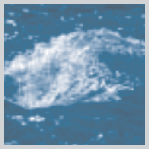
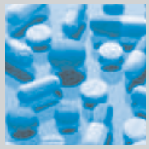
DENVER INSTRUMENT





Copper in Electroplating Copper Baths
(Redox Titration Method)

Introduction

Electroless copper baths, used in particular in the manufacture of printed circuits, contain copper salts, sodium hydroxide stabilising agents and formol, but many electroplating copper baths contain acids (H_2SO_4) or cyanide ion.

For these baths, copper determination can involve a redox titration instead of E.D.T.A.

Principle

The redox titration of copper ion involves a two-step reaction:

First step: oxidation of iodide ion I^- Cu^{2+} with iodine formation

$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$

Second step: titration of generated I_2 with thiosulphate ion

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

Regarding the 2 reactions, 1 mole of Cu^{2+} corresponds to 1 mole of $S_2O_3^{2-}$

The titration uses a combined platinum/reference electrode.

Electrode and reagents

MC3051Pt combined platinum/reference electrode (part no. E31M003)

CL114 connecting cable (part no. A94L114)

Potassium iodide solution

Dissolve 80 g of potassium iodide in 1000 ml of distilled water.

Glacial acetic acid

Sodium thiosulphate solution 0.1 mol/ (or 0.1N)

$Na_2S_2O_3$, $5H_2O$ has a molecular weight corresponding to 248.181 g/mol

To prepare a 0.1 equivalent/l (or 0.1 mol/) sodium thiosulphate solution; dissolve 24.8181 g of $Na_2S_2O_3$, $5H_2O$in 500 ml of freshly distilled water (or freshly boiled and cooled desionised water) and 2 or 3 drops of $CHCl_3$ and complete to 1000 ml using a volumetric flask

Wait for one day and filter the solution if necessary (precipitation of sulphur can occur)

Stock the solution in a brown glass flask

Look at the solution from time to time and filter and standardise again if necessary

This solution is also commercially available.

Distilled water.

Inflection Detection settings

CONTINUOUS IP MODE

Burette volume:	10 ml (see working range)
Stirring speed:	500 rpm
Working mode:	mV
Start timer:	5 min
Maximum volume:	10 ml
Stop point:	170 mV
Direction:	decreasing mV
Minimum speed:	0.1 ml/min
Maximum speed:	5.00 ml/min
Smoothing parameter:	5
Minimum ordinate:	200 mV
Maximum ordinate:	320 mV
Stop at last IP:	YES
Sample unit:	ml
Sample amount:	**(see working range)**
Dilution:	NO **(see working range)**
Result:	g/l
Molar weight:	159 g/mol
Reaction:	2Smp + 2Titr

Procedure

For a sulphuric acid/Copper bath

For an expected concentration of $CuSO_4$ close to 75 g/l, pipette 1 ml of sample, add 10 ml of distilled water and 15 ml of CH_3COOH and complete to 60 ml with distilled water.

Stir the solution and add 5 ml of KI solution.

The solution becomes dark yellow and cuprous iodide precipitates.

Run the titration.

The start timer set to 5 minutes allows a complete reduction of Cu^{2+}.

At the end of the titration, the solution may be colourless with a white precipitate of cuprous iodide.

The complete sample preparation and titration procedure change according to the sample composition.

As a general rule, the copper reduction (first step reaction) and the iodine reduction (titration) take place in acidic media (pH 2.00/4.00).

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Results

As indicated, 1 mole of Cu^{2+} corresponds to 1 mole of $S_2O_3^{2-}$

$$R(g/l) = Vtitr * Ctitr * 159.58 / Vsmp$$

Vtitr = Total volume of titrant used in ml

Ctitr = Concentration of titrant in mol/l

Vsmp = Sample volume in ml

159.58 = Molar weight of $CuSO_4$ in g/mol

3 determinations on the same bath

Mean:	74.20 g/l
Standard deviation:	0.2 g/l

Working range

The table below can be used as a guideline according to the copper concentration:

$CuSo_4$ conc. g/l	10	80	160
Sample ml	10	1	1
Burette capacity ml	10	10	25
KI added	5	5	10
Titrant used	6.25	5	10

This table takes into account the above-mentioned concentrations for reagents and titrant.

Instead of 1 ml for sample amount, it is possible to take 10 ml of sample diluted to 100 ml with a volumetric flask and use 10 ml of the diluted solution.

In this case, modify the Titration Manager settings as follows:

Sample unit:	ml
Dilution:	YES
Sample amount:	10
Final dilution amount:	100
Aliquot:	10

Notes

Procedure:

Addition of KSCN (potassium thiocyanate) avoids adsorption of I_2 on CuI and improves accuracy of the method.

Depending on the bath composition, it can be necessary to change the sample preparation. If the solution contains cyanide ion, add 3 ml of sulphuric acid and 1 ml of nitric acid to 1 ml of sample under a hood, gently boil until white fumes are released then add water and ammonium hydroxide to pH 6.00 and then glacial acetic acid.

To obtain a well-shaped titration curve as shown in the graph and a correct result, make sure sufficient glacial acetic acid is added.

Curve