



## 48<sup>th</sup> International Chemistry Olympiad

# Practical Part I.

26 July 2016  
Tbilisi, Georgia

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# Instructions

- Begin only when the **START** command is given. The exam contains two parts. You have 100 minutes to work on Part I (Task 1). After this you will have to leave the lab for 30 minutes.
- Part I of the exam (Task 1) contains **5** pages, its answer sheets have **3** pages.
- Follow the safety rules announced in the preparatory tasks. You get one warning for violations. On the second warning you will get disqualified.
- Wear your lab coat and safety goggles while in the lab. Ask your lab assistant for the gloves of your size when you need them.
- Use only the pen, marker pen and calculator provided. Do not write with the marker on paper; use it only to label glass or plastic labware.
- Make sure that your student code is on every answer sheet.
- All answers must be written in the appropriate boxes on the answer sheet. Anything written elsewhere will not be graded. Use the reverse of the exam sheets if you need scratch paper.
- You have no access to sinks in the lab. You are provided with a sufficient quantity of labware. Only a few items need to be used again. Wash these carefully with an appropriate solvent into the waste container. Use the brush if needed. Distilled water and paper tissues are freely available.
- Liquid waste is to be put into the container labeled "LIQUID WASTE". Do not put rubbish (tissues, plastic, etc.) in this container, but into the waste baskets in the lab.
- Chemicals and labware are not supposed to be refilled or replaced. Each such incident (other than the first in the entire exam, which you will be allowed) will result in the loss of 1 point from your 40 practical points.
- Raise your hand if you have a safety question or you need a restroom break or drinking water.
- When you have finished this part of the examination, put your answer sheet into the envelope provided and leave it on the table. Do not seal the envelope. You will not have further access to the answer sheets from this part.
- You must stop your work immediately when the **STOP** command is given. A delay in doing this may lead to cancellation of your exam. Do not leave your place until permitted by the lab assistants. You can keep the task text.
- The official English version of this examination is available on request only for clarification.

# Labware

Item	Quantity
<b>All tasks, on the table of common use</b>	
Latex gloves of different sizes, choose your size	-
<b>General equipment for all tasks, for each student, on the table</b>	
Test tube rack (60 holes)	1
Paper tissue (can ask for extra)	5
Permanent marker	1
Glass stirring rod, 20 cm	1
Polypropylene funnel, diam. 3.5 cm	1
Soft plastic cup	3
Strong plastic cup	1
<b>All tasks, for each student in the soft plastic cup</b>	
Caps for polystyrene test tubes	22
<b>Task 1, for each student, on the table</b>	
Rack for centrifuge tubes (21 holes)	1
Container with a screw cap for waste, 1 dm <sup>3</sup> , labeled "Liquid Waste, Test 1"	1
Paper filters in zip-bag	5
<b>Task 1, for each student, in the strong plastic cup</b>	
Pasteur pipettes	20
<b>Task 1, for each student, in the 60-hole rack</b>	
Polystyrene test tubes, 10 cm <sup>3</sup>	35

