

17. Electrogravimetric determination of copper in alloys

Electrogravimetry is electroanalytical method based on gravimetric determination of metallic elements, which are isolated on the cathode in form of metal or on the anode in form of metal oxide during electrolysis. This method employs two or three electrodes, and either a constant current or a constant potential is applied to the preweighed working electrode.

An electrode (half-cell) is a structure consisting of two conductive phases – one of these is a metal or a different solid conductor, and the other consists of electrolyte. Between the metal or any other solid conductor (electrode) and the solution, electrode processes take place, which are redox reactions.

Electrolysis is decomposition of electrolyte as a result of impact of direct current flowing through the electrolyzer. This term encompasses: the actual electrochemical reaction taking place on the metallic electrodes, which is associated with transport of charge, transport of ions to and from the electrode surface, secondary chemical reactions taking place near the electrode.

In electrogravimetry, we use **electrolytic cells** or structures consisting of two electrodes immersed in an electrolyte solution, to which an external source of electrical energy is connected. The electrode connected to the positive pole of this external source is the anode, while the electrode connected to the negative pole is the cathode. On the cathode, the reduction reaction takes place ($ox_1 + z_1e \rightarrow red_1$), and on the anode – the oxidation reaction ($red_2 \rightarrow ox_2 + z_2e$). In order to make sure that the reduction and oxidation reactions are taking place at the sufficient speed, it is necessary to apply the appropriate potential from the external source of electric energy. The cathode potential must be more negative than the ox_1/red_1 potential, while the anode potential must be more positive than the red_2/ox_2 potential.

Decomposition potential – the potential, which causes the occurrence of electrode reactions.

A typical electrolysis diagram is presented in Figure 1.

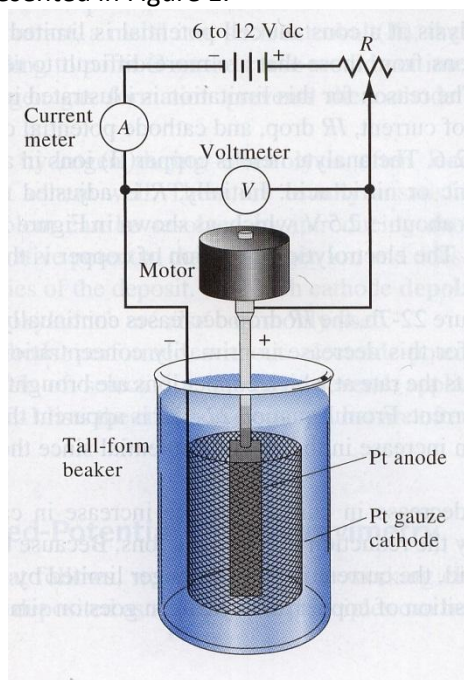


Fig. 1. Apparatus for electrodeposition of metals without cathode-potential control. Note that this is a two-electrode cell (Fig. 22-6 from [1]).

Electrogravimetric analysis provides precise and repeatable results. Determination is easy and the apparatus used is very simple.

Electrolysis is widely used to apply metallic coating to such items as truck fenders (chromium plating), cutlery (silver plating) and jewelry, which can be electrochemically coated with various noble metals. The Oscar statuette is an example of a nickel-plated item. The statuette is made of a tin, copper and antimony alloy,

electrochemically plated with copper, then – with nickel (to fill the metal pores) and then placed in a silver bath. Afterwards, the statuette is electrochemically coated with 24-karat gold. The quantity of gold can be determined by weighing the statuette before and after the final stage of electrolysis.

Parameters that influence the effectiveness of the electrolysis process:

- **The value of voltage applied to electrodes.** The voltage is selected so that the current intensity is high due to the speed of electrolysis.
- **The current intensity value.** It should provide the appropriate current density (current intensity per unit of electrode surface). Increase in the current density is advantageous as it accelerates the process of electrolysis.
- **Composition of the electrolyzed solution.** Most often, electrolysis of solutions containing nitric acid (V) or sulfuric acid (VI). Excessive acid concentration is not beneficial as the isolated metal can dissolve at the end of electrolysis.

Objective of the exercise

Quantification of the content of copper in brass.

Brass is an alloy of copper and zinc and other metals, having very good mechanical properties. It is used among others for the manufacture of machine parts including engineering, automotive and electrical engineering, for the production of everyday items such as fittings, door handles, fittings and much more. Due to its high resistance to corrosion, can be used for the manufacture of objects, which must have a high resistance to corrosive factors (such as propellers).

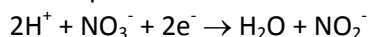
Analysis of brass during its production permits adjustment in the concentrations of metals to achieve a desired strength and corrosion resistance.

