ISR_4

PRACTICAL EXAM

51st — International Chemistry Olympiad France — Paris — 2019

Making science together!

2019-07-24

2018 ANNÉE DE LA CHIMIE de l'école à l'université 2019

Liberté • Égalité • Fraternité
RÉPUBLIQUE FRANÇAISE

MINISTÈRE DE L'ÉDUCATION NATIONALE ET DE LA JEUNESSE

MINISTÈRE DE L'ENSEIGNEMENT SUPÉRIEUR, DE LA RECHERCHE ET DE L'INNOVATION

General instructions

- This practical booklet contains 27 pages.
- Before the start of the practical exam, the **Read** command is given. You will have 15 minutes to read the exam booklet. You may only **read** during this time; **do not write nor use the calculator.**
- You may begin working as soon as the **Start** command is given. You will then have **5 hours** to complete the exam.
- You may work on the tasks in any order, but **starting with problem P1 is advised**.
- All results and answers must be clearly written **in pen in their respective designed areas** on the exam papers. Answers written outside the answer boxes will not be graded.
- If you need scratch paper, use the backside of the exam sheets. Remember that **nothing outside the designed areas will be graded**.
- 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 restroom or have a drink or snack), raise the appropriate card. A lab assistant will come to accompany you.
- Shelves above the benches are not to be used during the task for the purpose of equality.
- You must **follow the safety rules** given in the IChO regulations. 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 the nullification of your practical examination.
- Chemicals and labware, unless otherwise noticed, will be refilled or replaced without penalty only for the first incident. Each further incident will result in the deduction of 1 point from your 40 practical exam points.
- The lab supervisor will announce a 30 minutes warning before the **Stop** command.
- You must stop your work immediately when the **Stop** command is announced. Failure to stop working or writing by one minute or longer will lead to nullification of your practical exam.
- After the **Stop** command has been given, the lab supervisor will come to sign your answer sheet.
- After both the supervisor and you sign, place this exam booklet in the envelope and submit it for grading together with your product and thin-layer chromatography (TLC) plates.

Lab rules and safety

- You must wear a lab coat and keep it buttoned up. Footwear must completely cover the foot and the heel.
- 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 gums are not allowed.
- Work only in the designated area. Keep your work area and the common work areas tidy.
- No unauthorized experiments are allowed. No modification of the experiments is allowed.
- Do not pipette with your mouth. Always use a pipette filler bulb.
- Clean up spills and broken glassware immediately from both the bench and the floor.
- All waste must be properly discarded to prevent contamination or injury. Water solutions are eligible for sink disposal. Organic waste must be disposed of in the marked capped container.

לא להילחץ, השתדלו להנות, ובהצלחה!!!

Physical constants and equations

In these tasks, we assume the activities of all aqueous species to be well approximated by their respective concentration in mol L^{-1}. To further simplify formulae and expressions, the standard concentration $c° = 1$ mol L^{-1} is omitted.

Avogadro's constant:	$N_A = 6.022 \cdot 10^{23}$ mol^{-1}
Universal gas constant:	$R = 8.314$ J mol^{-1} K^{-1}
Standard pressure:	$p° = 1$ bar $= 10^5$ Pa
Atmospheric pressure:	$P_{atm} = 1$ atm $= 1.013$ bar $= 1.013 \cdot 10^5$ Pa
Zero of the Celsius scale:	273.15 K
Faraday constant:	$F = 9.649 \cdot 10^4$ C mol^{-1}
Watt:	1 W = 1 J s^{-1}
Kilowatt hour:	1 kWh = $3.6 \cdot 10^6$ J
Planck constant:	$h = 6.626 \cdot 10^{-34}$ J s
Speed of light in vacuum:	$c = 2.998 \cdot 10^8$ m s^{-1}
Elementary charge:	$e = 1.6022 \cdot 10^{-19}$ C
Electrical power:	$P = \Delta E \times I$
Power efficiency:	$\eta = P_{obtained}/P_{applied}$
Planck-Einstein relation:	$E = hc/\lambda$
Ideal gas equation:	$pV = nRT$
Gibbs free energy:	$G = H - TS$
	$\Delta_r G° = -RT \ln K°$
	$\Delta_r G° = -n\, F\, E_{cell}°$
	$\Delta_r G = \Delta_r G° + RT \ln Q$
Reaction quotient Q for a reaction a A(aq) + b B(aq) = c C(aq) + d D(aq):	$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
Henderson−Hasselbalch equation:	$pH = pK_a + \log\frac{[A^-]}{[AH]}$
Nernst–Peterson equation:	$E = E° - \frac{RT}{zF}\ln Q$
where Q is the reaction quotient of the reduction half-reaction	at $T = 298$ K, $\frac{RT}{F}\ln 10 \approx 0.059$ V
Beer–Lambert law:	$A = \varepsilon lc$
Rate laws in integrated form:	
- Zero order:	$[A] = [A]_0 - kt$
- First order:	$\ln[A] = \ln[A]_0 - kt$
- Second order:	$1/[A] = 1/[A]_0 + kt$
Half-life for a first order process:	$t_{1/2} = \ln 2/k$
Number average molar mass M_n:	$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$
Mass average molar mass M_w:	$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$
Polydispersity index I_p:	$I_p = \frac{M_w}{M_n}$

Note

The unit of molar concentration is either "M" or "mol L^{-1}":

1 M = 1 mol L^{-1} 1 mM = 10^{-3} mol L^{-1} 1 µM = 10^{-6} mol L^{-1}

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 statements

The GHS hazard statements (H-phrases) associated with the materials used are indicated in the problems. Their meanings are as follows.

Physical hazards

H225 Highly flammable liquid and vapor.
H226 Flammable liquid and vapor.
H228 Flammable solid.
H271 May cause fire or explosion; strong oxidizer.
H272 May intensify fire; oxidizer.
H290 May be corrosive to metals.

