The 3rd Metropolises Olympiad

Chemistry

Practical exam

September 4, 2018

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. 15 min for reading the set before you start to work.
- **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.**
- **Answers:** only in the answer boxes in the booklet, nothing else will be graded. Relevant calculations have to be shown when asked for.
- **Use only the calculator provided.**
- **More chemicals** needed? Ask your lab assistant. No penalty for this.
- **Questions** concerning safety, apparatus, chemicals, toilet break: **ask your lab assistant.**
- **Chemical waste** carefully pour in the sink at your working place.
- **Official English version: available** on request **for clarification only.** Ask your lab assistant.
- **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.**
- **Booklet with the tasks on Inorganic and Analytical chemistry and answer boxes:** 14 pages (incl. the cover sheet and Periodic table of elements).

Reagents

Reagent	Quantity	Placed in	Label
Task 1, at every workplace			
Potassium dichromate	10 g	Bottle with blue cap, 50 mL	$K_2Cr_2O_7$
Hydrochloric acid, concentrated	47 mL	Bottle with blue cap, 50 mL	HCl
Ethanol	11 mL	Bottle with blue cap, 50 mL	C_2H_5OH 11 ml
	20 mL	Bottle with blue cap, 50 mL	C_2H_5OH 20 ml
Zink, granules	175 g	Bottle with blue cap, 50 mL	Zn
Ammonia aqueous solution	250 mL	Bottle with blue cap, 250 mL	NH_3aq
Ammonium chloride	72 g	Bottle with blue cap, 250 mL	NH_4Cl
Task 2			
At every workplace			
Weighted sample of the complex	To be determined	Beaker, 25 mL	STUDENT CODE
Standard solution of cerium(IV) sulfate	50 mL	Bottle with blue cap, 50 mL	Ce^{4+} 0.0094 M
Hydrogen peroxide, 0.1%	50 mL	Bottle with blue cap, 50 mL	H_2O_2
Sulfuric acid, 2 M	100 mL	Bottle with blue cap, 100 mL	H_2SO_4
Mohr's salt solution	100 mL	Bottle with blue cap, 250 mL	Mohr's salt
Potassium hydroxide, 0.1 M	50 mL	Bottle with blue cap, 50 mL	KOH
Sodium hydroxide, standard solutin	100 mL	Bottle with blue cap, 100 mL	NaOH 0.0119 M
Per two participants			
Phenylanthranilic acid	20 mL	Dropper	PAA
Phenolphthalein	20 mL	Dropper	Phenolphthalein
Manganese dioxide (MnO_2), suspension	40 mL	Dropper	MnO_2
On the table of common use			
Formaldehyde (20%)	250 mL	Bottle with blue cap, 250 mL	HCHO (20%)

Glassware and equipment

Item	Quantity
Tasks 1 and 2	
At every workplace	
Support stand with two clamps, ring and burette clamp	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	
Task 1	
At every workplace	
Reflux condenser	1
Crystallizing dish	1
Separatory funnel	1
Adaptor for separatory funnel	1
Petry dish with your Student code	1
Glass rod	1
Spoon-spatula	1
Round-bottom flask, 500 mL	1
Funnel, 100 mm with your Student code	1
Funnel, 75 mm	1
Beakers, 600 mL with numbers and your Student code	3 (I, II, III)
Tube with charcoal	1
Piece of foil	1
Filter paper	2
On the table of common use	
Adaptor with Bunsen valve	
Squeezers	
Balances	
Under the fume hood of common use	
Support stand with rings for filtration	
Air blower with glass tubes for the solution bubbling	
Task 2, at every workplace	
Burette, 25 mL	1
Volumetric flask, 100 mL	1
Glass funnel, 36 mm (for filling the burette)	1
Beaker, 25 mL (under the burette and for formaldehyde)	1
Erlenmeyer flask (conical, flat-bottom), 250 mL	2
Graduated pipette, 10 mL	2
Cylinder, 10 mL	2
Cylinder, 50 mL	1
Red pipette filler (3-way bulb)	1
Watch glass	2
Fingertips to handle hot glassware and foil	3

Student code _____

Task 1. Multicolor chromium (12 marks).

Question	a	b	c	d	e	f	Total
Points	4	4	10	2	28	2	50
Result							

Long time ago, in 1797, the Frenchman Nicolas-Louis Vauquelin discovered a new element in a mineral mined in Ural Mountains region, Russia. The mineral, crocoite $PbCrO_4$, was also called «Siberian red lead», «red lead-ore». The element found in it, chromium, got its name due to variety of colors found in its compounds (Greek χρῶμα - colour). Doing this task you will enjoy discovering the amazing and diverse world of chromium complex compounds.

