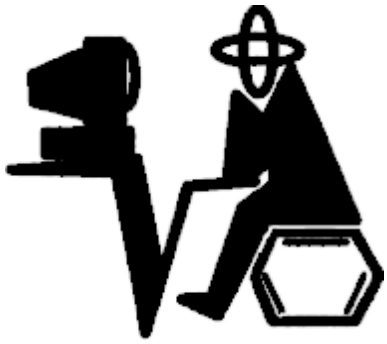
THE 50th INTERNATIONAL CHEMISTRY OLYMPIAD

May 2-8, 2016



PRACTICAL EXAMINATION

Moscow 2016

Name _____ Student code _____

General directions

1. You will have 15 min to read the exam text and plan your work before the start. It is forbidden to write any notes and/or start working during this time.

2. Always wear your lab coat and safety (or your own) goggles when being in the lab.

3. Handle solutions of acids and ammonia carefully!

4. Fill pipettes using pipette filler only. It is absolutely prohibited to suck solutions into the pipette by mouth.

5. Take into account that the amount of the provided solutions is limited. Spilled or completely used up solution will be replaced with penalty.

6. You are provided with clean dry burettes and pipettes. Do not spend the solutions for rinsing these.

7. Dispose the used solutions into the sinks (large or small).

8. When working do not interfere with other Olympiad participants. Keep your working place in order.

9. In case of broken glassware approach your lab assistant, who will help you in cleaning up the space and provide you with the substitution.

10. Use the back side of the booklet sheets for your draft work.

11. To optimize the usage of the sand baths, the students with even numbers start their work with the synthesis (Part 1), and those with odd numbers with analysis (Part 2). In any case, you will have to start fulfilling the other part of the exam in parallel during the filtrations present in both synthetic and analytical parts.

12. The total duration of the practical exam is 5 h (including the time for reading).Once the STOP command in given, you must immediately stop your work and deliver the Answer sheets and the product to you lab assistant.

Name _____ Student code _____

Equipment and glassware

For each student:

Laboratory stand with the burette clamp and ring	1
Graduated pipette, 10 mL	1
Pipette, 1 mL	1
Flat-bottom flask for titration	2
Volumetric flask with a stopper, 50 mL	1
Glass beakers, 50 mL (that labeled with the code contains the weighed amount of the complex)	3
Glass beaker, 150 mL	1
Glass beaker, 250 mL	1
Measuring cylinders, 10 mL	2
Funnel (3-4 cm) to fill the measuring cylinder with solutions	1
Funnel (6-7 cm)	1
Funnel (10 cm)	1
Paper filter «blue strip» (18 cm)	1
Paper filter «white strip» (9 cm)	3
KI weighed amount (3.32 g, in the small bag)	1
KI weighed amount (24 g, in the big bag)	1
$Na_2S_2O_3 \cdot 5H_2O$ weighed amount (4.95 g, in the small bag) for the synthesis	1
Ethylene diamine solution (1.5 g, as recalculated to the pure substance), in the Eppendorf tube	1
Spatula	1
Glass rod	1
Rubber finger guards (to handle hot beakers)	1
Wash bottle with distilled water	1
Burette	1
Pipette filler	1
Gloves (at the table in the lab center; choose the proper size: S, M, or L)	pair
Marker to label the beakers	1

Solutions, reagents and equipment to be shared between <u>two</u> students (at the bench between the working places of the students):

pH-Indicator paper	4
Acetone, in a vial	45 mL
Cylinder, 25 mL (for acetone)	
Barium iodide solution (0.01 mol), in a 30 mL amber glass vial	22 mL
H_2SO_4 solution (1 M), in a 30 mL amber glass vial	10 mL
H_2SO_4 solution (5 M), in an amber glass dropper	25 mL
Starch solution (0.5 %), in an amber glass dropper	5 mL
$CuSO_4 \cdot 5H_2O$ solution (0.25 g + 1 mL of water), in a vial	65 mL
HCl solution (0.2 M), in a vial	45 mL
KI solution (5 %), in a vial (for the Analytical part)	95 mL

Name _____ Student code _____

Solutions and equipment of general use:

Thiosulfate solution (0.025 M) for titration, in a carboy equipped with the siphon trap, located atop, 1 for 8 students

Ammonia solution (1.8 M), under the fume hood

Sulfuric acid solution (5 M) for refilling the drop bottles, under the fume hood

Sand bath, under the fume hood

Box with ice + beaker, 400 mL, with cold distilled water, under the fume hood or central table

Paper towel in rolls, on the table of general use

Name _____ Student code _____

Preparation and analysis of a copper complex

You will have to synthesize a complex compound of copper, titrimetrically determine the copper content in it and propose the complex composition and structure based on all the data available.