Health hazards

H301 Toxic if swallowed.
H302 Harmful if swallowed.
H304 May be fatal if swallowed and enters airways.
H311 Toxic in contact with skin.
H312 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.
H331 Toxic if inhaled.
H332 Harmful if inhaled.
H333 May be harmful if inhaled.
H334 May cause allergy or asthma symptoms or breathing difficulties if inhaled.
H335 May cause respiratory irritation.
H336 May cause drowsiness or dizziness.
H351 Suspected of causing cancer.
H361 Suspected of damaging fertility or the unborn child.
H371 May cause damage to organs.
H372 Causes damage to organs through prolonged or repeated exposure.
H373 May cause damage to organs through prolonged or repeated exposure.

Environmental hazards

H400 Very 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.
H412 Harmful to aquatic life with long-lasting effects.

Chemicals

For all problems

Chemicals	Labeled as	GHS hazard statements
Deionized water in: - Wash bottle (bench) - Plastic bottle (bench) - Plastic canister (hood)	**Deionized Water**	Not hazardous
Ethanol, in a wash bottle	**Ethanol**	H225, H319
Sample of white wine, 300 mL in amber plastic bottle	**Wine sample**	H225, H319

For problem P1

Chemicals	Labeled as	GHS hazard statements
4-nitrobenzaldehyde, 1.51 g in amber glass vial	**4-nitrobenzaldehyde**	H317, H319
Eluent A, 20 mL in glass vial	**Eluent A**	H225, H290, H304, H314, H319, H336, H410
Eluent B, 20 mL in glass vial	**Eluent B**	H225, H290, H304, H314, H319, H336, H410
Oxone® (potassium peroxomonosulfate salt), 7.87 g in plastic bottle	**Oxone®**	H314
Sample of 4-nitrobenzaldehyde for TLC	**TLC standard**	H317, H319

For problem P2

Chemicals	Labeled as	GHS hazard statements
1 M potassium thiocyanate solution, 20 mL in plastic bottle	**KSCN 1 M**	H302+H312+H332, H412
0.00200 M potassium thiocyanate solution, 60 mL in plastic bottle	**KSCN 0.00200 M**	Not hazardous
1 M perchloric acid solution, 10 mL in plastic bottle	**$HClO_4$**	H290, H315, H319
0.00200 M iron(III) solution, 80 mL in plastic bottle	**Fe(III) 0.00200 M**	Not hazardous
0.000200 M iron(III) solution, 80 mL in plastic bottle	**Fe(III) 0.000200 M**	Not hazardous
0.3% hydrogen peroxide solution, 3 mL in amber glass bottle	**H_2O_2**	Not hazardous

For problem P3

Chemicals	Labeled as	GHS hazard statements
0.01 M iodine solution, 200 mL in brown plastic bottle	**I_2**	H372
0.03 M sodium thiosulfate solution, 200 mL in plastic bottle	**$Na_2S_2O_3$**	Not hazardous
1 M NaOH solution, 55 mL in plastic bottle	**NaOH**	H290, H314
2.5 M sulfuric acid solution, 80 mL in plastic bottle	**H_2SO_4**	H290, H315, H319
0.5 M potassium iodide solution, 25 mL in plastic bottle	**KI**	H372
Potassium iodate, about 100 mg (exact mass written on the label), in glass vial	**KIO_3**	H272, H315, H319, H335
Starch solution, 25 mL in plastic bottle	**Starch**	Not hazardous

Equipment
For all problems

Personal equipment	Quantity
Pipette filler bulb (פיפטור כחול ידני עבור פיפטות)	1
Safety goggles	1
1 L plastic bottle for organic waste, labeled “**Organic waste**”	1
Paper towels	15 sheets
Precision wipers	30 sheets
Spatula (large)	1
Spatula (small)	1
Stopwatch (סטופר)	1
Pencil	1
Eraser	1
Black pen	1
Felt-tip pen for glassware (עט פרמננט לזכוכית)	1
Ruler	1

Shared equipment	Quantity
UV lamp for TLC visualization	2 per lab
Colorimeter (= spectrophotometer)	5 per lab
Gloves	All sizes (S, M, L, XL) available upon request to a lab assistant
Ice bucket	1 per lab

For problem P1

Personal equipment	Quantity
Laboratory stand with: - Clamp holder with small clamp - Clamp holder with large clamp	1 2 1
Erlenmeyer flask with ground joint, 100 mL (ארלנמייר עם לטש מחוספס לחיבור)	1
Erlenmeyer flask with ground joint, 50 mL (ארלנמייר עם לטש מחוספס לחיבור)	1
Reflux condenser	1
Hotplate stirrer	1
Glass cooling bath (קערת זכוכית גדולה עבור אמבט קירור)	1
Magnetic stirring bar	1
Suction flask (בקבוק יניקה לסינון עם חיבור ואקום)	1
Büchner funnel with rubber adapter	1
Zipped bag with 3 pieces of filter paper	1
Petri dish (צלוחית זכוכית שטוחה עם מכסה)	1
TLC elution chamber, labeled “**TLC elution chamber**”	1
Zipped bag with 3 TLC plates (with fluorescence indicator), labeled with Student Code	1
TLC graduated spotters (in Petri dish)(קפילרות קטנות)	4
Plastic tweezers (פינצטה סגולה)	1
Glass rod (מקל זכוכית)	1
Graduated cylinder, 25 mL (משורה)	1
Beaker, 150 mL (כוס כימית)	2

Plastic powder funnel (משפך מוצקים)	1
Disposable plastic pipette	2
Amber glass vial, for TLC sample, 1.5 mL, with stopper, labeled **C** and **R**	2
Pre-weighed amber glass vial, 10 mL, with stopper, labeled with **Student Code**	1
Magnetic stirring bar retriever	1