Procedure

1. Carefully check the reagents and glassware located at your workplace.

2. Place the bottle with the concentrated ammonia solution and the 600 ml beaker labeled **"participant code – I"** into the crystallizing dish (1, hereunder the numbers refer to fig. 1 and 2). Fill the crystallizing dish with ice. Place ammonium chloride into the beaker.

3. Fix the round-bottom flask (3) on the stand (2). Fix the reflux condenser (4) on the stand over the round-bottom flask (adjust its position so that it can easily enter the flask), but do not insert it into the flask! The distance between the flask and condenser should be such that you can easily place the 75 mm funnel into the flask. Take the hose attached to the lower joint (inlet) of the condenser and connect it to the tap water source. Direct the other hose into the sink. Open the water tap **slowly and carefully**. Make the water flow moderate.

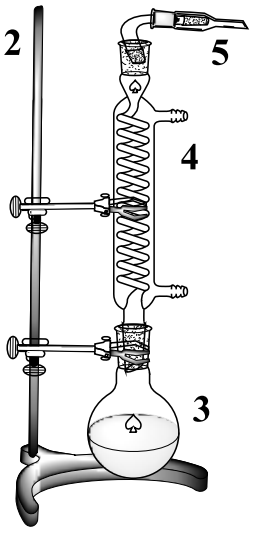

Fig 1. Apparatus for the first synthesis step
2 – support stand,
3 – round-bottom flask,
4 – reflux condenser,
5 – tube with charcoal

4. Place the given portion of potassium dichromate into the round-bottom flask (3) through the funnel. Remove the funnel and insert the reflux condenser (4) into the flask (3) leaving a small gap between the pieces of glassware. Pour through the condenser the given portion of the concentrated hydrochloric acid first, and then that of ethanol labeled **«C_2H_5OH 11 ml».** Once all the ethanol is introduced into the flask, immediately insert the reflux condenser into the flask and attach the tube with charcoal (5) to the upper end of the condenser as shown in fig, 1. Both add the alcohol and fit the condenser to the flask as fast as possible, since the reaction is exothermic and accompanied by the release of highly volatile substances and gases. The reaction is completed once the reaction mixture color changes to green. As soon as all the gaseous products are condensed in the flask, remove the tube with charcoal, remove the reflux condenser, turn off the water supply and disconnect the hose from the tap water source. Place free ends of both hoses into the sink. Slightly cool down the flask under tap water (down to relatively high temperature, still bearable to hand) and fix it back on the stand.

a. Write down equation of the reaction proceeding and the formula of the complex particle formed.

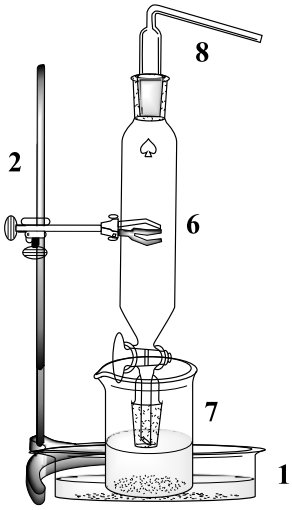

Fig. 2. Apparatus for the second synthesis step
1 – crystallizing dish,
2 – support stand,
6 – separatory funnel,
7 – beaker,
8 – adapter with Bunsen valve

5. Assemble the apparatus for the second synthesis step (fig. 2). Place all the given granulated zinc into the separatory funnel (6). Fix the funnel on the stand (2) over the beaker (7, labeled **"participant code – I"**) situated in the crystallizing dish (1) with ice. Using the 75 mm funnel,

transfer the solution obtained at the first synthesis step into the separatory funnel (6). To ensure complete transfer of the obtained compound, add 14 ml of water to the round-bottom flask (3) and pour out the obtained solution into the separatory funnel (6). (**Attention!** Measure water by using the **50** ml graduated cylinder **only**). Attach the Bunsen valve (8, overpressure relief valve). Deliver the round-bottom flask (3) to your laboratory assistant.

Attention! The Bunsen valves are located on the table of common use. Start doing this part of the protocol only when you get sure that there is a Bunsen valve available.

Wait till the reaction is complete, which can be distinguished by the reaction mixture color change from green to intensive light-blue.

b. Write down the equation of the reaction proceeding and the formula of the complex particle formed at this synthesis step.

