# Determination of Free Cyanide in a Copper Bath

Cyanide content determination in e.g. brass electroplating bath is very important to achieve optimum plating efficiency. Free cyanide is precipitated by silver nitrate, and the titration is monitored with a DP550 phototrode.

| | |
|---|---|
| **Sample** | Copper bath,<br>aliquots of 1 mL from diluted solution of 10 mL in 100 mL. |
| **Substance** | Free cyanide, $CN^-$ , M = 26.02,<br>z = 1 |
| **Chemicals** | 5 mL potassium iodide, KI, 10%<br>40 mL deion. water |
| **Titrant** | Silver nitrate, $AgNO_3$<br>c(1/2 $AgNO_3$) = 0.2 mol/L |
| **Standard** | Sodium chloride (see appl. M525) |
| **Instruments** | DL50 Graphix, DL53/DL55/DL58,<br>DL70ES/DL77<br>AT261, Printer |
| **Accessories** | Titration beakers ME-101974 |
| **Indication** | DP550 Phototrode with<br>DIN-Lemo Adapter ME-89600 |
| **Chemistry** | $Ag^+ + 2\ CN^- = Ag(CN)_2^-$<br>$Ag^+ + Ag(CN)_2^- = Ag[Ag(CN)_2]$<br>$AgI + 2\ CN^- = [Ag(CN)_2]^- + I^-$ |
| **Calculation** | R=Q*C/m ; CN in sample (g/L)<br>C=M/z<br>R2=R1*10 ; CN Bath content in g/L<br>R3=Q*C3 ; CN in sample (mg)<br>C3=M*1000/z |
| **Waste disposal** | Cyanide waste.<br>CAUTION: cyanide is toxic. |
| **Author** | R. Böhlen, MT-CH |

## Preparation and Procedures

**Sample preparation**

1. 10 mL bath are diluted to 100 mL with deion. water.
2. 1 mL aliquot is poured in the titration beaker.
3. Add 5 mL 10% potassium iodide solution (KI).
4. 40 mL deionized water is added to the sample.

A soluble complex $[Ag(CN)2]^-$ is first formed:

$$Ag^+ + 2\ CN^- = [Ag(CN)_2]^-$$

As long as free cyanide is still present, the solution remains clear, but the first excess of silver causes formation of a white solid that mark the endpoint:

$$Ag^+ + Ag(CN)_2^- = Ag[Ag(CN)_2]$$

For an accurate end-point determination, KI is used as an indicator. During titration, any silver iodide which would tend to form will be kept in solution by the excess of cyanide ion until the equivalence point is reached:

$AgI + 2\ CN^- = [Ag(CN)_2]^- + I^-$

After the EQP, the formation of yellow silver iodide will lead to a turbidity increase which indicates the endpoint.

## Remarks

The method was developed on the DL25 titrator and has been adapted for the DL5x-/DL7x-titrators.

**Chemicals**

10% Potassium iodide, KI:
50 g KI and 50 g NaOH are dissolved in deionized water, and diluted to 500 mL in a volumetric flask.

**CAUTION:** Cyanide is toxic. Wear safety googles and gloves, and work in a fume hood. NEVER add strong acid to the solution since cyanidric acid is formed and liberated as a gas from the solution.

**Literature**

1. Application note, DL25 Application Brochure "Petroleum and electroplating", ME-51724627.

2. Vogel's textbook of quantitative inorganic analysis, 4th edition, Longman Group Limited , 1978.

3. D.A. Skoog, D.M. West, "Fundamentals of Analytical Chemistry", Holt, Rinehart, and Winston, 1969.

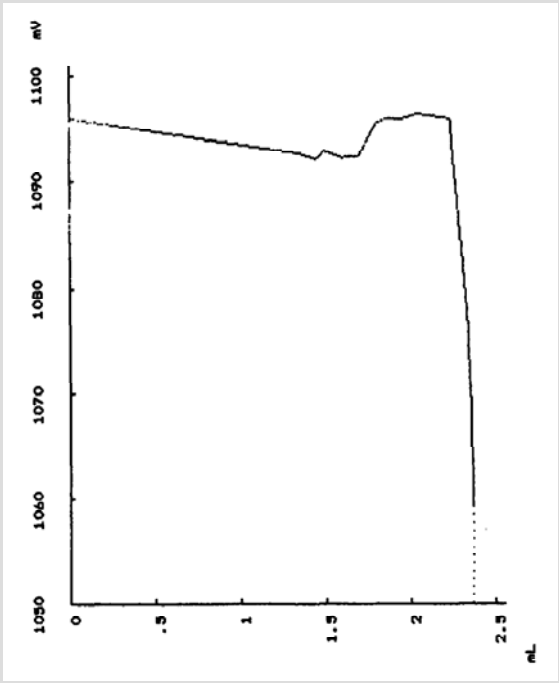
4. Application no. M525 in Application brochure18, "Standardization of Titrants", 2000.

