

40<sup>th</sup> International  
Chemistry Olympiad

# Practical tasks

15 July 2008  
Budapest, Hungary

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# Instructions

- This examination has **10** pages and **5** pages of answer sheets (8+4 for Task 1-2, 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 glassware 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 **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

<b>For common use in the lab:</b>
Heating block preadjusted to 70 °C under the hood
Distilled water (H <sub>2</sub> 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
<b>On each desk:</b>
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 <sup>3</sup> ) with polypropylene filter disc
Pipette bulb
14 graduated plastic Pasteur pipettes
Petri dish with etched competitor code
Burette
Stand and clamp
Pipette (10 cm <sup>3</sup> )
2 beakers (400 cm <sup>3</sup> )
Beaker and watchglass lid with filter paper piece for TLC
10 capillaries
2 graduated cylinders (25 cm <sup>3</sup> )
3 Erlenmeyer flasks (200 cm <sup>3</sup> )
Beaker (250 cm <sup>3</sup> )
2 beakers (100 cm <sup>3</sup> )
Funnel
Volumetric flask (100 cm <sup>3</sup> )
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

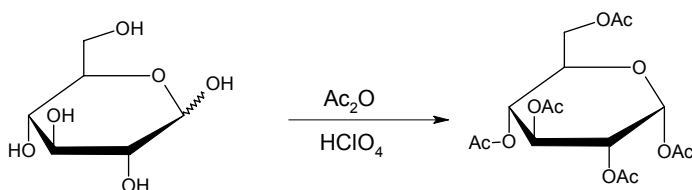
Sets for 4-6 people	R phrases	S phrases
0.025 mol/dm <sup>3</sup> ferroin solution	52/53	
0.2 % diphenylamine, (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NH solution in conc. H <sub>2</sub> SO <sub>4</sub>	23/24/25-33-35-50/53	26-30-36/37-45-60-61
0.1 mol/dm <sup>3</sup> K <sub>3</sub> [Fe(CN) <sub>6</sub> ] solution	32	
Pumice stone		
<b>On each desk:</b>		
50 mg anhydrous ZnCl <sub>2</sub> 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 <sub>6</sub> H <sub>12</sub> O <sub>6</sub> , preweighed in vial		
(CH <sub>3</sub> CO) <sub>2</sub> O in Erlenmeyer flask (12 cm <sup>3</sup> )	10-20/22-34	26-36/37/39-45
(CH <sub>3</sub> CO) <sub>2</sub> O in vial (10 cm <sup>3</sup> )	10-20/22-34	26-36/37/39-45
CH <sub>3</sub> COOH in vial (15 cm <sup>3</sup> )	10-35	23-26-45
CH <sub>3</sub> OH in vial (10 cm <sup>3</sup> )	11-23/24/25-39	7-16-36/37-45
30 % HClO <sub>4</sub> in CH <sub>3</sub> COOH in vial (1 cm <sup>3</sup> )	10-35	26-36/37/39-45
1:1 isobutyl acetate – isoamyl acetate in vial (20 cm <sup>3</sup> ), labeled as ELUENT	11-66	16-23-25-33
solid K <sub>4</sub> [Fe(CN) <sub>6</sub> ].3H <sub>2</sub> O sample with code in small flask	32	22-24/25
ZnSO <sub>4</sub> solution labeled with code and concentration (200 cm <sup>3</sup> )	52/53	61
0.05136 mol/dm <sup>3</sup> Ce <sup>4+</sup> solution (80 cm <sup>3</sup> )	36/38	26-36
1.0 mol/dm <sup>3</sup> H <sub>2</sub> SO <sub>4</sub> solution (200 cm <sup>3</sup> )	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

<b>Indication of Particular Risks</b>			
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		
<b>Combination of Particular Risks</b>			
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
<b>Indication of Safety Precautions</b>			
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.
<b>Combination of Safety Precautions</b>			
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 $\alpha$ -D-glucopyranose pentaacetate

