27TH BALTIC CHEMISTRY OLYMPIAD

PRACTICAL EXAMINATION

General instructions

- This practical exam booklet contains **18** pages.
- You may begin working as soon as the **START** command is given.
- You have **5 hours** to complete the exam.
- You may work on the tasks in any order, however starting with Problem **EXP1** is highly recommended.
- All results and answers must be clearly written **with pen into their respective boxes** on the exam papers. **Answers written outside the answer boxes will not be graded.**
- Do not use a pencil or a marker to write the answers. These results will not be graded also.
- You are allowed to use a calculator.
- You are provided with 3 sheets of draft paper. If you need more, use the backside of the exam sheets.
- **The official English version** of the exam booklet is available upon request and serves for clarification only.
- If you need to leave the laboratory (to use the toilet or have a drink or a snack), tell your lab assistant. He or she will come to accompany you.
- **You must follow all the safety rules**. If you break the safety rules, you will receive only one warning from the lab assistant. Any safety rule violation after the first warning will result in your dismissal from the laboratory and 0 marks for the entire practical examination.
- Chemicals and labware, unless otherwise noted, will be refilled or replaced without penalty only for the first item. Each further incident will result in the deduction of 1 point from your total practical exam points.
- The lab assistant will announce, when the last 30 minutes are left.
- You must stop your work immediately when the **STOP** command is announced. Failure to stop working or writing will lead to nullification of your practical exam.
- After the **STOP** command has been given, a lab assistant will come to sign your answer sheet. After you and lab assistant have signed the booklet, put it back to the envelope and leave it to your work area together with your product and TLC plate.

Lab rules and safety

- You must always wear safety gloves and lab coat while being in the laboratory. Always keep the lab coat buttoned up.
- Footwear must completely cover your foot and heel. High-heels are not allowed.
- Always wear safety glasses or prescription glasses when working in the lab. Do not wear contact lenses.
- Do not eat or drink in the lab. Chewing gum is not allowed.
- Work only in your designated area. Keep your work area and common work areas tidy.
- No unauthorized experiments are allowed. No modifications of the experiments are allowed. Any suspicious activity will result in warning or dismissal from the experiment depending on the severity of your actions.
- Do not pipet with your mouth. Always use a bulb pipette filler.
- Clean up spills immediately from from any surface (including floor). Let the lab assistant know of any occurring incidence like breaking glass.
- All waste must be properly discarded to prevent contamination or injury. Non-hazardous water soluble/miscible lab waste is allowed for sink disposal. Other lab waste must be disposed of in a marked capped container.

Periodic table

1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

Definition of GHS hazard statements

H224	Extremely flammable liquid and vapour
H225	Highly flammable liquid and vapour
H226	Flammable liquid and vapor
H272	May intensify fire; oxidiser
H290	May be corrosive to metals
H302	Harmful if swallowed
H303	May be harmful if swallowed
H304	May be fatal if swallowed and enters airways
H312	Harmful in contact with skin
H313	May be harmful in contact with skin
H314	Causes severe skin burns and eye damage
H315	Causes skin irritation
H317	May cause an allergic skin reaction
H318	Causes serious eye damage
H319	Causes serious eye irritation
H332	Harmful if inhaled
H333	May be harmful if inhaled
H335	May cause respiratory irritation
H336	May cause drowsiness or dizziness
H340	May cause genetic defects
H350	May cause cancer
H361	Suspected of damaging fertility or the unborn child
H373	May cause damage to organs through prolonged or repeated exposure
H400	Very toxic to aquatic life
H401	Toxic to aquatic life
H402	Harmful to aquatic life
H410	Very toxic to aquatic life with long lasting effects
H411	Toxic to aquatic life with long-lasting effects

Chemicals

For all problems

Chemical	Quantity	Note	Labelled as	GHS hazard statements
Deionized water	–	in wash bottle	**Water**	Not hazardous
Thymol blue solution (indicator)	–	in dropper bottle	**Indicator**	H319

