Uniting Elements, Strengthening Bonds, Shaping Tomorrow!

30th Baltic Chemistry Olympiad

Tartu, Estonia, May 4th–6th, 2024

Practical exam

Student's code:

Problem	**1**	**2**
Points		

May 4th, 2024

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Problem 1. Electrochemical copper deposition: checking the Faraday law.

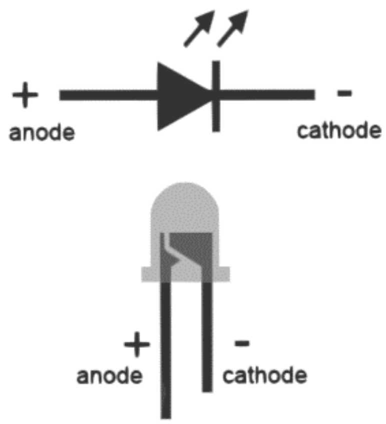
On your desk, you will find:

- 1 multimeter with a set of cables
- 4 connection cables
- 2 LEDs: red and blue
- 6 copper rods to use as electrodes
- 2 AA batteries and battery holder
- 1 beaker
- 1 holder for electrodes made of polymer foam
- 1 stopper

On the shared bench, you will find:

- 0.1 M $CuSO_4$ + 0.1 M H_2SO_4 electrolyte and 2 copper plating additives
- 5000 ppm Cl^- stock solution
- 10000 ppm PEG stock solution
- Deionized water bottles
- Analytical balance

Theoretical background

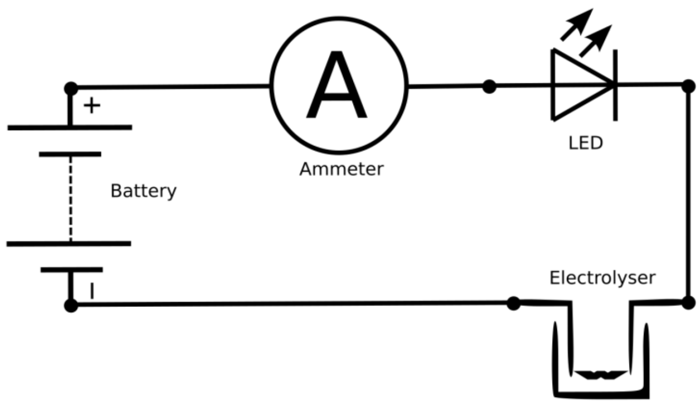


Cl^- is a well-known *accelerator* in Damascene copper plating and is used as diluted HCl acid. PEG – polyethylene glycol polymer with an average molar weight of 6000 Da – is a *suppressor* for copper plating. Together, they work in synergy to improve the characteristics of the copper plating process.

A light-emitting diode (LED) is a diode that converts electric energy into light when a current passes through it. The energy of the emitted light is proportional to the voltage drop through an LED. For instance, red LEDs have smaller voltage drops than blue LED ones.

Experimental procedure

Assemble the shown circuit to perform a copper deposition.



For each electrodeposition experiment, use 50 cm^3 of 0.1 M $CuSO_4$ + 0.1 M H_2SO_4 electrolyte. Using a stopper, run each deposition for 900 seconds (15.0 minutes). Use the multimeter to observe and write down the current values. Before and after each copper deposition weight corresponding copper rods used as anode and cathode. After each deposition, rinse and dry the used rods. Be careful not to wipe the fragile deposited layer of copper with paper. It is crucial to measure both deposited and dissolved copper amounts. Weigh carefully, and write the weight with 4 digits after the decimal delimiter. Pay attention that you can reuse anodes during the deposition process, but the cathodes should be taken every time a new one.

