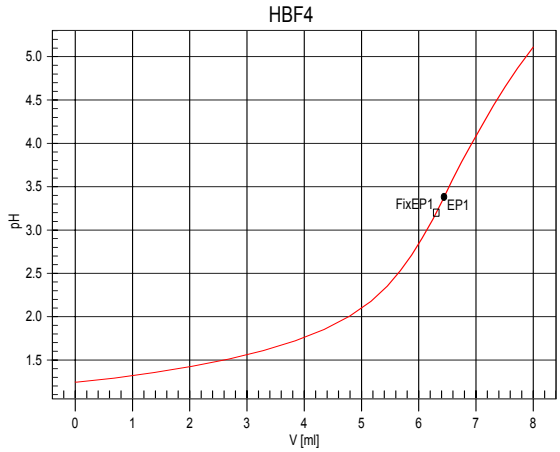

Fig. 5: *Titration curve free HBF_4.*