For Problem EXP1

Chemical	Quantity	Note	Labelled as	GHS hazard statements
(–)-menthol	0.500 g	starting material, in Eppendorf tube	**Menthol**	H303, H315, H319, H333,
	ca. 0.002 g	standard for TLC, in Eppendorf tube	**SM**	
Glacial acetic acid	5 cm^3	in graduated test tube with stopper	**CH_3COOH**	H226, H314, H402
Calcium hypochlorite solution	15 cm^3	in Erlenmeyer flask	**$Ca(ClO)_2$**	H272, H302, H313, H314, H318, H400, H410
Sodium bisulfite saturated solution	10 cm^3	in graduated test tube with stopper	**$NaHSO_3$**	H302, H313, H319
6 M sodium hydroxide solution	10 cm^3	in graduated test tube with stopper	**6 M NaOH**	H290, H314
Sodium chloride	–	in plastic bottle	**NaCl**	Not hazardous
Diethyl ether	50 cm^3	in Erlenmeyer flask	**Et_2O**	H224, H302, H336
Anhydrous magnesium sulfate	–	in plastic bottle	**$MgSO_4$**	H302, H312, H332
Eluent (petroleum ether/ethyl acetate 9:1 (v/v))	5 cm^3	in glass bottle	**TLC eluent**	H225, H304, H315, H319, H335, H336, H361, H373, H401, H411
Ethyl acetate	–	on bench in Erlenmeyer flask for sharing	**EtOAc**	H225, H319, H335, H336
Phosphomolybdic acid solution	–	on bench for sharing, for staining TLC plates	**PMA**	H225, H272, H314, H336

For Problem EXP2

Chemical	Quantity	Note	Labelled as	GHS hazard statements
Mayonnaise	20 g	in centrifuge tube	**Mayonnaise**	Not hazardous
0.01 M (exact concentration on bottle) sodium hydroxide solution	–	in glass bottle	**0.01 M NaOH**	H290, H314
Silver nitrate (purity 99.86%)	1 g	in plastic vial	**$AgNO_3$**	H272, H302, H314, H318, H400, H410
Potassium chromate	–	in plastic vial	**K_2CrO_4**	H315, H317, H319, H335, H340, H350, H373, H400, H410

Lab equipment and glassware:

For all problems

Equipment	Quantity
Balance	for sharing
Spatula	1
Plastic Pasteur pipette	7
Permanent marker	1

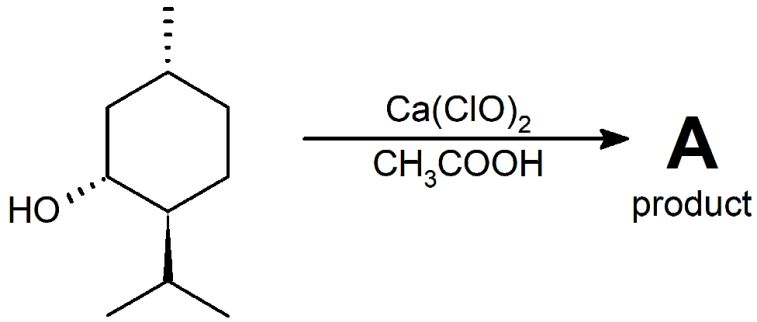
For Problem EXP1

Equipment	Quantity
Magnetic stirrer with stir bar	1
Laboratory stand with clamp holder, clamp and open metal ring	1 (each)
Three-neck round bottom flask + stopper	1 + 1
Round bottom or pear-shaped flask (100 cm^3) (One is labelled as **Product**)	2
Erlenmeyer flask	2
Separatory funnel	1
Glass funnel	1
Fritted glass filter funnel	1
Filtering adapter	1
Graduated cylinder	1
Thermometer	1
Syringe (20 cm^3) with needle	1
Rubber septum	1
Ice bath	1
Glass beaker (50 cm^3) with Petri dish lid	1
Tweezers, pencil, ruler	1 (each)
Filter paper	2
TLC plate (silica gel 60 F_{254})	2
Eppendorf tube (for product sample making for TLC analysis if needed)	1
Hot air gun	for sharing
Vacuum rotary evaporator with vacuum source	for sharing
Organic waste bottle (marked as **Organic waste**)	1