# Chemicals

Name	State	Conc.	Q-ty	Placed in	Labeled
<b>All tasks, for each student, on the table</b>					
Distilled water	Liquid	-	1 dm <sup>3</sup>	Wash bottle, 1 dm <sup>3</sup>	H <sub>2</sub> O dist.
<b>Task 1, for each student, on the table</b>					
Hexane	Liquid	-	25 cm <sup>3</sup>	Glass bottle with screw cap, 50 cm <sup>3</sup>	Hexane
Sodium hydroxide	Aqueous solution	1 M	80 cm <sup>3</sup>	Amber plastic bottle with screw cap, 125 cm <sup>3</sup>	NaOH
Nitric acid*	Aqueous solution	2 M	150 cm <sup>3</sup>	Glass bottle with dropper cap, 250 cm <sup>3</sup>	HNO <sub>3</sub>
<b>Task 1, for each student, in the 21-hole rack</b>					
5 unknowns	Aqueous solution	-	45 cm <sup>3</sup>	Centrifuge tubes, 50 cm <sup>3</sup>	Unknown No ___
Silver nitrate	Aqueous solution	0.1 M	25 cm <sup>3</sup>	Centrifuge tube, 50 cm <sup>3</sup>	AgNO <sub>3</sub>
Aluminium sulfate	Aqueous solution	0.3 M	25 cm <sup>3</sup>	Centrifuge tube, 50 cm <sup>3</sup>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
Barium nitrate	Aqueous solution	0.25 M	25 cm <sup>3</sup>	Centrifuge tube, 50 cm <sup>3</sup>	Ba(NO <sub>3</sub> ) <sub>2</sub>
Iron(III) nitrate	Aqueous acidic (HNO <sub>3</sub> ) solution	0.2 M	25 cm <sup>3</sup>	Centrifuge tube, 50 cm <sup>3</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub>
Potassium iodide	Aqueous solution	0.1 M	25 cm <sup>3</sup>	Centrifuge tube, 50 cm <sup>3</sup>	KI
Potassium iodate	Aqueous solution	0.1 M	25 cm <sup>3</sup>	Centrifuge tube, 50 cm <sup>3</sup>	KIO <sub>3</sub>
Magnesium chloride	Aqueous solution	0.2 M	25 cm <sup>3</sup>	Centrifuge tube, 50 cm <sup>3</sup>	MgCl <sub>2</sub>
Sodium carbonate	Aqueous solution	0.2 M	25 cm <sup>3</sup>	Centrifuge tube, 50 cm <sup>3</sup>	Na <sub>2</sub> CO <sub>3</sub>
Sodium sulfite	Aqueous solution	0.2 M	25 cm <sup>3</sup>	Centrifuge tube, 50 cm <sup>3</sup>	Na <sub>2</sub> SO <sub>3</sub>
Ammonia*	Aqueous solution	1 M	25 cm <sup>3</sup>	Centrifuge tube, 50 cm <sup>3</sup>	NH <sub>3</sub> (aq)

\* Nitric acid and ammonia solutions are needed in a subsequent task.

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# Task 1

You have 10 different compounds dissolved in water in 5 unknown solutions. Each numbered container contains two of the following compounds in aqueous solution (every compound is used, and each compound is used only once):

$\text{AgNO}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{KI}$ ,  $\text{KIO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{MgCl}_2$ ,  $\text{NH}_3$

You are given  $\text{HNO}_3$  solution,  $\text{NaOH}$  solution, hexane and the aqueous solutions of the 10 pure compounds listed above.

You can use empty test tubes and any of the liquids provided (including the unknowns) to identify the unknown samples. A funnel and filter paper can be used for separation.

Identify the compounds in the solutions **1-5**. Give the number of the solution that contains the individual compounds on the answer sheet. Indicate two observations caused by a chemical reaction for each compound in your unknown mixtures by giving the letter code of the appropriate observation (choose one or more from the list), and write appropriate balanced ionic equation(s) that explain the observation. At least one of the reactions has to be specific for clearly identifying the compound from this selection of unknowns.

Note: After the STOP signal close all the centrifuge test tubes containing the unknown mixtures with the blue caps labeled with the student code and leave these in the rack.



# 48<sup>th</sup> International Chemistry Olympiad

## Practical Part I.

### Answer Sheets

26 July 2016

Tbilisi, Georgia

**Task 1****13% of the total**

7	7	7	7	7	7	7	7	7	7	Sum: 70

Only fill out this table when you are ready with all your assignments. Use the following observation codes:

A - Formation of white precipitate  
 B - Formation of colored precipitate  
 (red, brown, yellow, black etc.)  
 C - Dissolution of precipitate  
 D - Color change in the solution  
 E - Formation of colored solution

F - Brown color in the organic phase  
 G - Purple color in the organic phase  
 H - Formation of colored gas  
 I - Formation of colorless and odorless gas  
 J - Formation of colorless and odorous gas  
 K - Change in the color of precipitate

Compound	No. of unknown	Formula of reaction partner(s)	Observation code(s)	Balanced net ionic equation(s)
NH <sub>3</sub>				
Fe(NO <sub>3</sub> ) <sub>3</sub>				
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>				
AgNO <sub>3</sub>				
KIO <sub>3</sub>				

Compound	No. of unknown	Formula of reaction partner(s)	Observation code(s)	Balanced net ionic equation(s)
Na <sub>2</sub> CO <sub>3</sub>				
MgCl <sub>2</sub>				
Na <sub>2</sub> SO <sub>3</sub>				
Ba(NO <sub>3</sub> ) <sub>2</sub>				
KI				

Replacements:

