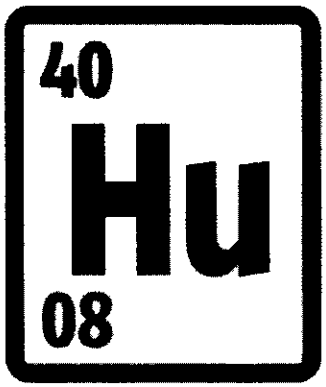



# 40th International Chemistry Olympiad

# Practical tasks

15 July 2008
Budapest, Hungary

# Instructions

- This examination is divided into two parts. 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 glassware and chemicals. You will then have **2 hours** to work on **Task 3**.
- This examination has **10** pages and **5** pages of answer sheets (**8+4** pages for Tasks 1-2; **2+1** pages for 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 **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 rough working paper.
- You will need to reuse some glassware during the exam. Clean them carefully at the sink closest to you.
- Use the labelled **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.
- Laboratory equipment and chemicals are not supposed to be **refilled or replaced**. Each such incident (other than the first, for which you will not be penalised) will result in the **loss of 1 point** from your 40 practical points.
- When you have finished each 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 ($H_2O$) in jugs for refill |
| Latex gloves (ask for a replacement if allergic to latex) |
| Labelled 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. |
| Tweezers |
| Spatula |
| Glass rod |
| Ceramic tile |
| Paper tissue |
| Spray bottle with distilled water |
| 9 Eppendorf vials in a foam stand |
| TLC plate in labelled ziplock bag |
| Plastic syringe (100 mL) with polypropylene filter disc |
| Pipette bulb |
| 14 graduated plastic Pasteur pipettes (**6** for Tasks 1 & 2; **8** for Task 3) |
| Petri dish with etched competitor code |
| Burette |
| Stand and clamp |
| Pipette (10 mL) |
| 2 beakers (400 mL) |
| Beaker and watchglass lid with filter paper piece for TLC |
| 10 capillaries |
| 2 graduated cylinders (25 mL) |
| 3 Conical flasks (200 mL) |
| Beaker (250 mL) |
| 2 beakers (100 mL) |
| Funnel |
| Volumetric flask (100 mL) |
| 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

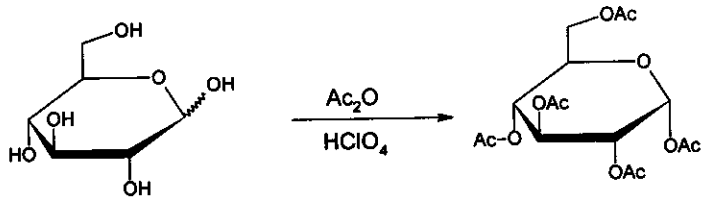
| **Sets for 4-6 people** | **R phrases** | **S phrases** |
|---|---|---|
| 0.025 mol/L ferroin solution | 52/53 | |
| 0.2 % diphenylamine, $(C_6H_5)_2NH$ solution in conc. $H_2SO_4$ | 23/24/25-33-35-50/53 | 26-30-36/37-45-60-61 |
| 0.1 mol/L $K_3[Fe(CN)_6]$ solution | 32 | |
| Pumice stone | | |
| **On 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, $C_6H_{12}O_6$, preweighed in vial | | |
| $(CH_3CO)_2O$ in conical flask (12 mL) | 10-20/22-34 | 26-36/37/39-45 |
| $(CH_3CO)_2O$ in vial (10 mL) | 10-20/22-34 | 26-36/37/39-45 |
| $CH_3COOH$ in vial (15 mL) | 10-35 | 23-26-45 |
| $CH_3OH$ in vial (10 mL) | 11-23/24/25-39 | 7-16-36/37-45 |
| 30 % $HClO_4$ in $CH_3COOH$ in vial (1 mL) | 10-35 | 26-36/37/39-45 |
| 1:1 isobutyl acetate – isoamyl acetate in vial (20 mL), labeled as ELUENT | 11-66 | 16-23-25-33 |
| solid $K_4[Fe(CN)_6].3H_2O$ sample with code in small flask | 32 | 22-24/25 |
| $ZnSO_4$ solution labeled with code and concentration (200 mL) | 52/53 | 61 |
| 0.05136 mol/L $Ce^{4+}$ solution (80 mL) | 36/38 | 26-36 |
| 1.0 mol/L $H_2SO_4$ solution (200 mL) | 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**

