48th International
Chemistry Olympiad

Practical Tasks
Part I.

26 July 2016

Tbilisi, Georgia

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
All tasks, on the table of common use	
Latex gloves of different sizes, choose your size	-
General equipment for all tasks, for each student, on the table	
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
All tasks, for each student in the soft plastic cup	
Caps for polystyrene test tubes	22
Task 1, for each student, on the table	
Rack for centrifuge tubes (21 holes)	1
Container with a screw cap for waste,1 dm^3, labeled “Liquid Waste, Test 1”	1
Paper filters in zip-bag	5
Task 1, for each student, in the strong plastic cup	
Pasteur pipettes	20
Task 1, for each student, in the 60-hole rack	
Polystyrene test tubes, 10 cm^3	35

Chemicals

Name	State	Conc.	Q-ty	Placed in	Labeled
All tasks, for each student, on the table					
Distilled water	Liquid	-	1 dm^3	Wash bottle, 1 dm^3	H_2O dist.
Task 1, for each student, on the table					
Hexane	Liquid	-	25 cm^3	Glass bottle with screw cap, 50 cm^3	Hexane
Sodium hydroxide	Aqueous solution	1 M	80 cm^3	Amber plastic bottle with screw cap, 125 cm^3	NaOH
Nitric acid*	Aqueous solution	2 M	150 cm^3	Glass bottle with dropper cap, 250 cm^3	HNO_3
Task 1, for each student, in the 21-hole rack					
5 unknowns	Aqueous solution	-	45 cm^3	Centrifuge tubes, 50 cm^3	Unknown No ___
Silver nitrate	Aqueous solution	0.1 M	25 cm^3	Centrifuge tube, 50 cm^3	$AgNO_3$
Aluminium sulfate	Aqueous solution	0.3 M	25 cm^3	Centrifuge tube, 50 cm^3	$Al_2(SO_4)_3$
Barium nitrate	Aqueous solution	0.25 M	25 cm^3	Centrifuge tube, 50 cm^3	$Ba(NO_3)_2$
Iron(III) nitrate	Aqueous acidic (HNO_3) solution	0.2 M	25 cm^3	Centrifuge tube, 50 cm^3	$Fe(NO_3)_3$
Potassium iodide	Aqueous solution	0.1 M	25 cm^3	Centrifuge tube, 50 cm^3	KI
Potassium iodate	Aqueous solution	0.1 M	25 cm^3	Centrifuge tube, 50 cm^3	KIO_3
Magnesium chloride	Aqueous solution	0.2 M	25 cm^3	Centrifuge tube, 50 cm^3	$MgCl_2$
Sodium carbonate	Aqueous solution	0.2 M	25 cm^3	Centrifuge tube, 50 cm^3	Na_2CO_3
Sodium sulfite	Aqueous solution	0.2 M	25 cm^3	Centrifuge tube, 50 cm^3	Na_2SO_3
Ammonia*	Aqueous solution	1 M	25 cm^3	Centrifuge tube, 50 cm^3	$NH_3(aq)$

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

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):

$AgNO_3$, $Al_2(SO_4)_3$, $Ba(NO_3)_2$, $Fe(NO_3)_3$, KI, KIO_3, Na_2CO_3, Na_2SO_3, $MgCl_2$, NH_3

You are given HNO_3 solution, 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.

<u>Identify</u> the compounds in the solutions **1**-**5**. <u>Give</u> the number of the solution that contains the individual compounds on the answer sheet. <u>Indicate two observations</u> 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 <u>write appropriate balanced ionic equation(s)</u> 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.

48th International Chemistry Olympiad

Practical Tasks 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_3				
$Fe(NO_3)_3$				
$Al_2(SO_4)_3$				
$AgNO_3$				
KIO_3				

Compound	No. of unknown	Formula of reaction partner(s)	Observation code(s)	Balanced net ionic equation(s)
Na_2CO_3				
$MgCl_2$				
Na_2SO_3				
$Ba(NO_3)_2$				
KI				

Replacements:

Item	Quantity	Lab assistant's signature	Student's signature

5p for locating each compound, 1 p for each relevant equation. Altogether 10x7p.

Subpoints for 1p: 0.4p for correct observation with appropriate reagent(s); 0.6p for the relevant balanced ionic equation (-0.1p for minor typos; maximum of -0.3p for poor balancing; maximum of 0.3p for an equation in other than ionic form)

The unknowns are identical mixtures for every student in different order. Most are mixed in 1:1 ratio by volume.

Characteristic reactions are marked with bold letters. One of these or equivalent has to be shown on the answer sheet.