6. As soon as the light-blue color of the solution is stabilized, carefully pour the chilled ammonia solution into the beaker containing ammonium chloride. Cover the beaker using the piece of foil with a hole; fix the foil pressing it by hand. Place the tip of the separatory funnel into the beaker through the foil hole. Get sure that the tip is immersed into the ammonia solution so that the liquid from the funnel enters the solution having no contact with air. However, avoid the contact of the funnel tip with the ammonium chloride crystals. Open the stopcock of the separatory funnel to mix the solutions. Lift up the Bunsen valve to let the solution pour out. P**erform all the subsequent steps under fume hood only.** Do not stir the beaker contents! Decant the supernatant liquid into the other beaker labeled **"participant code – II"**. Cover the latter beaker with foil. Place the glass tube into the beaker through the hole in foil and blow air through the mixture to bring the reaction to completion, which is manifested by the solution color change to dark-red as well as by pink fine crystal precipitate formation. Do not continue air blowing for more than 20 min. Deliver the beaker labeled **"participant code – I"** to your lab assistant.

The complex cation of the reaction product can be presented by two identical high symmetry polyhedra with a common vertex. The coordination environment of the central atom includes ligands of two types of: of the first type (one ligand), which is oxygen-containing (charged bridged ligand); and of the second type, which are molecular ligands. Beside the

counterions, the compound includes uncharged particles increasing the oxygen content by a factor 2. Long-term storage is accompanied by slow disappearance of the uncharged particles from the substance you have received.

c. Write down the equations of the proceeding reactions and the formulae of the complex particles formed at these synthesis steps. Draw the structural formula of the complex cation of the final reaction product.

7. Prepare a paper filter for the 100 mm funnel. When the reaction is completed, filter the obtained precipitate into the beaker labeled **"participant code-III"**. Wash the precipitate with alcohol (labeled "**C_2H_5OH 20 ml**") and place the filter with the product into the Petri dish labeled with your student code.

d. Weigh the filter with the product and write down the value.

Mass of the Petri dish with the filter and the product = _____ g

Mass of the Petri dish = _____ g

Mass of the filter with the product = _____ g

Deliver the Petri dish with the product and the beaker labeled **"participant code – III"** to your lab assistant.

e. Your product will be dried by the organizers and then re-weighted, whereas its quality will be checked spectrophotometrically.

f. Calculate the approximate value of the reaction yield using the determined mass of the filter with the reaction product and knowing that the mass of the initial potassium dichromate was 10 g. Assume that the mass of the wet filter is 10 g.

Calculation: Yield = _____ %

Task 2. Rhodochromium chloride analysis (20 marks).

Question	a	b	c	d	e	f	g	h	i	Total
Points	5	22	12	1	3	1	2	3	1	**50**
Result										

In this task you are expected to determine the chromium and ammonia content in rhodochromium chloride by titrimetric method. The sample of rhodochromium chloride for analysis was synthesized for you in advance in order to avoid interference between your titration results with those of the inorganic part (task 1). Ask your lab assistant for your sample of rhodochromium chloride. Transfer it quantitatively from the 25-mL beaker labeled with your student code into the 100-mL graduated flask and dissolve in distilled water in the presence of your lab assistant. Make sure the sample is dissolved completely. Bring up to the mark with distilled water and mix thoroughly.

Standardization of ammonium iron (II) sulphate (Mohr's Salt) with cerium (IV) sulfate

Fill the burette with the Mohr's salt solution using the funnel. Transfer with the 10-mL volumetric pipette a 5.0 mL aliquot of the cerium sulfate solution into the conical flask. Add with the cylinder 10 mL of 2M H_2SO_4 solution and 3 drops of indicator – phenylanthranilic acid. Wait till the reddish-brown color of solution appears. Titrate the prepared mixture with the Mohr's salt solution swirling the flask constantly. Repeat the titration until the coverage of 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 Mohr's salt solution used for titration of the standard cerium (IV) sulfate solution:

Titration number	$V_{initial}$, mL	V_{final}, mL	V_1, mL
1			
2			
3			
Your accepted volume, $V_{1,\,acc}$, mL:			

Determination of chromium content in rhodochromium chloride

Pipette a 10.0 mL aliquot of the prepared solution with another 10-mL volumetric pipette into the conical flask. Add 10 mL of 0.1M KOH, cover the flask with the watch glass and heat it on the hot-plate until the discoloration of the mixture and appearance of flocculent precipitate (adjust the left regulator of the hot-plate to «4»). Avoid excessive boiling. Remove the conical flask from the hot-plate. **Attention! Take off the gloves and use the fingertips!** Rinse the watch glass with distilled water.