For problem P2

Personal equipment	Quantity
Volumetric pipette, 10 mL	1
Graduated pipette, 10 mL	3
Graduated pipette, 5 mL	3
Test tube stand	1
Test tubes (מבחנות)	15
Test tube stopper (פקקים למבחנות)	7
Colorimeter cuvette, path length 1.0 cm	2
Beaker, 100 mL	2
Disposable plastic pipette	15

For problem P3

Personal equipment	Quantity
Laboratory stand with burette clamp	1
Burette, 25 mL	1
Glass transfer funnel (משפך זכוכית)	1
Erlenmeyer flask, 100 mL	3
Erlenmeyer flask, 250 mL	3
Beaker, 150 mL	1
Beaker, 100 mL	2
Volumetric flask, 100 mL, with stopper	1
Volumetric pipette, 50 mL	1
Volumetric pipette, 25 mL	1
Volumetric pipette, 20 mL	1
Graduated cylinder, 25 mL	1
Graduated cylinder, 10 mL	1
Graduated cylinder, 5 mL	1
Disposable plastic pipette	3
Parafilm	20 sheets

Problem P1 13% of total	Question	Yield	Purity	TLC	P1.1	P1.2	Total
	Points	12	12	8	2	3	37
	Score						

Problem P1. Greening the oxidation of nitrobenzaldehyde

For the last decades, chemists have tried to replace harmful reagents in oxidation processes in order to reduce hazardous waste treatment. In this problem, potassium peroxomonosulfate has been chosen as oxidizing agent, because it only produces non-toxic and non-polluting sulfate salts. It is provided here as Oxone®.
Furthermore, the reaction itself is performed in a mixture of water and ethanol, which are classified as green solvents.

Your task is to perform the oxidation of 4-nitrobenzaldehyde, to recrystallize the product, to compare TLC eluents and to check the purity of the product using TLC.

Note: Ethanol waste and eluent must be disposed of in the "Organic waste" bottle.

Procedure

I. Oxidation of 4-nitrobenzaldehyde

1. **<u>Mix</u>** 20 mL of water and 5 mL of ethanol.

2. **<u>Insert</u>** the magnetic bar (בוחש מגנטי) in a 100 mL **ground-joint** Erlenmeyer flask (ארלנמייר עם פתח בעל לטש מחוספס).

3. **<u>Transfer</u>** the pre-weighed 1.51 g of 4-nitrobenzaldehyde into the Erlenmeyer flask. **<u>Add</u>** all of the water/ethanol mixture prepared previously. **<u>Clamp</u>** (חברו עם התופסן) the Erlenmeyer flask to the stand. **<u>Start stirring</u>** the mixture, then **<u>add</u>** the pre-weighed 7.87 g of Oxone®.

4. According to figure **1**, **<u>Attach</u>** the reflux condenser by loosening the large clamp and adjusting the ground joints (חברו בעדינות את התופסן הגדול על המעבה). **<u>Raise</u>** your HELP card. A lab assistant will come to turn on the water and set the hotplate (כדי למנוע אסון בניסוי שלכם או של השכן שלכם).

5. **<u>Heat</u>** the reaction mixture with a <u>gentle</u> reflux for **45 minutes**. The mark on the heater corresponds to the necessary power to get a gentle reflux (מסומן לכם על הפלטה חץ לאן שצריך לכוון את החימום).

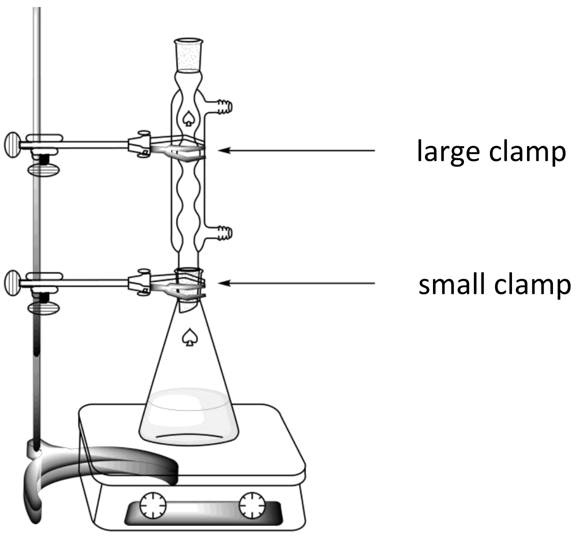


Figure 1. Setup for heating the reaction mixture under reflux

6. Then **turn off** the heating on the hotplate stirrer. **Remove** the hot plate and **let** the reaction mixture cool down for **10 minutes**.

Afterwards, **Place** the Erlenmeyer flask in a glass cooling bath filled with an ice-water mixture. **Let** it stand for another **10 minutes**.

7. **Set up** a vacuum filtration apparatus (see Figure **2**) using a Büchner funnel, a filter paper and a suction flask, that is secured (מחובר טוב) to the laboratory stand with a small clamp. **Raise** your HELP card. A lab assistant will come and show how to connect the suction flask to the vacuum source.