For Problem EXP2

Equipment	Quantity
Magnetic stirrer with stir bar	1
Laboratory stand with clamp holder and clamp	1 (each)
Burette	1
Titration flask (100 cm^3)	3
Volumetric flask (100 cm^3)	1
Container for weighing	1
Glass funnel	1
Glass rod	1
Beaker	3
Graduated cylinder	1
Waste bottle for $AgNO_3$ and K_2CrO_4 (marked as **Aquatic waste**)	1

Problem EXP1. Oxidation of (–)-menthol



starting material

Experimental procedure

1. Add (–)-menthol and glacial acetic acid to the three-neck round bottom flask, equipped with stir bar.

2. Close one side neck with stopper and another with rubber septum (fold it over a neck). Equip the flask top neck with thermometer. **Thermometer is fragile. Be gentle and careful. Be sure that the thermometer does not reach to the stir bar or it might break the thermometer when hitting the stir bar.**

3. Immerse the flask into ice-water bath. Turn stirring on.

4. Take 15 cm^3 of calcium hypochlorite solution using a syringe with needle, pierce the septum with the needle and add the calcium hypochlorite solution dropwise to the solution over a period of ~20 minutes. Maintain the temperature of the reaction between 15–20 °C. (See Figure 1.)

5. After addition of $Ca(ClO)_2$ solution, stir the reaction mixture at room temperature for additional 60 minutes.

6. Cool the mixture in an ice bath, remove the stopper and neutralize the excess of $Ca(ClO)_2$ by adding dropwise sodium bisulfite saturated solution with Pasteur pipette. Stop the neutralization when the temperature stops rising and the yellow colour of the mixture disappears.

7. Filter the reaction mixture (use fritted glass filter funnel, filtering adapter and 100 cm^3 unlabelled flask). (See Figure 2.)

8. Wash the precipitate several times with diethyl ether. Also rinse the flask with diethyl ether. Do not use more than 10−15 cm^3 of diethyl ether.

9. Add few drops of thymol blue indicator solution to the filtrate. Water layer should turn red or yellow.

10. Cool the mixture in an ice bath and add dropwise 6 M NaOH solution until the water layer turns and stays light-blue.

11. Add solid NaCl to the mixture until it is saturated.

12. Place a separatory funnel into a metal ring and place one Erlenmeyer flask under it. Filter the reaction mixture by gravity filtration into a separatory funnel.

13. Perform two 15 cm^3 extractions with diethyl ether. Combine the organic layers in one Erlenmeyer flask. Dry the organic layer over anhydrous magnesium sulfate for about 10 minutes. Filter off the used drying agent through filter paper and collect the filtrate in a pre-weighed round bottom flask which is labelled as **Product**. Give the flask with organic layer to the lab assistant. Product can be recovered from the filtrate by evaporating the solvent on a rotary evaporator. Record the yield.

14. Perform a TLC analysis. It is convenient to spot the product mixture for TLC analysis while it is still dissolved in diethyl ether. Analyse the product on TLC plate with two lanes: one lane for product and another one for starting material. Dissolve the starting material (**SM**) in Eppendorf tube in ethyl acetate. Use 9:1 petroleum ether/ethyl acetate (v/v) as the TLC developing solvent (**TLC eluent**) which is already prepared for your use. For visualisation of starting material and your product on TLC plate, dip the TLC plate for a moment into a phosphomolybdic acid solution (**PMA**) by holding it with tweezers. Take it out, let it dry on a napkin a while and then heat it with hot air gun. **The heat gun heats the blown-out air up to 500 °C. Do not direct the stream towards combustible materials or body parts.** With a pencil, circle all the visualised spots and calculate the R_f values for them. Write your student code on the top of the TLC plate and leave the plate on your working space.