Item	Quantity	Lab assistant's signature	Student's signature





## 48<sup>th</sup> International Chemistry Olympiad

# Practical Part II.

26 July 2016  
Tbilisi, Georgia

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# Instructions

- You have a 15 minute reading time before you start work. Begin reading only when the START command is given.
- Follow the safety rules announced in the preparatory tasks. You get one warning for violations. On the second warning you will get disqualified.
- Wear your lab coat and safety goggles while in the lab. Ask your lab assistant for the gloves of your size when you need them.
- Use only the pen, marker pen and calculator provided. Do not write with the marker on paper; use it only to label glass or plastic labware.
- Make sure that your student code is on every answer sheet.
- All answers must be written in the appropriate boxes on the answer sheet. Anything written elsewhere will not be graded. Use the reverse of the exam sheets if you need scratch paper.
- You have no access to sinks in the lab. You are provided with a sufficient quantity of labware. Only a few items need to be used again. Wash these carefully with appropriate solvent into the waste container. Use the brush if needed. Distilled water and paper tissues are freely available.
- Liquid waste is to be put into the container labeled "LIQUID WASTE". Do not put rubbish (tissues, plastic, etc.) in this container, but
- Chemicals and labware are not supposed to be refilled or replaced. Each such incident (other than the first in the entire exam, which you will be allowed) will result in the loss of 1 point from your 40 practical points.
- Raise your hand if you have a safety question or you need a restroom break or drinking water.
- When you have finished the examination, put your answer sheet into the envelope provided and leave it on the table. Do not seal the envelope.
- You must stop your work immediately when the STOP command is given. A delay in doing this may lead to cancellation of your exam. Do not leave your place until permitted by the lab assistants. You can keep the task text.
- The official English version of this examination is available on request only for clarification.

## Instructions specific for Part II

- The working time for Part II (Task 2 and 3) is 200 minutes.
- Start Part II with Task 2. When you are ready to start with Task 3, tell the lab assistant, and you will receive the chemicals and labware for Task 3. Reagents for Task 2 will be taken away from you at this point.
- Part II of the exam (Task 2-3) contains 10 pages, its answer sheets have 6 pages.
- Ask the lab assistants when you need your alcohol lamp lighted. Heat only glass test tubes. Close the alcohol lamp with the cap when finished.

# Labware

Item	Quantity
<b>General equipment for all tasks, for each student, on the table</b>	
Test tube rack (60 holes)	1
Paper tissue	5
Permanent marker	1
Glass stirring rod, 20 cm	1
Polypropylene funnel, diam. 3.5 cm	1
Soft plastic cups	3
Strong plastic cup	1
Caps for polystyrene test tubes	22
<b>Tasks 2 and 3, for each student, on the table</b>	
Container with a screw cap for waste, 3 dm <sup>3</sup> , labeled "Liquid Waste, Tests 2&3"	1
<b>Task 2, for each student, on the table</b>	
Storage box labeled "Task 2"	1
Laboratory stand with double burette clamp	1
Burette, 25.00 cm <sup>3</sup>	2
Graduated pipette, 10.0 cm <sup>3</sup>	1
Graduated pipette, 1.00 cm <sup>3</sup>	1
Bulb (Mohr) pipette, 10.00 cm <sup>3</sup>	1
Erlenmeyer flask, 100 cm <sup>3</sup>	2
Graduated cylinder, 10.0 cm <sup>3</sup>	2
Brush	1
Polypropylene funnel, 5.5 cm	1
<b>Task 2, for each student, in the storage box "Task 2"</b>	
Polystyrene test tubes, 10 cm <sup>3</sup>	8
Pipette filler	1
Pasteur pipettes for indicators	2
<b>Task 3, for each student, get from the lab assistants</b>	
Storage box labeled "Task 3"	1
<b>Task 3, for each student, in the storage box "Task 3"</b>	
Polystyrene test tubes, 10 cm <sup>3</sup>	20
Alcohol lamp	1
Test tube holders, wooden	1
Glass test tubes	10
Pasteur pipettes	10
Strong plastic cup	1

