

The 4th Metropolises Olympiad

Chemistry

Practical exam

September 3, 2019

Moscow, Russia

General directions

- **Lab safety:** follow the general rules accepted in chemistry labs; no eating or drinking in the lab.
- **Violation of lab safety rules:** you get one warning only; offend again: you are disqualified.
- **The exam includes two tasks:** on Analytical and Inorganic chemistry. You can start your work with any task.
- **Time:** 4 h 30 min to complete all the tasks. 30 min warning before the end.
- **When entering the lab** search for the table with your Student code.
- **Your student code:** get sure this is present on **every page**.
- **Use only the provided calculator, pen, and marker.**
- **Extra chemicals or glassware** needed? Ask your lab assistant (raise the colored “Help” card). No penalty for the first case. Each subsequent substitution will lead to a penalty of 1 point of 40 for the practical exam.
- **Questions** concerning safety, apparatus, chemicals, toilet break: **ask your lab assistant** (raise the colored “Help” card).
- **Chemical waste** carefully pour in the sink at your working place.
- **Answers:** only in the answer boxes in the booklet, nothing else will be graded. Relevant calculations have to be shown when asked for.
- Write down your answers only in the given **English or Russian version**. Use the version in your mother tongue for reading the text only.
- **After the stop signal:** put your booklet aside and leave it at your working place.
- **You must stop your work immediately after the stop signal has been given. A 2 min delay will result in zero points for the current task.**
- **During the Practical exam, some items of the glassware are expected to be used several times. Clean these carefully.**
- **This booklet with the tasks on Inorganic and Analytical chemistry and answer boxes: 16 pages** (incl. the cover sheet and Periodic table of elements).

Reagents

Reagent	Quantity	Placed in	Label
Task 1			
At every workplace			
Nickel chloride hexahydrate	7.14 g	Bottle with blue cap, 100 mL	NiCl ₂ ·6H ₂ O
Copper sulfate pentahydrate	5.00 g	Bottle with blue cap, 100 mL	CuSO ₄ ·5H ₂ O
Potassium iodide	3.50 g	Bottle with blue cap, 100 mL	KI (a)
Potassium iodide	3.50 g	Bottle with blue cap, 100 mL	KI (b)
Potassium iodide	28.00 g	Bottle with blue cap, 100 mL	KI (c)
Sodium thiosulfate pentahydrate	4.95 g	Bottle with blue cap, 100 mL	Na ₂ S ₂ O ₃ ·5H ₂ O (a)
Sodium thiosulfate pentahydrate	4.95 g	Bottle with blue cap, 100 mL	Na ₂ S ₂ O ₃ ·5H ₂ O (b)
Cobalt chloride hexahydrate	1.00 g	Weighing bottle, 15 mL	CoCl ₂ ·6H ₂ O
Potassium hexacyanoferrate(III)	1.40 g	Weighing bottle, 15 mL	K ₃ [Fe(CN) ₆]
At the table of common use			
1,2-ethylenediamine solution	500 mL	Volumetric flask and cylinder	NH ₂ CH ₂ CH ₂ NH ₂
Hydrogen peroxide solution	500 mL	Bottle and cylinder	H ₂ O ₂
Task 2			
At every workplace			
Weighted sample of the Cu ²⁺ и Ni ²⁺ salts	To be determined	Beaker, 25 mL	STUDENT CODE
Standard solution of potassium dichromate	0.0588g of salt	Volumetric flask, 100 mL	K ₂ Cr ₂ O ₇
Sodium thiosulfate solution	100 mL	Bottle with blue cap, 250 mL	Na ₂ S ₂ O ₃
Sulfuric acid, 2 M	80 mL	Bottle with blue cap, 100 mL	H ₂ SO ₄
Potassium iodide solution, 5%	150 mL	Bottle with blue cap, 250 mL	5% KI
Standard EDTA solution, 0.0500 M	80 mL	Bottle with blue cap, 100 mL	EDTA
Murexide indicator	5 g	Plastic centrifuge tube with screw cap	murexide
Starch, 1%	15 mL	Dropper, 30 mL	starch
Ammonium buffer solution, pH 10	15–20 mL	Dropper, 30 mL	buffer