NH_3

$AgNO_3$, B)	$2\ Ag^+ + 2\ OH^- = Ag_2O + H_2O$ *(if Ag^+ is not mixed with Fe^{3+})*
C)	$Ag_2O + H_2O + 4\ NH_3 = 2\ [Ag(NH_3)_2]^+ + 2\ OH^-$ *(if Ag^+ is not with Fe^{3+})*
$Fe(NO_3)_3$, B)	**$Fe^{3+} + 3\ OH^- = Fe(OH)_3$**
$Al_2(SO_4)_3$, A)	**$Al^{3+} + 3OH^- = Al(OH)_3$ (or $[Al(H_2O)_6]^{3+} + 3\ OH^- = Al(OH)_3 + 6\ H_2O$)**
$MgCl_2$, A)	**$Mg^{2+} + 2\ OH^- = Mg(OH)_2$**
NaOH, J)	**$NH_4^+ + OH^- = NH_3 + H_2O$**
(KIO_3) + $AgNO_3$, C)	**$AgIO_3 + 2\ NH_3 = [Ag(NH_3)_2]^+ + IO_3^-$**

$Fe(NO_3)_3$

NaOH, B)	**$Fe^{3+} + 3\ OH^- = Fe(OH)_3$**
NH_3, B)	**$Fe^{3+} + 3\ OH^- = Fe(OH)_3$**
KI, D) or E)	**$2\ Fe^{3+} + 2\ I^- = 2\ Fe^{2+} + I_2$**
$MgCl_2$, E)	**$Fe^{3+} + Cl^- = [FeCl]^{2+}$ (or $Fe^{3+} + 3\ Cl^- = FeCl_3$ etc.)**

$Al_2(SO_4)_3$

NaOH, A)	$Al^{3+} + 3\ OH^- = Al(OH)_3$ (or $[Al(H_2O)_6]^{3+} + 3\ OH^- = Al(OH)_3 + 6\ H_2O$)
C)	**$Al(OH)_3 + OH^- = [Al(OH)_4]^-$**
(NaOH +) HNO_3 A)	**$[Al(OH)_4]^- + H^+ = Al(OH)_3 + H_2O$**
$Ba(NO_3)_2$, A)	**$Ba^{2+} + SO_4^{2-} = BaSO_4$**
Na_2CO_3, A)	$Al^{3+} + 3\ OH^- = Al(OH)_3$ (or $[Al(H_2O)_6]^{3+} + 3\ OH^- = Al(OH)_3 + 6\ H_2O$)

$AgNO_3$

$NaOH$, B)	**$2\ Ag^+ + 2\ OH^- = Ag_2O + H_2O$**
KI, B)	**$Ag^+ + I^- = AgI$**
NH_3, B)	$2\ Ag^+ + 2\ OH^- = Ag_2O + H_2O$ *(if* Ag^+ *is not mixed with* Fe^{3+}*)*
C)	$Ag_2O + H_2O + 4\ NH_3 = 2\ [Ag(NH_3)_2]^+ + 2\ OH^-$ *(if* Ag^+ *is not with* Fe^{3+}*)*
$MgCl_2$, A)	**$Ag^+ + Cl^- = AgCl$**
Na_2CO_3, A) or B)	$2\ Ag^+ + CO_3^{2-} = Ag_2CO_3$
Na_2SO_3, A)	$2\ Ag^+ + SO_3^{2-} = Ag_2SO_3$
C)	**$Ag_2SO_3 + 3\ SO_3^{2-} = 2\ [Ag(SO_3)_2]^{3-}$**
KIO_3, A)	$Ag^+ + IO_3^- = AgIO_3$

KIO_3

$Na_2SO_3 + HNO_3$, B) or E) (+ hexane, G)	**$5\ SO_3^{2-} + 2\ IO_3^- + 2\ H^+ = I_2 + 5\ SO_4^{2-} + H_2O$**
$KI + HNO_3$, B) or E) (+ hexane, G)	**$5\ I^- + IO_3^- + 6\ H^+ = 3\ I_2 + 3\ H_2O$**
$AgNO_3$, A)	$Ag^+ + IO_3^- = AgIO_3$
$Ba(NO_3)_2$, A)	$Ba^{2+} + 2\ IO_3^- = Ba(IO_3)_2$

Na_2CO_3

HNO_3, I)	**$CO_3^{2-} + 2\ H^+ = H_2O + CO_2$**
$Ba(NO_3)_2$, A)	$Ba^{2+} + CO_3^{2-} = BaCO_3$
$+ HNO_3$, C), I)	**$BaCO_3 + 2\ H^+ = Ba^{2+} + H_2O + CO_2$**
$AgNO_3$, A) or B)	$2\ Ag^+ + CO_3^{2-} = Ag_2CO_3$
$+ HNO_3$, C), I)	**$Ag_2CO_3 + 2\ H^+ = 2\ Ag^+ + H_2O + CO_2$**
$MgCl_2$, A)	$Mg^{2+} + CO_3^{2-} = MgCO_3$
$+ HNO_3$, C), I)	**$MgCO_3 + 2\ H^+ = Mg^{2+} + H_2O + CO_2$**