1. Run two depositions: one with red and one with blue LED from 0.1 M $CuSO_4$ + 0.1 M H_2SO_4 electrolyte.

2. Run two depositions: one with red and one with blue LED from 0.1 M $CuSO_4$ + 0.1 M H_2SO_4 electrolyte with Cl^- and PEG. Add the necessary amount of stock solutions to the electrolyte for achieving a desired concentrations of 50 ppm of Cl^- and 100 ppm of PEG in electrolyte.

a) Calculate the faradaic efficiency for copper deposition in every electrodeposition experiment based on your measured data.

b) Calculate partial copper currents on the cathode and anode based on the measured data.

c) What is the cause of the difference in measured and calculated current for copper deposition if the Faraday law holds?

d) What is the synergistic effect of the additives based on your experimental data?

e) Predict whether a smaller or bigger amount of copper will deposit if a violet LED with an even higher voltage drop is used.

Problem 1. Answer sheet

a) and **b)**

Added Cl^- stock solution ________ cm^3

Added PEG stock solution ________ cm^3

Deposition 1 without additives, RED LED

Cathode before ____________ g   Cathode after _______________ g

Anode before ____________ g   Anode after _______________ g

Faradaic efficiency ___________ %

Cathode current ___________ mA

Anode current ___________ mA

Deposition 2 without additives, BLUE LED

Cathode before ____________ g   Cathode after _______________ g

Anode before ____________ g   Anode after _______________ g

Faradaic efficiency ___________ %

Cathode current ___________ mA

Anode current ___________ mA

Deposition 1 with additives, RED LED

Cathode before ____________ g   Cathode after _______________ g

Anode before ____________ g   Anode after _______________ g

Faradaic efficiency ___________ %

Cathode current ___________ mA

Anode current ___________ mA

Deposition 2 with additives, BLUE LED

Cathode before ____________ g   Cathode after _______________ g

Anode before ____________ g   Anode after _______________ g

Faradaic efficiency ___________ %

Cathode current ___________ mA

Anode current ___________ mA

c) The difference between measured and calculated current for copper deposition is (tick one answer):

☐ LED voltage drop issues.
☐ Electrode active surface area.
☐ Poor connection.
☐ Specific weather conditions and moon phase.

d) Synergistic effect of the additives (tick one answer):

☐ Acceleration.
☐ Suppression.
☐ Neither (no effect).

e) Violet~~UV~~ LED hypothetical effect (tick one answer):

☐ There will be less copper deposited.
☐ There will be more copper deposited.
☐ There will be a violet copper deposit on the electrode.

Problem 2. Iodometric determination of Cu^{2+} ions in solution

Introduction

Iodometric titration is a highly sensitive analysis method because even traces of I_2 can be determined using a starch indicator, which forms an intensely coloured bluish-violet complex with iodine. As the temperature rises, the sensitivity of the indicator decreases. For this reason, as well as for the volatility of I_2, iodometric titrations are performed only in cold solutions. Since I_2 is a medium-strength oxidizer and I^- ion is a medium-strength reducer, iodometry can be used for the quantitative determination of both oxidizers and reducers.

Working principle

Copper(II) salts react with iodide, resulting in the release of iodine. The released iodine is titrated with sodium thiosulfate solution.

Chemicals

- ✓ $CuSO_4$ solution
- ✓ Solid KI
- ✓ concentrated sulfuric acid
- ✓ distilled water
- ✓ …………… mol/dm^3 sodium thiosulfate ($Na_2S_2O_3$) solution
- ✓ 1% starch solution

Instruments for individual use

- ✓ burette
- ✓ pipette pump
- ✓ beaker
- ✓ Erlenmeyer flask (volume 200–300 cm^3)
- ✓ ground glass stopper for Erlenmeyer flask
- ✓ stand, clamp, clamp holder
- ✓ weighing paper
- ✓ distilled water bottle
- ✓ 25 cm^3 volumetric pipette
- ✓ test tube stand + one graduated conical test tube
- ✓ dropper bottle with starch solution
- ✓ measuring cylinder

Instruments shared with others

- ✓ dropper bottles with concentrated sulfuric acid solution
- ✓ scales
- ✓ plastic bottle filled with $Na_2S_2O_3$ solution with a known concentration