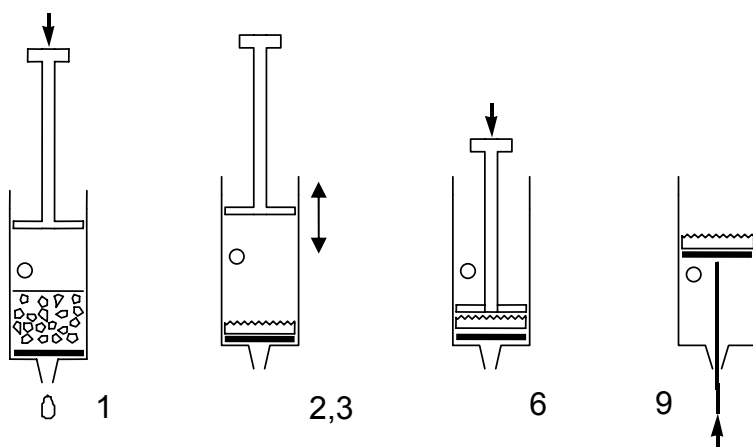


Caution: Use gloves while manipulating acetic acid and acetic anhydride. Let the lab supervisors know if any is spilled.

Add and mix 12 cm<sup>3</sup> of pure acetic acid to 12 cm<sup>3</sup> of acetic anhydride (provided in an Erlenmeyer flask) and add 3.00 g glucose (acetic anhydride is used in excess). Add with a Pasteur-pipette 5 drops of 30% HClO<sub>4</sub> dissolved in acetic acid. After the addition of the catalyst the solution might warm up considerably.

Let the mixture rest covered for 10 minutes and swirl it from time to time. Pour the reaction mixture into 100 cm<sup>3</sup> of water 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 two times with 10 cm<sup>3</sup> of water using the syringe and the porous polypropylene filter disc.

### Filtration using a plastic syringe



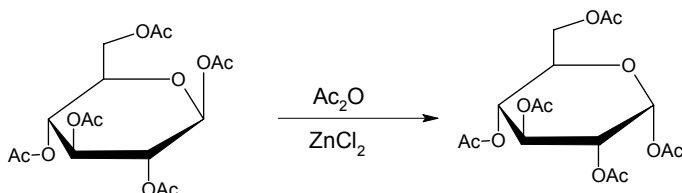
1. Pull out the piston. Fill the syringe from above with the suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.
2. Cover the hole with your finger and press in the piston as far as the hole.
3. Open the hole and draw the piston back. Do not draw in air through 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.
7. Wash the product twice with 10 cm<sup>3</sup> 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 (mass) of your product in g. ( $M(\text{C}) = 12 \text{ g/mol}$ ,  $M(\text{O}) = 16 \text{ g/mol}$ ,  $M(\text{H}) = 1.0 \text{ g/mol}$ )

### Synthesis of $\alpha$ -D-glucopyranose pentaacetate from $\beta$ -D-glucopyranose pentaacetate

An alternative synthesis of  $\alpha$ -D-glucopyranose pentaacetate starts from readily available  $\beta$ -D-glucopyranose pentaacetate. In this experiment we will study the kinetics of this reaction with thin layer chromatography.



Add  $1.5 \text{ cm}^3$  acetic anhydride to 50 mg of anhydrous  $\text{ZnCl}_2$  (preweighed in a test tube). Add 100 mg of pure  $\beta$ -D-glucopyranose pentaacetate (BPAG) and swirl until dissolved. Take three drops from this mixture into an Eppendorf tube, add  $0.5 \text{ cm}^3$  methanol and save it.

Place the test tube in the heating apparatus under the hood closest to your desk. Place the test tube in the heating block preadjusted to  $70^\circ\text{C}$ . 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 pipet after 2, 5, 10, and 30 minutes. Mix immediately each sample with  $0.5 \text{ cm}^3$  of methanol to stop the reaction in an Eppendorf tube.

Prepare a silica TLC plate with the collected samples to study the reaction kinetics. Apply the necessary reference compounds as well 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 (under the 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 labeled ziplock bag.
- d) Interpret your experimental findings answering the questions on the answer sheet.