Add with the cylinder 10 mL of 0.1% H_2O_2 to the warm solution in the conical flask. Swirl the flask, cover it with the watch glass and continue heating (adjust the hot-plate regulator to «5»). Bring the mixture to boiling, keep heating for other 5 min and then remove the conical flask from the hot-plate. **Attention! Use the fingertips!** Rinse the drops from the watch glass with distilled water into the flask. Add 5-10 drops of MnO_2 suspension (shake the suspension in the dropper before use). If the color of the solution did not turn into light-grey and there is no precipitate formed at the bottom of the flask, add a few more drops of MnO_2 suspension. Wait for 2-3 min swirling the flask from time to time. Add with the cylinder 10 mL of 2M H_2SO_4 solution and 3-4 drops of phenylanthranilic acid. Swirl the flask and wait till the reddish-brown color of solution appears (~ 1-2 min). Titrate the mixture with the Mohr's salt solution constantly swirling the flask until the color changes to grey-yellow. Repeat the titration as necessary.

b. Write down the volumes of the Mohr's salt solution used for titration:

Titration number	$V_{initial}$, mL	V_{final}, mL	V_2, mL
1			
2			
3			
Your accepted volume, $V_{2,\,acc}$, mL:			

Determination of ammonium in rhodochromium chloride

The formaldehyde method is among the most precise ones used for determination of ammonia salts. The ammonium cation reacts with formaldehyde with the formation of weak base – hexamethylentetramine (urotropin, $(CH_2)_6N_4$) and strong acid. The acid is then determined by direct titration with standard sodium hydroxide in the presence of phenolphthalein. The admixture of formic acid in the formaldehyde is excluded by preliminary titration of formaldehyde solution with standard sodium hydroxide solution.

Thoroughly wash the burette with distilled water and rinse with standard NaOH solution. Then fill the burette with the same NaOH solution. Pipette a 10.0 mL aliquot of the rhodochromium chloride solution into the conical flask. Add with the cylinder 10 mL of distilled water, cover the flask with the watch glass and heat it on the hot-plate until discoloration of the mixture and appearance of flocculent precipitate (adjust the left regulator of the hot-plate to «4»). Avoid excessive boiling. Remove the conical flask from the hot-plate. Cool the conical flask to room temperature.

Pour 5 mL of 20% formaldehyde from the 250-mL bottle on the table of common use into clean 25-mL beaker and add 2-3 drops of phenolphthalein indicator. Add dropwise the NaOH solution from the burete to the mixture in the beaker until the first indication of the light pink color appears.

Add the neutralized formaldehyde solution into the conical flask cooled down to room temperature and add 2-3 drops of phenolphthalein indicator. Swirl the flask and leave for 2-3 min. Titrate the mixture with the standard NaOH solution. Repeat the titration as necessary.

c. Write down the volumes of the sodium hydroxide solution used for titration:

Titration number	$V_{initial}$, mL	V_{final}, mL	V_3, mL
1			
2			
3			
Your accepted volume, $V_{3,\,acc}$, mL:			

d. Write down the reaction equation occurring upon heating of the complex solution (you have defined the formula in task 1) with potassium hydroxide:

e. Write down the reaction equations behind chromium determination occurring upon: 1) addition of hydrogen peroxide to the solution obtained after the decomposition of the complex, 2) heating of the mixture, 3) addition of sulfuric acid:

1. 2. 3.

f. Write down the reaction equation occurring upon standardization of the Mohr's salt by cerium (IV) sulphate solution. Calculate the concentration of the Mohr's salt (mol/L) from the titration results:

$c\ (Fe^{2+})$ = ____ mol/L

g. Write down the reaction occurring upon titration of the product of reaction 3 in question **e** with Mohr's salt. Calculate the concentration of chromium (mol/L):

c (Cr) = ____ mol/L

h. Write down the reactions of: 1) decomposition of rhodochromium chloride in a neutral medium, 2) interaction of ammonium salt with formaldehyde. Calculate the concentration of ammonium cation in mol/ L in the solution of rhodochromium chloride according to the formaldehyde method:

1.

2.

$c\ (NH_4^+)$ = ____ mol/L

i. Determine the ratio of ammonia and chromium in the given sample and the mass of the sample:

Cr : NH_3 = __ : __

m = ____ g

Student code _____

The Periodic table of elements 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 -