In the analytical part, you will be provided with a weighed amount of the same complex compound as you will obtain in the synthetic part.

Part I. Synthesis

Step 1. Using the 10-mL cylinder, transfer 10 mL of $CuSO_4 \cdot 5H_2O$ solution (0.25 g in 1 mL of water, in the clear glass vial, to be shared by two students) into a 50 mL beaker. Add 1.5 g of 1,2-ethylene diamine (the entire amount from the Eppendorf tube) to the same beaker with mixing. Place 10 mL of BaI_2 solution (in the amber glass vial, to be shared by two students, admeasure with the 10 mL cylinder) into **another** 50 mL beaker. Pour over the solution of the copper complex with ethylene diamine to the barium iodide solution in portions with mixing. Isolate the precipitate by filtration (the middle-size funnel, the 9 cm diameter filter) and wash it twice with ~5 mL portions of water (use the water from the wash bottle). You can collect the filtrate either in a beaker or in the conical flask. Combine the wash waters with the filtrate (Solution 1). Keep the Solution 1, since it will be used at step 3. Wash all the 50 mL beakers.

Answer the questions (Part A). You can do this later, when you have got spare time

A1. Write down the equation of the reaction between copper(II) ions and 1,2-ethylene diamine occurring in water solution:

A2. What will be the medium in the 1,2 ethylene diamine aqueous solution (tick one)?

☐ acidic ☐ close to neutral ☐ alkaline

A3. What will be the medium in the copper sulfate aqueous solution (tick one)?

☐ acidic ☐ close to neutral ☐ alkaline

A4. Write down the equations of the competing reactions observed upon interaction of copper(II) with ethylene diamine. Underline the prevailing process:

A5. Explain the reason behind the color change of the copper sulfate solution after addition of ethylene diamine solution. Tick the correct answer:

☐ Change of pH
☐ Formation of the precipitate
☐ Change of the coordination environment of copper
☐ Change of concentration of copper cations
☐ Completion of the redox reaction

A6. What is the coordination environment of copper in the initial and resultant solutions?

☐ octahedron ☐ square ☐ tetrahedron ☐cube

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Step 2. Dissolve the provided weighed amounts of 3.32 g of KI and 4.95 g of $Na_2S_2O_3 \cdot 5H_2O$ (in plastic bags) in 12 mL of water (preferably in the 250 mL beaker). With vigorously mixing, add the obtained solution to 20 mL of $CuSO_4 \cdot 5H_2O$ solution (as in Step 1) placed into a 50 mL beaker beforehand. Leave the precipitate formed for 15 min, then filter it off discarding the filtrate (the large-size funnel, the 9 cm diameter filter). You can collect the filtrate either in a beaker or in the conical flask.

Answer the questions (Part B)

B1. Write down the equation of the reaction observed at Step 2.

B2. Is it possible to obtain this poorly soluble compound in the same system without adding thiosulfate? Use the hereunder Latimer diagram (pH = 0) to answer this question.

$$Cu^{2+} \xrightarrow{0.16\ V} Cu^{+} \xrightarrow{0.52\ V} Cu$$

$$Cu^{2+} \xrightarrow{0.865\ V} CuI \xrightarrow{-0.185\ V} Cu$$

$$Cu^{2+} \xrightarrow{0.65\ V} CuBr \xrightarrow{0.03\ V} Cu$$

$$H_5IO_6 \xrightarrow{1.60\ V} IO_3^- \xrightarrow{1.85\ V} HIO \xrightarrow{1.44\ V} I_2 \xrightarrow{0.54\ V} I^-$$

$$SO_4^{2-} \xrightarrow{0.16\ V} H_2SO_3 \xrightarrow{0.40\ V} S_2O_3^{2-} \xrightarrow{0.60\ V} S \xrightarrow{0.14\ V} H_2S$$

Tick the correct variant: ☐ possible ☐ impossible

B3. What is the role of thiosulfate in this process (tick the correct answer)?

☐ oxidizing agent
☐ reducing agent
☐ ligand
☐ thiousulfate is needed to keep the pH constant

Step 3. Label the 250 mL beaker with the marker. Prepare the solution of 24 g of KI (in the zip-bag) in 30 mL of water in this beaker and transfer (as completely as possible) the precipitate obtained at Step 2 into it. Heat up the suspension to nearly boiling at the sand bath. You should observe complete dissolving of the precipitate (Solution 3).