## Task 2

Insert this remark in your translation if your students do not know this kind of pipette.

Hint: The pipette has two graduation marks. Stop at the second mark to measure out exact volumes. Do not let all the solution to 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 out the composition of the stoichiometric precipitate that 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 redox indication, 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  $K_4[Fe(CN)_6] \cdot 3H_2O$  ( $M = 422.41$  g/mol) sample in the small Erlenmeyer flask and quantitatively transfer it into the  $100.00$  cm<sup>3</sup> volumetric flask. Take  $10.00$  cm<sup>3</sup> portions of the hexacyanoferrate(II) solution. Add  $20$  cm<sup>3</sup>  $1$  mol/dm<sup>3</sup> sulfuric acid and two drops of the ferroin indicator solution to each sample before titration. Titrate with the  $0.05136$  mol/dm<sup>3</sup>  $Ce^{4+}$  solution. Repeat titration as necessary. Cerium(IV) is a strong oxidant under acidic conditions forming  $Ce(III)$ .

- Report the  $Ce^{4+}$  solution volumes 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  $10.00$  cm<sup>3</sup> of the hexacyanoferrate(II) solution and add  $20$  cm<sup>3</sup>  $1$  mol/dm<sup>3</sup> sulfuric acid. Add three drops of indicator solution (diphenyl amine) 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 zinc solution volumes consumed.
- Interpret the titration 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:  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Sn}^{2+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$

Anions:  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ ,  $\text{S}^{2-}$ ,  $\text{HS}^-$ ,  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ ,  $\text{MnO}_4^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$

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

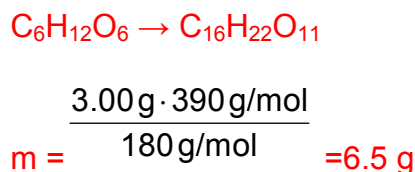
**Task 1****10% of the total**

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

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

The samples are dried by the organizers. Full pts for a 60-100% yield, linear scale between 0-60% yield. The typical yield is 70%.  
 Purity is checked by solubility (acetone) and TLC. If there is no insoluble material and no impurity is detectable by TLC, the full points for the yield are received.  
 If there is a considerable (easily visible) amount of insoluble material or impurity on the TLC plate, then 0 point is received for the yield (only possible in case of intentional contamination).  
 5 points off if filter disc is submitted.

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



Theoretical yield:

c) Sketch your developed TLC plate and leave on your desk to be evaluated,

If both standards and all samples are present and labeled: 5 pts  
 If any sample is missing: 2 pts, if more than one is missing: 0 pt.  
 Loading of the plate: if over- or underloading does not interfere with the evaluability: 4 pts, if interfering, but evaluation is still possible: 2 pts, if evaluation is not possible: 0 pt  
 If the development is appropriate (minor tilting is acceptable): 3 pts. If erratically developed, but still evaluable (the two isomers separate): 1 pt, otherwise 0 pt.

Name:

Code: XXX-

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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  $\beta$ -D-glucopyranose pentaacetate can be used for the preparation of pure  $\alpha$ -D-glucopyranose pentaacetate.

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

Solutions: a, a (2 pts. each)

Name:

Code: XXX-

## Task 2

15 % of the total

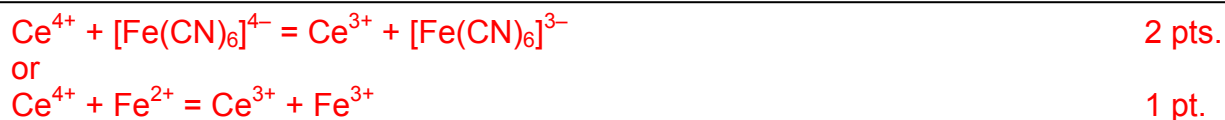
2a	2b	2c	2d	2e	Task 2
25	4	25	6	5	65

a)  $\text{Ce}^{4+}$  consumptions:

Full marks (25 pts.) if  $V_1$  is within  $0.15 \text{ cm}^3$  of the expected value recalculated from the  $\text{K}_4[\text{Fe}(\text{CN})_6]$  mass. Zero marks if deviation is more than  $0.50 \text{ cm}^3$ . Linear scale is applied in between.

