

### 13. Iodometric determination of copper in alloys

Copper is one of the most important metals. Because of its very good electric, as well as thermal conductivity it finds applications mainly in electric and electronic industry. Limited sources of copper cause that it is a strategic material. Poland is the tenth world producer of copper (almost half a million pure metal annually)<sup>1</sup>. The ores of Cu rarely contain more than 1% of this element, this increases the costs of exploitation and makes them expensive.

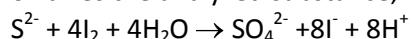
Many important alloys contain copper, like bronze<sup>2</sup> or brass<sup>3</sup>, but it is also added to silver<sup>4</sup> and gold (copper improves their mechanical properties), even to aluminum. The alloy of copper with nickel, containing 5 to 25% of Ni is widely used for production of coins in many countries, also in Poland (our coins from 10 gr to 1 zł and the cores of 2 and 5 zł, while the smallest face-values are made of manganese brass). The composition of alloy strongly affects its properties, in particular mechanical ones and chemical resistivity, so the ability to determine it is important branch of chemical quantitative analysis.

Copper is a semi-precious metal, its oxidizing potential is higher than that of hydrogen, and it does not dissolve in non-oxidizing acids. However, it is easy to dissolve it in nitric acid, both diluted (HNO<sub>3</sub> is reduced to NO) and concentrated (HNO<sub>3</sub> is reduced to NO<sub>2</sub>). Easy, fast, precise and cheap method of the quantitative determination of copper is iodometry.

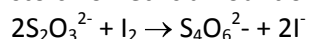
Iodometry belongs to the group of volumetric redoxometric methods of analysis. It has wide applications in analysis of reducing organic compounds, for example sugars containing the aldehyde group –CHO, which is easy to be oxidized to the carboxylic group –COOH. This is the case of glucose (see Task no. 12).

In iodometry, the end-point is detected when elemental iodine appears or disappears. However, iodine, I<sub>2</sub>, is almost insoluble in water. Addition of KI causes formation of I<sub>3</sub><sup>-</sup> ions (I<sub>2</sub>+I<sup>-</sup>→I<sub>3</sub><sup>-</sup>), and solubility of iodine increases.

In iodometry, the solution of iodine in aqueous KI is often used (direct titrations). This is possible if iodine oxidizes the analyzed substance, like in the following reaction:



Much more often the indirect or reverse titrations are applied. The example of the indirect titration is analysis of copper. Its idea is oxidizing iodides to iodine, while Cu<sup>2+</sup> ions are reduced to Cu<sup>+</sup>. Comparison of the standard potentials for both the half-reactions (Cu<sup>2+</sup>/Cu<sup>+</sup> E<sup>0</sup>=+0.17 V, I<sub>2</sub>/I<sup>-</sup> E<sup>0</sup>=+0.54 V) suggests that it is iodine that oxidizes Cu<sup>+</sup> ions, i.e. iodine is the oxidizer, not copper. The reality is different, because copper(I) iodide, CuI, is almost insoluble in water (K<sub>so</sub>=10<sup>-12</sup>). This means that the concentration of Cu<sup>+</sup> ions in solution is very low, and consequently the standard potential of the process Cu<sup>2+</sup>/Cu<sup>+</sup> much higher (ca. +0.88 V, remember that there is excess of iodide anions in solution). In consequence, the reaction which is observed when I<sup>-</sup> ions are added to Cu<sup>2+</sup> in solution is 2Cu<sup>2+</sup> + 4I<sup>-</sup> → 2CuI↓ + I<sub>2</sub> and one observes that the stoichiometric amount of iodine is formed. Iodine can be titrated using thiosulfate solution:



The only difficulty in analysis of copper alloys is that an oxidizing (nitric) acid must be used for dissolving the sample. The excess of this acid remaining in solution will oxidize the iodide anions to iodine (or higher, to the oxygen acids of iodide). So, we will first precipitate and separate copper as hydroxide Cu(OH)<sub>2</sub>, and dissolve it in a non-oxidizing acid (H<sub>2</sub>SO<sub>4</sub>) before the analysis. This difficulty can be avoided if one dissolves the alloy in as small amount of HNO<sub>3</sub> as possible and performing analysis in diluted solution.

Presence of iron can disturb this analysis. In aim to eliminate it first one adds hydrogen peroxide H<sub>2</sub>O<sub>2</sub> (to oxidize Fe<sup>2+</sup> ions to Fe<sup>3+</sup>) and after ammonia. This leads to precipitation of colloidal Fe(OH)<sub>3</sub>, which can be easily filtered. Copper is present in the filtrate because amino complex of copper is soluble in water. If the pH is correct, the filtrate will be dark-blue.

<sup>1</sup> In 2010.

<sup>2</sup> Bronzes are the alloys of copper with tin and also other metals; they usually contain 80-90% Cu.

<sup>3</sup> Brasses are the alloys of copper with Zn (up to 40%), often with addition of other metals, like Mn, Ni, Pb etc. Those with high contents of Ni are used for springs, ferrules and jewellery. After polishing they are imitating silver and are used for production of sugar-bowls, plates, cups, cutlery etc.

<sup>4</sup> Typical jewellery alloy is silver of 925 standard, i.e. containing 7.5% Cu.

## Procedure

1. Weigh ca. 0.09-0.12 g of the alloy using an analytical balance, place it in a beaker (**if the alloy contains iron**) of 200-250 mL in volume or in Erlenmeyer flask (**if the alloy does not contain iron**) and add concentrated  $\text{HNO}_3$  drop by drop until the sample dissolves completely (do it in the fume hood).
2. (**If the alloy contains iron**) Dilute the sample to ca. 100 mL with distilled water. Add few drops of hydrogen peroxide  $\text{H}_2\text{O}_2$  in order to oxidize  $\text{Fe}^{2+}$  ions to  $\text{Fe}^{3+}$ . Next add slowly concentrated ammonia mixing the content of the beaker with glass rod until brown, jelly-like precipitate of  $\text{Fe}(\text{OH})_3$  appears. Check the pH using indicator paper – it should be basic.
3. (**If the alloy contains iron**) Filter the solution using “soft” paper filter and wash it with small amount of diluted (ca. 0.1 M) ammonia. Only the filtrate will be used in further analysis.
4. (**If the alloy does not contain iron**) Add ca. 100 mL of distilled water.
5. Add slowly concentrated ammonia solution, continuously mixing, until dark-blue color of amino complex of copper appears.
6. Next add concentrated acetic acid, drop by drop, until the dark-blue color disappears. To the resulting pale-blue solution add ca. 2 mL of the acid in excess.
7. Add one small teaspoonful of solid KI. Close the flask and store in a dark place during ca. 15 min.
8. Titrate the reduced iodine using 0.05 M sodium thiosulfate. When solution becomes light-yellow, add 2-3 mL of starch solution (the solution becomes dark) and finish the titration until the solution is milk-like.
9. Perform the procedure three times.

## Calculations and report

- Calculate the mass of copper, independent for each analysis. Calculate its content in the alloy (expressed as weight%).
- Calculate the arithmetic mean of the obtained results.

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### *Sources:*

Internet, in particular Wikipedia  
textbooks