**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 (H₂SO₄) 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⁻ with iodine formation

\[
2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI} + \text{I}_2 + \text{H}_2\text{O}
\]

Second step: titration of generated I₂ with thiosulphate ion

\[
\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}
\]

Regarding the 2 reactions, 1 mole of Cu²⁺ corresponds to 1 mole of S₂O₃²⁻.

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)

Na₂S₂O₃, 5H₂O has a molecular weight corresponding to 248.181 g/mol

To prepare a 0.1 equivalent/l (or 0.1 mol/l) sodium thiosulphate solution; dissolve 24.8181 g of Na₂S₂O₃, 5H₂O in 500 ml of freshly distilled water (or freshly boiled and cooled desionised water) and 2 or 3 drops of CHCl₃ 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**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burette volume</td>
<td>10 ml</td>
</tr>
<tr>
<td>(see working range)</td>
<td></td>
</tr>
<tr>
<td>Stirring speed</td>
<td>500 rpm</td>
</tr>
<tr>
<td>Working mode</td>
<td>mV</td>
</tr>
<tr>
<td>Start timer</td>
<td>5 min</td>
</tr>
<tr>
<td>Maximum volume</td>
<td>10 ml</td>
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<tr>
<td>Stop point</td>
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</tr>
<tr>
<td>Direction</td>
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<tr>
<td>Minimum speed</td>
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<td>Maximum speed</td>
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<td>Maximum ordinate</td>
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<tr>
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<tr>
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<td>ml</td>
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<tr>
<td>Sample amount</td>
<td></td>
</tr>
<tr>
<td>(see working range)</td>
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</tr>
<tr>
<td>Dilution</td>
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<tr>
<td>(see working range)</td>
<td></td>
</tr>
<tr>
<td>Result</td>
<td>g/l</td>
</tr>
<tr>
<td>Molar weight</td>
<td>159 g/mol</td>
</tr>
<tr>
<td>Reaction</td>
<td>2Smp + 2Titr</td>
</tr>
</tbody>
</table>

**Procedure**

*For a sulphuric acid/Copper bath*

For an expected concentration of CuSO₄ close to 75 g/l, pipette 1 ml of sample, add 10 ml of distilled water and 15 ml of CH₃COOH 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 Cu²⁺.
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).

Copper in Electroplating Copper Baths (Redox Titration Method)

**Results**

As indicated, 1 mole of Cu$^{2+}$ corresponds to 1 mole of S$_2$O$_3^{2-}$.

\[
R(g/l) = \frac{V_{titr} \times C_{titr} \times 159.58}{V_{smp}}
\]

- $V_{titr}$ = Total volume of titrant used in ml
- $C_{titr}$ = Concentration of titrant in mol/l
- $V_{smp}$ = 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:

<table>
<thead>
<tr>
<th>CuSO$_4$ conc. g/l</th>
<th>10</th>
<th>80</th>
<th>160</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample ml</td>
<td>10</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Burette capacity ml</td>
<td>10</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>KI added</td>
<td>5</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Titrant used</td>
<td>6.25</td>
<td>5</td>
<td>10</td>
</tr>
</tbody>
</table>

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 Cul 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**

\[
\text{milliVolts vs. milliliters}
\]

![Graph image]