Average volume consumed ( $V_1$ ):

b) The titration reaction:



Calculation of sample mass:

$$m = c_{\text{Ce}} V_1 10 \cdot M \quad 2 \text{ pts.}$$

Actual sample masses will be distributed with the exam copies.

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

c) Zinc consumptions:

Full marks (25 pts.) if  $V_2$  is within  $0.15 \text{ cm}^3$  of the expected value recalculated from  $\text{K}_4[\text{Fe}(\text{CN})_6]$  mass, zinc concentrations and empirical ratio. Zero marks if the deviation is more than  $0.50 \text{ cm}^3$ . Linear scale is applied in between.

Average volume consumed ( $V_2$ ):

d) Mark the correct answer.

The diphenyl amine indicator changes in colour at the end point

- a) because the concentration of the  $\text{Zn}^{2+}$  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.

Name:

Code: XXX-

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

Solutions: b, b, a (2 pts. each)

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

The mole ratio of the zinc:hexacyanoferrate(II) in the precipitate can be evaluated as:

$$n_{\text{Zn}}/n_{\text{Fe}(\text{CN})_6} = \frac{10c_{\text{Zn}}V_2M}{m}$$

Values for  $c_{\text{Zn}}$  are distributed according to country color (found on seating plan)  
Red/Pink: 0.0500    Green: 0.0450    Blue: 0.0475    Yellow/Ivory: 0.0525

The empirical ratio obtained from the experiments is 1.489.

Calculating the zinc/hexacyanoferrate(II) ratio: 3 pts.

Cations are needed to make the precipitate neutral and only potassium is present.

The precipitate is  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ . 2 pts.

Any other reasonable calculation giving the same result is accepted.

Hydrogen instead of potassium ( $\text{H}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$  or  $\text{KHZn}_3[\text{Fe}(\text{CN})_6]_2$ ) is also acceptable.

Mistakes in units, dilution factors, significant figures (not 3 or 4 in 2b) carry a penalty of 1 pt. in each calculation.

The formula of the precipitate:

Name:

Code: XXX-

---

Items replaced or refilled:

Student signature:

Supervisor signature:



Name:

Code: XXX-

**Task 3****15 % of the total**

Task 3
108

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

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>
Cation								
Anion								

6 pts for each correctly identified ion except for  $\text{HCO}_3^-$  and  $\text{HS}^-$  which are worth 12 pts, bringing up the total to 108 points.

Partial points will be awarded in the following cases:

Anions:

$\text{AgNO}_3$ : Full points if  $\text{NO}_3^-$  is the only anion shown. 3 pts for  $\text{ClO}_4^-$  only. 3 pts if fluoride appears together with nitrate and/or perchlorate. Otherwise 0 pt.

$\text{Pb}(\text{CH}_3\text{COO})_2$ : 3 pts if  $\text{NO}_3^-$  and/or  $\text{ClO}_4^-$  appear together with  $\text{CH}_3\text{COO}^-$ . 1 pt for nitrate and/or perchlorate on their own. Otherwise 0 pt.

3 pts for  $\text{CO}_3^{2-}$  instead of  $\text{HCO}_3^-$ , and for  $\text{S}^{2-}$  instead of  $\text{HS}^-$ .

Cations:

In the case of all alkali metal compounds, 2 pts for an incorrect alkali metal.

1 pt for  $\text{Ca}^{2+}$  or  $\text{Sr}^{2+}$  instead of  $\text{Ba}^{2+}$ .

# Solution

The solutions received by the students contain the following compounds. The country colours can be found on the laboratory seating plan.