# Chemicals

Name	State	Conc.	Q-ty	Placed in	Labeled
<b>Task 2, for each student, on the table</b>					
Nitric acid	Aqueous solution	2 M	.*	Glass bottle with dropper cap, 250 cm <sup>3</sup>	HNO <sub>3</sub>
<b>Task 2, for each student, in the storage box "Task 2"</b>					
Water sample solution	Aqueous solution	To be determined	100 cm <sup>3</sup>	Glass bottle with screw cap, 100 cm <sup>3</sup>	Water sample
Sodium fluoride	Aqueous solution	9 mg/dm <sup>3</sup> in fluoride	50 cm <sup>3</sup>	Glass bottle with screw cap, 50 cm <sup>3</sup>	F <sup>-</sup> , 9 mg/dm <sup>3</sup>
Zirconyl Alizarin indicator	Acidic aqueous solutions	0.055% ZrOCl <sub>2</sub> , 0.028% Alizarin Red S	10 cm <sup>3</sup>	Glass bottle with screw cap, 25 cm <sup>3</sup>	Zirconyl Alizarin
Sodium chloride	Aqueous solution	0.0500 M	50 cm <sup>3</sup>	Glass bottle with screw cap, 50 cm <sup>3</sup>	NaCl, 0.0500 M
Ammonium iron(III) sulfate dodecahydrate	Aqueous acidic solution	20 g/dm <sup>3</sup>	10 cm <sup>3</sup>	Dropper, 15 cm <sup>3</sup>	Fe <sup>3+</sup> ind.
Silver nitrate	Aqueous solution	To be determined	200 cm <sup>3</sup>	Amber glass bottle, 250 cm <sup>3</sup>	AgNO <sub>3</sub>
Ammonium thiocyanate	Aqueous solution	See exact concentration on the label	100 cm <sup>3</sup>	Glass bottle with screw cap, 100 cm <sup>3</sup>	NH <sub>4</sub> SCN, X.XXXX M
Potassium chromate	Aqueous solution	10%	5 cm <sup>3</sup>	Dropper, 15 cm <sup>3</sup>	K <sub>2</sub> CrO <sub>4</sub>
<b>Task 3, for each student, on the table</b>					
Ethanol	Liquid	95 %	150 cm <sup>3</sup>	Glass bottle with dropper cup, 250 cm <sup>3</sup>	C <sub>2</sub> H <sub>5</sub> OH
<b>Task 3, for each student, in the storage box "Task 3"</b>					
Organic unknowns 1 to 8	Liquid	-	0.5 cm <sup>3</sup>	Syringes, 2 cm <sup>3</sup>	1 to 8
Potassium permanganate	Aqueous solution	0.13 %	5 cm <sup>3</sup>	Amber glass bottle, 50 cm <sup>3</sup>	KMnO <sub>4</sub>
Ammonium cerium(IV) nitrate reagent	2.0 M HNO <sub>3</sub> aqueous solution	28.6 %	5 cm <sup>3</sup>	HDPE bottle, 30 cm <sup>3</sup>	Ce(IV)
Acetonitrile	Liquid	-	45 cm <sup>3</sup>	Glass bottle, 50 cm <sup>3</sup>	CH <sub>3</sub> CN

Name	State	Conc.	Q-ty	Placed in	Labeled
2,4-Dinitrophenylhydrazine reagent	Sulfuric acid solution in aqueous ethanol	3 %	20 cm <sup>3</sup>	HDPE bottle, 30 cm <sup>3</sup>	DNPH
Iron(III) chloride	0.5 M HCl aqueous solution	2.5 %	1 cm <sup>3</sup>	HDPE bottle, 30 cm <sup>3</sup>	FeCl <sub>3</sub>
Hydroxylamine hydrochloride	Ethanolic solution	0.5 M	10 cm <sup>3</sup>	HDPE bottle, 30 cm <sup>3</sup>	NH <sub>2</sub> OH× HCl
Sodium hydroxide	Aqueous solution	6 M	5 cm <sup>3</sup>	HDPE bottle, 30 cm <sup>3</sup>	NaOH
Hydrochloric acid	Aqueous solution	1 M	25 cm <sup>3</sup>	HDPE bottle, 30 cm <sup>3</sup>	HCl

\*In the quantity left after doing Task 1.