Simultaneously bring the wash waters obtained at Step 1 (Solution 1) to boiling. With intense mixing, add this hot solution to the boiling Solution 3. You should immediately observe precipitation. Cool the obtained mixture down to room temperature (you can use tap water to cool the beaker). Filter off the precipitate (large-size funnel, 18 cm diameter filter), twice wash with chilled water (in the on-ice beaker, under the fume hood or central table) using less than 20 mL. Finally wash the precipitate with 20 mL of acetone (in a clear glass vial, to be shared by two students). Place the precipitate on the yet wet filter into the 150 or 250 mL beaker. Write down your student number on the beaker with the marker and deliver together with the Answer Sheets to your Lab assistant at the end of the exam.

Name _____ Student code _____

Part II. Analysis (separate determination of copper(I) and copper(II) in the complex compound)

You are expected to analyze the dry complex compound pre-synthesized by the Science Committee (each student is provided with an individual weighed amount).

1. Mesh with the glass rod the weighed amount of the complex compound placed in the 50 mL beaker with your student code, add 10 mL of 0.2 M HCl solution using the cylinder and keep mixing manually for about 5 min. Observe the color change of the solid phase.

2. Filter the suspension through the paper filter (9 cm diameter) collecting the filtrate into the 50 mL volumetric flask. Transfer the entire precipitate on the filter using ~5 mL of 0.2 M HCl solution. Wash the precipitate (containing CuI and dark admixtures) on the filter with several 1.5–2-mL portions of water. Collect the wash waters in the volumetric flask as well. If the filtrate becomes opaque, stop washing. The total volume of the filtrate must not exceed that of the volumetric flask. You will further use the precipitate for copper(I) determination.

3. Determination of copper(II). Bring the filtrate in the volumetric flask to the mark with water and mix. Take off a 10.0 mL aliquot, add 5 mL of 5 % KI solution (with the cylinder), about 1 mL of 1 M sulfuric acid (with 1 mL pipette), wait 3-5 min till CuI is precipitated and titrate with standard thiosulfate solution (0.025 M) till light straw-yellow color of the suspension. Then add few drops of 0.5 % starch solution till blue coloration appears and continue titrating till the first discoloration of the suspension.

Repeat titration as necessary.

Write down the titration results in the Table:

The burette reading, mL		Volume consumed for copper(II) titration, mL
V_1	V_2	

The accepted volume (copper(II) titration): _____ mL

Answer the questions (Part C)

C1. Write down the equation of the reaction of iodide oxidation with copper (II):

C2. Write down the equation of the reaction of iodine titration with thousulfate:

C3. Calculate the amount of copper (II) in the weighed amount:

$n(Cu^{2+})$, mol =

4. Determination of copper (I). Wash the precipitate on the filter with 1.8 M ammonia solution (in 1.5–2-mL portions) collecting the filtrate into the 50 mL volumetric flask. The total amount of the ammonia solution wash waters should be of about 30 mL. There should be only a small amount of the dark precipitate insoluble in ammonia (admixture) left on the filter. Bring the obtained solution to the mark with water in the flask.

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5. Transfer a 10.0 mL aliquot of the filtrate into the titration flask and neutralize it with the 5 M sulfuric acid from the drop bottle (the blue solution must turn into colorless or yellowish suspension upon neutralization). If needed, you can refill your drop bottle with 5 M sulfuric acid from the bottle located under the fume hood. Add 10 mL of water, and then 5 mL of 5 % KI solution. Titrate with thiosulfate as described above.

Write down the titration results into the Table:

The burette reading, mL		Volume consumed for copper(I) titration, mL
V_1	V_2	

The accepted volume (copper(I) titration): _____ mL

Answer the questions (Part D)

D1. Write down the equation of the reaction of copper(I) iodide dissolving in ammonia:

D2. Write down the equations of the copper involving reactions observed in the titration flask upon copper(I) determination:

1)

2)

D3. Calculate the amount of copper(I) in the weighed amount (mol):

$n(Cu^+)$, mol =

D4. Calculate the molar ratio of copper(I) and (II) in the starting complex compound:

$n(Cu^+) : n(Cu^{2+}) =$

D5. Propose equation of a possible reaction of complex compound dissolving in the diluted hydrochloric acid solution. Take into account possible formation of protonated copper complexes with ethylene diamine:

D6. Write down the reaction equations of interaction of the obtained compound with:

a) acidified potassium permanganate solution:

b) sodium sulfide solution:

When finished with the exam, deliver the Answer Sheets 4–8 and the product to your Lab Assistant.