Country colour	1	2	3	4	5	6	7	8
Blue	AgNO <sub>3</sub>	KHCO <sub>3</sub>	NH <sub>4</sub> ClO <sub>4</sub>	NaOH	NaHS	Pb(OAc) <sub>2</sub>	BaI <sub>2</sub>	MgSO <sub>4</sub>
Green	Pb(OAc) <sub>2</sub>	NH <sub>4</sub> ClO <sub>4</sub>	NaOH	NaHS	MgSO <sub>4</sub>	KHCO <sub>3</sub>	AgNO <sub>3</sub>	BaI <sub>2</sub>
Ivory	NH <sub>4</sub> ClO <sub>4</sub>	Pb(OAc) <sub>2</sub>	KHCO <sub>3</sub>	BaI <sub>2</sub>	AgNO <sub>3</sub>	MgSO <sub>4</sub>	NaHS	NaOH
L.Blue	NaHS	MgSO <sub>4</sub>	BaI <sub>2</sub>	NH <sub>4</sub> ClO <sub>4</sub>	Pb(OAc) <sub>2</sub>	AgNO <sub>3</sub>	NaOH	KHCO <sub>3</sub>
L.Green	BaI <sub>2</sub>	NaHS	MgSO <sub>4</sub>	AgNO <sub>3</sub>	NaOH	NH <sub>4</sub> ClO <sub>4</sub>	KHCO <sub>3</sub>	Pb(OAc) <sub>2</sub>
Pink	MgSO <sub>4</sub>	NaOH	AgNO <sub>3</sub>	Pb(OAc) <sub>2</sub>	KHCO <sub>3</sub>	BaI <sub>2</sub>	NH <sub>4</sub> ClO <sub>4</sub>	NaHS
Red	NaOH	BaI <sub>2</sub>	Pb(OAc) <sub>2</sub>	KHCO <sub>3</sub>	NH <sub>4</sub> ClO <sub>4</sub>	NaHS	MgSO <sub>4</sub>	AgNO <sub>3</sub>
Yellow	KHCO <sub>3</sub>	AgNO <sub>3</sub>	NaHS	MgSO <sub>4</sub>	BaI <sub>2</sub>	NaOH	Pb(OAc) <sub>2</sub>	NH <sub>4</sub> ClO <sub>4</sub>

The problem can be approached in many ways. Intuition is very helpful in the tentative assignment of some compounds in the early phases of the work. A systematic solution is given here for the blue Country colour.

All solutions are colourless (NaHS may be slightly yellowish because of polysulfide impurity). Solutions **1**, **3**, **6**, **7**, and **8** are practically neutral (pH paper reading about 5-6). Solution **2** is basic (pH = 9) while solutions **4** and **5** are very strongly basic (pH > 11).

We can exclude all ions that only form coloured compounds in aqueous solutions: Cr<sup>3+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and MnO<sub>4</sub><sup>-</sup>. (In principle we should also exclude Mn<sup>2+</sup> but its solutions have a very light pink colour that might be mistaken for colourless. The yellowish solution is strongly basic hence its colour cannot be attributed to iron.) The compounds of H<sup>+</sup>, Sn<sup>2+</sup>, Sn<sup>4+</sup>, Sb<sup>3+</sup>, Bi<sup>3+</sup>, and HSO<sub>4</sub><sup>-</sup> with the possible counter-ions could only exist in markedly acidic solutions; therefore they can also be safely excluded.

Thus the list of possible ions is:

Cations: NH<sub>4</sub><sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Sr<sup>2+</sup>, Ag<sup>+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>.

Anions: OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, S<sup>2-</sup>, HS<sup>-</sup>, Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>.

The unknown solutions react with each other as follows ( $\downarrow$  = precipitate;  $\uparrow$  = volatile product; “no change” means even when boiled, unless indicated otherwise):