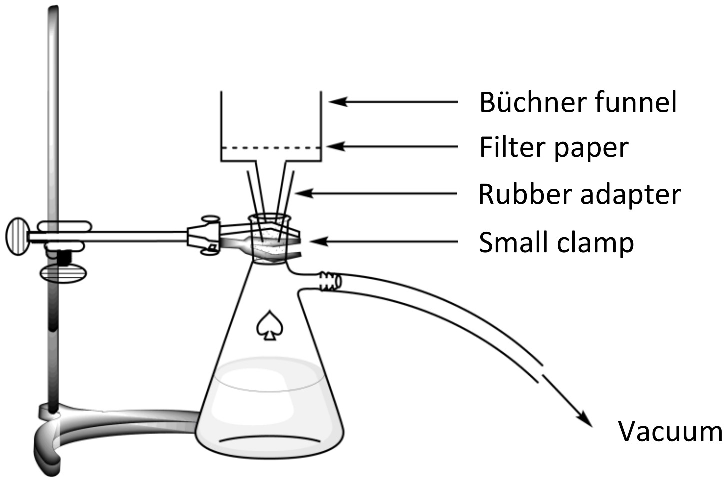


Figure 2. Setup for the vacuum filtration

8. **Wet** the filter paper with water and **ensure** that it covers all the holes of the Büchner funnel.

9. **Pour** the suspension of the crude product into the Büchner funnel and **apply** vacuum. **Wash** the solid thoroughly with deionized water (at least 4×20 mL).

10. **Let** air suck through the precipitate for 5 minutes to pre-dry the product. **Disconnect** the vacuum source. **Use** the small spatula to transfer one tip of spatula (על קצה הספטולה) of the product to the 1.5 mL amber glass vial, **labeled C**. **Close** the vial and **save** it for part III.

11. **Transfer** all of the remaining solid into the 50 mL ground-joint Erlenmeyer flask (ארלנמייר אחר עם לטש עבור הגיבוש בשלב הבא).

12. **Discard** the filtrate in the "Organic waste" bottle and **wash** both the suction flask and the Büchner funnel with ethanol and water. **Use** the "Organic waste" bottle to dispose of ethanol waste.

II. Recrystallization of the product

1. **Prepare** a crystallization solvent from 9 mL of water and 21 mL of ethanol.

2. **Perform** the recrystallization of the crude product contained in the 50 mL ground-joint Erlenmeyer flask using the appropriate amount of the crystallization solvent (עם כמות מתאימה לגיבוש מחדש), using the same setup as for the reflux heating (see Figure **1**): **Raise** your HELP card. A lab assistant will come to turn on the water and set the hotplate. **Add** the solvent from the top of the condenser.

3. Once the product has crystallized, **use** the same procedure as described previously (I.7 to I.10) to collect the solid. **Use** the small spatula to transfer one tip of spatula (על קצה הספטולה) of the recrystallized product in the 1.5 mL amber glass vial, **labeled R**. **Close** the vial and **save** it for part III.

4. **Transfer** the purified solid to the pre-weighed vial labeled with your Student Code. **Close** the vial.

5. **Discard** the filtrate (התסנין) to the "Organic waste" bottle and **raise** your HELP card. A lab assistant will come to turn off the water of the condenser.

III. TLC analysis

1. **Prepare the elution chamber. Add** eluent **A** to the elution chamber to about 0.5 cm in height. Cover it with a Petri dish. **Wait** for the eluent to saturate the atmosphere in the elution chamber.

2. **Prepare your samples**. You are provided a sample of 4-nitrobenzaldehyde in an amber glass vial (וייל כהה מזכוכית) labeled **TLC standard** (referred as **S** on the TLC). You have also kept a small sample of your crude product (vial **C**) and your recrystallized product (vial **R**) in two other amber glass vials. **Add** about 1 mL of ethanol to each of the vials in order to dissolve the samples.

3. **Prepare your TLC plate**. Use a pencil to **draw** carefully the start line (1 cm above the bottom of the plate) and **mark** the positions in order to spot the 3 samples. **Label** them **S** (Starting material), **C** (Crude product) and **R** (Recrystallized product), as described in Figure **3**.

On the top left of the plate, **write** your **Student Code**. On the top right of the plate, **write** the eluent you use (first **Eluent A**, then **Eluent B**). **Spot** the three samples on the plate, using capillary spotters.

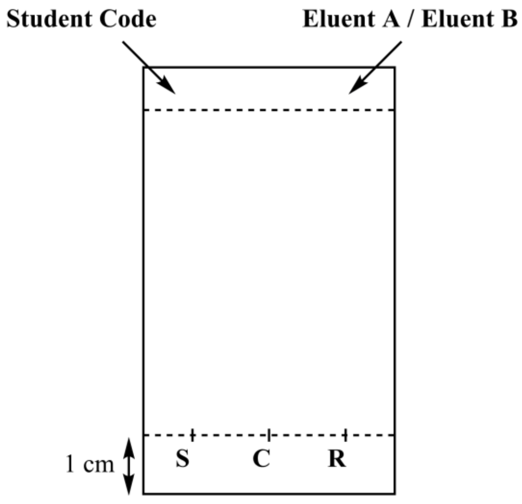


Figure 3. TLC plate preparation

4. **Perform the TLC analysis**. Using tweezers (פינצטה), **insert** the TLC plate into the elution chamber and **cover** it with the Petri dish. **Let** the eluent **reach** approximately 1 cm below the top of the plate. Using tweezers, **remove** the plate, mark the eluent front with a pencil and let the plate air-dry.

5. **<u>Visualize the TLC plate.</u>** **<u>Place</u>** the TLC plate under the UV lamp kept on the common bench. With a pencil, **<u>circle</u>** all the visible spots.