### Periodic table with relative atomic masses

1 H 1.008																	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 -																														
<table border="1"> <tbody> <tr> <td>57 La 138.9</td> <td>58 Ce 140.1</td> <td>59 Pr 140.9</td> <td>60 Nd 144.2</td> <td>61 Pm -</td> <td>62 Sm 150.4</td> <td>63 Eu 152.0</td> <td>64 Gd 157.3</td> <td>65 Tb 158.9</td> <td>66 Dy 162.5</td> <td>67 Ho 164.9</td> <td>68 Er 167.3</td> <td>69 Tm 168.9</td> <td>70 Yb 173.0</td> <td>71 Lu 175.0</td> </tr> <tr> <td>89 Ac -</td> <td>90 Th 232.0</td> <td>91 Pa 231.0</td> <td>92 U 238.0</td> <td>93 Np -</td> <td>94 Pu -</td> <td>95 Am -</td> <td>96 Cm -</td> <td>97 Bk -</td> <td>98 Cf -</td> <td>99 Es -</td> <td>100 Fm -</td> <td>101 Md -</td> <td>102 No -</td> <td>103 Lr -</td> </tr> </tbody> </table>																		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 -
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 -																																	

# Task 2

## Determination of fluoride and chloride content in mineral water

Georgia is world famous for its splendid mineral waters. Many of these are used to cure various diseases. Manufacturers have to carefully control the ionic composition of waters, fluoride and chloride being among the most important ions.

### Visual colorimetric detection of fluoride

The method of fluoride determination is based on the decrease in the color intensity of zirconium(IV)-Alizarin Red S complex in the presence of fluoride ions due to formation of a more stable colorless complex. The equilibrium is achieved in about 20 minutes after the reagent addition. The fluoride concentration is determined visually by comparing the color developed in the sample with those in the calibration solutions.

Transfer  $9.0 \text{ cm}^3$  of mineral water from the sample into the plastic test tube labeled "X".

Calculate how much of the  $9.0 \text{ mg/dm}^3$  standard fluoride solution you will need to prepare a set of calibration solutions with the following fluoride ion content: 0.0; 1.0; 2.0; 3.5; 5.0; 6.5; 8.0  $\text{mg/dm}^3$  (calculate for  $9.0 \text{ cm}^3$  of each solution).

Using the  $1.0 \text{ cm}^3$  and  $10.0 \text{ cm}^3$  graduated pipettes, add the calculated amounts of the standard fluoride solution to the test-tubes, then add  $1.0 \text{ cm}^3$  of Zirconyl Alizarin indicator into each test tube, and bring the volume in each calibration test tube to the  $10.0 \text{ cm}^3$  mark with distilled water (the mark is shown in the figure with the arrow).



**2.1.1.** Report the fluoride volumes used in your dilutions.

Mix the obtained solutions in the test tubes. Set the tube rack aside for at least 20 minutes.

**2.1.2.** Compare the color of the sample and the calibration solutions looking on them from the top down and from the front. Select the concentration of the standard that is closest to the fluoride concentration of the water sample.

Note: the rack with the test tubes will be photographed by the lab staff after the whole exam is finished.

## Standardization of silver nitrate solution by the Mohr method

Transfer  $10.0 \text{ cm}^3$  of the standard  $0.0500 \text{ mol/dm}^3$  NaCl solution into an Erlenmeyer flask using the bulb (Mohr) pipette. Add approximately  $20 \text{ cm}^3$  of distilled water and 10 drops of 10% aqueous  $\text{K}_2\text{CrO}_4$  solution.

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Fill a burette with the silver nitrate solution. Titrate the contents of the flask with the silver nitrate solution while vigorously mixing the solution containing the precipitate formed. The final titrant drops are added slowly with vigorous swirling of the flask. The titration is complete when the faint color change visible on titrant addition does not disappear in the pure yellow suspension. Take the final burette reading. Repeat the titration as necessary.

- 2.2.1. Report your volumes on the answer sheet.
- 2.2.2. Write balanced chemical equations for the titration of NaCl with AgNO<sub>3</sub> and for the end-point indication reaction.
- 2.2.3. Calculate the concentration of the AgNO<sub>3</sub> solution from your measurement.
- 2.2.4. The Mohr titration method requires a neutral medium. Write down equations for the interfering reactions that take place at lower and at higher pH.

### Chloride determination by the Volhard method

Wash the bulb (Mohr) pipette with distilled water. Wash the Erlenmeyer flasks first with a small portion of the ammonia solution left over from Task 1 to help removing the silver salt precipitate and then with distilled water. (In case you used up all the ammonia solution in the first task, you can get a refill without penalty.)