$MgCl_2$

$NaOH$, A)	**$Mg^{2+} + 2\ OH^- = Mg(OH)_2$**
NH_3, A)	**$Mg^{2+} + 2\ OH^- = Mg(OH)_2$**
$AgNO_3$, A)	**$Ag^+ + Cl^- = AgCl$**
Na_2CO_3, A)	$Mg^{2+} + CO_3^{2-} = MgCO_3$
$Fe(NO_3)_3$, E)	**$Fe^{3+} + Cl^- = [FeCl]^{2+}$ (or $Fe^{3+} + 3\ Cl^- = FeCl_3$ etc.)**

Na_2SO_3

HNO_3, J	**$SO_3^{2-} + 2\ H^+ = H_2O + SO_2$**
$KIO_3 + HNO_3$, B) or E) (+hexane, G)	**$5\ SO_3^{2-} + 2\ IO_3^- + 2\ H^+ = I_2 + 5\ SO_4^{2-} + H_2O$**
$Ba(NO_3)_2$, A)	$Ba^{2+} + SO_3^{2-} = BaSO_3$
$+ HNO_3$, C)	**$BaSO_3 + 2\ H^+ = Ba^{2+} + SO_2 + H_2O$**
$AgNO_3$, A)	**$2\ Ag^+ + SO_3^{2-} = Ag_2SO_3$**
C)	**$Ag_2SO_3 + 3\ SO_3^{2-} = 2\ [Ag(SO_3)_2]^{3-}$**
$KI + KIO_3$, D)	**$I_2 + SO_3^{2-} + H_2O = 2\ I^- + SO_4^{2-} + 2\ H^+$**

$Ba(NO_3)_2$

$Al_2(SO_4)_3$, A)	**$Ba^{2+} + SO_4^{2-} = BaSO_4$**
KIO_3, A)	$Ba^{2+} + 2\ IO_3^{-} = Ba(IO_3)_2$
Na_2CO_3, A)	$Ba^{2+} + CO_3^{2-} = BaCO_3$
Na_2SO_3, A)	$Ba^{2+} + SO_3^{2-} = BaSO_3$
+ HNO_3, C)	**$BaSO_3 + 2\ H^{+} = Ba^{2+} + SO_2 + H_2O$**

KI

$Fe(NO_3)_3$, E) or D)	**$2\ Fe^{3+} + 2\ I^{-} = 2\ Fe^{2+} + I_2$**
$AgNO_3$, B)	**$Ag^{+} + I^{-} = AgI$**
KIO_3, + HNO_3, B) or E) (+hexane, G)	**$5\ I^{-} + IO_3^{-} + 6\ H^{+} = 3\ I_2 + 3\ H_2O$**

48th International Chemistry Olympiad

Practical Tasks

Part II.

26 July 2016

Tbilisi, Georgia

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 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 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 7 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
General equipment for all tasks, for each student, on the table	
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
Tasks 2 and 3, for each student, on the table	
Container with a screw cap for waste,3 dm^3, labeled “Liquid Waste, Tests 2&3”	1
Task 2, for each student, on the table	
Storage box labeled “Task 2”	1
Laboratory stand with double burette clamp	1
Burette, 25.00 cm^3	2
Graduated pipette, 10.0 cm^3	1
Graduated pipette, 1.00 cm^3	1
Bulb (Mohr) pipette, 10.00 cm^3	1
Erlenmeyer flask, 100 cm^3	2
Graduated cylinder, 10.0 cm^3	2
Brush	1
Polypropylene funnel, 5.5 cm	1
Task 2, for each student, in the storage box “Task 2”	
Polystyrene test tubes, 10 cm^3	8
Pipette filler	1
Pasteur pipettes for indicators	2
Task 3, for each student, get from the lab assistants	
Storage box labeled “Task 3”	1
Task 3, for each student, in the storage box “Task 3”	
Polystyrene test tubes, 10 cm^3	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
Task 2, for each student, on the table					
Nitric acid	Aqueous solution	2 M	-*	Glass bottle with dropper cap, 250 cm^3	HNO_3
Task 2, for each student, in the storage box "Task 2"					
Water sample solution	Aqueous solution	To be determined	100 cm^3	Glass bottle with screw cap, 100 cm^3	Water sample
Sodium fluoride	Aqueous solution	9 mg/dm^3 in fluoride	50 cm^3	Glass bottle with screw cap, 50 cm^3	F^-, 9 mg/dm^3
Zirconyl Alizarin indicator	Acidic aqueous solutions	0.055% $ZrOCl_2$, 0.028% Alizarin Red S	10 cm^3	Glass bottle with screw cap, 25 cm^3	Zirconyl Alizarin
Sodium chloride	Aqueous solution	0.0500 M	50 cm^3	Glass bottle with screw cap, 50 cm^3	NaCl, 0.0500 M
Ammonium iron(III) sulfate dodecahydrate	Aqueous acidic solution	20 g/dm^3	10 cm^3	Glass bottle, 15 cm^3	Fe^{3+} ind.
Silver nitrate	Aqueous solution	To be determined	200 cm^3	Amber glass bottle, 250 cm^3	$AgNO_3$
Ammonium thiocyanate	Aqueous solution	See exact concentration on the label	100 cm^3	Glass bottle with screw cap, 100 cm^3	NH_4SCN, X.XXXX M
Potassium chromate	Aqueous solution	10%	5 cm^3	Glass bottle, 15 cm^3	K_2CrO_4
Task 3, for each student, on the table					
Ethanol	Liquid	95 %	150 cm^3	Glass bottle with dropper cup, 250 cm^3	C_2H_5OH
Task 3, for each student, in the storage box "Task 3"					
Organic unknowns 1 to 8	Liquid	-	0.5 cm^3	Syringes, 2 cm^3	1 to 8
Potassium permanganate	Aqueous solution	0.13 %	5 cm^3	Amber glass bottle, 50 cm^3	$KMnO_4$
Ammonium cerium(IV) nitrate reagent	2.0 M HNO_3 aqueous solution	28.6 %	5 cm^3	HDPE bottle, 30 cm^3	Ce(IV)
Acetonitrile	Liquid	-	45 cm^3	Glass bottle, 50 cm^3	CH_3CN