Equipment and glassware

Item	Quantity
Tasks 1 and 2	
At every workplace	
Support stand with clamp(s) and burette clamp(s)	1
Magnetic stirrer with heating	1
Wash-bottle with distilled water	1
Permanent marker	1
Goggles	1
On the table of common use	
Gloves (choose the appropriate size)	
Paper towels	
Paper filters	
Task 1	
At every workplace	
Beaker, 100 mL	2
Beaker, 250 mL	2
Burette, 10 mL	1
Glass rod	1
Spatula	1
Cylinder, 100 mL	1
Funnel, d 75 mm	1
Piece of foil	1
Schott filter	1
Bunsen flask	1
Petri dish for products, labeled with Student code	2
Weighing bottle for products, labeled with Student code	2
Stirring bar	1
Crystallizing dish	1 for 2 part.
Magnet rod for removing stirring bar	1 for 2 part.
Task 2	
At every workplace	
Burette, 25 mL	1
Volumetric flask, 100 mL	1
Volumetric flask with potassium dichromate solution, 100 mL	1
Glass funnel, 36 mm (for filling the burette)	1
Beaker, 50 mL (for the burette)	1
Erlenmeyer flask (conical flat-bottom), 250 mL	2
Volumetric pipette, 10 mL	1
Cylinder, 10 mL	1
Cylinder, 50 mL	1
3-Way bulb	1
Watch glass, 80 mm	2
Piece of aluminum foil, 30×30 cm	2
Spoon-spatula (for murexide)	1

Task 1. Chemical kaleidoscope (20 marks)

Question	1	2	3	4	5	6	7	8	9	10	11	Total
Points	1	1	1	1	1	2	1	3	1	1	1	100
Result												
Question	12	13	14	15	16	17	18	19	20	21		
Points	1	4	1	3	1	2	25	8	16	25		
Result												

Kaleidoscope (from the Greek. Καλός - beautiful, εἶδος – form, shape, σκοπέω – to look to, to examine) is an optical instrument (a toy), most often in the form of a tube consisting of several mirrors located relative to each other at a certain angle, and colored glass. When the tube is rotated, colored pieces of glass are repeatedly reflected in the mirrors, thus creating changing symmetrical patterns.

Complex particles consist of a central atom and ligands similar to the "glass pieces of kaleidoscope." Changes in the mutual arrangement of the ligands in a particle and oxidation state of the central atom as well as replacement of the ligands result in modified color, solubility, and crystal shape in the resulting compound.

In this task, you will create different pictures of the chemical kaleidoscope.

Part 1

Place all the given sample of nickel chloride hexahydrate into a 250-mL beaker.

1. Calculate the volume of water that must be added to the given amount of the salt to prepare the 10.5 mass % solution. Measure the calculated amount and transfer into the beaker.

Calculation:

$$V(\text{H}_2\text{O}) = \text{_____ mL}$$

Note. If you fail with calculations, approach your lab assistant (raise the "Help" card) who will provide you with the required amount of water.

2. Calculate the volume of the 50 mass % aqueous 1,2-ethylenediamine solution (density of 0.99 g/mL) that must be added to the solution prepared in i. 1 to obtain the complex compound with the molar ratio Ni:en=1:3.

Calculation:

$$V = \text{_____ mL} \quad V + 10\% \text{ excess} = \text{_____ mL}$$

Note. If you fail with calculations, approach your lab assistant (raise the “Help” card) who will provide you with the required amount of the 1,2-ethylenediamine solution.

Once the nickel chloride hexahydrate is completely dissolved in water (mind the solution color change), add with stirring the 1,2-ethylenediamine solution in a 10 % excess (as compared to the calculated value) to the prepared solution. Observe the change of the solution color (solution 1).

