Application Bulletin

Of interest to: Metals, Electroplating industry A C 10

Titrimetric analysis of cadmium plating baths

Summary

This Bulletin describes titrimetric methods for the determination of cadmium, free sodium hydroxide, sodium carbonate and total cyanide. The free cyanide can be calculated from the total cyanide and the Cd content.

Apparatus and accessories

- Titrino or Titrando with Dosino or Dosimat
- Magnetic swing-out stirrer
- Exchange units
- Photometer (610 nm) or
  Cu ISE 6.0431.140 with Ag/AgCl reference electrode 6.0726.107 (KCl 3 mol/L) and electrode cable 6.2106.020
- Combined pH glass electrode 6.0255.100 with electrode cable 6.2104.020
- Ag Titrode with Ag_2S coating 6.0430.100

Reagents

These are described under the individual analyses.

1. Determination of cadmium

1.1. By means of photometric titration (Photometer)

Reagents:

- *c*(Na_2EDTA) = 0.1 mol/L
- *w*(formaldehyde) = 30%
- Buffer solution pH = 10:
  Dissolve 114 mL *w*(NH_3) = 25% and 14 g NH_4Cl in dist. H_2O and fill up to 200 mL.
- Colored indicator:
  Dissolve 100 mg each eriochrome black T and vitamin C in dist. H_2O and fill up to 100 mL.
- *w*(KCN) = 6.5%

Analysis:

Place a 1.0 ... 2.0 mL bath sample, containing approx. 50 mg Cd in a beaker, add 1 mL KCN, approx. 80 mL dist. H_2O, 20 mL buffer solution pH = 10 and 0.25 mL colored indicator. Slowly add 4 mL formaldehyde and, while stirring allow to react for 1 min (to set Cd free from the cyanide complex). Finally titrate with *c*(Na_2EDTA) = 0.1 mol/L using the Photometer.

Calculations:

1 mL *c*(Na_2EDTA) = 0.1 mol/L = 11.241 mg Cd
g/L Cd = EP1 * C01 / C00

C00 = Sample size in mL
C01 = 11.241

Figures:

```
'pa
751 GPD Titrino          05268   751.0011
date  2000-05-30    time  16:01         5
MET  U              AB93 Cd
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                     60 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                    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 for Cd determinations

```
'fr
751 GPD Titrino          05268   751.0011
date  2000-05-30    time  16:01         5
U(init)          325 mV MET U     AB93 Cd
smpl size        2.0 ml
EP1            7.308 ml             316 mV
Cadmium        41.07 g/l
stop V reached
          ============
```

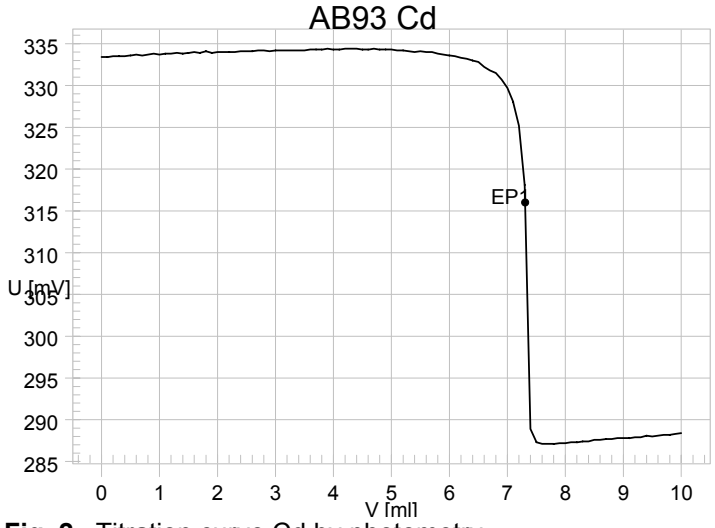

Fig. 2 Titration curve Cd by photometry

1.2. By means of potentiometric titration (Cu ISE)

Reagents:

- $c(Na_2EDTA)$ = 0.1 mol/L
- $Cu(NH_4)_2EDTA$, c = 0.1 mol/L (Merck No. 105217)
- Buffer solution pH = 10; see under 1.1
- $w(HNO_3)$ = 65%

Analysis:

Work under a fume cupboard, toxic HCN is set free!!!
Put 5.0 mL bath sample into a Kjeldahl flask and add approx. 10 mL dist. H_2O. Tilting back and forth, carefully add HNO_3 until the solution becomes definitely acidic. Heat up the solution under a fume cupboard and cook until all cyanide is destroyed and entirely removed. After cooling, rinse the solution with dist. H_2O into a 50 mL graduated flask, fill up to the mark and mix.
Pipet 10.0 ... 20.0 mL of the treated sample solution (corresponding to 1 ... 2 mL original bath) into a beaker and complete to approx. 40 mL with dist. H_2O. Add 5 mL buffer solution pH = 10 and 1 mL $Cu(NH_4)_2EDTA$ and, while stirring allow to react for 1 min. Finally titrate with $c(Na_2EDTA)$ = 0.1 mol/L in the MET mode of the titrator, using the Cu ISE.

Calculations:

1 mL $c(Na_2EDTA)$ = 0.1 mol/L = 11.241 mg Cd
g/L Cd = EP1 * C01 / C00

C00 = Sample size in mL (original sample)
C01 = 11.241

Figures:

```
'fr
751 GPD Titrino          05268   751.0011
date  2000-05-31    time  09:38         2
U(init)          -67 mV MET U     AB93 Cd
smpl size        2.0 ml
EP1            7.438 ml            -110 mV
Cadmium        41.81 g/l
stop V reached
          ============
```

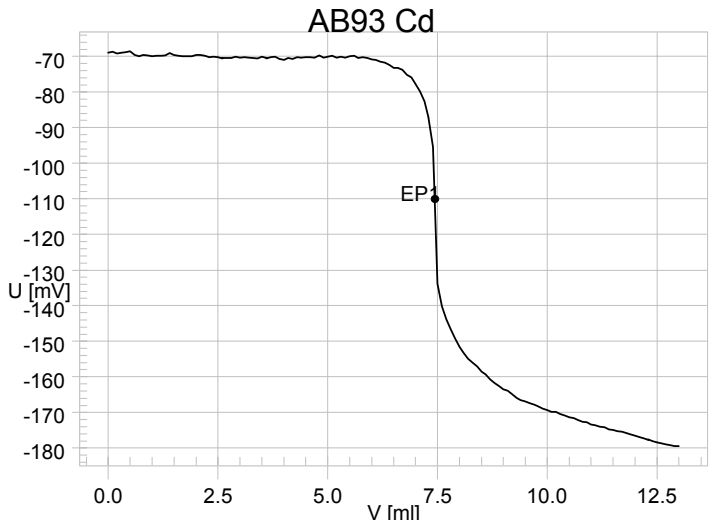

Fig. 3 Titration curve Cd by potentiometry

2. Determination of free NaOH and carbonate

Reagents:

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

Analysis:

Put approx. 50 mL dist. H_2O and 2.0 mL bath sample into a glass beaker. After addition of 5 mL $BaCl_2$ solution, titrate with c(HCl) = 1 mol/L, using the pH glass electrode, until shortly after the second endpoint.

Calculations:

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

g/L NaOH = EP1 * C01 / C00
g/L Na_2CO_3 = (EP2 - EP1) * C02 / C00

C00 = Sample size in mL (2)
C01 = 40
C02 = 106

Remarks:

- The titration has to be stopped after reaching the second endpoint, otherwise toxic HCN may be set free. It is best to work under a fume cupboard!

Figures:

```
'pa
751 GPD Titrino          05268   751.0011
date  2000-05-31    time  12:42         3
DET  U             AB93 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                     6 ml
  stop U                   OFF mV
  stop EP                    9
  filling rate            max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                        5
  EP recognition:            2
  fix EP1 at U             OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
            ------------
```

Fig. 4 Parameter report Titrino for NaOH, Na_2CO_3

