Workplace _____ Surname _____

57th International Mendeleev Chemistry Olympiad

1–6 May 2023

Astana, Kazakhstan

Practical exam

Astana, May 5, 2023

Workplace _____ Surname _____

General instructions

1. During the practical tour, you are required to wear the lab coat and safety goggles (you can wear your prescribed glasses instead).
2. Handle the solutions containing acids and bases very carefully!
3. Use the 3-way pipette bulb when filling pipettes. Pipetting with your mouth is strictly forbidden.
4. You have sufficient, but limited amount of solutions to work with. In case of spillage or re-fill with an extra portion of a solution, penalty points will be deducted.
5. Working with burettes:

   a) The burettes stopcocks are open. Close the stopcock before using them for the first time.

   b) If there is an air bubble at the bottom part of the burette after filling it up, place the burette into vertical position and gently shake it. If this does not help, approach your lab assistant.

   c) The burette may leak. Place a 50 mL beaker under the burette.
6. Dispose of aqueous solutions in a plastic waste container. If it is full, empty the container in the *red waste container* under the fume hood labeled with **Inorganic waste**. Only dispose the chloroform waste in the *red container* under the fume hood labeled with **Organic waste**.
7. For your convenience, the work stations are marked with red tape. While working, do not interfere with other contestants. Keep your workstation clean and ordered.
8. In case you have broken some of your glassware items, ask the lab assistant to remove the debris and provide you with the replacement.
9. You can use the backside of the exam sheets as draft paper.
10. The total duration of the experimental exam is 5 h. There is a countdown timer on the screen. When you hear the STOP signal, you must stop working immediately and hand in all your papers.

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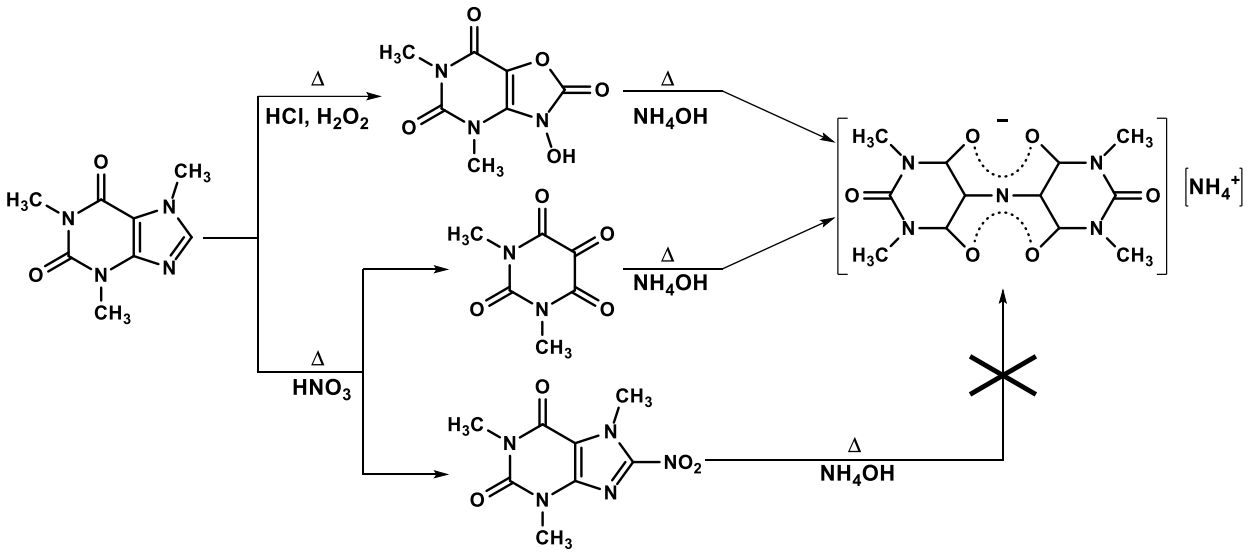
Mendeleev's tea

Introduction

Tea holds a special place in Kazakh culture. It is a source of large number of biologically active substances, including those with a tonic effect. Caffeine is the most known of these. Besides, it is also a valuable chemical and pharmaceutical raw material.