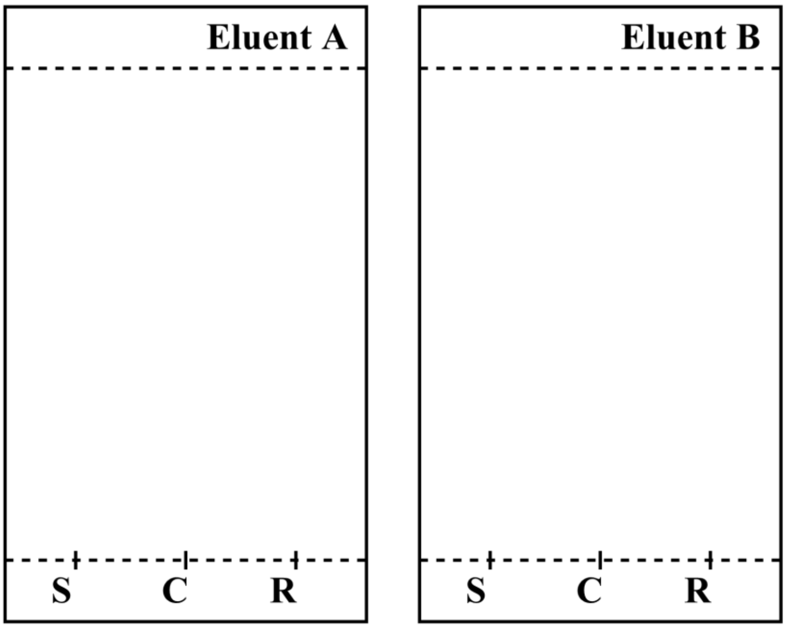
6. **<u>Discard the eluent into the "Organic waste" bottle.</u>**

7. **<u>Repeat</u>** steps 1, 3, 4, 5, and 6 with eluent **B**.

8. **<u>Place</u>** your plates in the zipped bag with your Student Code.

Results of your TLC analysis (you **<u>may complete</u>** the schemes with your results)

You **may** use these drawings to make a scheme of your TLC plates that may help you answer the following questions. **The scheme will not be graded**.



At the end of the examination, your lab supervisor will pick up the following items:

- Glass vial labeled with your **Student Code** containing your recrystallized product;
- TLC plates A and B in zipped bag labeled with your **Student Code**.

Submitted items		
Recrystallized product	□	
TLC plate A	□	
TLC plate B	□	
Signatures	______________ Student	______________ Lab Supervisor

Questions

1. **Propose** a structure for the final organic product from the reaction of 4-nitrobenzaldehyde and Oxone®.

2. Based on your results on the TLC analysis, **answer** the following questions.

- Which eluent is better to follow the reaction progress?

□ **A**	□ **B**

- The crude product (C) contains traces of 4-nitrobenzaldehyde.

□ **True**	□ **False**

- The recrystallized product (R) contains traces of 4-nitrobenzaldehyde.

□ **True**	□ **False**

Problem P2 14% of total	Question	Calibration	Iron determination	P2.1	P2.2	P2.3	Stoichiometry determination	P2.4	P2.5	Total
	Points	10	6	3	4	3	9	3	2	40
	Score									

Problem P2. The iron age of wine

Iron is an element which can naturally be found in wine. When its concentration exceeds 10 to 15 mg per liter, iron(II) oxidation to iron(III) may lead to quality loss, through the formation of precipitates. It is therefore necessary to assess the iron content of the wine during its production.

Given the very low concentration of iron species, a colored complex of iron(III) with thiocyanate SCN^- as a ligand is used to quantify the iron amount, through spectrophotometric measurements.

Your task is to determine the total iron concentration of the white wine provided using spectrophotometry, and to determine the stoichiometry of the thiocyanate – iron(III) complex.

WARNING – חשוב לקרוא

- In this task, you are provided with **two** iron(III) solutions and **two** potassium thiocyanate solutions of **different concentrations**. Be very careful not to confuse them.

- Once the solutions are ready for spectrophotometric measurements, record the absorbance **no later than one hour** after the addition of thiocyanate.

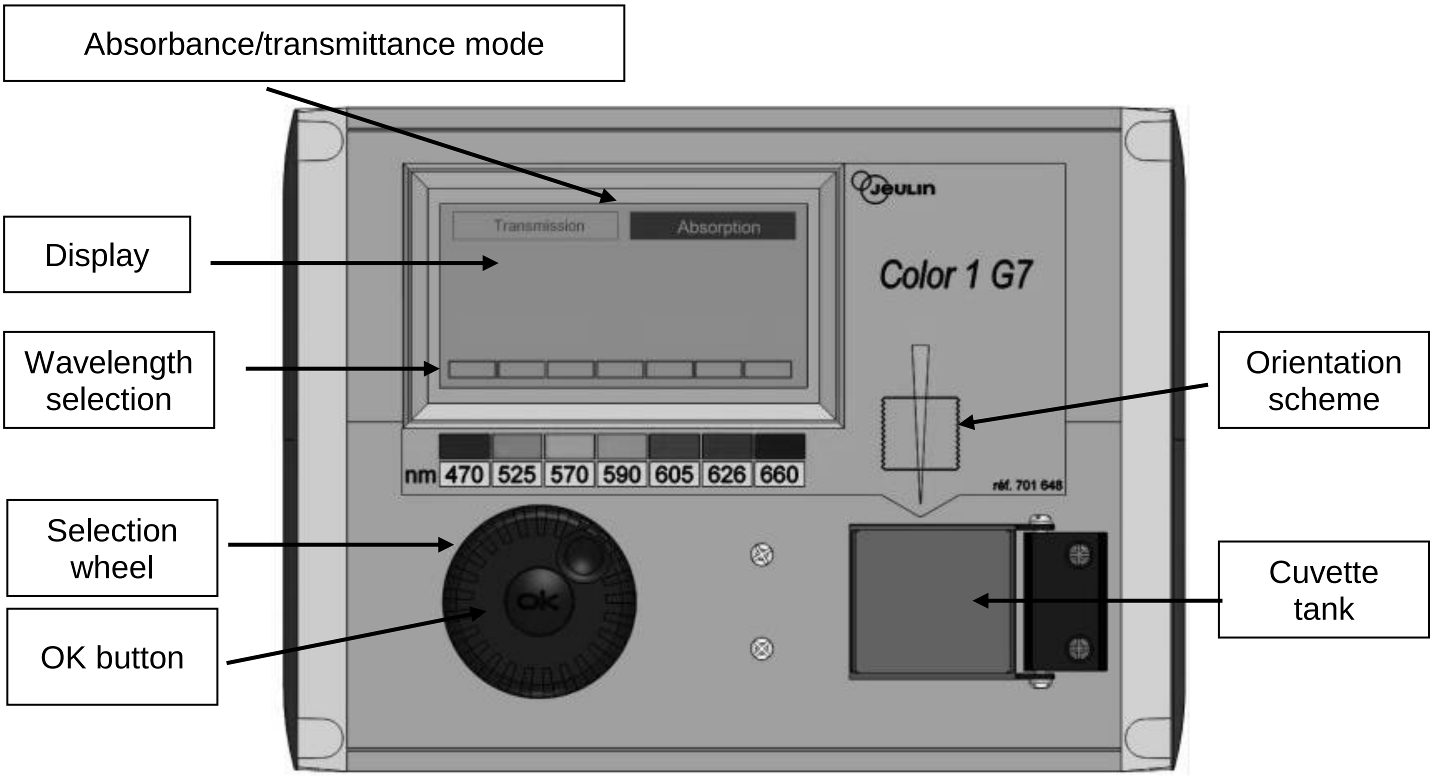
- When you need a colorimeter (**ספקטרופוטומטר**), raise your HELP card. A lab assistant will give you a colorimeter labeled. You will have the exclusive use of this colorimeter for up to **15 minutes**. The lab assistant will take it back as soon as you have finished or when the 15 minutes are over. If no colorimeter is available at the precise moment, you will be added to a waiting-list.

