# Application Bulletin

Of interest to: Electroplating industries, Metals A 10

## Potentiometric analysis of tin plating baths


### *Summary*

Potentiometric titration methods for the analysis of acid and alkaline tin plating baths are presented. Following methods are described:
tin(II) / tin(IV) / total tin, free fluoroboric acid or free sulfuric acid, chloride in acidic tin baths, free hydroxide and carbonate in alkaline tin baths.


### *Apparatus and accessories*

- Titrino or
  Titrando with Dosino or Dosimat
- Magnetic swing-out stirrer
- Exchange unit(s)
- Pt Titrode 6.0431.100 with electrode cable 6.2104.020
- Comb. pH glass electrode 6.0255.100
- Ag Titrode with $Ag_2S$ coating 6.0430.100

### *Reagents*

These are described under the individual analyses.

### *1. Iodometric tin determination*

To increase the accuracy of this analysis, 10.0 mL bath sample is pipetted into a 100 mL graduated flask, filled up to the mark with distilled water and mixed well.

***Reagents:***

- *c*(Iodine solution) = 0.05 mol/L
- *w*(HCl) = 36%
- Iron powder p.a.

#### *1.1. Tin(II)*

Add 15 mL HCl and 50 mL dist. $H_2O$ to 10.0 mL diluted sample (corresponding to 1 mL original bath) in a beaker and titrate with *c*(iodine solution) = 0.05 mol/L against the Pt Titrode.

### *1.2. Tin(IV) and total tin*

In compliance with the tin content, pipet between 10.0 - 50.0 mL of the diluted sample (1 - 5 mL original bath) into a wide-necked Erlenmeyer flask and add 50 mL HCl. Stirring well, add ca. 1 g iron powder in small portions and when reaction subsides, warm up until the iron powder is entirely dissolved. Cool immediately and titrate with *c*(iodine solution) = 0.05 mol/L against the Pt Titrode.

***Calculations:***

1 mL *c*(Iodine solution) = 0.05 mol/L = 5.9345 mg Sn

g/L Sn = EP1 x C01 / C00

C00 = sample size in mL original bath
C01 = 5.9345

***Figures:***

```
'pa
751 GPD Titrino          05268   751.0011
date  2000-06-05    time  10:26         4
MET  U              AB90 Sn.
parameters
>titration parameters
  V step                  0.10 ml
  dos.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                     6 ml
  stop U                   OFF mV
  stop EP                    9
  filling rate            max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       30 mV
  EP recognition:    greatest
  fix EP1 at U             OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ------------
```

**Fig. 1** Parameter report Titrino, iodometric tin determination

```
'fr
751 GPD Titrino          05268   751.0011
date  2000-06-05    time  10:26         4
U(init)          391 mV MET U    AB90 Sn.
smpl size        1.0 ml    id#1    Sn(II)
EP1            3.030 ml             290 mV
Sn             17.98 g/l
stop V reached
          ------------
```

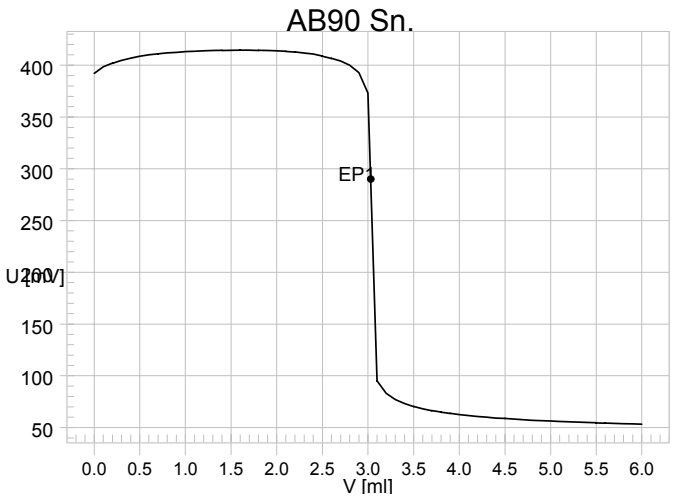


**Fig. 2** Titration curve iodometric tin determination

## 2. Free fluoroboric acid or free sulfuric acid

***Reagents:***

- *c*(NaOH) = 1 mol/L
- Sodium sulfate p.a.