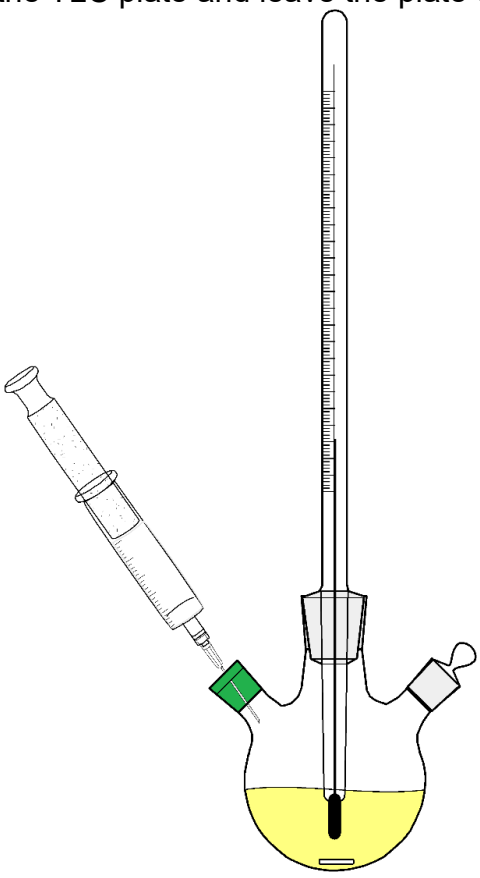


Figure 1. Synthesis apparatus

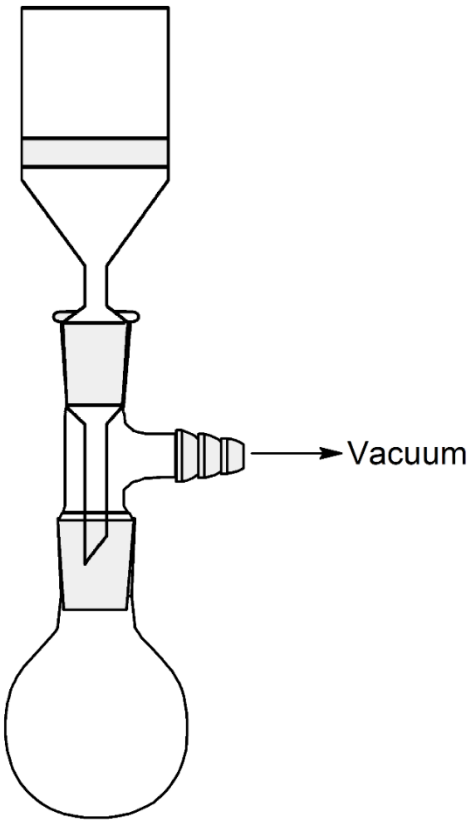


Figure 2. Filtration apparatus

Problems and answers

EXP1. 1. Yield calculations.

Mass of empty flask labelled as **Product**:	g
Mass of flask with product:	g
Mass of product:	g
Calculations: Yield of your synthesis:	%

EXP1. 2. TLC analysis.

Based on the TLC analysis, your synthesis product contains:

	YES	**NO**
Starting material (**SM**)		
Product (**A**)		

Calculation of the R_f (**SM**):

R_f (**SM**) =

Calculation of the R_f (**A**):

R_f (**A**) =

EXP1. 3. Draw the structure of the product **A** including stereochemistry.

EXP1. 4. Write down the chemical reaction which occurs in the excessive $Ca(ClO)_2$ neutralization step.

EXP1. 5. How many stereoisomers and diastereomer pairs are existing for **a)** menthol, **b)** product **A**?

a) for menthol:	**b)** for product **A:**

EXP1. 6. 2,4-dinitrophenylhydrazine is another well-known TLC staining agent besides phosphomolybdic acid. Is it suitable for staining menthol or product **A**? Write the reaction(s) which occur upon staining these compounds with 2,4-dinitrophenylhydrazine.

