

Student code:



23rd Chemistry Olympiad of the Baltic States

Daugavpils, Latvia

April 24-26, 2015



University of Daugavpils
<http://du.lv/en>



University of Latvia
<http://www.lu.lv/eng/>



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PRACTICAL EXAMINATION, ENGLISH (used for translation and clarification)

" Scientia Vinces "

" Through knowledge you win "

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Introduction

General information

- Keep your safety or optical glasses on, while working in laboratory. Fill pipettes only with a bulb. Food is strongly prohibited in the laboratory.
- Participants must follow safety rules, be polite and keep instruments and your working place in neat order. Do not hesitate to ask laboratory assistant about safety.
- You will have 10 minutes before start of practical tasks for reading. During this reading time you are not allowed to write. In this time you may check your lab equipment present, if something is missing immediately inform lab assistant. You are not allowed to start practical experiments during this reading time.
- **You can only start to work once the START command is given.**
- **You are given 4 hours to complete your experimental work and fill the answer sheets.** You will be notified 15 minutes before the end of practical examination. You must stop working once the “STOP” signal is given. If you are late 5 min or more, your work will be disqualified and you will be given 0 points for practical examination.
- **Write your code** (found on your working place) **in designated areas on ALL of your answer sheets.**
- All results should be written in boxed areas in answer sheets. Information written in other parts of answer sheets will not be graded. Back side of answer sheets can be used as draft but it will not be graded.
- Ask lab assistant if you need clean copy of answer sheets, but it will be in English.
- Do not leave the laboratory without permission.
- You can only use materials given to you in the laboratory.
- Number of decimal places in calculations must be in accordance with experimental error and data analysis principles. You will be penalized for inaccurate calculations, even if your experimental skills are faultless.

Utilization of spilled chemicals and broken glassware

- All filtrates of organic compounds, washing liquids and other waste materials should be placed in waste containers.
- When disposing waste, look for the appropriate waste container.
- Broken glassware should be placed in waste basket.

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Problem 1. Analysis of hydrates (20 marks)

Reagents and equipment

Reagent / equipment	Amount	Label
100 mL volumetric flask	2	
0.0500 M EDTA solution	500 mL	0.0500 M EDTA
Ammonia buffer solution pH = 10	100 mL	pH = 10
25 mL burette	1	
Laboratory stand	1	
White paper A5	2	
Erlenmeyer (conical) flasks, 250 mL	3	
10 mL Mohr's pipette	1	
Distilled (deionized) water in washing bottle	1	Clean H ₂ O
Cleaning towel (from paper)	5	
Weighting bottle	1	
Weighting bottle	1	Hydrate mixture, exact mass
Funnel for transferring solid substances into volumetric flask	1	
Funnel for burette	1	
Pipette filling bulb	1	
Indicator eriochrome black T with spatula	1	
Solid ZnSO ₄ · z H ₂ O	~ 2 g	On table

Introduction

Magnesium is the eight most abundant element in the Earth crust but it only occurs naturally in combination with other elements, where it invariably has a +2 oxidation state. It is found in large deposits of magnesite, dolomite, and other minerals, and in mineral waters. One of magnesium minerals is epsomite or Epsom salt which is hydrate of magnesium sulfate. Epsom salt has been traditionally used as a component of bath salts. Epsom salt can also be used as a beauty product. Athletes use it to soothe sore muscles, while gardeners use it to improve crops.

Zinc is element which is very similar to magnesium, as it also has stable oxidation state of +2 and has similar ion radius as magnesium. Zinc sulfate historically known as "white vitriol". It is a colorless solid that is a common source of soluble zinc ions. Zinc sulfate is used to supply zinc in animal feeds, fertilizers, and agricultural sprays.

In this laboratory problem you will have to analyze mixture of magnesium sulfate hydrate and zinc sulfate hydrate. 1st part of laboratory task was performed by organizers who analyzed magnesium sulfate hydrate and zinc sulfate hydrate by thermogravimetry (TG). Hydrates were heated from ambient conditions to 400°C and mass changes were recorded. Corresponding graphs are shown in figure 1 on next page.