Name	State	Conc.	Q-ty	Placed in	Labeled
2,4-Dinitrophe-nylhydrazine reagent	Sulfuric acid solution in aqueous ethanol	3 %	20 cm^3	HDPE bottle, 30 cm^3	DNPH
Iron(III) chloride	0.5 M HCl aqueous solution	2.5 %	1 cm^3	HDPE bottle, 30 cm^3	$FeCl_3$
Hydroxylamine hydrochloride	Ethanolic solution	0.5 M	10 cm^3	HDPE bottle, 30 cm^3	$NH_2OH\times HCl$
Sodium hydroxide	Aqueous solution	6 M	5 cm^3	HDPE bottle, 30 cm^3	NaOH
Hydrochloric acid	Aqueous solution	1 M	25 cm^3	HDPE bottle, 30 cm^3	HCl

*In the quantity left after doing Task 1.

Periodic table with relative atomic masses

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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											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 -

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 cm^3 of mineral water from the sample into the plastic test tube labeled "X".

Calculate how much of the 9.0 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 mg/dm^3 (calculate for 9.0 cm^3 of each solution).

Using the 1.0 cm^3 and 10.0 cm^3 graduated pipettes, add the calculated amounts of the standard fluoride solution to the test-tubes, then add 1.0 cm^3 of Zirconyl Alizarin indicator into each test tube, and bring the volume in each calibration test tube to the 10.0 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 cm^3 of the standard 0.0500 mol/dm^3 NaCl solution into an Erlenmeyer flask using the bulb (Mohr) pipette. Add approximately 20 cm^3 of distilled water and 10 drops of 10% aqueous K_2CrO_4 solution.

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 $AgNO_3$ and for the end-point indication reaction.

2.2.3. Calculate the concentration of the $AgNO_3$ 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^3 aliquot of the mineral water from the sample into an Erlenmeyer flask using the bulb (Mohr) pipette. Add 5 cm^3 of 2 mol/dm^3 nitric acid using a graduated cylinder. Add 20.00 cm^3 of the silver nitrate solution from the burette and mix well the suspension. Add appr. 2 cm^3 of the indicator (Fe^{3+}) 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^- ions with SCN^- 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_4SCN and that for the end-point indication reaction.

2.3.3. Calculate the chloride concentration (in mg/dm^3) in the water sample from your measurements.

2.3.4. If Br^-, I^-, and F^- 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?

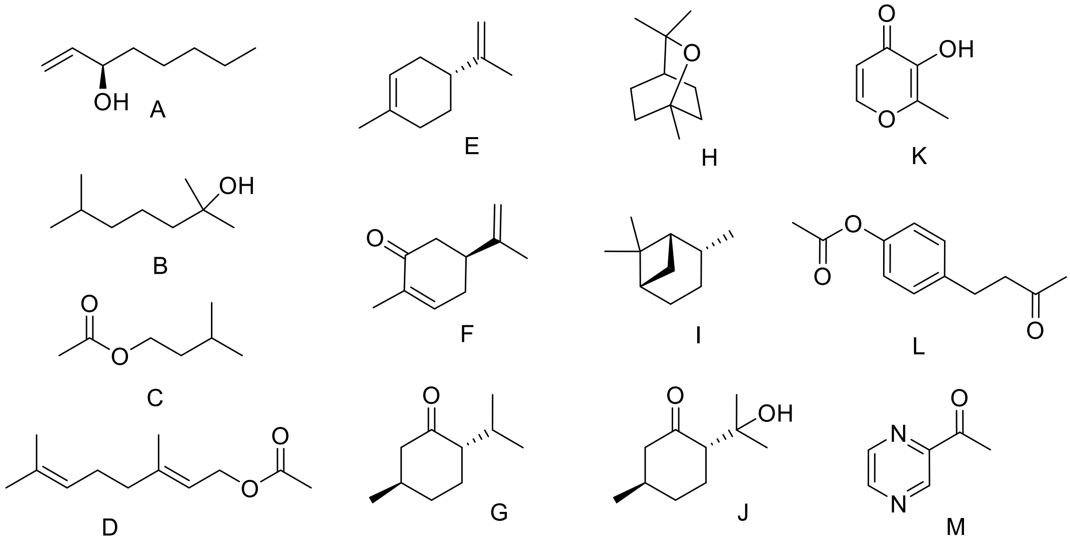
2.3.5. When trying to determine the concentration of Cl^- in the presence of other halides, an analyst added some potassium iodate and sulfuric acid to the sample and boiled the solution. Afterwards he reduced the excess of iodate to iodine by boiling the sample with phosphorous acid H_3PO_3. What interfering 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 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 Roman numeral 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