- You can call for the colorimeter **only three times** for this problem.

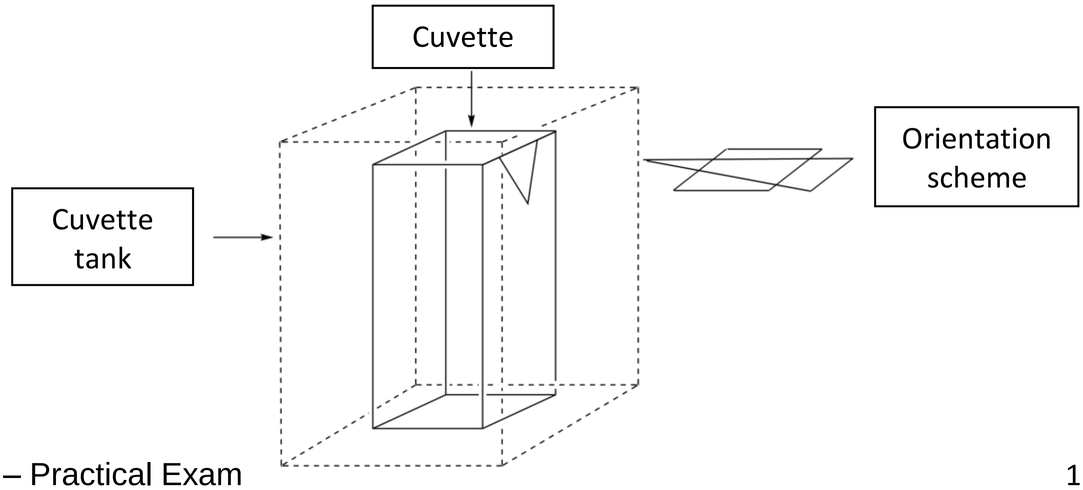
- Instructions for the colorimeter are presented on the following page.

- השימוש ביין הוא לצרכי הבחינה בלבד. לא לשימוש עצמי

Instructions for the use of the colorimeter (ספקטרופוטומטר)



- Plug in the colorimeter (ספקטרופוטומטר).
- Check that “Absorbance” is highlighted. If not, turn the selection wheel until a dashed line (קו מקווקו) appears around “Absorbance” and then press the OK button.
- Turn the selection wheel until a dashed line appears around the desired wavelength (470 nm). Press the OK button.
- Place the cuvette with about 3 cm in height of the blank solution in the tank. Be careful to choose the correct orientation (look at the orientation scheme on the colorimeter, the beam is in the direction of the yellow arrow, see figure below), and to push the cuvette down until the final position. Close the lid (מכסה).
- Turn the selection wheel until a dashed line appears around “Absorbance” and then press the OK button. Using the selection wheel, highlight “Calibration” and press the OK button.
- Wait until the display reads 0.00 (or –0.00).
- Place the cuvette with about 3 cm in height of the analyzed solution in the tank. Close the lid.
- Read the absorbance value.



I. Determination of the iron content in the wine

In this part, you will need the <u>0.000200 M</u> iron(III) solution and the <u>1 M</u> potassium thiocyanate solution.

Procedure

1. **<u>Prepare</u>** 6 test tubes (מבחנות) by adding to each test tube the required volumes of the provided solutions, as described in the table below.

Tube #	**1**	**2**	**3**	**4**	**5**	**6**
0.000200 M iron(III) solution	1.0 mL	2.0 mL	4.0 mL	6.0 mL		
1 M perchloric acid solution	1.0 mL	1.0 mL	1.0 mL	1.0 mL	1.0 mL	1.0 mL
Wine					10.0 mL	10.0 mL
Hydrogen peroxide solution					0.5 mL	0.5 mL
Deionized water	9.5 mL	8.5 mL	6.5 mL	4.5 mL		1.0 mL

2. **<u>Stopper</u>** the tubes (אטמו את המבחנות עם הפקקים המתאימים) and **<u>mix well</u>**.