```
'fr
751 GPD Titrino          05268   751.0011
date  2000-05-31    time  12:42         3
U(init)         -309 mV DET U    AB93 OH-
smpl size        2.0 ml
EP1            1.963 ml            -209 mV
EP2            3.409 ml             -33 mV
NaOH           39.26 g/l
Na2CO3         76.64 g/l
manual stop
           ------------
```

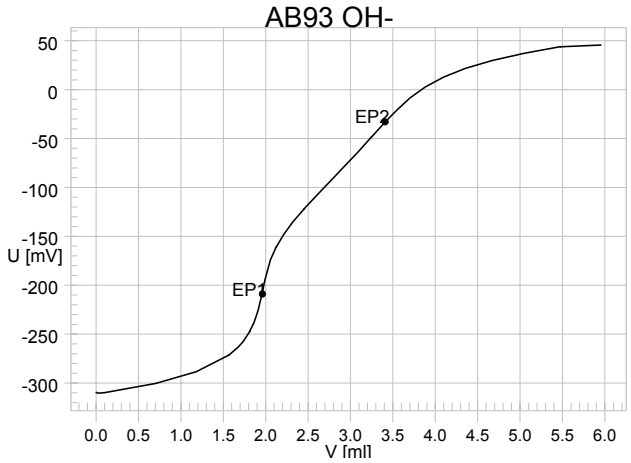

Fig. 5 Titration curve NaOH / Na_2CO_3

3. Determination of total cyanide

Reagents:

- *c*($AgNO_3$) = 0.1 mol/L
- *c*(NaOH) = 2 mol/L
- *w*(potassium iodide) = 10%

Analysis:

Place approx. 50 mL dist. H_2O and 2 mL NaOH into a glass beaker. Then add 1.0 mL bath sample and 2 mL KI solution, and titrate with *c*($AgNO_3$) = 0.1 mol/L using the Ag Titrode.

Calculations:

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

g/L „cyanide“ = EP1 * C01 / C00

C00 = Sample size in mL (1)
C01 = 5.204 or 9.802 or 13.024

Figures:

```
'pa

751 GPD Titrino          05268   751.0011
date  2000-05-31    time  13:15         5
DET  U              AB93 CN-
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                   13 ml
  stop U                  OFF mV
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                       5
  EP recognition:    greatest
  fix EP1 at U            OFF mV
  pK/HNP:                 OFF
>preselections
  req.ident:              OFF
  req.smpl size:          OFF
  activate pulse:         OFF
          ============
```

Fig. 6 Parameter report Titrino for the cyanide determination

```
'fr
751 GPD Titrino          05268   751.0011
date  2000-05-31     time  13:15         5
U(init)          204 mV DET U     AB93 CN-
smpl size        2.0 ml
EP1           10.019 ml              20 mV
Cyanid         13.03 g/l
stop V reached
            ============
```

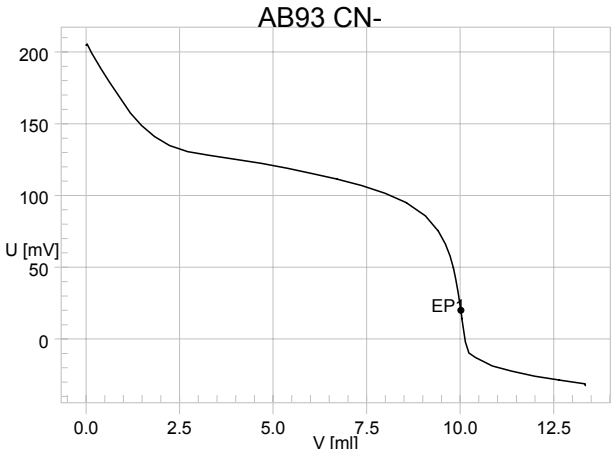

Fig. 7 Titration curve total cyanide

4. Calculation of free cyanide

To calculate the free cyanide, the content of cyanide combined with Cd must be subtracted from the total cyanide content. According to the formula $K_2Cd(CN)_4$ this corresponds to 0.926 g CN per g Cd.

Free cyanide; g/L CN = (g/L total-CN) - (g/L Cd * 0.926)

Literature

- Metrohm Application Bulletin No. 101
- Metrohm Ti Application Note No. T-22, T-23, T-24
- Wild,P.W.
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  Eugen G. Leuze Verlag, D-88348 Saulgau/Württ. 1972
- Jelinek,T.W.
  Prozessbegleitende Analytik in der Galvanotechnik
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