$KMnO_4$ test (Baeyer test)

Place appr. 1 cm^3 of 95% ethanol in a plastic test tube and add 1 drop of an unknown. Add 1 drop of $KMnO_4$ 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^3 of 95% ethanol in a plastic test tube. Add 1 cm^3 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^3 of 0.5 mol/dm^3 ethanolic hydroxylamine hydrochloride solution with 5 drops of 6 mol/dm^3 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^3 of 1 mol/dm^3 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. Stopper the test tubes with a green cap after completing the test to prevent a 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**.

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.

48th 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^- content (mg/dm^3)	0.0	1.0	2.0	3.5	5.0	6.5	8.0
Calculated volume of F^- solution (cm^3)							

2p

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

15p, 5p for adjacent values.

F^- content (mg/dm^3)	0.0	1.0	2.0	3.5	5.0	6.5	8.0

2.2.1. Report your titration volumes.

Titration no.	1	2				
Initial burette reading, cm^3						
Final burette reading, cm^3						
Volume spent, cm^3						

Your accepted volume, V_1: cm^3

30p on a sliding scale

2.2.2. Write a balanced chemical equation for the titration of NaCl with $AgNO_3$ and that for the end-point indication reaction.

Titration reaction:

$Cl^- + Ag^+ \longrightarrow AgCl\downarrow$

Indication reaction:

$CrO_4^{2-} + 2\ Ag^+ \longrightarrow Ag_2CrO_4\downarrow$

2p

2.2.3. Calculate the concentration of the $AgNO_3$ solution from your measurement.

Your work:

$c(Ag^+) = c(Cl^-)10.0\ cm^3 / V_1$

2 p

$c(Ag^+)$:

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: $2\ CrO_4^{2-} + 2\ H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$ (dichromic or chromic acids also accepted),

or $Ag_2CrO_4 + H^+ \rightarrow 2Ag^+ + HCrO_4^-$

High pH: $2\ Ag^+ + 2\ OH^- \longrightarrow Ag_2O + H_2O$

2p

2.3.1. Report your volumes on the answer sheet.

Titration no.	1	2				
Initial burette reading, cm^3						
Final burette reading, cm^3						
Volume spent, cm^3						

Your accepted volume, V_2: cm^3 — 30p on a sliding scale

2.3.2. Write a balanced chemical equation for the back titration with NH_4SCN and that for the end-point indication reaction.

Titration reaction:

$Ag^+ + SCN^- \longrightarrow AgSCN\downarrow$

Indicatio[n]:

$SCN^- + Fe^{3+} \longrightarrow Fe(SCN)^{2+}$ or analogous reaction

2p

2.3.3. Calculate the chloride concentration (in mg/dm^3) in the water sample from your measurements.

Your work:

$c(Cl^-) = [20.00\ cm^3\ c(Ag^+) - V_2\ c(SCN^-)]\ M(Cl) / 10.00\ cm^3$

4p, 3p if in different unit

$c(Cl^-)$: mg/dm^3

2.3.4. If Br^-, I^-, and F^- 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^- ☐ I^- ☐ F^- ☐ none

Br^-, I^-

2p, 1p if 1 mistake committed

2.3.5. When trying to determine the concentration of Cl^- 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_3PO_3. What interfering anions were removed by this operation?

☐ Br^- ☐ I^- ☐ F^- ☐ none

Br^-, I^-

2p

Write the reaction equations of these ions with iodate.