***Analysis:***

Dilute 10.0 mL bath sample to approx. 50 mL with dist. $H_2O$ in a beaker. While stirring dissolve approx. 5 g $Na_2SO_4$ and titrate afterwards with *c*(NaOH) = 1 mol/L against the comb. pH glass electrode. The flat potential jump at pH = approx. 3.2 is evaluated.

***Calculations:***

1 mL *c*(NaOH) = 1 mol/L = 87.81 mg $HBF_4$ or 49.037 mg $H_2SO_4$

g/L $HBF_4$ = EP1 x C01 / C00
g/L $H_2SO_4$ = EP1 x C02 / C00

C00 = Sample size in mL original sample (10)
C01 = 87.81
C02 = 49.037

***Figures:***

```
'fr
751 GPD Titrino          05268   751.0011
date  2000-06-06    time  08:23         3
pH(init)       1.82    DET pH   AB90 SO4
smpl size       5.0 ml
EP1+           9.932 ml               3.33
H2SO4          97.41 g/l
#EP's not corresponding
stop V reached
          ------------
```

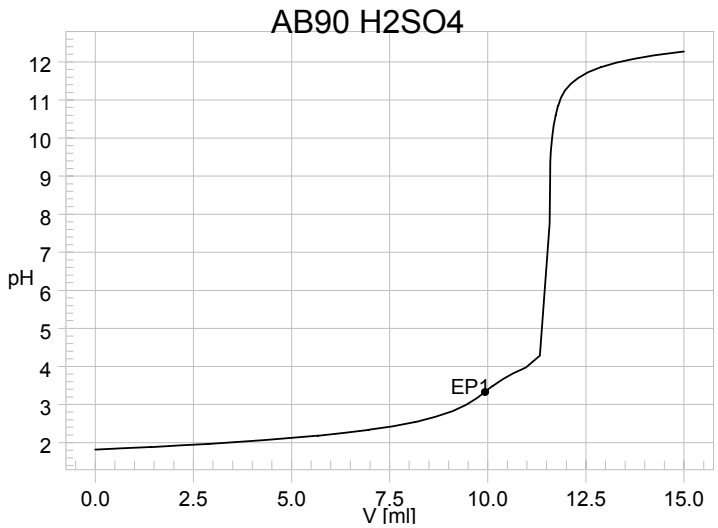


**Fig. 3** Titration curve free sulfuric acid

## 3. Chloride determination in acidic tin baths

***Reagents:***

- *c*($AgNO_3$) = 0.1 mol/L
- *w*($HNO_3$) = 65%

***Analysis:***

Pipet 5.0 mL bath solution into a beaker and dilute to approx. 50 mL with dist. $H_2O$. Add 2 mL $HNO_3$ and titrate with $c(AgNO_3)$ = 0.1 mol/L against the Ag Titrode ($Ag_2S$-coating).

***Calculations:***

1 mL $c(AgNO_3)$ = 0.1 mol/L = 3.5453 mg Chloride

g/L Chloride = EP1 x C01 / C00

C00 = sample size in mL original bath (5)
C01 = 3.5453

***Figures:***

```
'fr
751 GPD Titrino          05268   751.0011
date  2000-06-06    time  09:02         5
U(init)          236 mV DET U     AB90 Cl
EP1            3.473 ml              97 mV
Chlorid        12.31 g/l
stop V reached
          ============
```