You will extract caffeine from a tea sample and oxidize it to murexide, which is used as an indicator in complexometric titrations. The oxidation of caffeine with HNO_3 or a mixture of HCl/H_2O_2 is given below:



After basifying the reaction mixture, a tetramethyl derivative of murexide is formed. You can use it as an indicator for the titrimetric determination of calcium in a pharmaceutical preparation.

Attention! The exam includes *3 independent* parts. In parts 1 and 2 you should obtain the products to be used in subsequent parts. However, to compensate for any possible losses during these steps, you will be provided with the pure products of Parts 1 and 2. In other words, you will start every new part '*from scratch'*, which will allow marking all parts independently.

Part 1 is time-consuming! You can use the waiting periods to complete other parts. Still, **you must not leave the heating plate with boiling suspension unattended!** The solution can spill over or evaporate under strong heat leading to the beaker damage.

Equipment and labware for all parts

For each participant:

- Stand with clamp and ring
- 0.5 L wash bottle with distilled water (or two 0.25 L bottles)
- Large porcelain bowl for solid waste
- Waste container for liquids (but not for organic solvents; dispose of chloroform waste in the red canisters labeled with **Organic waste** under the fume hood)
- Cloth gloves for handling hot things
- Nitrile or latex gloves
- Goggles

To be shared by 2 participants:

- Heating plate
- Paper tissues

For the whole lab (at the instructor's desk):

- Permanent black markers
- Balance
- Small spatulas
- Sheets of paper for handling the product

Under the fume hood

- Drop-bottles with concentrated HCl and concentrated NH_3
- Metal tongs (to remove the evaporating dish from the heating plate)
- Test-tube rack

Part 1. Extraction of caffeine from black tea

Reagents

- Granules of black tea
- MgO
- 2 M H_2SO_4
- Chloroform
- 2 M NaOH

Equipment

- Non-sterile cotton wool
- Mortar with pestle for grinding tea - 1 pc.
- 100 mL graduated cylinder for water - 1 pc.
- 150 mL beaker for collecting extracts - 3 pcs.
- 400 mL beaker - 3 pcs.
- 25 mL graduated cylinder - 1 pc.
- Glass rod – 1 pc.
- Large glass funnel - 2 pcs.
- Filter paper, white label, d = 15 cm - 8 pcs. (also used in **Part 3**)
- 250 mL separatory funnel with stopper - 1 pc.
- 100 mL evaporating dish - 1 pc.
- Metal spatula - 1 pc.

Keep grinding the given amount (12.5 g) of black tea using the mortar and pestle for 5-10 min, and then transfer it to a 400 mL beaker with MgO (which is added to adsorb the tannins). Add 150 mL of water and carefully stir the suspension. Place the beaker on the heating plate, adjust the heating to maximum and bring the suspension to boiling. ATTENTION! *The suspension foams, and can overflow from the beaker*. When the suspension starts boiling, decrease the heating power and boil for 15 min, occasionally stirring with the glass rod. Meanwhile, prepare the filtration funnel: add a piece of cotton to the big filtration funnel and place it onto the metal ring attached to the stand. Place a clean 400 mL beaker beneath.

After boiling, decant the hot solution over the cotton. Pay attention that the solid residue remains in the beaker!

Add 70 mL of water to the beaker containing the ground tea, boil the suspension for 15 min and decant over a clean piece of cotton. Repeat the procedure for the third time.

Combine the aqueous filtrates and add 12-13 mL of 2 M sulfuric acid. Label the beaker with the permanent marker, place it on the heating plate and evaporate the liquid to approximately half the initial volume.