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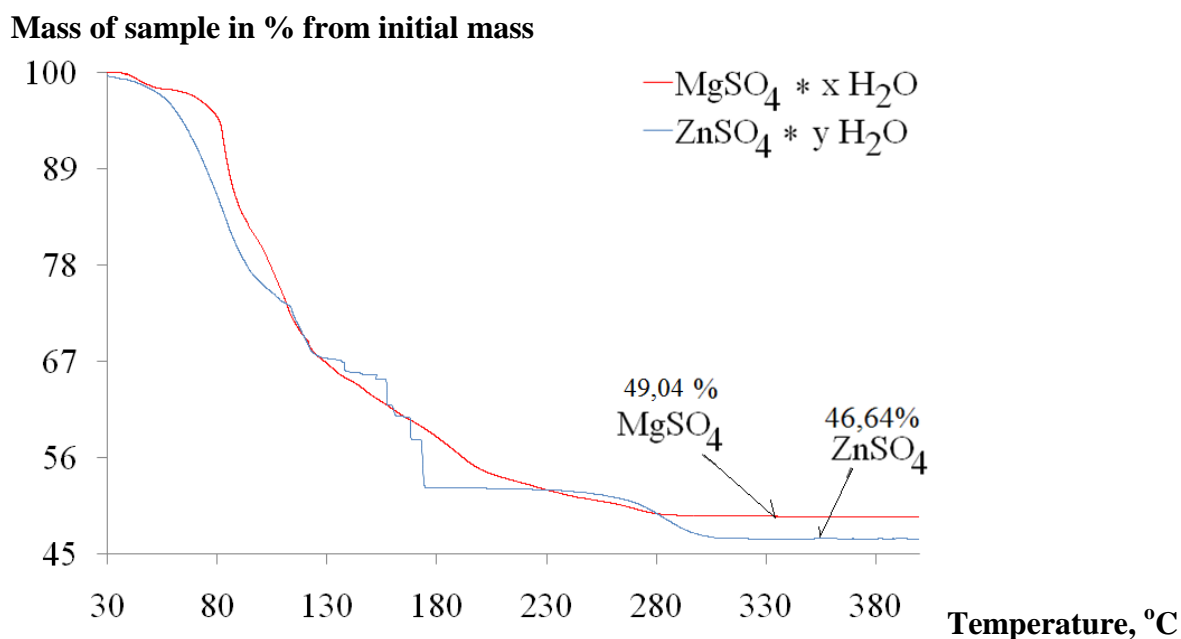


Figure 1. Mass changes in % from starting mass during heating

1.1. Use data from figure 1. and calculate composition of magnesium and zinc sulfate hydrates, find values of x and y . $M(\text{ZnSO}_4) = 161 \text{ g/mol}$; $M(\text{MgSO}_4) = 120 \text{ g/mol}$; $M(\text{H}_2\text{O}) = 18 \text{ g/mol}$.

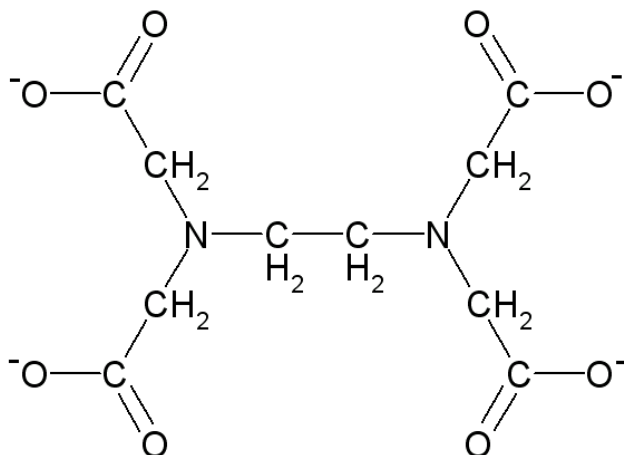
Composition of $\text{MgSO}_4 \cdot x \text{H}_2\text{O}$	Composition of $\text{ZnSO}_4 \cdot y \text{H}_2\text{O}$
<p>$x =$</p>	<p>$y =$</p>

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Composition of zinc sulfate hydrate seems to be unrealistic. So you have to analyze composition of zinc sulfate by titration with EDTA.



EDTA is hexadentate ligand. Its structural formula is shown bellow.



1.2. In structure above circle atoms which binds to metal ions when EDTA anion reacts with metal ions.

Procedure for titration for determination of $\text{ZnSO}_4 \cdot z \text{H}_2\text{O}$ composition.

1. Weight approximately 2 grams of $\text{ZnSO}_4 \cdot z \text{H}_2\text{O}$ on analytical balance and record mass of sample.

Exact mass of $\text{ZnSO}_4 \cdot z \text{H}_2\text{O}$ _____ grams
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2. Quantitatively transfer weighted ZnSO_4 sample into 100 mL volumetric flask till mark with distilled/deionized water.
3. Transfer 10.0 mL of prepared ZnSO_4 solution to Erlenmeyer (conical) flask. Add approximately 10 mL of buffer solution (pH = 10) to solution in Erlenmeyer flask.
4. Add small amount of indicator eriochrome black T (it is provided in solid state as mixture with sodium chloride). Solution turns pink.
5. Titrate solution with 0.05000 M EDTA solution until color changes to light blue. Record your results in Table 1.
6. Circle numbers of those three results you will use for further calculations and calculate value of z (number of moles of water). Show z calculation example in one case bellow table.