Transfer a 10.0 cm<sup>3</sup> aliquot of the mineral water from the sample into an Erlenmeyer flask using the bulb (Mohr) pipette. Add 5 cm<sup>3</sup> of 2 mol/dm<sup>3</sup> nitric acid using a graduated cylinder. Add 20.00 cm<sup>3</sup> of the silver nitrate solution from the burette and mix well the suspension. Add appr. 2 cm<sup>3</sup> of the indicator (Fe<sup>3+</sup>) solution with the Pasteur pipette.

Fill the second burette with the standard ammonium thiocyanate solution (see the exact concentration on the label). Titrate the suspension with this solution while vigorously swirling. At the end point one drop produces a faint brown color that is stable even after intense mixing. Take the final burette reading. Repeat the titration as necessary.

Note. The AgCl precipitate exchanges Cl<sup>-</sup> ions with SCN<sup>-</sup> ions from the solution. If you titrate too slowly or with breaks, the brown color disappears with time, and too much titrant is spent for the titration. Therefore when approaching the endpoint you should add the titrant at a *constant* slow rate swirling the flask *constantly* so that the suspension would stay white. The appearance of faint brown color will mean reaching the endpoint.

- 2.3.1. Report your volumes on the answer sheet.
- 2.3.2. Write down balanced chemical equations for the back titration with NH<sub>4</sub>SCN and that for the end-point indication reaction.
- 2.3.3. Calculate the chloride concentration (in mg/dm<sup>3</sup>) in the water sample from your measurements.
- 2.3.4. If Br<sup>-</sup>, I<sup>-</sup>, and F<sup>-</sup> ions are present in the sample in addition to chloride, the concentration of which ion(s) will contribute to the result of the Volhard titration?

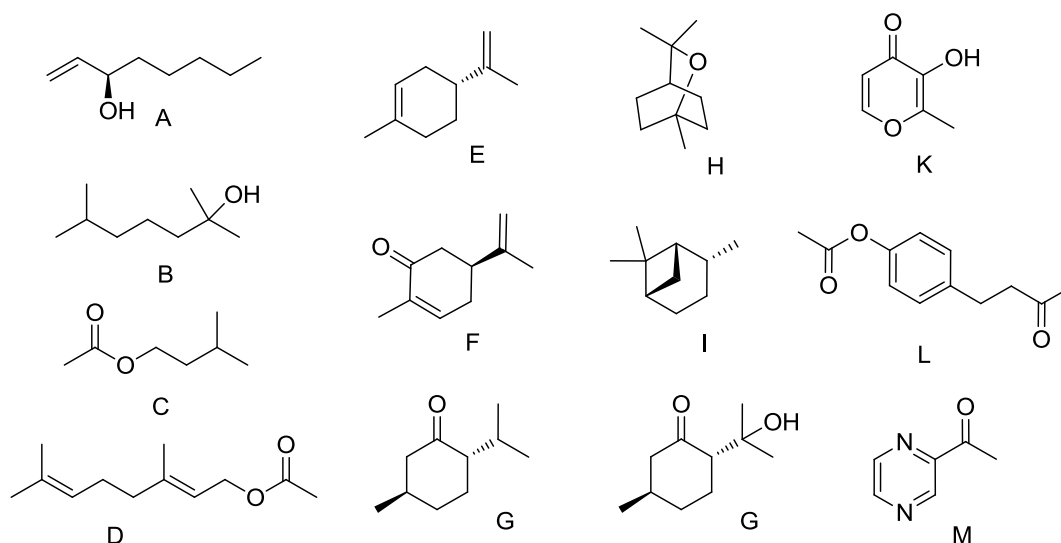
- 
- 2.3.5.** When trying to determine the concentration of  $\text{Cl}^-$  in the presence of other halides, an analyst added some potassium iodate and sulfuric acid to the sample and boiled the solution. Afterwards he reduced the excess of iodate to iodine by boiling the sample with phosphorous acid  $\text{H}_3\text{PO}_3$ . What interfering anions were removed by this operation? Write the chemical equations for the reactions of these ions with iodate.



# Task 3

## Identifying flavors and fragrances

Tourists coming to Georgia admire many specialties, local cuisine occupying one of the top positions in the list of adventures. Excellent meat, fresh vegetables and greens, ripe fruits, home-made jams... What else is needed to satisfy true gourmets? Of course, unique flavors and fragrances!



You are given 8 samples of unknown organic compounds (labeled 1 to 8), which are industrially used as flavors and fragrances. All samples are pure individual compounds. Their possible structures are found among **A-M** given here.

