

XXVIII INTERNATIONAL CHEMISTRY OLYMPIAD

The Experimental Examination

Moscow, 1996, Tuesday, July 16

Please carefully read the texts of problems and study the layout of answer forms before you begin the experimental work.

Attention!

In the laboratory room you must wear safety eye glasses or your own glasses, and use a special pipette filler(bulb) to fill pipettes. Taking off glasses or filling a pipette by mouth will get you a warning from the laboratory supervisor. Repeated faults of this kind will invoke a penalty of 5 points subtracted from the total score of a current problem. The third violation is considered a major fault incompatible with further experimental work, and the person who fails to observe vital safety rules will be dismissed from the laboratory with zero score for the whole experimental examination.

Directions:

1. Please specify your surname, personal code (it is indicated at the working place), and team in the upper right corner of your answer sheet.
1. The work must begin only when the senior supervisor gives a START command.
1. You have 3 hours for Problem 1 in an analytical laboratory, and 2 hours for Problem 2 in an organic chemistry laboratory, including the time needed to fill in the answer sheet forms with your results. You must stop your work and give the filled answer sheets to the supervisor immediately after the STOP command is given. A delay in doing this by 3 minutes will lead to the cancellation of the current problem and will result in zero points for this problem.
1. All experimental and other necessary data must be given in the corresponding boxes in the form. Data written elsewhere cannot be marked. Do not use the back of your answer sheet to write anything. If you need more paper for work, request it from the supervisor.
1. Use only the pen provided in the laboratory.

1. In experiments in the analytical laboratory use only the deionized water, except for cooling purposes.
1. The number of significant digits in numerical answers must conform to the rules of evaluation of experimental errors. The inability to perform calculations correctly will result in penalty points, even if your experiment is flawless.

Problem 1.

Iodometric Determination of Copper(II) and Iron(III) in a Sample of a Technological Solution

Reagents [on bench or shelf]

- $\text{K}_2\text{Cr}_2\text{O}_7$, 0.008333 M [the volumetric flask is labeled "0.05000/6 M"]
- KI, 20% [mass percent]
- HCl, 1 M
- H_2SO_4 , 1 M
- $\text{Na}_4\text{P}_2\text{O}_7$, 5% [mass percent]
- Starch, 1% [mass percent]
- $\text{Na}_2\text{S}_2\text{O}_3$ (to be standardized)
- The solution to be analyzed in 100 mL volumetric flask

(mL = cm^3 throughout)

Glassware and accessories

- A 25 mL burette
- 2 10 mL pipettes
- A 100 mL volumetric flask
- 2 250 mL Erlenmeyer (conical) flasks
- A watch glass
- 2 10 mL graduated cylinders
- 2 25 mL graduated cylinders
- A 100 mL graduated cylinder
- A bulb-type safety pipette filler or pipette pump dispenser
- A wash bottle and a dropper bottle with deionized/distilled water

Procedure

1. Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ solution

1. 10 mL of 1 M solution of H_2SO_4 and 2 mL of 20% KI solution are placed into an Erlenmeyer (conical) flask (the solution must remain colorless).
2. 10.00 mL of $\text{K}_2\text{Cr}_2\text{O}_7$ solution is added.
3. The Erlenmeyer (conical) flask is covered with a watch glass and kept in a dark place for 3 to 5 min.

4. 100 mL of water is added to the flask.
5. The mixture is titrated immediately with $\text{Na}_2\text{S}_2\text{O}_3$ solution until the color of mixture changes to pale yellow. Then, 10 drops of starch solution are added. The titration continues until blue colour disappears completely.
6. It is recommended that the titration (steps 1 through 5) is repeated two more times

Do the following and fill in the answer sheet form

1. Write the balanced equations for the reactions involved in the standardization of the $\text{Na}_2\text{S}_2\text{O}_3$ solution.
2. Calculate the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ solution, and show all calculations.

2. The determination of copper

1. The solution to be analyzed in a 100 mL volumetric flask is diluted with water to the mark and mixed.
2. A 10.00 mL aliquot of the diluted solution is placed into an Erlenmeyer (conical) flask.
3. To the flask add: 20 mL of 5% solution of $\text{Na}_4\text{P}_2\text{O}_7$, 7 mL of 1 M solution of HCl, and 10 mL of 20% solution of KI. A precipitate may form upon the addition of the $\text{Na}_4\text{P}_2\text{O}_7$
4. The Erlenmeyer (conical) flask is covered with a watch glass and left in a dark place for 3-5 min.
5. The mixture is titrated immediately with $\text{Na}_2\text{S}_2\text{O}_3$ solution until the color of suspension changes to pale yellow. Then, 10 drops of starch solution are added. The titration continues until the blue colour disappears leaving an off-white suspension.
6. It is recommended that the titration (steps 2 through 5) is repeated two more times.