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Table 1

No.	Initial volume, mL	End volume, mL	Used volume, mL	z value
1.				
2.				
3.				
4.				

1.3. Example of z calculation (titration result No. ___)

1.4. Calculate average $z_{avg.}$ value (from three results) and random error for z abbreviated as Δz . Fill table 2. It is known that:

$$\Delta z = \frac{S_n \cdot 4,30}{\sqrt{3}}, \text{ where } S_n - \text{standard deviation}$$

$$S_n = \sqrt{\frac{(z_1 - z_{avg.})^2 + (z_2 - z_{avg.})^2 + (z_3 - z_{avg.})^2}{2}}$$

Table 2

Average value $z_{avg.}$	S_n	Δz

1.5. Calculate difference of z between your average value and value obtained from TG measurements.

Difference =

1.6. Compare difference calculated in 1.5. and value of random error Δz and comment on possible systematic error:

There is systematic error if compare titration results with TG results: YES / NO (circle correct).

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Third part of this laboratory experiment is to determine composition of $\text{MgSO}_4 \cdot x \text{H}_2\text{O}$ (x value as calculated in 1.1.) and $\text{ZnSO}_4 \cdot z \text{H}_2\text{O}$ (z value as determined in previous titration) mixture.

Procedure for titration for determination of mixture composition

1. Record mass of hydrate sample provided to you. Written on weighting bottle.

Exact mass of hydrate mixture _____ grams

2. Quantitatively transfer hydrate mixture sample into 100 mL volumetric flask till mark with distilled/deionized water.
3. Transfer 10.0 mL of prepared solution to Erlenmeyer (conical) flask. Add approximately 10 mL of buffer solution (pH = 10) to solution in Erlenmeyer flask.
4. Add small amount of indicator eriochrome black T (it is provided in solid state as mixture with sodium chloride). Solution turns pink.
5. Titrate solution with 0.05000 M EDTA solution until color changes to light blue. Record your results in Table 3.
6. Circle numbers of those titration results you will use for calculation average titration value.

Table 3

No.	Initial volume, mL	End volume, mL	Used volume, mL
1.			
2.			
3.			
4.			

1.7. Calculate average volume of EDTA solution used.

Average volume of EDTA solution used: _____ mL

1.8. Calculate mass fraction of $\text{ZnSO}_4 \cdot z \text{H}_2\text{O}$ in mixture.

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Mass fraction of $\text{ZnSO}_4 \cdot z \text{H}_2\text{O}$ in hydrate mixture is _____ %

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Problem 2. Synthesis of β -naphthol orange (20 marks)

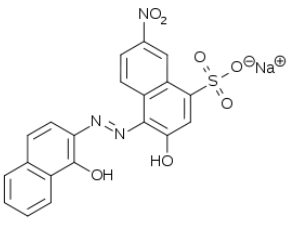
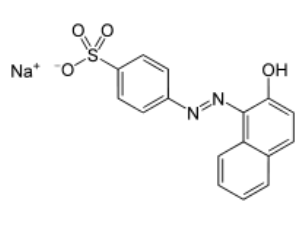
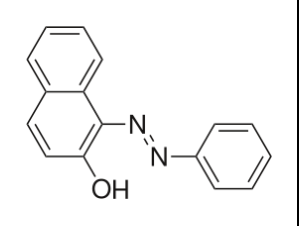
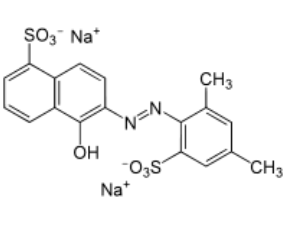
Reagents and equipment

Reagent / equipment	Amount	Label
Gloves	2 pairs	
Laboratory balance (d = ± 0.1 g)	1 on table	
100 mL conical flask	1	
2 M NaOH solution	On table	2 M NaOH
Graduated pipette 10 mL	1	
Universal indicator paper	..	Universal indicator
Glass rod	1	
Electrical stove	1	
Graduated cilinder 25 mL	1	
2 M HCl	On table	2 M HCl
NaNO ₂ solid	On table	NaNO ₂
Sulfanilic acid	On table	Sulfanilic acid
Ice	2 kg (per student) = 40 kg	
Dropping pipette	1	
Filter paper (exact size discs)	3 pieces	
Buchner funnel	1 per table	
Bunzen flask	1 per table	
250 mL beakers	2	
Thermometer (measure temp. <10°C)	1	
2-naphthol	On table	2-naphthol / β -naphthol
NaCl solid	On table	NaCl
Petri dish	1	

Introduction

Acid orange 7, also known as 2-naphthol orange and Orange II, is an azo-dye. It can be synthesized from sulfanilic acid and inorganic reagents.