Prepare four pleated filter papers, a dry and clean glass funnel and a 400 mL beaker. Once the evaporation is over, leave the beaker with hot suspension on the plate and filter the solution through the prepared filter papers into a new beaker in four portions. Use a new filter for each portion.

When the filtrate cools down, transfer it into the separatory funnel, fixed using the metal ring or clamp. Add 15 mL of chloroform to the filtrate and close the separatory funnel with the stopper. Hold the separatory funnel stopper with one hand, and the stopcock with the other. Carefully shake it 2-3 times, which will result in pressure increase inside the separatory funnel. To drop the excessive pressure, hold the funnel vertically with the stopcock up, open the stopcock (do not direct the funnel tip towards people) and release the organic vapors. Repeat the shaking several times, always releasing the excessive pressure as described above.

Fix the separatory funnel onto the metal ring or in the clamp. Remove the stopper and wait until the liquids separate into two phases. Carefully drain the lower phase (chloroform) into a clean 150 mL beaker. Repeat the extraction with chloroform four more times.

Discard the remaining water phase from the separatory funnel in the waste container. Transfer the chloroform extract back to the separatory funnel, add 15 mL of 2M NaOH solution and shake. Wait until the phases separate and drain the lower phase into a clean beaker. Discard the aqueous phase in the waste container. Transfer the chloroform phase in the separatory funnel again and add 15 mL of water. Shake the funnel, let the phases separate and drain the organic layer into a clean beaker. Under the fume hood transfer the chloroform phase from the beaker into a clean 100 mL evaporating dish. Evaporate the organic solution completely, thus obtaining the dry product. Show the evaporated product to the lab assistant and ask for an empty plastic tube. Weigh out the empty test tube together with the lab assistant. Write down the value into the table below and ask for your lab assistant’s signature.

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Write down the product color: _____ Lab assistant's signature _____

Under the lab assistant's control, transfer the product using the spatula first to the sheet of paper (near the balance), and then into the plastic tube. Hand the latter over to the lab assistant for weighing.

	Mass, g	Signature of the lab assistant
Empty plastic tube		
Plastic tube with the isolated product		

Mass of product: _____ g

Once **Part 1** is complete, the lab assistant keeps the test tube.

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Part 2. Murexide test

Reactants

- H_2O_2, 3%
- HCl, conc. (under the hood)
- NH_3, conc. (under the hood)
- Caffeine (in a 2 mL plastic test tube)

Equipment

- 100 mL evaporating dish (the same as in **Part 1**)
- Drop bottle with conc. HCl and conc. NH_3 (under the hood)
- Glass funnel that fits both 10 mL graduated cylinder and test tube (1 pc.)
- 10 mL graduated cylinder for the solution of H_2O_2 (the same as in **Part 1**)
- 15-20 mL test tubes (for colorimetry)
- 2 mL plastic tube with caffeine

Transfer the caffeine from the test tube labeled with «Caffeine» into the 100 mL evaporating dish. Add 2 mL of 3% H_2O_2 and 3 drops of conc. HCl. Transfer the dish onto the heating plate under the fume hood and keep evaporating to dryness (about 15 min). Continue heating until the orange-yellow product is formed (1-2 min). Once the product is formed, add a few drops of conc. NH_3 until the purple-violet coloration of the product stops increasing its intensity. Carefully rinse with distilled water the entire product into a test tube. Bring to the mark (5 mL).

Give the test tube to the lab assistant for colorimetric studies reflecting the product yield.