The organic compounds in your unknown samples are readily soluble in ether, and insoluble in dilute aqueous NaOH and HCl. These compounds, but the unknown No. 6, are insoluble in water, the latter being slightly soluble ( $3.5 \text{ g/dm}^3$ ).

- 3.1.** Perform test reactions described below to identify the samples **1-8**. Indicate the results of the tests by giving the letter code of the appropriate observation (choose one or more from the list). Fill in all cells of the table. Use + and - to indicate positive and negative tests.
- 3.2.** Identify the unknowns based on the test results and the information given above. Write the structure codes (of **A** to **M**) of the identified samples in the appropriate box.

## Test procedures

### KMnO<sub>4</sub> test (Baeyer test)

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Place appr. 1 cm<sup>3</sup> of 95% ethyl alcohol in a plastic test tube and add 1 drop of an unknown. Add 1 drop of KMnO<sub>4</sub> solution and shake the mixture. Treat the test as positive if the permanganate color disappears immediately after shaking.

3.3. Write the reaction scheme for a positive Baeyer test with one of the compounds **A-M**.

### **Cerium(IV) nitrate test**

Place 2 drops of the **Ce(IV) reagent** into a glass test tube, add 2 drops of acetonitrile and then 2 drops of an unknown (the sequence is important!). Shake the mixture. In the case of positive test the mixture color promptly changes from yellow to orange-red.

Note 1. Use only glass test tubes to perform the test. In case you need to wash the glass test tubes, carefully choose the appropriate solvent. Use caps to prevent the strong odor.

Note 2. Comparison with blank (no unknown) and reference (with ethanol) tests is recommended for adequate interpretation.

Note 3. Ce(IV) ions initially form brightly colored coordination compounds with alcohols. Complexes formed from primary or secondary alcohols react further (within 15 seconds to 1 hour) with the disappearance of the color.

### **2,4-dinitrophenylhydrazine (2,4-DNPH) test**

Add only 1 drop of an unknown to 1 cm<sup>3</sup> of 95% ethanol in a plastic test tube. Add 1 cm<sup>3</sup> of the DNPH reagent to the prepared solution. Shake the mixture and let it stand for 1-2 min. Observe formation of yellow to orange-red precipitate if the test is positive.

3.4. Write the reaction scheme for a positive 2,4-DNPH test with one of the compounds **A-M**.

### **Ferric hydroxamate test**

Ask a lab assistant to light up your alcohol lamp. Mix 1 cm<sup>3</sup> of 0.5 mol/dm<sup>3</sup> ethanolic hydroxylamine hydrochloride solution with 5 drops of 6 mol/dm<sup>3</sup> sodium hydroxide aqueous solution in a glass test tube. Add 1 drop of an unknown and use the alcohol lamp to heat the mixture to boiling while gently swirling the test tube to avoid splashes of the reaction mixture. Allow it to cool down slightly and add 2 cm<sup>3</sup> of 1 mol/dm<sup>3</sup> HCl solution. Add 1 drop of 2.5% iron(III) chloride solution. Observe appearance of magenta color if the test is positive. Close the alcohol lamp with the cap when finished.

Note 1. Use glass test tubes only to perform the test; use the test tube holder when heating. In case you need to wash the glass test tubes, use an appropriate solvent. Use caps to prevent the strong odor.

Note 2. Fe(III) ions form a colored 1:1 complex with hydroxamic acids (R-CO-NHOH).

3.5. Write the reaction scheme for a positive ferric hydroxamate test with one of the compounds **A-M**.

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Note: After the STOP signal reattach the corresponding needles on the syringes with the unknown compounds, and place them into the plastic cup and leave them on the table.



# 48<sup>th</sup> International Chemistry Olympiad

## Practical Part II.

### Answer Sheets

26 July 2016

Tbilisi, Georgia

**Task 2****14% of the total**

2.1.1	2.1.2	2.2.1	2.2.2	2.2.3	2.2.4	2.3.1	2.3.2	2.3.3	2.3.4	2.3.5	Sum
2	15	30	2	2	2	30	2	4	2	4	95

2.1.1. Report the fluoride volumes used in your dilutions.

F <sup>-</sup> content (mg/dm <sup>3</sup> )	0.0	1.0	2.0	3.5	5.0	6.5	8.0
Calculated volume of F <sup>-</sup> solution (cm <sup>3</sup> )							

2.1.2. Circle the concentration of the standard that is closest to the fluoride concentration of the water sample.

F <sup>-</sup> content (mg/dm <sup>3</sup> )	0.0	1.0	2.0	3.5	5.0	6.5	8.0
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2.2.1. Report your titration volumes.