Stages of work

1. Pipette 25.00 cm^3 of $CuSO_4$ solution into the Erlenmeyer flask using the volumetric pipette.
2. Add 25 cm^3 of distilled water using the measuring cylinder.
3. Add 5 cm^3 of concentrated sulfuric acid solution using the graduated conical test tube.
4. Weigh 0.7 g of solid KI and add it to the solution in the Erlenmeyer flask (light blue solution turns brown). Mix the solution by shaking.
5. Start titration with $Na_2S_2O_3$ solution until the solution changes its colour into light yellow.
6. When the solution has turned into light yellow, add 3 drops of 1% starch solution.
7. Titrate with sodium thiosulfate solution until the color turns whitish pink.
8. Repeat the experiment until obtaining three matching results (max. difference 0.05 cm^3).
9. Fill in the answer sheet.

Tips:

- Carefully consider which glassware needs to be washed with distilled water and which needs to be rinsed with the corresponding solution.
- You must wear a lab coat and safety glasses in the laboratory all the time!
- Mark your glassware with a marker to avoid mixing up containers.

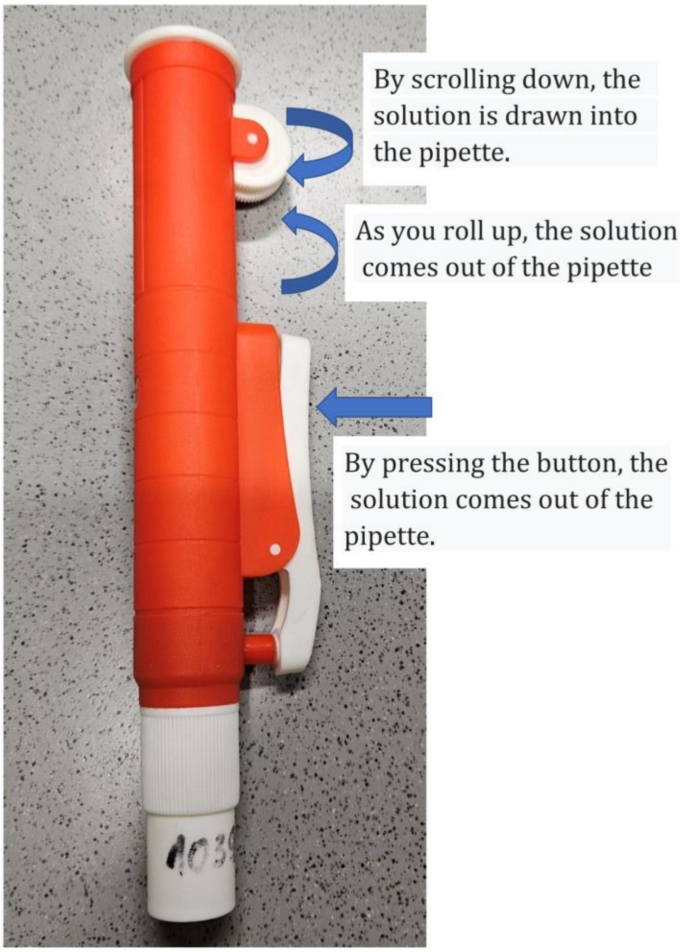


Figure. Pipette pump.

Problem 2. Answer sheet

a) Write down the average volume (cm^3) of sodium thiosulfate solution used to titrate the 25.00 cm^3 sample. Give the answer with 4 significant figures.

b) Calculate the concentration of copper ions (M) in the $CuSO_4$ solution. Give the answer with 4 significant figures.

$c(Cu^{2+})$ = ... M

c) How many grams of $CuSO_4 \cdot 5H_2O$ were dissolved in 100.0 cm^3 of $CuSO_4$ solution? Give the answer with 4 significant figures.

$m(CuSO_4 \cdot 5H_2O)$ = ... g

d) Write a balanced ionic equation for the reaction of copper(II) ions and iodide ions.

e) Write a balanced ionic equation for the reaction of iodine and thiosulfate ions.