3. **<u>Add</u>** 1.0 mL of 1 M potassium thiocyanate solution in tubes **1**, **2** **3**, **4** and **5**. **<u>Do not</u>** add this solution to test tube **6**. **<u>Stopper</u>** and **<u>mix well</u>**. **<u>Immediately</u>** proceed to the next step.

4. When all the tubes are ready, **<u>raise</u>** your HELP card to get a colorimeter (ספקטרופוטומטר) from a lab assistant.

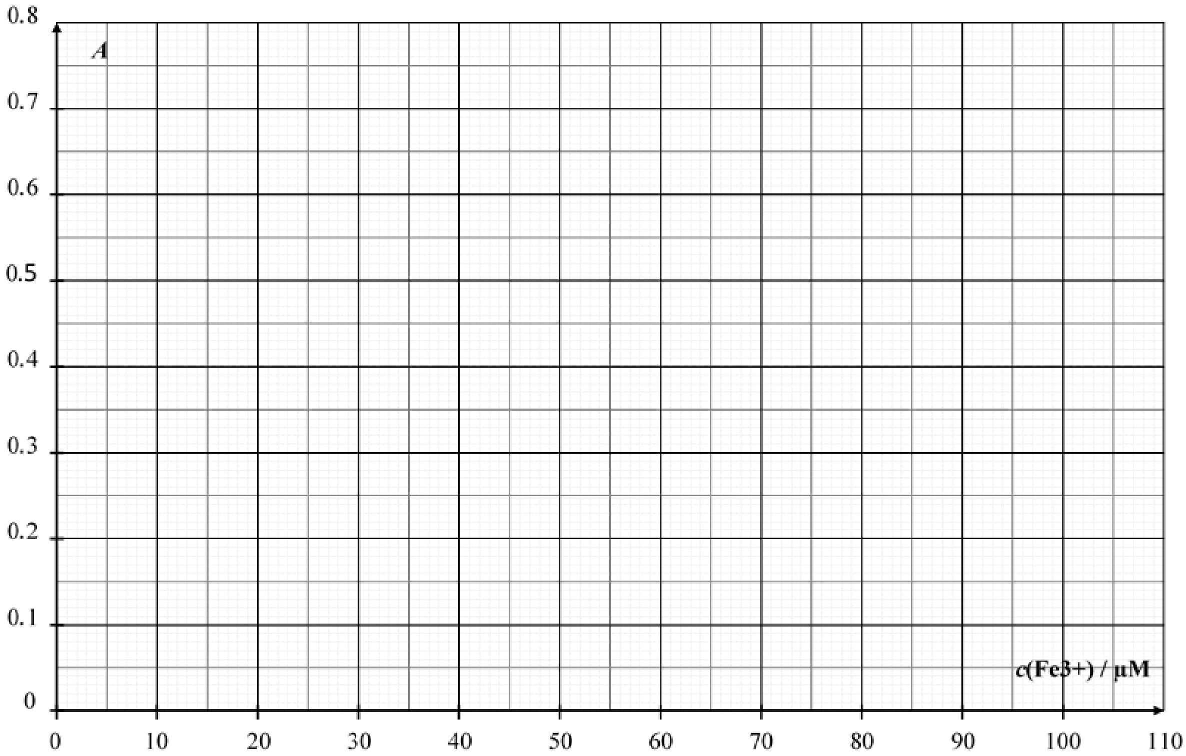
5. **<u>Prepare</u>** the colorimeter using the procedure described previously (see page 16). **<u>Set</u>** the wavelength at 470 nm. **<u>Use</u>** deionized water for the blank.

6. **<u>Record</u>** the absorbance of each tube (**1** to **6**) at this wavelength. **<u>Report</u>** the results in the following table. **<u>Raise</u>** your HELP card to return the colorimeter.

Tube #	**1**	**2**	**3**	**4**	**5**	**6**
Absorbance (at 470 nm)						
Analytical concentration of Fe^{3+} in the tube $c(Fe^{3+})$ / **μM**	16	32	64	96		
Colorimeter code						

Questions

1. **Plot** the absorbance *A* of tubes **1** to **4** as a function of the analytical concentration of Fe^{3+} in the test tube.



- In the following, check the boxes of the data you will consider for your calibration curve.

Tube #	**1**	**2**	**3**	**4**
Absorbance values used for the calibration curve				

2. Using the previous plot and the data you have chosen, **draw** the calibration straight line on the previous plot. **Determine** the analytical concentration (in µmol L^{-1}) of Fe^{3+} in tube **5**.

$c(Fe^{3+})_{TUBE\ 5}$ = ________________ µmol L^{-1}

If you could not calculate $c(Fe^{3+})$, the value $c(Fe^{3+})$ = 50 µmol L^{-1} can be used in the rest of the problem.

3. **Calculate** the mass concentration, in mg per liter, of iron in the studied white wine.

c_m(iron) = ________________ mg L^{-1}

II. Determination of the complex stoichiometry

In this part, you will need the <u>0.00200 M</u> iron(III) solution and the <u>0.00200 M</u> potassium thiocyanate solution.

Procedure

In part I of this problem, we used the color of the iron(III)-thiocyanate complex to determine the concentration of iron in the sample of wine. Part II of this problem aims at investigating the stoichiometry of the $[Fe_a(SCN)_b]^{(3a-b)+}$ complex (coordination of water is not shown), where *a* and *b* are integers no greater than 3.

You are provided with the following aqueous solutions for this part:

- 0.00200 M iron(III) solution (already acidified) (80 mL)
- 0.00200 M potassium thiocyanate solution (80 mL)

You also have test tubes (with stoppers that you can wash and dry), graduated pipettes (פיפטות עם שנתות), a spectrophotometer cuvette, a colorimeter (upon request) (ספקטרופוטומטר), and any other labware on your bench that you think is useful.