Do the following and fill in the answer sheet form

3. Write the balanced equations for the reactions involved in the determination of Cu^{2+} ion.
4. Calculate the mass of copper in the solution under analysis, and show all calculations.

3. The determination of total amount of copper and iron

1. A 10.00 mL aliquot of the solution [prepared in 2(1)] to be analyzed is placed into an Erlenmeyer (conical) flask.
2. 2 mL of 1 M HCl solution and 10 mL of 20% KI solution are added.
3. The Erlenmeyer (conical) flask is covered with a watch glass and kept in a dark place for 3 to 5 min.
4. The mixture is titrated immediately with $\text{Na}_2\text{S}_2\text{O}_3$ solution until the color of suspension changes to pale yellow. Then, 10 drops of starch solution are added. The titration continues until the blue colour disappears leaving an off-white suspension.
5. It is recommended that the titration (steps 1 through 4) is repeated two more times.

Do the following and fill in the answer sheet form

5. Write the balanced equations for the reactions involved in the determination of Fe^{3+} ion.
6. Calculate the mass of iron in the solution under analysis, and show all calculations.

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<i>filled by supervisor !</i>	Laboratory No.		Solution No.	
	Penalty for safety rules violation			

The Solution Report Form

1. Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ solution

Write the balanced equations for the reactions involved in the standardization of the $\text{Na}_2\text{S}_2\text{O}_3$ solution in the space below:

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2. The volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution used for titration

V_1, mL	V_2, mL	V_3, mL	$V_{\text{mean}}, \text{mL}$

calculations:

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The concentration of $\text{Na}_2\text{S}_2\text{O}_3$ solution, M	
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3. Write the balanced equations for the reactions involved in the determination of Cu^{2+} ion

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4. The volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution used for the titration of copper

V_1, mL	V_2, mL	V_3, mL	V_{mean}, mL

<i>calculations:</i>

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The mass of copper in the initial solution [g]	
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5. Write the balanced equations for the reactions involved in the determination of Fe^{3+} ion

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6. The volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution used for the titration of iron and copper

V_1, mL	V_2, mL	V_3, mL	$V_{\text{mean}}, \text{mL}$

Calculations:

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Mean volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution used for the titration of iron, mL	
The mass of iron in the initial solution [g]	

Experimental problem 1. Answers and score points (points are given in shaded square brackets)

1.

Equation	Points	Notes
<input type="text" value="x"/>	[5]	
<input type="text" value="x"/>	[5]	

3.

Equation	Points	Notes
<input type="text" value="x"/>	[5]	i ,
<input type="text" value="x"/>	[5]	i ,
<input type="text" value="x"/>		i ii ,

5.

Equation	Points	Notes
<input type="text" value="x"/>	[5]	i
<input type="text" value="x"/>		
<input type="text" value="x"/>		i ii ,

2, 4 and 6. (see also note v)

Each value of both masses and the value of $\text{Na}_2\text{S}_2\text{O}_3$ concentration can give maximum [25] points depending on the relative accuracy of the result and the number of decimal digits given in the answer.

Points depend on the relative accuracy $|\delta|$ as:

- $|\delta| \leq 2\%$ [25]
- $2\% < |\delta| \leq 4\%$ [20]
- $4\% < |\delta| \leq 5\%$ [15]
- $5\% < |\delta| \leq 6\%$ [10]
- $6\% < |\delta| \leq 8\%$ [7]
- $8\% < |\delta| \leq 10\%$ [5]
- $|\delta| > 10\%$ [0]

The number of significant digits (N) in the answer must be 3 or 4. Otherwise, points ascribed to the result are evaluated as:

- $N = 1$ or 2 the result is recalculated to 4 significant digits and evaluated; [5- N] points are subtracted
- $N > 4$ [$N-4$] points are subtracted from the points calculated basing on the relative accuracy

Numerical error in calculations invokes a penalty of [2] points, subtracted after the recalculation using the raw data and the course of calculations written in the answer sheet.

Incorrectly written calculation formulae means the value of 0 points for the corresponding item

Each result is estimated according to the following sequence

- Is the calculation formula correct?
- Are the calculations correct?
- Are the resulting values correct?
- What is the number of significant digits?

Maximum total points for the problem are [100]

Problem 2.