3. Write down equation of the reaction between nickel(II) ions and 1,2-ethylenediamine in the aqueous solution:

4. Write down equation of the reaction of 1,2-ethylenediamine dissolution in water:

5. Write down equation of the reaction of nickel chloride dissolution in water:

6. Write down equations of the competing reactions occurring when aqueous solutions of nickel chloride and 1,2-ethylenediamine are mixed. Underline the prevailing process.

7. Why did the color of the nickel chloride solution change upon addition of the ethylenediamine solution? Tick the correct answer:

- the pH value changed
- a precipitate was formed
- the coordination sphere of nickel changed
- the concentration of nickel ions changed
- a redox reaction occurred

8. Sometimes emergencies at chemical plants make a real threat to the environment. Suppose a mixture of approximately equal amounts of ethylenediamine and ammonia has been discharged into a river. Nickel cations were added to bind the pollutants, still in the amount allowing complete binding of either entire ethylenediamine or entire ammonia.

A) Which of the substances will be mostly retained in the aqueous solution?

- ethylenediamine
- ammonia
- ethylenediamine and ammonia in comparable amounts

B) The above result is due to:

- a higher stability of the ethylenediamine complex
- a higher stability of the ammonia complex
- approximately equal stability of both complexes

C) The above ratio of the complexes stability is observed because:

- the central atom in the complex particles has the same coordination number
- the ions have the same coloration
- the central atom is surrounded by the atoms of the same element
- the chelate cycle is formed
- the central atom is situated in the same polyhedron
- the coordination number of the central atom in the complex particles is different.

Part 2

In a 100-mL beaker, dissolve the given amount of potassium iodide (KI (a)) in 10 mL of water (solutions 2). Add 1/3 of the solution 1 to the prepared solution 2, mix and place on ice to initiate

crystallization (solution 3). Then remove the beaker containing the solution from the ice and store at room temperature for crystallization. In not less than 30 minutes, filter off the precipitate formed in the solution 3 through the Schott filter (ask your lab assistant to switch on the vacuum line). Wash the precipitate with 5 mL of water. Transfer the obtained crystals into the weighing bottle I labeled with your student code.

9. Write down equation of the reaction occurring in this part of the task:

10. If the same crystallization were conducted at 0°C, the precipitate would contain several crystal types. Write down the chemical formula of the major admixture.

Part 3

In a 100-mL beaker, dissolve the given amount of sodium thiosulfate pentahydrate in 10 mL of water (solution 4). Add with mixing $\frac{1}{2}$ of the remaining amount of the solution 1 to the prepared solution 4. Filter off the formed precipitate using the paper filter. Wash the precipitate with 5 mL of distilled water. Transfer the precipitate on the filter into the Petri dish I labeled with your student code.

11. Write down equation of the reaction occurring in this part of the synthesis:

12. Compare the colors of the obtained precipitates. Draw the chemical formula of the ion responsible for the coloration of the complexes:

Part 4

In a 100-mL beaker, dissolve the given amount of copper sulfate pentahydrate in 20 mL of water (solution 5). In the other 100-mL beaker, dissolve the given amounts of (KI (b)) and sodium

thiosulfate pentahydrate in 10 mL of water (solution 6). Add with mixing the solution 6 to the solution 5. Let the formed precipitate 7 stand for 5 minutes.

With mixing and heating at the magnetic stirrer, add the weighed amount of (KI (c)) to the suspension containing the precipitate 7 (solution 8). Continue heating up to nearly boiling, still avoid boiling! (it is recommended to adjust the heating regulator at “4” or “5”).

Caution! Hot solution and hot magnetic stirrer plate!

In parallel, heat the remaining part of the solution 1 up to nearly boiling. Add with mixing and heating the hot solution 1 to the solution 8.

Caution! Hot solutions! Use rubber fingerstalls when pouring the hot solution.

Let the solution cool down. Filter off the formed precipitate using the paper filter and wash 3 times with ~5 mL portions of distilled water. Transfer the precipitate on the filter into the Petri dish II labeled with your student code.