	<b>1</b> AgNO <sub>3</sub>	<b>2</b> KHCO <sub>3</sub>	<b>3</b> NH <sub>4</sub> ClO <sub>4</sub>	<b>4</b> NaOH	<b>5</b> NaHS	<b>6</b> Pb(OAc) <sub>2</sub>	<b>7</b> BaI <sub>2</sub>	<b>8</b> MgSO <sub>4</sub>
<b>1</b> AgNO <sub>3</sub>	—	—	—	—	—	—	—	—
<b>2</b> KHCO <sub>3</sub>	$\downarrow$ light yellow $\uparrow$ neutral, odourless	—	—	—	—	—	—	—
<b>3</b> NH <sub>4</sub> ClO <sub>4</sub>	no change	$\downarrow$ white crystals (*)	—	—	—	—	—	—
<b>4</b> NaOH	$\downarrow$ brown-black	no change	boiling: $\uparrow$ basic, odour of ammonia	—	—	—	—	—
<b>5</b> NaHS	$\downarrow$ black solution turns acidic	no change	boiling: $\uparrow$ basic, odour of NH <sub>3</sub> , H <sub>2</sub> S	no change	—	—	—	—
<b>6</b> Pb(OAc) <sub>2</sub>	$\downarrow$ white crystals	$\downarrow$ white $\uparrow$ neutral, odourless	no change	$\downarrow$ white	$\downarrow$ black	—	—	—
<b>7</b> BaI <sub>2</sub>	$\downarrow$ yellow	$\downarrow$ white $\uparrow$ (**)	no change	no change	no change	$\downarrow$ yellow	—	—
<b>8</b> MgSO <sub>4</sub>	$\downarrow$ white crystals	no change (***)	no change	$\downarrow$ white	no change (****)	$\downarrow$ white	$\downarrow$ white	—

(\*): upon boiling, the formation of NH<sub>3</sub> is detectable by its odour and by pH paper.

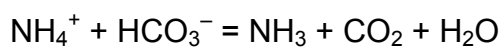
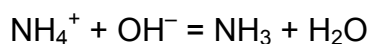
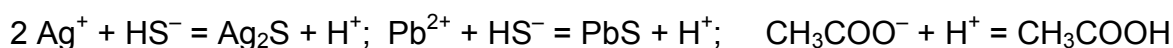
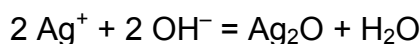
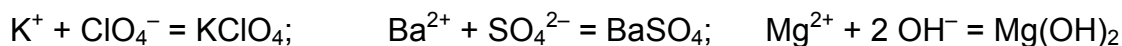
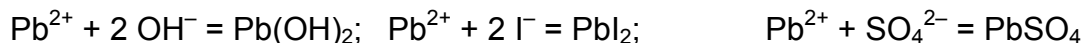
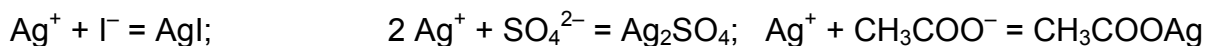
(\*\*): gas bubbles are usually not observed when **2** is in excess.

(\*\*\*): upon boiling, an odourless gas evolves and a white precipitate forms.

(\*\*\*\*): upon boiling, a white precipitate forms and the odour of H<sub>2</sub>S appears.



$\text{Mg}^{2+} + 2 \text{HCO}_3^- = \text{MgCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$  (more accurately, basic carbonates of variable composition are formed)



Two groups of the observed phenomena give instant clues to the identification of some of the ions.

First, the reactions of **2** are often accompanied with the formation of a colourless and odourless gas that can only be  $\text{CO}_2$ . Thus **2** contains  $\text{CO}_3^{2-}$  or  $\text{HCO}_3^-$ .

Second, there are only 3 dark precipitates that can form from the given ions:  $\text{Ag}_2\text{O}$ ,  $\text{Ag}_2\text{S}$ , and  $\text{PbS}$ . This fact, together with the pH of the solutions, instantly identifies the cation of **1** as  $\text{Ag}^+$ , the cation of **6** as  $\text{Pb}^{2+}$ , the anion of **4** as  $\text{OH}^-$ , and the anion of **5** as sulfide or hydrosulfide (confirmed by the distinct smell of the solution).

The choice between the latter two can be made by measuring the pH of the solution formed in the reaction of **5** with an excess of **1** or **6**. In the case of **1**, the reaction mixture is strongly acidic. Thus the anion of **5** is  $\text{HS}^-$ .