Qualitative determination of paracetamol in a sample of unknown drug

Introduction

There are three organic compounds which are the most widely used as pain relieving drugs: acetylsalicylic acid (*ortho*-acetoxybenzoic acid, phenacetine (*para*-ethoxy- acetanilide), and paracetamol (*para*-hydroxyacetanilide). Paracetamol is now the most popular, being the base of a large number of well known patented pharmaceuticals (panadol, solpadeine, coldrex, calpol, efferalgan etc.), as it is now considered as the safest and highly efficient drug.

You were given a sample of unknown drug which is claimed to contain paracetamol. Your task is to prove or disprove this claim experimentally. To do this you shall have to prepare an authentic sample of *para*-hydroxyacetanilide, and run a thin layer chromatography test.

Reagents

- *Para*-aminophenol, 3.10 g in a weighing beaker
- Acetic anhydride, 4.00 ml in an Erlenmeyer (conical) flask
- Ethanol
- Eluent (heptane:ethyl acetate:ethanol = 41:47:12, by volume)
- Sample of unknown drug in a test tube, 1% solution in ethanol
- Water (use tap water for all purposes)

Glassware and accessories

- Pyrex glass round-bottom flask, 50 ml
- Reflux condenser
- Hot plate
- Weighing beaker (weighing bottle)
- Pyrex glass beakers, 50 or 100 ml
- Thick-wall conical flask with inlet for suction filtration
- Glass frit filter (sintered glass filter) with rubber ring
- Large beaker for chromatography
- Aluminium thin layer chromatography (TLC) plates covered with silica containing UV indicator
- Small forceps for handling TLC plates

- Glass test tubes
- Glass funnel
- Glass capillaries in a container (shared by 2 students)
- Glass rod with flat end
- Stainless steel spatulas, 2 items
- Support stands with clamps and holders
- Rubber tubing
- Container with ice or ice cold water (may be shared by several students)
- UV cabinet for the development of chromatograms (mounted on a separate table and shared by all students in a room)
- Electronic balances (used by the supervisor)

Procedure

Preparation of para-hydroxyacetanilide

A 50 ml round bottom flask is equipped with reflux condenser and installed on a laboratory stand over a hot plate. Note that the space between the top of the hot plate and the bottom of the flask should be about 1-1.5 cm. Use two clamps to properly support the flask and condenser. Remove the hot plate. Do not turn on the hot plate until you finish adding reagents and reassembling the apparatus. With the reflux condenser temporarily removed, 3.10 g of *para*-aminophenol is placed in the flask using a funnel (use a glass rod to push it through the funnel, if necessary). Water

(10 ml) is then added through the same funnel. The condenser is mounted back, and acetic anhydride (4.00 ml) is carefully poured into the reaction mixture through the condenser (**warning!** acetic anhydride has a strong irritating smell. In case of spill immediately wash hands with water and ask the supervisor to help with the disposal of spilled compound). Carefully stir the contents by slightly relieving the clamps and swirling the flask 2-3 times. Be careful as the mixture and the flask get very hot. Place the flask back over the hot plate. Switch the hot plate on. (**Caution!** many laboratory places are equipped with small hot plates which have no temperature controls and switches. These plates are switched on/off by inserting or removing the plug from the socket. Please consult your supervisor in case you have any doubts about the functioning of this or any electric laboratory equipment). The reaction mixture is heated for 15 minutes beginning from the time when you plug in the hot plate. Then, the heater is switched off (pull the plug from the socket), and removed from the apparatus (**warning!** the plate is still very hot. Touch only plastic casing and move the plate completely out of your reach.) Cool the mixture by immersing the flask into a bath with cold tap water. You may do this immediately after you remove the plate as the flask is made of highly durable glass. After approximately five minutes remove the condenser and pour the contents of the reaction flask into an empty 100 ml pyrex glass beaker. Put the beaker into a metal dish filled with ice and water. Carefully rub the walls of the beaker with a spatula until small white crystals of crude product are formed.

Assemble a suction filtration device: put the frit filter onto a rubber ring stopper and secure into a heavy-walled suction flask. Connect the flask to a water aspirator (suction vacuum pump) and turn on water to create a vacuum (each time you turn on the aspirator, be sure to fully turn on the tap to ensure stable operation of the vacuum pump. Do not leave the pump switched on when not in use. **Caution!** Never turn off the water tap if your device is under vacuum. Always disconnect the flask from vacuum pump by carefully pulling off the rubber tubing from the vacuum flask).