$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

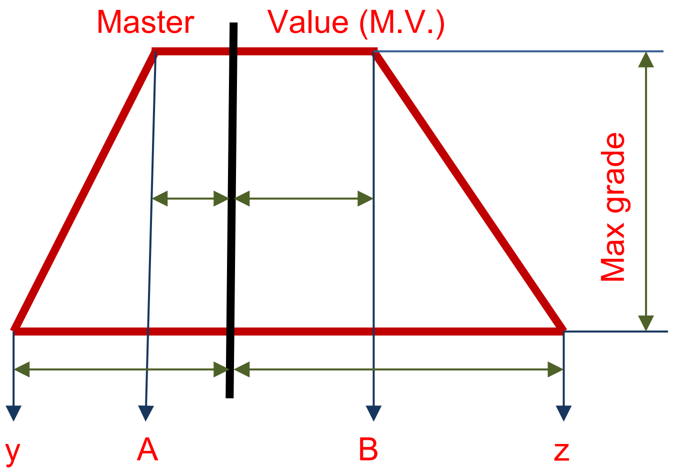
$10Br^- + 2IO_3^- + 12H^+ \rightarrow 5Br_2 + I_2 + 6H_2O$ (IBr also accepted)

2p

Replacements:

Item	Quantity	Lab assistant's signature	Student's signature

Grading scheme for the titration results



If A< Value < B, then Grade = Max grade
If Value < y, then Grade = 0, If Value > z, then Grade = 0
If y < Value < A, then Grade = Max grade × (Value – y)/(A – y)
If B < Value < z, then Grade = Max grade × (z – Value)/(z – B)

Question	M.V., mL	A, mL	B, mL	y, mL	z, mL	Max grade
2.2.1.	10.0	9.9	10.15	9.8	10.4	30p
2.3.1.	Theoretical values	–0.1	+0.3	–0.3	+0.8	30p

Task 3 13% of the total

3.1.	3.2.	3.3.	3.4.	3.5.	Sum
32	16	4	4	4	60

3.1. Indicate the results and observations of tests by giving the Roman numerals 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.

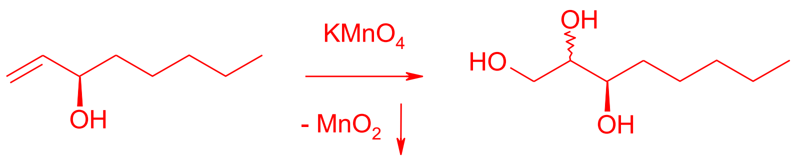
I – Immediate disappearance of purple color
II – Slow disappearance of purple color
III - Disappearance of yellow color
IV – Formation of a brown or black precipitate
V - Formation of a white precipitate
VI - Formation of a yellow or orange-red precipitate
VII - Appearance of orange or red color in solution
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**)	I, IV	X	I, IV	II, IV	X	II, IV	X	I, IV
Ce(IV) nitrate test result (+/–)	+	+	–	–	–	–	–	–
Ce(IV) nitrate test observations (**I-X**)	VII	VII	III, V	III	X	X or III	X	III
2,4-DNPH test result (+/–)	–	–	–	+	–	–	–	–
2,4-DNPH test observations (**I-X**)	X	X	X	VI	X	X	X	X
Fe(III) hydroxamate test result (+/–)	–	–	–	–	+	–	–	+
Fe(III) hydroxamate test observations (**I-X**)	X	X	X	X	VIII	X	X or IX	VIII

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

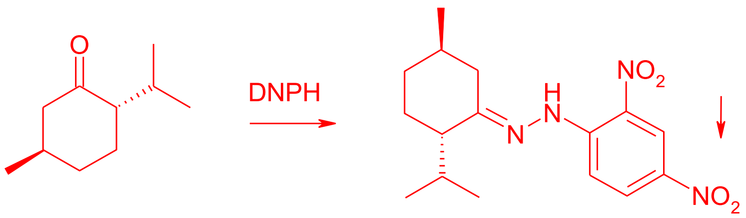
Sample No.	1	2	3	4	5	6	7	8
Structure code	**A**	**B**	**E**	**G**	**C**	**H**	**I**	**D**