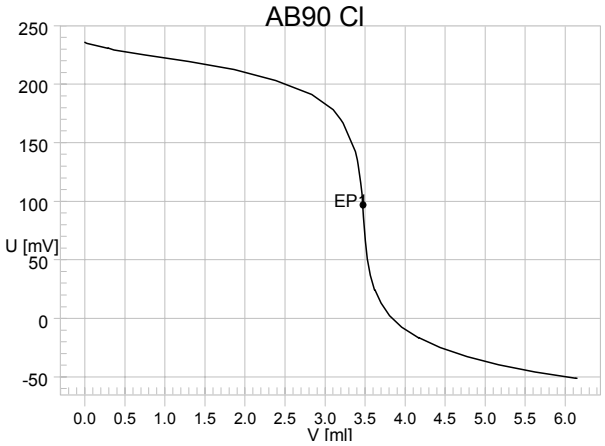


**Fig. 4** Titration curve chloride determination

## *4. Free hydroxide and carbonate in alkaline baths*

***Reagents:***

- $c$(HCl) = 1 mol/L
- $w(BaCl_2)$ = 25%

***Analysis:***

Add 50 mL $BaCl_2$ to 10.0 mL bath sample in a wide-necked Erlenmeyer flask and boil for a short time. Allow to cool and slowly titrate the still warm solution with $c$(HCl) = 1 mol/L against the comb. pH glass electrode.

***Calculations:***

Two endpoints are obtained. The consumption up to EP1 corresponds to NaOH, between EP1 and EP2 to tin and between EP2 and EP3 to carbonate.

1 mL $c$(HCl) = 1 mol/L = 40.0 mg NaOH or 106.0 mg $Na_2CO_3$

g/L NaOH = EP1 x C01 / C00
g/L $Na_2CO_3$ = (EP3 - EP2) x C02 / C00

C00 = Sample size in mL original sample (10)
C01 = 40
C02 =106

***Figures:***

```
'pa
751 GPD Titrino          05268   751.0011
date  2000-06-06    time  10:43        6
DET  U             AB90 OH-
parameters
>titration parameters
  meas.pt.density           4
  min.incr.              10.0 µl
  dos.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                   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:          OFF
  activate pulse:         OFF
          ------------
```

**Fig. 5** Parameter report Titrino, free NaOH and carbonate

```
'fr
751 GPD Titrino          05268   751.0011
date  2000-06-06    time  10:43        6
U(init)         -277 mV DET U    AB90 OH-
smpl size       10.0 ml
EP1            6.911 ml            -77 mV
EP2           11.657 ml            196 mV
EP3           14.329 ml            286 mV
NaOH           27.64 g/l
Na2CO3         28.32 g/l
stop V reached
          ------------
```

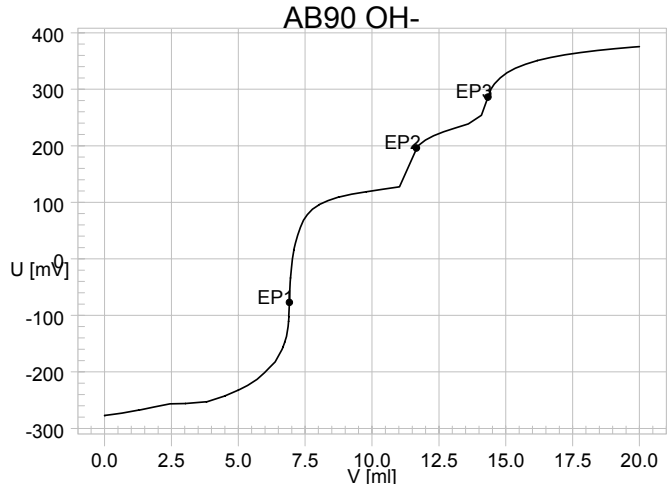


**Fig. 6** Titration curve NaOH / (Sn) / $Na_2CO_3$

## *Literature*


- Metrohm Ti Application Note No. T-5, T-21, T-23
- Wild,P.W.
  Moderne Analysen für die Galvanik
  Eugen G. Leuze Verlag, D-88348 Saulgau/Württ. 1972
- Jelinek,T.W.
  Prozessbegleitende Analytik in der Galvanotechnik
  Eugen G. Leuze Verlag, D-88348 Saulgau/Württ. 1999
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