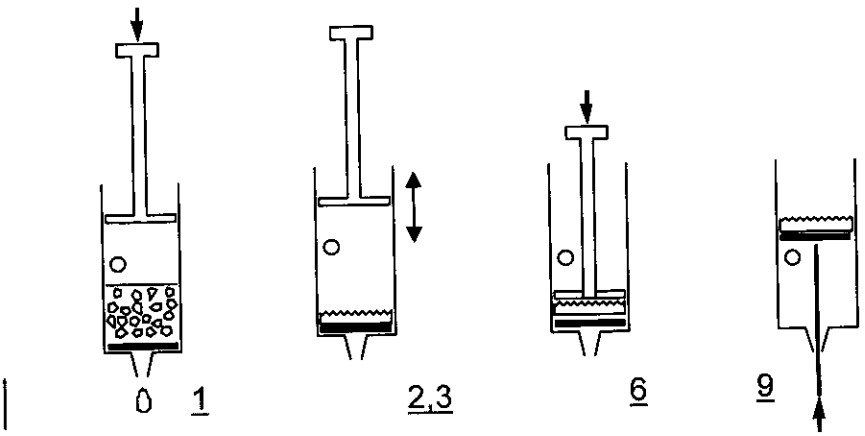



*Caution: Use gloves while manipulating acetic acid and acetic anhydride. Let the lab supervisors know if any is spilled.*

Add and mix 12 mL of pure acetic acid to 12 mL of acetic anhydride (provided in a conical flask) and add 3.00 g glucose (acetic anhydride is in excess). Add (with a Pasteur pipette) 5 drops of 30% $HClO_4$ dissolved in acetic acid. After the addition of the catalyst the solution might warm up considerably.

Leave the mixture covered for 10 minutes and swirl it from time to time. Pour the reaction mixture into 100 mL of water (either tap or distilled) in a beaker. Scratch the wall of the beaker with a glass rod to initiate crystallization, and let it crystallize for 10 minutes. Filter and wash the product twice with 10 mL of water using the syringe and the porous polypropylene filter disc.

**Filtration using a plastic syringe**



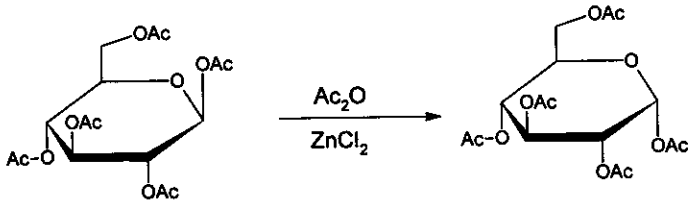

1. Pull out the piston. Fill the syringe from above with the suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.
2. Cover the hole with your finger and press in the piston as far as the hole.
3. Open the hole and draw the piston back, taking care not to draw 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.
7. Wash the product twice with 10 mL 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 it, weigh it and check it for purity.

**b)** Calculate the theoretical yield of your product in grams. (*FW*(C) = 12 g/mol, *FW*(O) = 16 g/mol, *FW*(H)= 1.0 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 mL acetic anhydride to 50 mg of anhydrous $ZnCl_2$ (preweighed in a test tube). Add 100 mg of pure β-D-glucopyranose pentaacetate (BPAG) and swirl until dissolved. Take three drops from this mixture into an Eppendorf tube, add 0.5 mL methanol and save it.

Place the test tube in the heating block (in the fume hood) which has been preadjusted to 70°C. Mix the contents of the test tube from time to time. During the reaction take three drops of sample from the mixture with a Pasteur pipette after 2, 5, 10, and 30 minutes. Transfer each sample to an Eppendorf tube, immediately add 0.5 mL of methanol and mix to stop the reaction.

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

**c)** Copy your plate on the answer sheet and place your plate in the labelled ziplock bag for evaluation.

**d)** Interpret your experimental findings by answering the questions on the answer sheet.

# Task 2

*Caution: You have been provided a 10 mL pipette with **two** graduation marks. To deliver an accurate volume, fill the pipette to the upper mark and drain it carefully to the lower mark. Do not let all the solution drain out of the pipette!*

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 determine the empirical formula of the precipitate (which is stoichiometric and contains no water of crystallization).