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



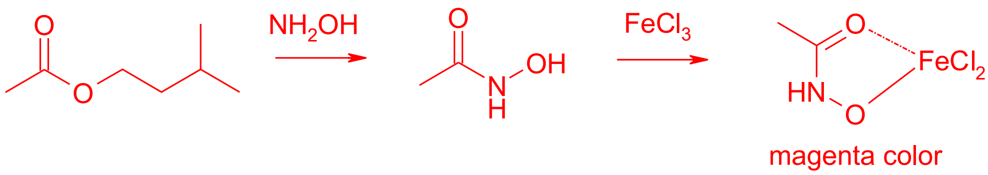
Or analogous 4p

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



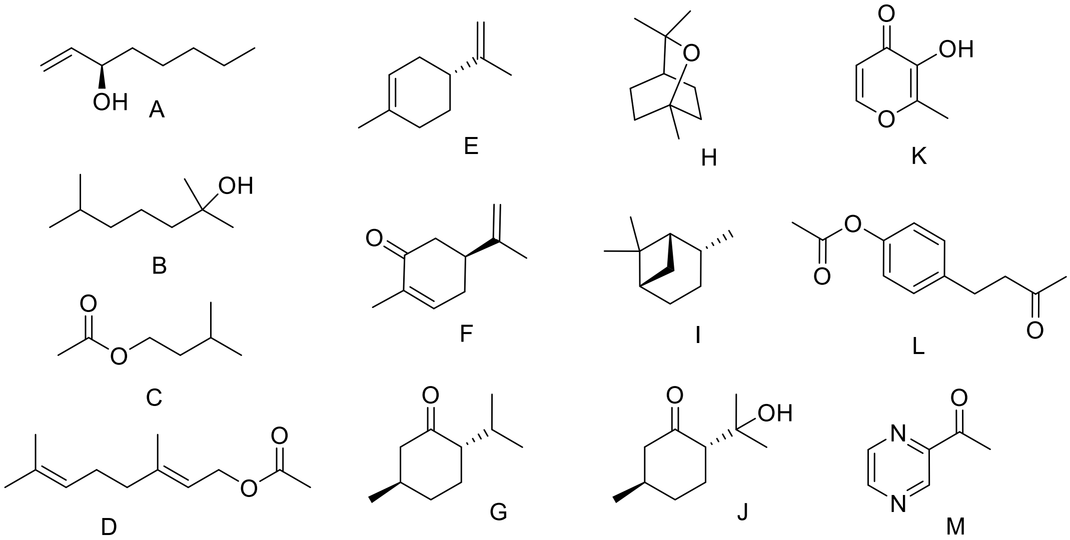
4p

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



Or analogous 4p (any 1:1 hydroxamate – Fe(III) complex is acceptable)

The problem can be approached in many ways. A systematic solution for one variant of the unknown compounds encoding is given below (other variants are processed similarly).



Step 1. Solubility data analysis.

The data given allow excluding compounds K (presence of phenol-like moiety) and M (presence of azine nitrogen) soluble in aqueous NaOH and aqueous HCl, respectively.

Step 2. Tests for the functional groups.

2.1 Unsatured compounds excluding those aromatic give positive Baeyer test, and those with keto- or aldehyde group give positive 2,4-DNPH test

2.2 For avoiding mistakes in true-positive / false-positive interpretation the precise description of true-positive tests is given in the test procedures.

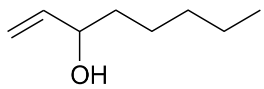
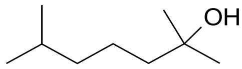
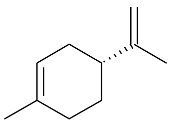
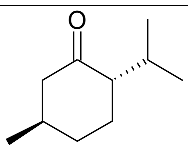
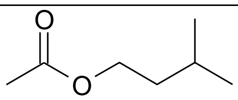
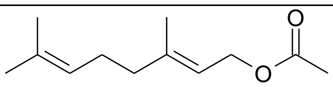
2.3 The information given in the Notes after the test procedures CLEARLY indicates the following prompts:

Note	Prompt
Comparison with blank (no unknown) and reference (with ethanol) tests is recommended for adequate interpretation of the test.	The cerium(IV) nitrate test is one for alcohols
Brightly colored Ce(IV) coordination compounds bearing C_{sp3}-O→Ce(IV) moiety have the formation constant in the range of 0.51 (MeOH, kinetically unstable) to 2.76 (t-BuOH, kinetically stable).	Red color appearing as a result of a positive cerium(IV) nitrate test can disappear due to further oxidation of alcohols by Ce(IV) in the case of primary and secondary alcohols
Brightly colored Fe(III)-hydroxamic acids coordination compounds have the formation constants $K_1 \sim 42$; $K_2 \sim 2.5$; $K_3 \sim 1.2 \cdot 10^{-2}$ (for acetohydroxamate in ethanol–water 1:1 mixture).	The ferric hydroxamate test is the one for the compounds capable of forming the hydroxamic acids in the reaction with NH_2OH. ONLY ESTERS are appropriate candidates for the positive test. Amides (J) do not afford hydroxamic acid under NH_2OH treatment, thus giving negative test.

The results of the experimental work can be summed up in the hereunder table.

# of sample	$KMnO_4$	$Ce(NH_4)_2(NO_3)_6$	2,4-DNPH	Ferric Hydroxamate Test
1	+	+	–	–
2	–	+	–	–
3	+	–	–	–
4	–	–	+	–
5	–	–	–	+
6	–	–	–	–
7	–	–	–	–
8	+	–	–	+

Analysis of the table allows unanimously identifying **A**, **B**, **E**, C, and **G**. **L** (Ferric hydroxamate and 2,4-DNPH), **J** (2,4-DNPH and Cerium(IV) nitrate test), and **F** ($KMnO_4$ and 2,4-DNPH tests) can be excluded from further consideration, since these provide for two positive tests each.

#	Structure	$KMnO_4$	$Ce(NH_4)_2(NO_3)_6$	2,4-DNPH	Ferric Hydroxamate Test
1		+	+	–	–
2		–	+	–	–
3		+	–	–	–
4		–	–	+	–
5		–	–	–	+
6	?	–	–	–	–
7	?	–	–	–	–
8		+	–	–	+

Step 3. Choosing of right structures of the samples 6 and 7 based on additional data given.