The evolution of  $\text{CO}_2$  in the reaction with  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  also identifies the anion of **2** as  $\text{HCO}_3^-$ . (in accord with the moderately basic pH)

The reaction of **3** and **4** yields ammonia. **4** is obviously not a solution of  $\text{NH}_3$  itself. Thus the cation of **3** is  $\text{NH}_4^+$ .

**2+4** do not form either a precipitate or ammonia. The cations of **2** and **4** are  $\text{Na}^+$  or  $\text{K}^+$ .

**2+5** do not form either a precipitate or ammonia. The cation of **5** is an alkali metal.

**3** is the only solution that does not give a precipitate with  $\text{Ag}^+$ . Accordingly, it can be ammonium nitrate, fluoride, or perchlorate. But it does give a precipitate with **2**, a hydrocarbonate of  $\text{Na}^+$  or  $\text{K}^+$ . Thus the anion of **3** is  $\text{ClO}_4^-$  and the cation of **2** is  $\text{K}^+$ .

**4** does not give a precipitate with  $\text{NH}_4\text{ClO}_4$ . The cation of **4** is  $\text{Na}^+$ .

**5** does not give a precipitate either with  $\text{NH}_4\text{ClO}_4$  ( $\text{K}^+$ ) or with a mixture of  $\text{KHCO}_3$  and  $\text{NaOH}$  ( $\text{Li}^+$ ). The cation of **5** is  $\text{Na}^+$ .

**7** forms no precipitate or ammonia with  $\text{NaOH}$  but gives a precipitate with  $\text{KHCO}_3$ . **7** cannot be an alkali metal perchlorate because it forms yellow precipitates with **1** and **6**. Thus the cation of **7** is  $\text{Ba}^{2+}$  and the anion of **7** is  $\text{I}^-$ .

At room temperature **8** gives a precipitate with  $\text{OH}^-$  but not with  $\text{HS}^-$  which means it can only be a salt of a Group 2A metal. Thus the reaction of **8** with  $\text{BaI}_2$  is obviously one

between  $\text{Ba}^{2+}$  and the anion of **8**. The latter is very likely  $\text{SO}_4^{2-}$  but  $\text{HCO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  are also theoretically possible. The solution of **8** is unchanged upon boiling and gives a white precipitate with  $\text{Ag}^+$ . This excludes both  $\text{HCO}_3^-$  and  $\text{H}_2\text{PO}_4^-$ . Thus the anion of **8** is  $\text{SO}_4^{2-}$ . This instantly identifies the cation of **8** as  $\text{Mg}^{2+}$ .

**6** is a soluble compound of lead. The anion could be  $\text{CH}_3\text{COO}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , or  $\text{ClO}_4^-$ . The slight odour of acetic acid might give a clue. Unlike **1**, the reaction of an excess of **6** with  $\text{HS}^-$  does not yield a markedly acidic solution which shows that **6** is a salt of a weak acid. If **6** were a nitrite, it would give a yellowish precipitate with  $\text{Ag}^+$ . It would also react with  $\text{NH}_4\text{ClO}_4$  upon heating with the evolution of  $\text{N}_2$  (and nitrogen oxides from the reaction with  $\text{HS}^-$  would also be noticeable). The absence of these reactions indicates that the anion of **6** is  $\text{CH}_3\text{COO}^-$ .

Soluble salts of silver are even less numerous, the only choices are  $\text{NO}_3^-$ ,  $\text{F}^-$ , and  $\text{ClO}_4^-$ . The anion can be examined if one removes the silver ions from the solution of **1** with an excess of  $\text{NaOH}$ . The  $\text{Ag}_2\text{O}$  precipitate quickly separates from the solution which can be easily poured off. This solution, containing the anion of **1**, does not give a precipitate with  $\text{BaI}_2$  which rules out  $\text{F}^-$ . The solubility of  $\text{KClO}_4$  is quite significant; therefore the absence of a precipitate with  $\text{KHCO}_3$  is inconclusive. The anion of **1** is therefore either  $\text{NO}_3^-$  or  $\text{ClO}_4^-$ .