2.1. Choose correct structure for 2-naphthol orange from structures provided bellow. Mark correct structure with X.

Additional safety information

- The sulfanilic acid is an irritant to skin, eyes, and other mucous membranes. Flush any skin surface with copious amounts of water upon exposure. You may want to wear gloves during this procedure.

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- Sodium hydroxide is caustic and corrosive to all tissues. Flush any skin surface with copious amounts of water upon exposure. The concentrated HCl is also caustic! Gloves should be used.
- Sodium nitrite is used extensively as a preservative for smoked and cured meats, however in large quantities, it is toxic to humans, and irritating to our skin and mucous membranes. Again, wearing gloves would protect your hands.
- 2-Naphthol is highly toxic and can be readily absorbed through the skin. Contact with the skin can cause peeling and discoloration. Actually, gloves would be a really good idea here!
- Both acetone and ethanol are flammable organic solvents.
- The product, Orange II, is not hazardous, but will stain your skin orange! Why not wear gloves so as not to become orange.

2.2. Diazotization of Sulfanilic Acid

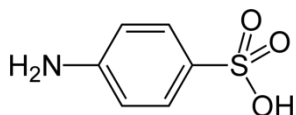
1. Weigh 2.5 g of sulfanilic acid, and place it in a 100-mL Erlenmeyer (conical) flask. Add 6.5 mL of 2 mol/L aqueous NaOH solution. Test solution pH with universal indicator paper, solution should be basic. Heat solution gently on a hot plate, just until the sulfanilic acid dissolves.
2. Cool the flask under running tap water.
3. Weight stoichiometric amount (to sulfanilic acid) of sodium nitrite, dissolve it in 12 mL of water and add to reaction mixture in conical flask.

a) Calculation of sodium nitrite mass:

4. Prepare an acidic ice solution in a 250 mL beaker by putting ~10-12 chunks of ice and 13 mL of 2 M HCl into it. Add dropwise and mixing with glass rod the sulfanilic acid/sodium nitrite solution in this cold solution, follow temperature changes in reaction mixture. Do not allow temperature to rise over 10°C, use more ice if necessary.
5. Watch for a white, powdery precipitate to form. If the precipitate does not form, add a few more drops of HCl until you see it forming. This is your "diazonium suspension".

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b) Write reaction equation for diazotization of sulfanilic acid:



2.3. Orange II Synthesis

1. Cool 22,5 mL of 2M NaOH solution in a 250 mL beaker. Add stoichiometric mass of 2-naphthol (M = 144.17 g/mol) to this cold NaOH solution and stir with your glass rod to dissolve.

a) Calculation of 2-naphthol mass:

2. Pour the diazonium salt suspension (from step 2.2.5.) into this solution with stirring. Stir for 5-10 minutes, until thoroughly mixed and you cannot see any further solid coming out of solution.
3. Add 12.5 grams of sodium chloride to reaction mixture and **cool it in ice bath for 1 hour**. The orange solid that forms is the Orange II dye that we are seeking.
4. Collect the solid product by suction filtration, and "wash" it with small amount of cold water while it is still in the suction apparatus and the suction is flowing.

Reaction equation:

β -naphthol (draw structural formula) +

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5. If you are not able to do 2.4. part (due timing or other reasons), place filtered precipitate on preweighed Petri dish. Report mass of precipitate and ask lab assistant signature for conformation. Allow the moist dye to dry overnight. **YOU DO NOT HAVE TO DO THIS IF YOU ARE ABLE TO DO 2.4. PART - RECRYSTALLIZATION.**

Mass of precipitate:	Lab assistant's signature:
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2.4. Recrystallization of product

1. Dissolve product obtained in part 2.4. in small amount of hot water and heat solution till boiling. Place vial with obtained clear solution in ice bath and observe formation of crystals.
2. Filter these crystals by suction filtration and transfer precipitate on preweighed Petri dish. Report mass of precipitate and ask lab assistant signature for conformation. Allow the moist dye to dry overnight.

Mass of precipitate:	Lab assistant's signature:
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2.5. Additional questions

1. Calculate theoretical yield of product (in grams):

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2. Calculate percentage yield of product using mass from 2.3.5. or 2.4.2. questions:

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3. Temperature in this reaction is important factor as it must be kept below 10°C . Why is diazonium salt so unstable, draw structure of compound which can be formed if temperature rises?

End of practical examination.