## Results

| | CN- | n | Comments |
|---|---|---|---|
| Mean value | 26.84 g/L | 6 | DL25 application note in |
| Standard deviation s | 0.346 g/L | | DL25 Application brochure "Petroleum products and electroplating" ME-51 724 627 |
| Rel. standard deviation srel | 1.29 % | | |

## Table of measured values

## Titration curve



## Method

```
Method    25002      Free CN- in Cu bath
          Version    17-01-2001  10:50
```

```
Title
   Method ID  . . . . . . . . . . . . . 25002
   Title      . . . . . . . . . . . . . Free CN- in Cu bath
   Date/time  . . . . . . . . . . . . . 17-01-2001  10:50
Sample
   Sample ID  . . . . . . . . . . . . . Cu bath
   Entry type . . . . . . . . . . . . . Fixed volume
      Volume [mL] . . . . . . . . . . . 1.0
   Molar mass M . . . . . . . . . . . . 26.01
   Equivalent number z  . . . . . . . . 1
   Titration stand  . . . . . . . . . . Stand 1
   Temperature sensor . . . . . . . . . Manual
Stir
   Speed [%]  . . . . . . . . . . . . . 50
   Time [s] . . . . . . . . . . . . . . 10
EQP titration
   Titrant/Sensor
      Titrant . . . . . . . . . . . . . 1/2AgNO3
      Concentration [mol/L] . . . . . . 0.2
      Sensor  . . . . . . . . . . . . . DP550
      Unit of meas. . . . . . . . . . . mV
   Predispensing  . . . . . . . . . . . to volume
      Volume [mL] . . . . . . . . . . . 1.5
      Wait time [s] . . . . . . . . . . 20
   Titrant addition . . . . . . . . . . Dynamic
      dE(set) [mV]  . . . . . . . . . . 4.0
      dV(min) [mL]  . . . . . . . . . . 0.02
      dV(max) [mL]  . . . . . . . . . . 0.2
   Measure mode . . . . . . . . . . . . Equilibrium controlled
      dE [mV] . . . . . . . . . . . . . 0.5
      dt [s]  . . . . . . . . . . . . . 1.0
      t(min) [s]  . . . . . . . . . . . 5.0
      t(max) [s]  . . . . . . . . . . . 30.0
   Recognition
      Threshold . . . . . . . . . . . . 200
      Steepest jump only  . . . . . . . No
      Range . . . . . . . . . . . . . . No
      Tendency  . . . . . . . . . . . . Negative
   Termination
      at maximum volume [mL]  . . . . . 20.0
      at potential  . . . . . . . . . . No
      at slope  . . . . . . . . . . . . No
      after number EQPs . . . . . . . . Yes
         n =  . . . . . . . . . . . . . 1
      comb. termination criteria  . . . No
   Evaluation
      Procedure . . . . . . . . . . . . Standard
      Potential 1 . . . . . . . . . . . No
      Potential 2 . . . . . . . . . . . No
      Stop for reevaluation . . . . . . Yes
          Condition . . . . . . . . . . neq=0
```

```
Calculation
   Formula  . . . . . . . . . . . . . . R=Q*C/m
   Constant . . . . . . . . . . . . . . C=M/z
   Decimal places . . . . . . . . . . . 2
   Result unit  . . . . . . . . . . . . g/L
   Result name  . . . . . . . . . . . . Sample content
   Statistics . . . . . . . . . . . . . Yes
Calculation
   Formula  . . . . . . . . . . . . . . R2=R1*10
   Constant . . . . . . . . . . . . . .
   Decimal places . . . . . . . . . . . 2
   Result unit  . . . . . . . . . . . . g/L
   Result name  . . . . . . . . . . . . Bath content
   Statistics . . . . . . . . . . . . . Yes
Calculation
   Formula  . . . . . . . . . . . . . . R3=Q*C3
   Constant . . . . . . . . . . . . . . C3=M*1000/z
   Decimal places . . . . . . . . . . . 2
   Result unit  . . . . . . . . . . . . mg
   Result name  . . . . . . . . . . . . CN in sample
   Statistics . . . . . . . . . . . . . No
Report
   Output . . . . . . . . . . . . . . . Printer
   Results  . . . . . . . . . . . . . . No
   All results  . . . . . . . . . . . . Yes
   Raw results  . . . . . . . . . . . . No
   Table of measured values . . . . . . Yes
   Sample data  . . . . . . . . . . . . No
   E - V curve  . . . . . . . . . . . . Yes
   dE/dV - V curve  . . . . . . . . . . Yes
   d2E/dV2 - V curve  . . . . . . . . . No
   log dE/dV - V curve  . . . . . . . . No
   E - t curve  . . . . . . . . . . . . No
   V - t curve  . . . . . . . . . . . . No
   dV/dt - t curve  . . . . . . . . . . No
```