Titration no.	1	2				
Initial burette reading, cm <sup>3</sup>						
Final burette reading, cm <sup>3</sup>						
Volume spent, cm <sup>3</sup>						

Your accepted volume,  $V_1$ :                      cm<sup>3</sup>

2.2.2. Write a balanced chemical equation for the titration of NaCl with AgNO<sub>3</sub> and that for the end-point indication reaction.

Titration reaction:

Indication reaction:

2.2.3. Calculate the concentration of the AgNO<sub>3</sub> solution from your measurement.

Your work:

$c(\text{Ag}^+)$ :

**2.2.4.** The Mohr titration method requires a neutral medium. Write equations for the interfering reactions that take place at lower and at higher pH.

Low pH:

High pH:

**2.3.1.** Report your volumes on the answer sheet.

Titration no.	1	2				
Initial burette reading, cm <sup>3</sup>						
Final burette reading, cm <sup>3</sup>						
Volume spent, cm <sup>3</sup>						

Your accepted volume,  $V_2$ :                      cm<sup>3</sup>

**2.3.2.** Write a balanced chemical equation for the back titration with NH<sub>4</sub>SCN and that for the end-point indication reaction.

Titration reaction:

Indication reaction:

**2.3.3.** Calculate the chloride concentration (in mg/dm<sup>3</sup>) in the water sample from your measurements.

Your work:

$c(\text{Cl}^-)$ :                      mg/dm<sup>3</sup>

2.3.4. If Br<sup>-</sup>, I<sup>-</sup>, and F<sup>-</sup> ions are present in the sample in addition to chloride, the concentration of which ion(s) will contribute to the result of the Volhard titration? Tick the appropriate box(es).

Br<sup>-</sup>       I<sup>-</sup>       F<sup>-</sup>       none

2.3.5. When trying to determine the concentration of Cl<sup>-</sup> in the presence of other halogens, an analyst added some potassium iodate and sulfuric acid to the sample and boiled the solution. Afterwards he reduced the excess of iodate to iodine by boiling the sample with phosphorous acid H<sub>3</sub>PO<sub>3</sub>. What interfering anions were removed by this operation?

Br<sup>-</sup>       I<sup>-</sup>       F<sup>-</sup>       none

Write the reaction equations of these ions with iodate.

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Replacements:

Item	Quantity	Lab assistant's signature	Student's signature

**Task 3****13% of the total**

<b>3.1.</b>	<b>3.2.</b>	<b>3.3.</b>	<b>3.4.</b>	<b>3.5.</b>	Sum
32	16	4	4	4	60

**3.1.** Indicate the results and observations of tests by giving the letter codes of the appropriate observations in the table. Fill in all cells of the table. Use + and - to indicate positive and negative tests. Choose one or more codes from the list below.

**I** - Immediate disappearance of purple color

**II** - Slow disappearance of purple color

**III** - Disappearance of yellow color

**IV** - Formation of a brown or black precipitate

**V** - Formation of a white precipitate

**VI** - Formation of a yellow or orange-red precipitate

**VII** - Appearance of orange or red color in solution

**VIII** - Appearance of magenta color

**IX** - The unknown compound is insoluble in ethanol

**X** - no visible changes

Sample No.	1	2	3	4	5	6	7	8
Baeyer test result (+/-)								
Baeyer test observations (I-X)								
Ce(IV) nitrate test result (+/-)								
Ce(IV) nitrate test observations (I-X)								
2,4-DNPH test result (+/-)								
2,4-DNPH test observations (I-X)								
Fe(III) hydroxamate test result (+/-)								
Fe(III) hydroxamate test observations (I-X)								

**3.2.** Write the structure codes (of **A** to **M**) of the identified samples in the appropriate boxes when you are certain in your assignments.



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Sample No.	1	2	3	4	5	6	7	8
<b>Structure code</b>								

3.3. Write the reaction scheme for a positive Baeyer test with one of the compounds **A-M**.

3.4. Write the reaction scheme for a positive 2,4-DNPH test with one of the compounds **A-M**.

3.5. Write the reaction scheme for a positive ferric hydroxamate test with one of the compounds **A-M**.