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

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

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

**a)** Report your $Ce^{4+}$ solution titres.

**b)** Give the equation for the titration reaction. Calculate the mass of your $K_4[Fe(CN)_6].3H_2O$ sample.

### The reaction between zinc ions and potassium hexacyanoferrate(II)

Take 10.00 mL of the hexacyanoferrate(II) solution and add 20 mL 1 mol/L sulfuric acid. Add three drops of indicator solution (diphenyl amine) and two drops of $K_3[Fe(CN)_6]$ solution. Note that 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.

**c)** Report your zinc solution titres.

**d)** Interpret the titration by answering the questions on the answer sheet.

**e)** Determine the empirical formula of the precipitate.

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

# Task 3

*Cautions:*

- *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. Each 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: $OH^-$, $CO_3^{2-}$, $HCO_3^-$, $CH_3COO^-$, $C_2O_4^{2-}$, $NO_2^-$, $NO_3^-$, $F^-$, $PO_4^{3-}$, $HPO_4^{2-}$, $H_2PO_4^-$, $SO_4^{2-}$, $HSO_4^-$, $S^{2-}$, $HS^-$, $Cl^-$, $ClO_4^-$, $MnO_4^-$, $Br^-$, $I^-$

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

Identify the compounds in the solutions **1-8**. You may 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 a supersaturated solution for a while. Don't draw negative conclusions too hastily, wait 1-2 minutes where 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 start reactions that do not take place at room temperature.

## Solubility Table at 25 °C

| | $NH_4^+$ | $Li^+$ | $Na^+$ | $Mg^{2+}$ | $Al^{3+}$ | $K^+$ | $Ca^{2+}$ | $Cr^{3+}$ | $Mn^{2+}$ | $Fe^{2+}$ | $Fe^{3+}$ | $Co^{2+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Zn^{2+}$ | $Sr^{2+}$ | $Ag^+$ | $Sn^{2+}$ | $Sn^{4+}$ | $Sb^{3+}$ | $Ba^{2+}$ | $Pb^{2+}$ | $Bi^{3+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3COO^-$ | | | | | | | | | | | | | | HR | | | 1.0 | ↓ | ↓ | ↓ | | | ↓ |
| $C_2O_4^{2-}$ | | | 3.6 | ↓ | | | ↓ | | ↓ | ↓ (Y) | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ |
| $NO_2^-$ | HR | | | | 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) | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ |
| $H_2PO_4^-$ | | | | | 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. Accurately known values between 0.1 and 4 are shown only.
Precipitates whose colour significantly differs from that of their hydrated ions: (**B**) = black, (**P**) = purple, (**W**) = white, ((**Y**)) = pale yellow, (**Y**) = yellow.

Name: Code: AUS-

# Task 1

# 10% of the total

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

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

(Official Use Only):

**b)** Calculate the theoretical yield of your product in grams.

Theoretical yield:

**c)** Sketch your developed TLC plate. Leave the TLC plate in the labeled ziplock bag on your desk to be evaluated.

**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 synthesis of pure α-D-glucopyranose pentaacetate.

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

Name: Code: AUS-

# Task 2

# 15 % of the total

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

**a)** $Ce^{4+}$ titration:

Average titre ($V_1$):

**b)** The titration reaction equation:

Calculation of sample mass:

$K_4[Fe(CN)_6].3H_2O$ mass ($m$):

**c)** Zinc titration:

Average titre ($V_2$):

**d)** Mark the correct answer.

The diphenyl amine indicator changes in colour at the end point

- ☐ a) because the concentration of the $Zn^{2+}$ ions increases.
- ☐ b) because the concentration of the $[Fe(CN)_6]^{4-}$ ions decreases.
- ☐ c) because the concentration of the $[Fe(CN)_6]^{3-}$ 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 reduction potential for the hexacyanoferrate(III) - hexacyanoferrate(II) system is lower than the reduction potential of the indicator.

- ☐ a) True
- ☐ b) False

**e)** Determine the empirical formula of the precipitate. Show all working.

The empirical formula of the precipitate:

Items replaced or refilled: Student signature: Supervisor signature:

Name: Code: AUS-

# 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 | | | | | | | | |