Color (to be filled by the assistant) _____ Signature of the lab assistant_____

Part 3. Complexometric determination of calcium in calcium gluconate tablets

Reagents

- Powdered calcium gluconate tablets
- Standard solution of Na_2EDTA, 0.025 M
- NaOH, 2 M (use the solution from **Part 1**)
- HCl, 2 M
- Murexide indicator

Equipment

- 10 mL graduated cylinder - 1 pc.
- 25 mL graduated cylinder - 1 pc. (the same as in **Part 1**)
- 150 mL beaker (the same as in **Part 1**)
- 100 mL graduated cylinder (the same as in **Part 1**)
- 100 mL volumetric flask with a stopper - 1 pc.
- 100-125 mL conical flask for titration - 1 pcs.
- 100 mL vial with lid for EDTA - 1 pc.
- 25 mL burette with a stopcock - 1 pc.
- Small glass funnel for filling up the burette - 1 pc.
- 10 mL Mohr or graduated pipette - 1 pc.
- 3-Way pipette bulb - 1 pc.
- Plastic tube with the indicator (murexide)
- Micro spatula for the indicator (located at the lab assistants' table, 2-3 per lab)
- Glass rod (the same as in **Part 1**)
- Funnel for filtration (the same as in **Part 1**)
- Filter paper, white label, d = 15 cm - 1 pc.

Transfer the powdered calcium gluconate tablets from the plastic tube labeled with your workspace number into a 150 mL beaker. Add 5 mL of 2M hydrochloric acid and mix thoroughly usin the glass rod. Add 50 mL water and filter the suspension through the paper filter. Wash the filter with water and transfer the filtrate into the volumetric flask. Bring with water to the mark. Transfer with pipette a 10 mL aliquot of the solution into the conical flask for titration. Add 5 mL of 2 M NaOH using the graduated cylinder and 10-15 mL of water. Mix the solution. With the tip of the spatula, add the solid murexide indicator until the solution has a clearly visible color. Mix until the indicator is dissolved and titrate with the standard

EDTA solution until the color changes from pink to lilac. Keep the overtitrated solution as a reference for the subsequent titrations. Repeat titrations as needed.

Write down your results in the table:

The burette reading, mL		Titration volume of the EDTA solution, mL
Initial	Final	

The accepted EDTA volume (mL): _____

Determine the content of calcium gluconate monohydrate $C_{12}H_{22}CaO_{14}\cdot H_2O$ in your sample (mg):

Answer_____ mg

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Theoretical questions

1. Beside the major compound, there are some excipients in the calcium gluconate tablets.

   1.1. Which excipient interferes most with the determination of the concentration of calcium in the procedure above, if the filtration step of the tablet suspension is omitted?

   ☐ silicon dioxide ☐ starch ☐ magnesium stearate ☐ talc

   1.2. What is the way to eliminate the interference of the excipient?

   ☐ increase pH ☐ increase the ionic strength of the solution

   ☐ decrease pH ☐ decrease the ionic strength of the solution

2. Write down the reaction equation behind the color change during the complexometric titration of calcium. Denote the free form of the murexide as Ind, and EDTA as Y^{4-}.

3. The distribution constant K_D of caffeine between chloroform and water is:

$$K_D = \frac{[\text{Caffeine}]_{(\text{org.})}}{[\text{Caffeine}]_{(\text{aq.})}} = 6.8.$$

Determine the recovery (%) of caffeine from 150 mL of aqueous solution by a single extraction with 75 mL of chloroform.

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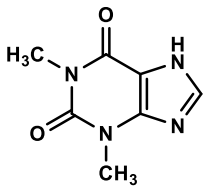
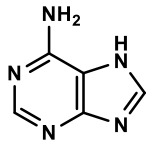
Calculation:

Answer _____%

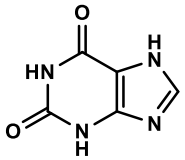
4. Tick the compounds that give a negative murexide test.