13. Write down equation of the reaction occurring in this part of the synthesis:

14. Draw the chemical formula of the particle responsible for the coloration of the solution 8.

Part 5

In a 100-mL beaker, dissolve the given amount of cobalt chloride hexahydrate in 5 mL of water. Once the dissolution complete (mind the solution coloration), add with mixing 3 mL of 50% 1,2-ethylenediamine solution. Observe the color change (solution 9).

Fill the 10-mL burette with 2 mL of the H_2O_2 solution. Cover the beaker containing the solution 9 with the piece of aluminum foil; make a hole for the burette tip in the center of the foil. Adjust the burette so that its tip is below the foil, still does not touch the solution. With stirring at the magnetic stirrer, add dropwise 1 mL of the hydrogen peroxide solution to the beaker (add every new drop only once the reaction with the preceding one is complete). Then keep the prepared solution 10 boiling for 10 minutes with the foil over the beaker.

Caution! Hot solution! Splashing and gas evolution possible!

Cool down the solution. In the other 100-mL beaker, dissolve the given amount of potassium hexacyanoferrate(III) in 5 mL of water (solution 11). Add the solution 11 to the solution 10, place the beaker into the crystallizing dish with ice and let it stand for 10-20 minutes. Filter off the obtained crystals under reduced pressure (ask your lab assistant to switch on the vacuum line). Wash the precipitate with 5 mL of distilled water.

Transfer the prepared precipitate into a 100-mL beaker, add 10 mL of water, cover with foil and heat with mixing up to nearly boiling. Do not boil the solution! Cool the solution down to room temperature, and then continue cooling in the crystallizing dish with ice. Filter off the obtained precipitate under reduced pressure (ask your lab assistant to switch on the vacuum line) and transfer the product into the weighing bottle II labelled with your student code.

15. Write down equations of the reactions occurring in this part of the task:

16. Tick the hydrogen peroxide role:

- medium
- catalyst
- oxidizing agent
- reducing agent
- acid
- base

17. Draw all isomers of the cobalt-containing particle.

18-21. Leave the prepared precipitates placed in the weighing bottles and Petri dishes labelled with your student code at your workplace.

Task 2. Cupronickel (20 marks)

Question	a	b	c	d	e	f	g	h	i	j	k	Total
Points	17	30	20	3	2	1	3	2	5	5	2	90
Result												

You are expected to titrimetrically determine the copper and nickel content in the given mixture of the metal salts. The total content of the metals in the sample can be found by complexometric titration, whereas that of copper by substitutive redox titration.

Standardization of thiosulfate solution with potassium dichromate

Add distilled water to the concentrated dichromate solution in volumetric flask. Bring up to the mark and mix well. Use the prepared potassium dichromate solution for standardization of sodium thiosulfate.

Fill the burette with sodium thiosulfate solution using the funnel. Transfer with the volumetric pipette a 10.0 mL aliquot of the potassium dichromate solution into a 250-mL conical flask. Add 10 mL of 2M H₂SO₄ and 20 mL of 5% KI using appropriate cylinders. Cover the flask with the watch glass, wrap with a piece of aluminum foil and keep the flask covered for 5 minutes. Add approximately 20 mL of water to the flask. Titrate the prepared mixture with the thiosulfate solution swirling the flask constantly until pale-yellow coloration. Then add 3 drops of 1% starch solution (**don't stir the starch solution**) and continue titrating with agitation until purple-grey coloration disappears. Repeat the titration as needed to attain reproducible results (the number of titrations is not graded).

Note: you are provided with dry and clean burettes and pipettes. Do not spend the solutions for rinsing the glassware.

a. Write down the volumes of thiosulfate solution used for titration of the standard potassium dichromate solution:

Titration number	V _{init} , mL	V _{final} , mL	V ₁ , mL
1			
2			
3			
Your accepted volume V ₁ , mL:			

Preparation of the sample solution for determination of metals

Ask your lab assistant for the sample labeled with your student code. Transfer the sample quantitatively into the **empty** 100-mL graduated flask. Add distilled water to dissolve the sample completely. Bring up to the mark with water and mix thoroughly.