Transfer all of the crystalline precipitate onto the glass frit filter (sintered glass filter) using a spatula. Any remaining solid can be washed out with small portions of ice cold water (as small as possible, as the compound possesses a slight solubility in water, and the losses of dissolved compound must not outweigh the losses due to incomplete transfer of product to the filter). The product in the filter is carefully washed with 2-3 portions of 2-3 ml of cold water by: a) disconnecting the vacuum suction flask from the aspirator (open to the atmosphere); b) addition of water and carefully mixing it with the precipitate using a spatula; c) reapplying the vacuum by reconnecting to the aspirator; d) pressing the precipitate with the flat tip of a glass rod to squeeze out as much water as possible. After the final washing, the suction is continued for 10 more minutes.

Several crystals of material are used for the chromatography test (see below). All other precipitate is moved to a sheet of filtering paper in a Petri dish, and spread out over the filter in a thin layer, and allowed to dry on a shelf (to exclude accidental spills). For rapid drying it is critical to spread the crystals as thinly as possible, break all large pieces, and to stir it and spread again every 3-5 minutes. This will expose all wet crystals to the air. It has been determined from numerous repetitions of this procedure, that after 30 min the product will contain no more than 5% water. This small amount of water retained in the product can be considered insignificant in evaluating the results of this preparation.

Chromatography test.

(If by some reason you have failed to obtain *para*-hydroxyacetanilide, you can obtain a sample for chromatography from your supervisor)

While still wet, several crystals of the material obtained by you are dissolved in a tube containing 1-2 ml of ethanol. The unknown drug is already dissolved in ethanol and given to you as a 1% solution. These solutions are used for thin layer chromatography as described below. (Note that you are given a spare plate for a repeat experiment in case of accidental faults. It should only be used if you consider the results of the first chromatogram as inappropriate. The use of this sheet is not considered a fault and not subject to penalty.)

Take an aluminum TLC plate covered with silica. Using a sharp pencil draw a start line and marks for sample spots. A small spot of each solution is placed on this TLC plate using a capillary. (**Warning!** Broken small glass capillaries are extremely hazardous for eyes and unprotected skin. Never leave the capillaries on a bench unattended. Immediately dispose of the used capillaries into a specially marked container. Never use your mouth to fill or empty a capillary). The spots are allowed to dry for 1-2 minutes.

The plate is placed into a beaker containing the eluent (heptane : ethyl acetate : ethanol) and allowed to be eluted. Use forceps to move the plate in and out of the beaker.

After the elution, remove the plate from the flask, mark the front of eluent, and allow it to dry under the hood for 5 minutes.

Examine the chromatogram under UV light in a special cabinet (**Warning!** you must be attended by the supervisor during this operation. The UV light is potentially harmful to your skin. Do the identification of the compound and unknown as fast as possible, preferably no longer than 1-2 minutes. You may decide to wear rubber gloves to protect your hands.) Outline the dark spots (if there are any) with a sharp pencil.

Weighing of sample

After you complete the chromatography, your product should be almost dry and is ready for weighing. Ask your supervisor to weigh an empty weighing beaker (weighing bottle). Put the dry product into the tared weighing beaker/bottle and give it to the supervisor for reweighing. The supervisor must write the weights on your answer sheet. Calculate the weight of the product.

Do the following and fill in the answer sheet form

1. Draw the structures of three main pain relieving drugs listed above.
2. Draw the reaction equation involved in the preparation of *para*-hydroxyacetanilide. Calculate the stoichiometric amounts of reagents needed for the reaction. How much acetic anhydride is taken in excess over the stoichiometry? The density of acetic anhydride is 1.08 g/ml.
3. Calculate the yield of product obtained by you.
4. Calculate and compare the values of R_f of unknown drug and your product.
5. From your experimental results is it possible that paracetamol is contained in your product? Yes or No (check the correct box on the answer page)

Surname	
Personal code	
Team	

Penalty scores for violation of safety rules (filled by supervisor during the work on the problem)	
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The Solution Report Form

Acetylsalicylic acid	Phenacetine	Paracetamol

2. Reaction equation

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(fill in all blank cells)

	Stoichiometry	Procedure			
	<i>mol</i>	<i>mol</i>	<i>g</i>	<i>ml</i>	excess, %
p-aminophenol	1		3.10		
acetic anhydride				4.00	

3. Fill in immediately after weighing

Weight of empty beaker, <i>g</i>	(filled by supervisor)
Weight of beaker with product, <i>g</i>	(filled by supervisor)
Weight of product, <i>g</i>	

Theoretical yield	<i>g</i>	
Actual yield	<i>g</i>	%

4. Chromatography data

	Retention, <i>mm</i>	Retention factor R_f
Eluent		
Product		
Unknown drug		

5. Place a checkmark in box at the correct statement.

Yes, the sample is likely to contain paracetamol

No, the sample contains no paracetamol