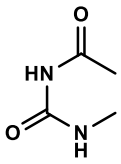
☐ theophylline



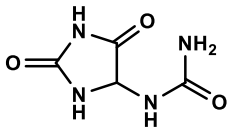
☐ adenine



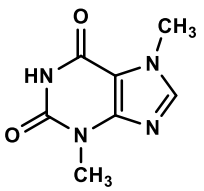
☐ xanthine



☐ 1-acetyl-3-methylurea



☐ allantoin



☐ theobromine

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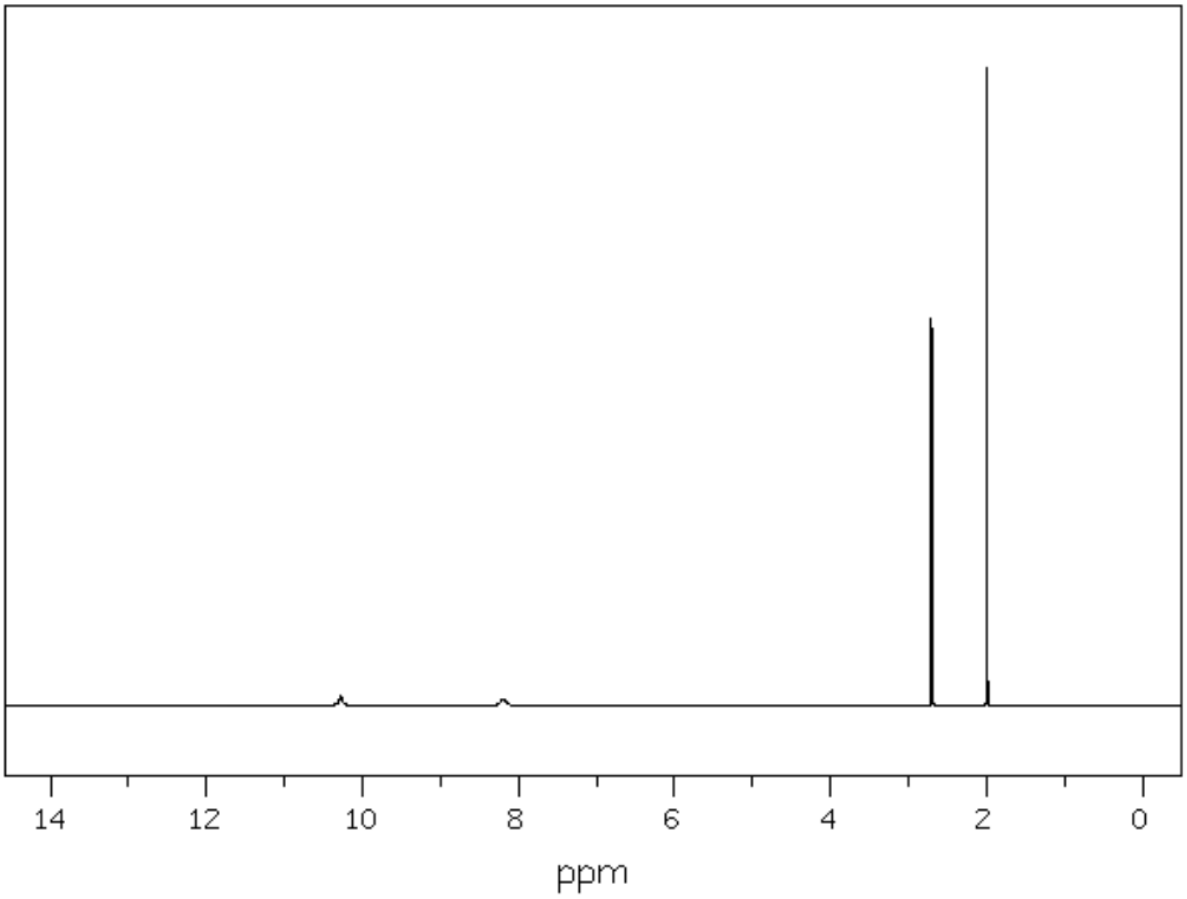
5. Below you can find the ^{1}H NMR spectrum of one of the compounds listed in question 4. Draw the structural formula and assign the signals.



Chemical shift, ppm (intensity)	Multiplicity	Structure of the compound and the assignment
10.3 (1H)	broad singlet	
8.20 (1H)	broad singlet	
2.71 (3H)	doublet	
1.99 (3H)	singlet	