Copper is isolated as a metal on the cathode from acidic solutions containing 3-4 % of sulfuric acid and 1-3 % of nitric acid. The cathode reaction is as follows: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}^0$

Precision of electrogravimetric determination depends on the form of the metal deposit isolated on the electrode. This should be a fine-crystalline deposit, covering the electrode with a compact layer. If the current density is too small, the fine-crystalline deposit that is formed does not cover the entire surface of the electrode and it easily falls off. If the current density is too high, the deposit is dark and spongy, it does not adhere well to the electrode surface and is easily oxidized with oxygen contained in the air. Isolation of hydrogen as an additional product on the cathode and decomposition of the metal hydrides that are formed result in loosening of the metal deposit layer and making it spongy. Isolation of hydrogen can be reduced, if the so-called depolarizer is added to the solution. This role is played by nitrate (V) ions. The process of reduction of nitrate ions on the platinum cathode takes place as follows: $\text{NO}_3^- + 10\text{H}^+ + 8\text{e}^- \rightarrow \text{NH}_4^+ + 3\text{H}_2\text{O}$
The potential for reduction of nitrite (V) ions is higher than the potential for reduction of hydrogen.

Lead present in some Cu alloys is isolated on the anode in form of PbO_2 . The content of HNO_3 should be higher, if the deposit of PbO_2 is isolated quantitatively simultaneously with copper. The process of oxidation of Pb^{2+} ions on the platinum anode takes place as follows: $\text{Pb}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2 + 4\text{H}^+ + 2\text{e}^-$

During electrolysis, formation of nitrite is also possible:



Nitrite ions prevent complete deposition of copper and are removed by urea:



Reagents:

- Metal alloy sample, such as brass
- Nitric acid (V), concentrated
- 1M H_2SO_4
- 2M HNO_3
- Acetone or ethanol
- Urea

The measurement system consists of:

- A measurement dish with electrodes (a grid cathode made of platinum and plate Pt anode)
- A magnetic mixer
- A stabilized power supply

Procedure

1. Dissolution of the alloy

Weigh out precisely 0.15-0.25 g of the alloy, put in a 250 cm³ beaker, add 15 cm³ water and 5-7 cm³ concentrated nitric acid (V) (work under a hood). Dissolve the alloy, heating the solution until the brownish fumes of nitric oxides no longer appear. If the solution is entirely clear, there is no tin in the alloy being analyzed, and it is possible to follow to the next step, that is, electrogravimetric determination of copper and – if possible - lead. A white deposit or turbidity (“haze”) indicates the presence of tin in the alloy being analyzed. If the white sediment appears, the solution with the sediment is to be heated for about half an hour (under a cover, preventing boiling) to ensure the quantitative isolation of β-stannic acid and filtrated through a hard filter.

2. Electrogravimetric determination of copper

Dilute the solution with water to the volume of about 80 cm³ and add ca. 20 cm³ of 2M H₂SO₄.

Attention:

Any manipulations with the grid Pt cathode should be performed very carefully – it is delicate and expensive.

Avoid the short-circuit between anode and cathode – the generator can be destroyed. The current can be switched on only under teacher’s supervision.

Prior to commencement of analysis, it is necessary to wash the Pt electrodes in 2M nitric acid (V), then flush the electrodes thoroughly with distilled water, wash with anhydrous acetone or ethanol and dry in a dryer for 5 minutes at the temperature of 105-110°C. The cathode should be cooled down to room temperature (ca. 1 min) and weighed precisely using analytical scales. The electrodes are to be placed in the solution so that they were completely immersed and there was space for magnetic stirrer under the anode. Turn on the mixer and conduct electrolysis at the voltage of 3-3.5 V. After 25-30 minutes, add a small amount of urea, add about 20 cm³ water and continue electrolysis. After next 5-10 minutes check whether copper has been isolated completely: for instance add ammonia and sodium diethylditiocarbamate to a drop of solution on china, glass or filter paper – brown color means the presence of copper(II) ions. After the end of electrolysis, the cathode is to be raised above the surface of the solution **immediately after turning off the current** and flushed with distilled water. If turned off too early, some copper may dissolve in the acidic electrolyte. Turn off the electrolyzer, the cathode with the copper sediment and flush thoroughly with water after disconnecting from the electrolyzer. The cathode with isolated copper is to be washed with acetone or ethanol and dried for 3-4 minutes in the temperature of 105-110°C. After cooling in essicator, it is to be weighed using analytical scales.

The copper sediment on the cathode should be salmon pink. Darkening of the sediment indicates that other metals of a relatively low isolation potential have been settling along with copper, or it may result from partial oxidation of copper.

Calculations and report

1. Calculate the percentage content of copper on the basis of the cathode mass increase:

$$\chi_{\text{Cu}} = \frac{a}{b} \cdot 100 \%$$

where: a – the mass of precipitated copper, g; b – the weight of brass, g.

The report should contain a very short description of the determination method, the type of sample analyzed, a description of preparation of the sample for measurement, equations of reactions taking place on the electrodes and results of calculations in % of the content of copper and lead in the alloy analyzed.

Sources:

D.A. Skoog, D.M. West, F.J. Holler, S.R. Crouch “Fundamentals of Analytical Chemistry” 2004
Internet, mainly www.chem.uky.edu