Among all compounds in the list, only H and I cannot give any positive test, the attribution requiring consideration of the solubility data. Sample 7 in the above table is soluble in ether only (attributed as I), whereas Sample 6 is partially soluble in water (attributed as H).

The final assignment is given below.

Sample No	1	2	3	4	5	6	7	8
Structure code	A	B	E	G	C	H	I	D

1 points for each test (1p × 4 tests × 8 unknowns=32p)

2 points for each correct assignment (2p× 8 unknowns=16p)

Appendix A

Hazard codes, provided by Globally Harmonized System of Classification and Labeling of Chemicals (not to be printed for students)

Substance	Name	GHS Hazard Statement
C_6H_{14}	Hexane	225, 304, 315, 336, 361f, 373, 411
NaOH	Sodium hydroxide	290, 314
HNO_3	Nitric acid	272, 290, 314
$AgNO_3$	Silver nitrate	272, 290, 314, 400, 410
$Al_2(SO_4)_3$	Aluminium sulfate	290, 318
$Ba(NO_3)_2$	Barium nitrate	272, 302+332, 319
$Fe(NO_3)_3$	Iron(III) nitrate	314
KI	Potassium iodide	302, 315, 319
KIO_3	Potassium iodate	272, 315, 319, 335
$MgCl_2$	Manganese chloride	-
Na_2CO_3	Sodium carbonate	-
Na_2SO_3	Sodium sulfite	-
NH_3	Ammonia	221, 280, 314, 331, 400, 410
NaF	Sodium fluoride	301, 315, 319
$ZrOCl_2$ + $C_{14}H_7NaO_7S$	Zirconyl Alizarin indicator	314
NaCl	Sodium chloride	-
$NH_4Fe(SO_4)_2{\times}12H_2O$	Ammonium iron(III) sulfate dodecahydrate	315, 319
NH_4SCN	Ammonium thiocyanate	302, 312, 332, 412
K_2CrO_4	Potassium chromate	301, 315, 317, 319, 335, 400, 410
$C_8H_{16}O$	1-Octen-3-ol, Matsutake alcohol	302, 315, 319
$C_9H_{20}O$	2,6-Dimethyl-2-heptanol, Dimetol, Freesiol	302, 318
$C_7H_{14}O_2$	Isoamyl Acetate	226
$C_{12}H_{20}O_2$	Geranyl acetate	315, 319, 335
$C_{10}H_{16}$	Limonene	226, 315, 317, 410
$C_{10}H_{14}O$	(+)-Carvone	-
$C_{10}H_{18}O$	(−)-Menthone	315, 317
$C_{10}H_{18}O$	1,8-Cineole	226
$C_{10}H_{18}$	Pinane	226
$C_{10}H_{18}O_2$	8-Hydroxy-p-menthan-3-one	315, 317
$C_6H_6O_3$	Maltol	302, 315, 319, 335
$C_{12}H_{14}O_3$	Raspberry ketone acetate	-
$C_6H_6N_2O$	2-Acetylpyrazine	315, 319, 335
$KMnO_4$	Potassium permanganate	400, 410
$Ce(NH_4)_2(NO_3)_6$	Ammonium cerium(IV) nitrate	272, 290, 302, 314, 317, 400, 410

CH_3CN	Acetonitrile	225, 302, 312, 319, 332
$C_6H_6N_4O_4$	2,4-Dinitrophe-nylhydrazine	228, 302
$FeCl_3$	Iron(III) chloride	290, 302, 315, 318
$NH_2OH{\cdot}HCl$	Hydroxylamine hydrochloride	290, 302, 312, 315, 317, 319, 373, 400, 410
HCl	Hydrochloric acid	290, 315, 319, 335

Appendix B

Hazard Statement Descriptions

Statement	**Description**
H221	Flammable gases
H225	Highly flammable liquid and vapour
H272	May intensify fire; oxidizer
H226	Flammable liquid and vapour
H228	Flammable solid
H280	Gases under pressure
H290	May be corrosive to metals
H301	Acute toxicity, oral
H302	Acute toxicity, oral
H302+332	Harmful if swallowed or if inhaled
H304	May be fatal if swallowed and enters airways
H312	Acute toxicity, dermal
H314	Causes severe skin burns and eye damage
H315	Causes skin irritation
H317	Skin sensitisation
H318	Causes serious eye damage
H319	Causes serious eye irritation.
H331	Acute toxicity, inhalation
H332	Acute toxicity, inhalation
H335	May cause respiratory irritation
H336	May cause drowsiness or dizziness
H361f	Suspected of damaging fertility
H373	May cause damage to organs through prolonged or repeated exposure
H400	Acute aquatic toxicity
H410	Chronic aquatic toxicity
H411	Toxic to aquatic life with long lasting effects
H412	Chronic aquatic toxicity