Determination of copper content in the sample

Rinse the volumetric pipette with distilled water. Transfer with the volumetric pipette a 10.0 mL aliquot of the prepared sample solution into 250-mL conical flask. Add 5 mL of 2M H₂SO₄ and 20 mL of 5% KI using the appropriate cylinders. Cover the flask with the watch glass and wrap with the piece of aluminum foil. Keep the flask covered for 5 minutes. Add approximately 20 mL of water to the flask. Titrate the suspension with the standard thiosulfate solution swirling the flask constantly until pale-yellow coloration. Then add 5 drops of 1% starch solution and continue titrating with agitation until the purple-grey coloration disappears and does not come back for at least 30 seconds.

Repeat the titration as needed to attain reproducible results (the number of titrations is not graded).

b. Write down the volumes of thiosulfate solution used for sample solution titration:

Titration number	V _{init} , mL	V _{final} , mL	V ₂ , mL
1			
2			
3			
Your accepted volume V ₂ , mL:			

Determination of the total content of copper and nickel in the sample

Wash the burette with distilled water and rinse with a small portion of the EDTA solution. Fill the burette with the same EDTA solution. Transfer with the volumetric pipette a 10.0 mL aliquot of the sample solution into a 250-mL conical flask. Add approximately 20 mL of distilled water and 30–40 mg of murexide indicator using the spatula (one full spoon), mix thoroughly. Make sure the intense yellow color is achieved. Start titrating the prepared solution with the standard EDTA solution until the light-green color of the solution appears. Then add 15 drops of the ammonium buffer solution and continue titrating till blue or purple coloration. Repeat the titration as needed to attain reproducible results (the number of titrations is not graded).

c. Write down the volumes of the EDTA solution used for the sample solution titration:

Titration number	V_{init} , mL	V_{final} , mL	V_3 , mL
1			
2			
3			
Your accepted volume V_3 , mL:			

d. Write down the balanced equations of the reactions: 1) between potassium dichromate and potassium iodide under experiment conditions; 2) upon titration with sodium thiosulfate:

1)
2)

e. Propose the side reactions taking place, if the iodometric titration is conducted in 1) alkali media; 2) highly acidic media:

1)
2)

f. Write down the balanced equation(s) of the reaction(s) taking place upon addition of potassium iodide to the aliquot of the sample solution:

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g. Calculate the concentrations of the standard potassium dichromate and sodium thiosulfate solutions (use the titration results):

$$c(\text{K}_2\text{Cr}_2\text{O}_7) = \quad \text{mol}\cdot\text{L}^{-1}$$

$$c(\text{Na}_2\text{S}_2\text{O}_3) = \quad \text{mol}\cdot\text{L}^{-1}$$

h. Calculate the mass of copper (mg) in the given sample (use the titration results):

$$m(\text{Cu}) = \quad \text{mg}$$

i. Calculate the mass of ammonium chloride and the volume of 25% ammonia solution (density of $0.907 \text{ g}\cdot\text{mL}^{-1}$) to prepare 1 L of a buffer solution with pH 10 and total content of the components of $1 \text{ mol}\cdot\text{L}^{-1}$. $\text{p}K_b(\text{NH}_3) = 4.76$.

$$m(\text{NH}_4\text{Cl}) = \quad \text{g}$$

$$V(\text{NH}_3) = \quad \text{mL}$$

j. Determine the dominating form of ethylenediaminetetraacetic acid (H_4Y) at pH 10 and calculate the corresponding mole fraction. Acidity constants of H_4Y : $K_1 = 1.02\cdot 10^{-2}$, $K_2 = 2.14\cdot 10^{-3}$, $K_3 = 6.92\cdot 10^{-7}$, $K_4 = 5.50\cdot 10^{-11}$.

$$n = \underline{\hspace{2cm}}$$

$$\alpha (\text{H}_n\text{Y}^{-(n-4)}) = \underline{\hspace{2cm}} \%$$

k. Calculate the mass of nickel (mg) in the given sample (use the titration results):

$$m(\text{Ni}) = \underline{\hspace{2cm}} \text{ mg}$$

Periodic table with relative atomic masses

1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -