

40th International Chemistry Olympiad

Practical tasks

15 July 2008
Budapest, Hungary

Instructions

- This examination has **10** pages and **5** pages of answer sheets (8+4 for Task 1-2 (including cover page, instruction, lists of apparatus, chemicals and risk & safety phrases), 2+1 for Task 3).
- You have **3 hours** to complete **Tasks 1 and 2**. After that you will have to leave the laboratory for a short **break** while the assistants exchange your glasswares and chemicals. You will then have **2 hours** to work on **Task 3**.
- Begin only when the **START** command is given. You **must stop** your work immediately when the **STOP** command is given after each part. A delay in doing this by 3 minutes will lead to cancellation of your experimental exam.
- Follow the **safety rules** given in the IChO regulations. At all times while you are in the laboratory you **must wear safety glasses** or your own glasses if they have been approved, and use the **pipette filler bulb** provided. Use **gloves** when handling the organic liquids.
- You will receive only **ONE WARNING** from the laboratory supervisor if you break safety rules. On the **second occasion** you will be dismissed from the laboratory with a **resultant zero score for the entire experimental examination**.
- Do not hesitate to ask a demonstrator if you have any questions concerning safety issues or if you need to leave the room.
- Use only the pen and calculator provided.
- Write your **name and code** on each answer sheet. Do not attempt to separate the sheets.
- All **results must** be written in the **appropriate areas** on the answer sheets. Anything written elsewhere will not be graded. Use the reverse of the sheets if you need scratch paper.
- You will need to reuse some glassware during the exam. Clean them carefully at the sink closest to you.
- Use the labeled **waste containers** under the hood for the disposal of organic liquids from Task 1 and all liquids from Task 3.
- The number of **significant figures** in numerical answers must conform to the rules of evaluation of experimental errors. Mistakes will result in penalty points, even if your experimental technique is flawless.
- Chemicals and laboratory ware are not supposed to be **refilled or replaced**. Each such incident (other than the first, which you will be allowed) will result in the **loss of 1 point** from your 40 practical points.
- When you have finished a part of the examination, you must put your answer sheets into the envelope provided. **Do not seal the envelope**.
- The official English version of this examination is available on request only for clarification.

Apparatus

For common use in the lab:
Heating block preadjusted to 70 °C under the hood
Distilled water (H ₂ O) in jugs for refill
Latex gloves (ask for a replacement if allergic to latex)
Labeled waste containers for Task 1 (organic liquids) and Task 3 (all liquids)
Container for broken glass and capillaries
On each desk:
Goggles
Heat gun
Permanent marker
Pencil and ruler
Stopwatch, ask supervisor about operation if needed. (You can keep it.)
Tweezers
Spatula
Glass rod
Ceramic tile
Paper tissue
Spray bottle with distilled water
9 Eppendorf vials in a foam stand
TLC plate in labeled ziplock bag
Plastic syringe (100 cm ³) with polypropylene filter disc
Pipette bulb
14 graduated plastic Pasteur pipettes
Petri dish with etched competitor code
Burette
Stand and clamp
Pipette (10 cm ³)
2 beakers (400 cm ³)
Beaker and watchglass lid with filter paper piece for TLC
10 capillaries
2 graduated cylinders (25 cm ³)
3 Erlenmeyer (conical) flasks (200 cm ³)
Beaker (250 cm ³)
2 beakers (100 cm ³)
Funnel
Volumetric flask (100 cm ³)
30 test tubes in stand*
Indicator paper pieces and pH scale in ziplock bag*
Wooden test tube clamp*
2 plugs for test tubes*

* Only handed out for Task 3

Chemicals

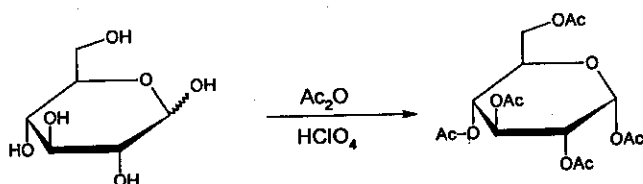
Sets for 4-6 people	R phrases	S phrases
0.025 mol/dm ³ ferroin solution	52/53	
0.2 % diphenylamine, (C ₆ H ₅) ₂ NH solution in conc. H ₂ SO ₄	23/24/25-33-35-50/53	26-30-36/37-45-60-61
0.1 mol/dm ³ K ₃ [Fe(CN) ₆] solution	32	
Pumice stone		
On each desk:		
50 mg anhydrous ZnCl ₂ in a small test tube (in the foam stand, labeled with code)	22-34-50/53	36/37/39-26-45-60-61
100 mg β-D-glucopyranose pentaacetate (labelled as BPAG)		
3.00 g anhydrous glucose, C ₆ H ₁₂ O ₆ , preweighed in vial		
(CH ₃ CO) ₂ O in Erlenmeyer flask (12 cm ³)	10-20/22-34	26-36/37/39-45
(CH ₃ CO) ₂ O in vial (10 cm ³)	10-20/22-34	26-36/37/39-45
CH ₃ COOH in vial (15 cm ³)	10-35	23-26-45
CH ₃ OH in vial (10 cm ³)	11-23/24/25-39	7-16-36/37-45
30 % HClO ₄ in CH ₃ COOH in vial (1 cm ³)	10-35	26-36/37/39-45
1:1 isobutyl acetate – isoamyl acetate in vial (20 cm ³), labeled as ELUENT	11-66	16-23-25-33
solid K ₄ [Fe(CN) ₆].3H ₂ O sample with code in small flask	32	22-24/25
ZnSO ₄ solution labeled with code and concentration (200 cm ³)	52/53	61
0.05136 mol/dm ³ Ce ⁴⁺ solution (80 cm ³)	36/38	26-36
1.0 mol/dm ³ H ₂ SO ₄ solution (200 cm ³)	35	26-30-45
Sample solutions for Task 3 (to be handed out at the start of Task 3)	1-26/27/28-32-35-50/53	24/25-36/39-61

Risk and Safety Phrases

Indication of Particular Risks			
1	Explosive when dry	33	Danger of cumulative effects
10	Flammable	34	Causes burns
11	Highly Flammable	35	Causes severe burns
22	Harmful if swallowed	39	Danger of very serious irreversible effects
32	Contact with concentrated acids liberates very toxic gas		
Combination of Particular Risks			
20/22	Harmful by inhalation and if swallowed	36/38	Irritating to eyes and skin
23/24/25	Toxic by inhalation, in contact with skin and if swallowed	50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
26/27/28	Very Toxic by inhalation, in contact with skin and if swallowed	52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment
Indication of Safety Precautions			
7	Keep container tightly closed	30	Never add water to this product
16	Keep away from sources of ignition - No smoking	33	Take precautionary measures against static discharges
22	Do not breathe dust	36	Wear suitable protective clothing
23	Do not breathe fumes/vapour	45	In case of accident or if you feel unwell, seek medical advice immediately (show label where possible)
25	Avoid contact with eyes	60	This material and/or its container must be disposed of as hazardous waste
26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice	61	Avoid release to the environment.
Combination of Safety Precautions			
24/25	Avoid contact with skin and eyes	36/37/39	Wear suitable protective clothing, gloves and eye/face protection
36/37	Wear suitable protective clothing and gloves		

Task 1

Synthesis of α -D-glucopyranose pentaacetate

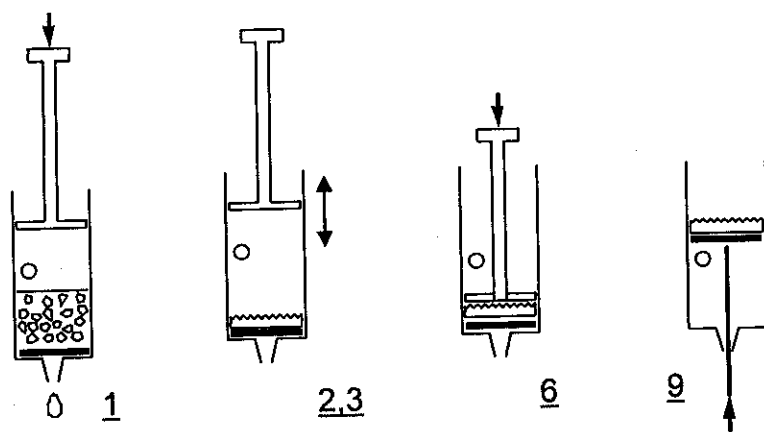


Caution: Use gloves while manipulating acetic acid and acetic anhydride. Let the lab supervisors know if any is spilled.

Add and mix 12 cm³ of pure acetic acid to 12 cm³ of acetic anhydride (provided in an Erlenmeyer (conical) flask) and add 3.00 g glucose (acetic anhydride is in excess). Add, with a Pasteur-pipette, 5 drops of 30% HClO₄ dissolved in acetic acid. After the addition of the catalyst the solution might warm up considerably.

Cover the reaction flask and let the mixture rest for 10 minutes and swirl it from time to time. Pour the reaction mixture into 100 cm³ of water in a beaker. Scratch the wall of the beaker with a glass rod to initiate crystallization, and leave it to crystallize for 10 minutes. Filter and wash the product twice with 10 cm³ of water using the plastic syringe and the porous polypropylene filter disc.

Filtration using a plastic syringe

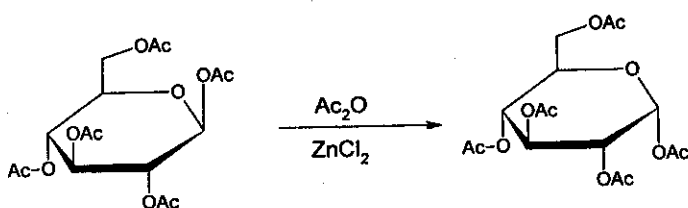


1. Pull out the piston. Fill the syringe from above with the suspension to be filtered. The syringe can be filled to the level of the hole (see 1). Replace piston.
2. Cover the hole with your finger and press in the piston as far as the hole.
3. Open the hole and draw the piston back. Do not draw in air through the filter.
4. Repeat steps 2-3 a few times to expel the liquid.
5. Repeat steps 1-4 until all solids are on the filter.
6. Press the piston against the filter cake and squeeze out the liquid (see 6).
7. Wash the product twice with 10 cm³ of water, repeating steps 1-4.
8. Press the piston against the filter cake and squeeze out the water.
9. Pull the piston out with the hole closed to lift out the filter cake. (Pushing with the end of the spatula can help).

- a) Place your product in the open Petri dish marked with your code. Leave it on your table. The organizers will dry, weigh and check your product for purity.
- b) Calculate the theoretical yield (mass) of your product in g. ($M(C) = 12 \text{ g/mol}$, $M(O) = 16 \text{ g/mol}$, $M(H) = 1.0 \text{ g/mol}$)

Synthesis of α -D-glucopyranose pentaacetate from β -D-glucopyranose pentaacetate

An **alternative** synthesis of α -D-glucopyranose pentaacetate starts from readily available β -D-glucopyranose pentaacetate. In this experiment we will study the kinetics of this reaction with thin layer chromatography.



Add 1.5 cm^3 acetic anhydride to 50 mg of anhydrous ZnCl_2 (preweighed in a test tube). Add 100 mg of pure β -D-glucopyranose pentaacetate (BPAG) to the above test tube and swirl until dissolved. Take three drops from this test tube and put them into an Eppendorf tube. Add 0.5 cm^3 methanol to the mixture in the Eppendorf tube and save it.

Take the test tube to the heating apparatus under the fumehood closest to your desk. Place the test tube in the heating block preadjusted to 70°C . Swirl the contents of the test tube from time to time. Then, take samples of three drops **each** from the mixture in this test tube with a Pasteur pipet **after** 2, 5, 10, and 30 minutes and put them into the Eppendorf tubes provided. Mix **each** sample immediately with 0.5 cm^3 of methanol to stop the reaction in the Eppendorf tubes.

Prepare a silica TLC plate with the collected samples to study the reaction kinetics. Apply the necessary reference compound as well to help in the identification of the spots on the plate. Mark the spots with a pencil, and develop the TLC plate in isobutyl acetate/ isoamyl acetate (1:1) eluent. Heat the TLC plate with a heat-gun (under the hood!) to visualise the spots (the colour is stable). (You can ask for a second TLC plate without penalty points if needed for proper evaluation).

- c) Sketch the spots of the plate on the answer sheet and place your TLC plate in the labeled ziplock bag. Leave the TLC plate in the ziplock bag on the table to be collected.
- d) Interpret your experimental findings by answering the questions on the answer sheet.

Task 2

Hint: The pipette given has two graduation marks. Stop at the second mark to measure out exact volumes. **Do not let all the solution run out.**

When potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$ is added to a solution containing zinc ions, an insoluble precipitate forms immediately. Your task is to find the composition of the stoichiometric precipitate that contains no water of crystallization.

The precipitation reaction is quantitative and quick enough that it can be used in a titration. The end point can be detected using redox indication. However, the concentration of the potassium hexacyanoferrate (II) solution has to be determined first.

Preparation of $K_4[Fe(CN)_6]$ solution and determination of its exact concentration

Dissolve the solid $K_4[Fe(CN)_6] \cdot 3H_2O$ ($M = 422.41$ g/mol) sample in the small Erlenmeyer (conical) flask and quantitatively transfer into the 100.00 cm³ volumetric flask. Put 10.00 cm³ of the hexacyanoferrate (II) solution into a conical flask. Add 20 cm³ of the 1 mol/dm³ sulfuric acid and two drops of the ferroin indicator solution before titration. Titrate with the 0.05136 mol/dm³ Ce^{4+} solution. Repeat titration as necessary. Cerium (IV) is a strong oxidant under acidic conditions forming Ce (III).

- Report the volumes of the Ce^{4+} solution consumed.
- Give the equation for the titration reaction. What was the mass of your $K_4[Fe(CN)_6] \cdot 3H_2O$ sample?

The reaction between zinc ions and potassium hexacyanoferrate (II)

Take 10.00 cm³ of the hexacyanoferrate (II) solution and add to it 20 cm³ 1 mol/dm³ sulfuric acid. Add three drops of the indicator solution (diphenylamine) and two drops of $K_3[Fe(CN)_6]$ solution. The indicator only works if the sample contains some hexacyanoferrate (III), $[Fe(CN)_6]^{3-}$.

Titrate slowly with the zinc solution. Continue until a bluish violet colour appears. Repeat titration as necessary.

- Report the volumes of zinc solution consumed.
- Interpret the titration by answering the questions on the answer sheet.
- Determine the formula of the precipitate.

Caveat: Best marks are not necessarily awarded to measurements reproducing theoretically expected values.

Task 3

Caution: Handle all unknown solutions as if they were toxic and corrosive. **Discard them only in the appropriate waste container.**

The heat gun heats the expelled air up to 500 °C. **Do not direct the stream towards combustible materials or body parts.** Be careful with the hot nozzle.

Always place a single piece of pumice into liquids before heating to avoid bumping. Never point the mouth of a heated test tube towards a person.

You have eight unknown aqueous solutions. Each solution contains only one compound. The same ion may appear in more than one solution. Every compound formally consists of one type of cation and one type of anion from the following list:

Cations: H^+ , NH_4^+ , Li^+ , Na^+ , Mg^{2+} , Al^{3+} , K^+ , Ca^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} ,
 Zn^{2+} , Sr^{2+} , Ag^+ , Sn^{2+} , Sn^{4+} , Sb^{3+} , Ba^{2+} , Pb^{2+} , Bi^{3+}

Anions: OH^- , CO_3^{2-} , HCO_3^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$, NO_2^- , NO_3^- , F^- , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- ,
 SO_4^{2-} , HSO_4^- , S^{2-} , HS^- , Cl^- , ClO_4^- , MnO_4^- , Br^- , I^-

You have test tubes and heating but no additional reagents apart from distilled water and pH paper.

Identify the compounds in the solutions 1-8. You can use the solubility table for **some** of the anions on the next page. If you are unable to identify an ion exactly, give the narrowest selection possible.

Remarks:

The unknown solutions may contain minor impurities arising from their exposure to air. The concentration of all solutions is around 5 % by mass so you can expect clearly observable precipitates from the main components. In some cases, precipitation does not occur instantaneously; some substances may remain in an oversaturated solution for a while. **Don't draw negative conclusions too hastily**, wait 1-2 minutes, if necessary. Always look carefully for all signs of a reaction.

Keep in mind that heating accelerates all processes, increases the solubility of most substances, and may initiate reactions that do not take place at room temperature.

Solubility Table at 25 °C

	NH ₄ ⁺	Li ⁺	Na ⁺	Mg ²⁺	Al ³⁺	K ⁺	Ca ²⁺	Cr ³⁺	Mn ²⁺	Fe ²⁺	Fe ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Sr ²⁺	Ag ⁺	Sn ²⁺	Sn ⁴⁺	Sb ³⁺	Ba ²⁺	Pb ²⁺	Bi ³⁺		
CH ₃ COO ⁻														HR			1.0	↓	↓	↓				↓	
C ₂ O ₄ ²⁻			3.6	↓					↓	↓ (Y)	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
NO ₂ ⁻	HR				HR					↓ R				HR	↓		0.41 ((Y))	↓ R	↓	↓				↓	
NO ₃ ⁻																									
F ⁻		0.13		↓	0.5		↓	4.0	1.0	↓ (W)	↓ (W)	1.4	2.6	↓	1.6	↓			↓		0.16	↓	↓	↓	
SO ₄ ²⁻							0.21									↓	0.84		↓		↓	↓	↓		
PO ₄ ³⁻	HR	↓		↓	↓	↓	↓	↓	↓	↓ (W)	↓	↓ (P)	↓	↓	↓	↓	↓ (Y)	↓	↓	↓	↓	↓	↓	↓	
HPO ₄ ²⁻		↓		↓	↓	↓	↓	↓	↓	↓ (W)	↓ (W)	↓ (P)	↓	↓	↓	↓	↓ (Y)	↓	↓	↓	↓	↓	↓	↓	
H ₂ PO ₄ ⁻					HR		1.0	HR	HR		↓ (W)	HR		↓	↓	HR	↓ (Y)	↓	↓	↓	HR	↓	↓	↓	
ClO ₄ ⁻						2.1																			
MnO ₄ ⁻	HR							HR	↓ R	R		HR					0.91	R		R		↓ R			
Br ⁻																	↓ ((Y))						0.98		
I ⁻											R			↓ R			↓ (Y)	1.0					↓ (Y)	↓ (B)	

No entry: Soluble compound ↓: Insoluble compound R: Redox reaction at room temperature
 HR: Soluble at room temperature. In hot solution a reaction with an observable effect (not necessarily a precipitate) takes place.
 Solubilities in g (substance) / 100 g water. Only accurately known values between 0.1 and 4 are shown.
 Precipitates whose colour significantly differs from that of their hydrated ions: (B) = black, (P) = purple, (Y) = pale yellow, (Y) = yellow.

Name: _____

Code: MAS- _____

Task 1

10% of the total

1a	1b	1c	1d	Task 1
30	2	12	4	48

a) Yield of the product in g, measured by the organizer:

b) Calculate the theoretical yield of your product in g.

Theoretical yield:

c) Sketch your developed TLC plate. Place your TLC plate in the labeled ziplock bag and leave it on your desk to be evaluated.

Name: _____

Code: MAS- _____

d) Interpret your experiment and choose the correct answer.

The acetylation reaction of glucose is exothermic.

- a) Yes
- b) No
- c) Cannot be decided based on these experiments

The isomerisation reaction of β -D-glucopyranose pentaacetate can be used for the preparation of pure α -D-glucopyranose pentaacetate.

- a) Yes
- b) No
- c) Cannot be decided based on these experiments

Name: _____

Code: MAS- _____

Task 2

15 % of the total

2a	2b	2c	2d	2e	Task 2
25	4	25	6	5	65

a) Ce^{4+} consumptions:

Average volume consumed (V_1):

b) The titration reaction:

Calculation of sample mass:

$\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ mass (m):

c) Zinc consumptions:

Average volume consumed (V_2):

Name:

Code: MAS-

d) Mark the correct answer.

The diphenylamine indicator changes colour at the end point

- a) because the concentration of the Zn^{2+} ions increases.
- b) because the concentration of the $[\text{Fe}(\text{CN})_6]^{4-}$ ions decreases.
- c) because the concentration of the $[\text{Fe}(\text{CN})_6]^{3-}$ ions increases.
- d) because the indicator is liberated from its complex.

Which form of the indicator is present before the end point?

- a) Oxidized
- b) Reduced
- c) Complexed to a metal ion

At the beginning of the titration the redox potential for the hexacyanoferrate(II) - hexacyanoferrate(III) system is lower than the redox potential of the diphenyl amine indicator.

- a) True
- b) False

e) Determine the formula of the precipitate. Show your work.

The formula of the precipitate:

Items replaced or refilled:

Student signature:

Supervisor signature:

Name: _____

Code: MAS- _____

Task 3

15 % of the total

Task 3
108

Only fill out this table when you are ready with all your assignments.

	1	2	3	4	5	6	7	8
Cation								
Anion								