

The 1st Metropolises Olympiad

Chemistry

Practical task on *Analytical* Chemistry

September 06, 2016

Moscow, Russia

General Directions

- **safety rules** follow ones adopted at the International Chemistry Olympiad, no eating or drinking in the lab.
- **violating safety rules** you get one warning only; offend again: you are disqualified.
- **the exam includes two parts.** One student in each team starts with the Organic chemistry task, whereas the other with the Analytical chemistry task.
- **time** 2 h 15 min to complete each part, 15 min break in between. 30 min warning before the end of each part. You will be guided to the break area and back to the lab.
- **when entering the lab** search for the table with your student code.
- **your student code** get sure this is present on **every page**.
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- **use only the pen, pencil and calculator provided.**
- **more chemicals** needed? Ask your lab assistant. No penalty for this with an exception of the hereunder.
- **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.
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- **You must stop your work immediately after the stop signal has been given. A 5 min delay will result in zero points for the current task.**

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Specific directions for the Analytical chemistry task

- **problem and answers booklet for the Analytical chemistry task** 8 pages (incl. cover sheet and Periodic table of elements)

Reagents

Reagent	Quantity	Placed in	Labeled
On each working place			
Sample (a mixture of glucose and sucrose)	To be determined	50 mL Volumetric flask	Sample and your student code
Hydrochloric acid, 2 M	15 mL	30 mL Amber glass vial with ground joint cap	HCl 2 M
Sodium thiosulfate, 0.1 M	100 mL	125 mL Plastic bottle with screw cap	Na ₂ S ₂ O ₃
Sodium hydroxide solution, 2 M	15 mL	30 mL Amber glass drop bottle	NaOH 2 M
Sodium hydroxide solution, 0.1 M	125 mL	125 mL Plastic bottles with screw cap	NaOH 0.1 M
Starch (0.5-1%)	10 mL	30 mL Amber glass drop bottle	Starch
Distilled water	500 mL	500 mL wash bottle	-
On the table of common use			
Iodine (0.05 M solution in I ₂ , 2.4% KI)	1 L (to be shared by 4 students)	Volumetric flask and burette	I ₂
Methyl Red	10 mL (to be shared by 4 students)	30 mL Amber glass drop bottle	Methyl red
Sodium hydroxide solution, 0.1 M	125 mL	125 mL Plastic bottles with screw cap	NaOH 0.1 M

Labware and equipment

Item	Quantity
On each working place	
Laboratory stand with burette clamp	1
50 mL beaker	1
25 mL cylinder	1
100 mL beaker	1
5 mL pipette	2
20 mL Bulb (Mohr) pipette	1
Pipette filler	1
25 mL burette	1
Glass funnel	1
100 mL Erlenmeyer (conical flat-bottom) flask	2
50 mL Volumetric flask	2
Gloves	1 pair

Question	1	2	3	4	5	6	7	Total
Techn. points	20	20	1	1	1	3	4	50

Titrimetric determination of glucose and sucrose in a mixture (20 points)

Concentration of reducing sugars is determined by iodometric back titration. The iodine excess is titrated by a standard thiosulfate solution using starch as an indicator. The **glucose** concentration is determined in the initial mixture, whereas the **sucrose** concentration is found as from the total amount of reducing sugars determined in the same mixture subjected to hydrolysis.

Procedure

Dissolve the given sample in the 50 mL volumetric flask labeled «Sample and your student code» in distilled water (from the wash bottle) and bring up to the mark with water. Take an aliquot of this solution for sucrose hydrolysis. Use the remaining solution for titrimetric determination of glucose (glucose determination and hydrolysis can be done simultaneously).

A. Iodometric determination of a reducing sugar concentration (back titration)

Using pipette place 5.00 mL of the analyzed sugar solution (prior to and after hydrolysis) into a conical titration flask and add 12.5 mL of the standard iodine solution from the burette of common use. Then, using measuring cylinder add 25 mL of 0.1 M NaOH solution with agitation. Store the solution for 10 min allowing complete oxidation of the sugar. Add 1.50 mL of 2 M HCl and titrate the iodine excess with the standard thiosulfate solution till pale-yellow coloration appears. Then add 2-3 drops of 1 % starch solution and continue titrating with agitation till blue coloration disappears.

1. Write down the volumes of thiosulfate solution used for glucose titration:

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

B. Sucrose hydrolysis

Using 20 mL bulb (Mohr) pipette transfer an aliquot of the solution from the volumetric flask labeled «Sample and your student code» into the 100 mL beaker and add 10 mL of 2 M hydrochloric acid solution with measuring cylinder or 5 mL pipette. Heat the beaker with the mixture on the magnetic stirrer for 8–10 min at about 70°C.

Notes.

1. Since the magnetic stirrer heats up slowly, adjust the regulator first to full power, and then to about ¼ of full power.
2. Avoid boiling the solution. Temperature of 70 °C can be distinguished by condensate formation on the beaker walls.

When finished with heating, cool the beaker down to room temperature under tap water and neutralize the mixture with 2M NaOH solution in the presence of Methyl Red till yellow coloration appears (Note. The Methyl Red indicator is located at the table of common use). Transfer the reaction mixture in the other volumetric flask and bring up to the mark with water. Use the obtained solution for the determination of the total amount of reducing sugars as described in Section A.

2. Write down the volumes of thiosulfate solution used for glucose and sucrose titration:

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

3. Write down the reaction equation for glucose oxidation (use molecular formulae, pay attention to stoichiometry!).

4. Write down the reaction equation for sucrose hydrolysis (use molecular formulae for sugars).

5. Write down the equation of iodine reaction with alkali.

6. Calculate the amount of glucose in the given sample

Formula for calculation of the glucose concentration (mol/L, in 50 mL flask), based on the titration results:

Glucose amount in the given sample _____ mg.

7. Calculate the amount of sucrose

Formula for calculation of the sucrose concentration (mol/L, in 50 mL flask), based on the titration results:

Sucrose amount in the given sample _____ mg.

IUPAC Periodic Table of the Elements																	
1 H hydrogen [1.007; 1.009]	2	Key: atomic number Symbol name standard atomic weight										13	14	15	16	17	18 He helium 4.003
3 Li lithium [6.938; 6.997]	4 Be beryllium 9.012											5 B boron [10.80; 10.83]	6 C carbon [12.00; 12.02]	7 N nitrogen [14.00; 14.01]	8 O oxygen [15.99; 16.00]	9 F fluorine 19.00	10 Ne neon 20.18
11 Na sodium 22.99	12 Mg magnesium 24.31	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 26.98	14 Si silicon [28.08; 28.09]	15 P phosphorus 30.97	16 S sulfur [32.05; 32.08]	17 Cl chlorine [35.44; 35.46]	18 Ar argon 39.95
19 K potassium 39.10	20 Ca calcium 40.08	21 Sc scandium 44.96	22 Ti titanium 47.87	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.38(2)	31 Ga gallium 69.72	32 Ge germanium 72.63	33 As arsenic 74.92	34 Se selenium 78.96(3)	35 Br bromine 79.90	36 Kr krypton 83.80
37 Rb rubidium 85.47	38 Sr strontium 87.62	39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.96(2)	43 Tc technetium	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57-71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium [204.3; 204.4]	82 Pb lead 207.2	83 Bi bismuth 208.0	84 Po polonium	85 At astatine	86 Rn radon
87 Fr francium	88 Ra radium	89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium		114 Fl flerovium		116 Lv livermorium		
			57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
			89 Ac actinium	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

- IUPAC 2009 Standard atomic weights abridged to four significant digits (Table 4 published in *Pure Appl. Chem.* 83, 359-396 [2011]; doi:10.1351/PAC-REP-10-09-14). The uncertainty in the last digit of the standard atomic weight value is listed in parentheses following the value. In the absence of parentheses, the uncertainty is one in that last digit. An interval in square brackets provides the lower and upper bounds of the standard atomic weight for that element. No values are listed for elements which lack isotopes with a characteristic isotopic abundance in natural terrestrial samples. See PAC for more details.

- Claims for the discovery of all the remaining elements in the last row of the Table, namely elements with atomic numbers 113, 115, 117 and 118, and for which no assignments have yet been made, are being considered by a IUPAC and IUPAP Joint Working Party.

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Specific directions for the Organic chemistry task

- **problem and answers booklet for the Organic chemistry task** 8 pages (incl. cover sheet and Periodic table of elements)
- **each extra Portion of the aldehyde or 2,4-dinitrophenylhydrazine:** a penalty of 1point out of 40.

List of Chemicals

Reagent	Quantity	Placed in	Labeled
On each working place			
2,4-Dinitrophenylhydrazine	200 mg each, 2 vials	small amber glass vial	2,4-DNPH
Sulfuric acid, concentrated	1 mL each, 2 bottles	plastic bottle with screw cap	H ₂ SO ₄
Aldehyde solution, 1 mmol in ethanol	4 mL each, 2 bottles	30 mL plastic bottle with screw cap	Aldehyde 1 and Aldehyde2
Ethanol	30 mL	large amber glass vial	Ethanol
Distilled water	500 mL	500 mL wash bottle	-

Labware and equipment

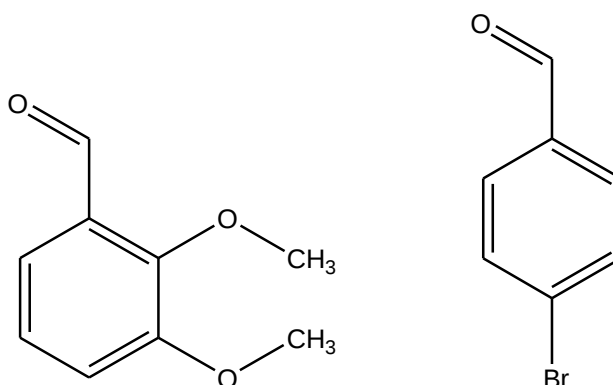
Item	Quantity
On each working place	
Glass weighing bottle labeled "Product 1 and your student code"	1
Glass weighing bottle labeled "Product 2 and your student code"	1
Lab stand with a clamp and ring	1
50 or 100 mL beaker	2
Magnetic stirrer	1
Stirring bar	2
Glass filter	2
Adapter	1
250 mL round bottom flask	1
Water-jet pump	1
2 mL pipette	2
5 mL pipette	2
Pipette filler	1
Spatula	1
25 mL measuring cylinder	1
Filter paper	3
Glass rod	1
Tweezers	1
pH indicator papers	1
Balances	1
On the tables for the common use	
Filter paper	
Gloves	

Question	1	2	3	4	5	Total
Techn. points	50	12	6	6	6	80

Synthesis of hydrazones (20 points)

Aldehydes and ketones are among most commonly used organic compounds. Application of these substances often requires easy methods of their identification. Hydrazones are produced as a result of hydrazine interaction with aldehydes or ketones under appropriate conditions. Due to well characterized properties and distinctive appearance, hydrazones are often used for such identification.

In this task you will have to identify two substituted benzaldehydes (shown below) by studying the products of their reactions with 2,4-dinitrophenylhydrazine.



Procedure

A. Preparation of 2,4-dinitrophenylhydrazones

Attention! Do not try to carry out two syntheses simultaneously!

Equip the 50 (or 100) mL beaker with the magnetic bar. Fix the beaker on the stirrer using the metal ring attached to the stand. Place the content of on a vial labeled “2,4-DNPH” into the beaker and start stirring carefully. **Only in the presence of your lab assistant**, carefully pour the concentrated sulfuric acid (1 mL) from **one** plastic bottle with screw cap onto the solid. Using pipettes add 1.6 mL of water and 4 mL of ethanol to the reaction mixture. Then using a pipette

add slowly the whole solution of one of the aldehydes (**you can start with any of the aldehydes!**). Bright precipitate starts forming at once. Continue stirring for 10 min, then add 10 mL of water and stir for another 3 min.

B. Product separation and purification

Assemble the filtering apparatus: fix the found-bottom flask to the stand, attach the vacuum hose to the adapter, place the latter into the flask, and apply the glass filter to the adaptor. Transfer the reaction product together with the stirring bar onto the filter. Turn on the water-jet pump and filter out the precipitate. Put a little amount of water in the beaker and transfer the leftover product onto the filter. Wash the solid on the filter 3 times with 20 mL water portions mixing the suspension the with glass rod. Then wash the solid three times with 5 mL portions of ethanol. Dry out the solid on the filter with working water-jet pump, loosening and squeezing the product with the glass rod from time to time. **(Once you have arranged vacuum drying of the first product, you can start synthesizing the second one – see Section C).** After *ca.* 20-40 min carefully transfer the dried powder into the pre-weighed weighing bottle labeled with the same product number as the aldehyde sample for the final drying in the air (**do not close the weighing bottle!**). Put the weighing bottle with the product in a safe place (e.g. on the shelf).

Always remove the vacuum hose from the adaptor before turning off the water-jet pump! Keep the water-jet pump turned off when not using it.

As soon as your product seems dry, remove the stirring bar with tweezers and weigh the product. Fill in Table 1.

Note: The products you have synthesized will be further re-examined by the lab staff.

C. Synthesis, separation and purification of the second product

Move the clamp with the filtering apparatus aside and continue drying the first product. Meanwhile, put the magnetic stirrer on the stand base and repeat the above synthetic and purification procedures with the other starting aldehyde. When finished, fill in the second column of Table 1.

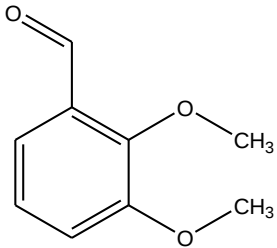
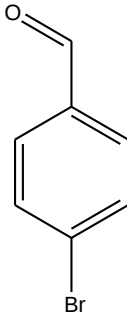
1. Table 1. Weighing results.

Weighing bottle 1	Weighing bottle 2
Mass of empty weighing bottle _____ mg	Mass of empty weighing bottle _____ mg
Mass of weighing bottle with the product _____ mg	Mass of weighing bottle with the product _____ mg
Mass of product _____ mg	Mass of product _____ mg

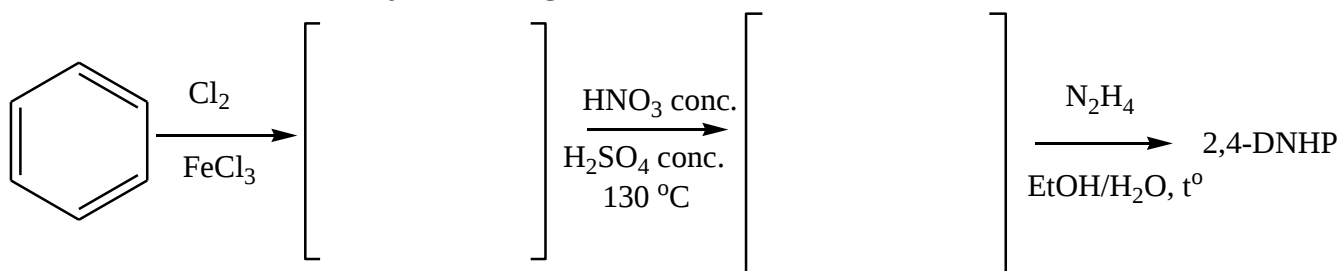
2. Write down the structures of 2,4-dinitrophenylhydrazine and the products.

A hydrazone color is mainly dependent on the substituents present in the benzene ring. The electron-donor groups are responsible for the wavelength of maximum absorption closer to the red range of the spectrum, whereas the electron-acceptor ones do not produce strong effect.

3. Based on the above information, assign numbers **1** or **2** to appropriate aldehydes. Calculate the percent yields of both hydrazones.

	
Number: _____	Number: _____
Yield calculation:	Yield calculation:
Yield Number 1 _____ %	
Yield Number 2 _____ %	

The scheme of 2,4-DNHP synthesis is given below.



4. Draw the structures of the intermediates.

5. Choose the mechanism of the latter reaction from the variants given below (tick the appropriate box)

- ☐ Aromatic nucleophilic substitution
- ☐ Nucleophilic substitution $\text{S}_{\text{N}}1$
- ☐ Nucleophilic substitution $\text{S}_{\text{N}}2$
- ☐ Free radical reaction
- ☐ Electrophilic substitution in aromatic ring

Replacement or extra chemicals	Lab assistant signature	Penalty
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

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11 Na sodium 22.99	12 Mg magnesium 24.31	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 26.98	14 Si silicon [28.08; 28.09]	15 P phosphorus 30.97	16 S sulfur [32.05; 32.08]	17 Cl chlorine [35.44; 35.46]	18 Ar argon 39.95
19 K potassium 39.10	20 Ca calcium 40.08	21 Sc scandium 44.96	22 Ti titanium 47.87	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.38(2)	31 Ga gallium 69.72	32 Ge germanium 72.63	33 As arsenic 74.92	34 Se selenium 78.96(3)	35 Br bromine 79.90	36 Kr krypton 83.80
37 Rb rubidium 85.47	38 Sr strontium 87.62	39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.96(2)	43 Tc technetium	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57-71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium [204.3; 204.4]	82 Pb lead 207.2	83 Bi bismuth 208.0	84 Po polonium	85 At astatine	86 Rn radon
87 Fr francium	88 Ra radium	89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium		114 Fl flerovium		116 Lv livermorium		
			57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
			89 Ac actinium	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

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