2,4-dinitrophenylhydrazine is suitable for:

	YES	**NO**
Menthol		
Product (**A**)		

Reaction(s):

EXP1. 7. Which of the compounds, either menthol or product **A** has a lower melting point? Provide an explanation.

☐ Menthol ☐ Product **A** has a lower melting point.
Explanation:

Problem EXP2. Determination of salt and vinegar in mayonnaise

Mayonnaise is generally made of oil, water, eggs, edible acids and seasonings. With titration, it is possible to determine acidity and salt content of mayonnaise.

Part I: Acidity of mayonnaise

Experimental procedure

1. Weigh approximately 2 g of mayonnaise into the titration flask. Add 50 cm^3 of deionized water and thymol blue indicator. Stir well.
2. Titrate with the sodium hydroxide solution until the first visible colour change of the indicator. Repeat if necessary.

Problems and answers

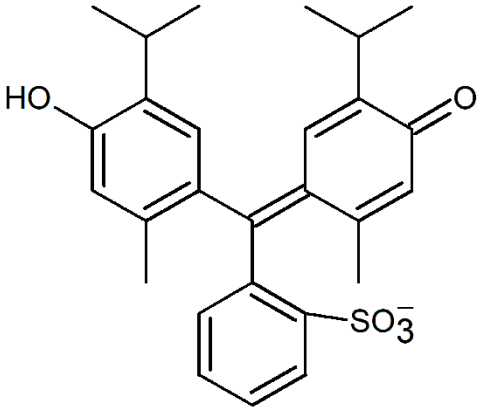
EXP2. 1. Enter the accepted values of the titration into the table. (You do not need to fill in all the rows.)

Analysis No.	Mass of mayonnaise (g)	NaOH solutin consumption (cm^3)
1		
2		
3		

EXP2. 2. Calculate the content of acids (expressed as acedic acid) in g per 100 g of mayonnaise.

Content of acids:

EXP2. 3. The other colour change for thymol blue takes place in very acidic (pH of 1.2−2.8) solutions. Write the other two structures of thymol blue (for pH < 1.2 and pH > 9.6), when the structure in solution with pH 2.8−8.0 is:



pH < 1.2	pH > 9.6

Part II: Determination of NaCl in mayonnaise

Mohr method of determination of chlorides by titration with $AgNO_3$ is one of the oldest titration methods still in use. Chorides are titrated with the silver nitrate solution in the presence of potassium chromate. The method can also be used for determination of bromides or other halides.

Experimental procedure

1. Prepare the titrant, 100 cm^3 of $AgNO_3$ solution with approximate concentration of 0.030 M. Write down the amount of weighed $AgNO_3$ for later calculations.

2. Prepare 10% potassium chromate solution in water that will be used as an indicator.

3. Weigh approximately 2 g of mayonnaise into the titration flask. Add 50 cm^3 of deionized water and ~0.5 cm^3 potassium chromate indicator solution. Stir well.

4. Titrate with the silver nitrate solution until the first visible colour change of the indicator. Repeat if necessary.

Problems and answers

EXP2. 4. Enter the accepted values of the titration into the table. (You do not need to fill in all the rows.)

Analysis No.	Mass of mayonnaise (g)	$AgNO_3$ solution consumption (cm^3)
1		
2		
3		

EXP2. 5. Calculate the exact concentration (mol/dm^3) of the titrant.

Mass of $AgNO_3$:	g
Exact concentartion of titrant:	

EXP2. 6. Calculate the content of chlorides (expressed as NaCl content) in g per 100 g of mayonnaise.

Content of chlorides:

EXP2. 7. Write the reactions taking place in the titration.

EXP2. 8. Write the dissociation reaction of the compound that indicates the end of the titration. Calculate the molar solubility of the same compound (K_{sp} is $1.1 \cdot 10^{-12}$).