1. **<u>Fill</u>** the first three lines of the following table with volume values that will allow you to determine the stoichiometry of the complex, by spectrophotometric measurements. *You don't have to fill all the columns*. **<u>Calculate</u>** the molar fraction of iron(III) in each tube, using the following formula.

$$x(\mathrm{Fe^{3+}}) = \frac{V_{\mathrm{Fe(III)}}}{V_{\mathrm{Fe(III)}} + V_{\mathrm{SCN^-}}}$$

Tube #	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Volume of 0.00200 M iron(III) solution $V_{Fe(III)}$ / mL									
Volume of 0.00200 M potassium thiocyanate solution V_{SCN^-} / mL									
Molar fraction in iron(III) $x(Fe^{3+})$									
Absorbance (at 470 nm)									
Colorimeter code									

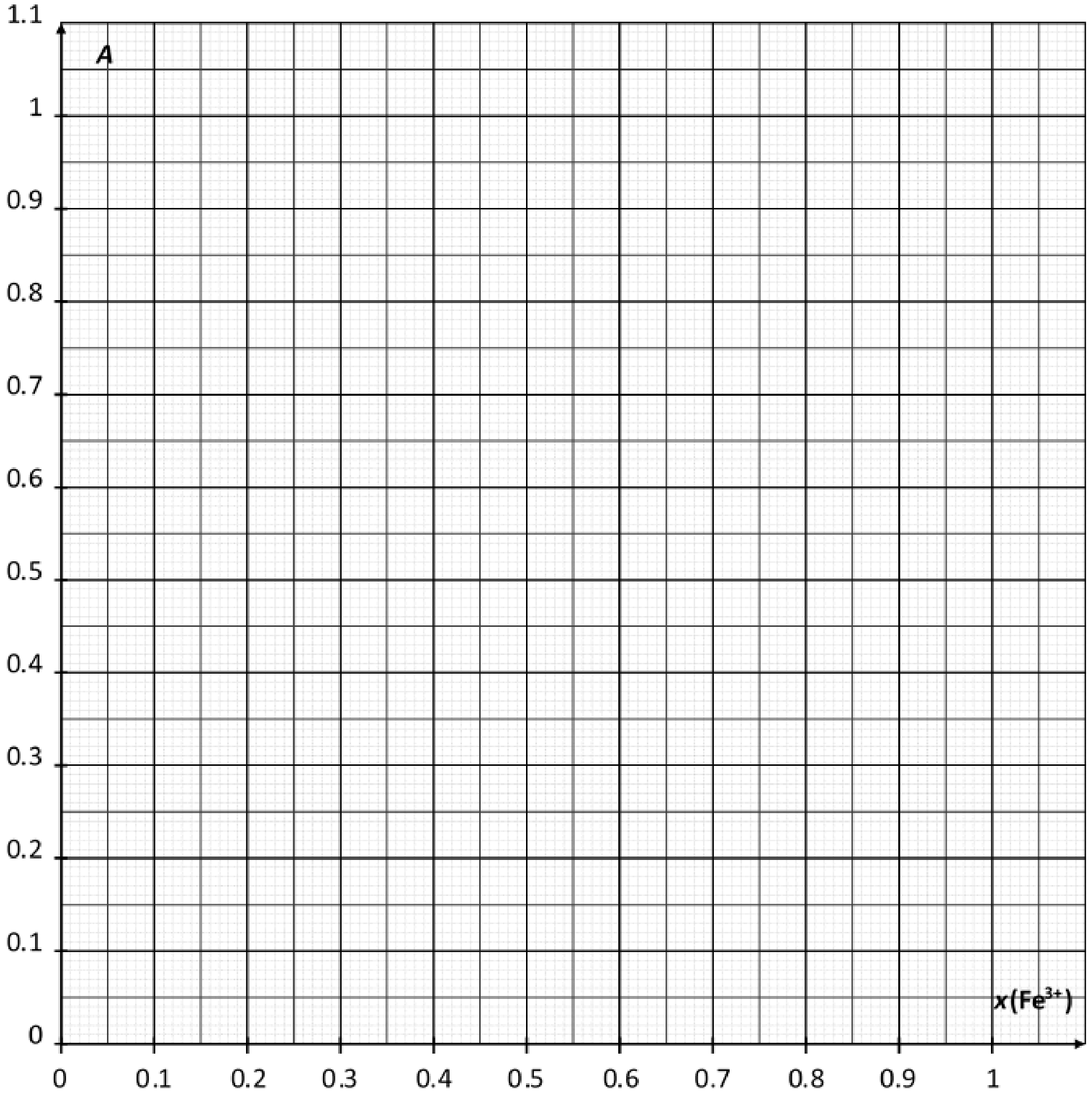
2. **<u>Prepare</u>** the test tubes. When all the test tubes are ready, **<u>immediately raise</u>** your HELP card to get a colorimeter from a lab assistant.

3. **<u>Prepare</u>** the colorimeter using the procedure described previously (see page 16). **<u>Set</u>** the wavelength at 470 nm. **<u>Use</u>** deionized water for the blank.

4. **Record** the absorbance of each test tube at this wavelength. **Report** the results in the previous table.

Questions

4. **Plot** the absorbance *A* of the tubes as a function of the molar fraction of iron(III) $x(Fe^{3+})$.



5. Based on the results of the experiments you carried out, **determine** the stoichiometry of the complex $[(Fe)_a(SCN)_b]^{(3a-b)+}$.

a = _______	***b*** = _______

Problem P3 13% of total	Question	Titration I	Titration II	Titration III	P3.1	P3.2	P3.3	P3.4	P3.5	Total
	Points	10	10	8	4	4	2	2	2	42
	Score									

Problem P3. Wine for keeping

Sulfur dioxide, SO_2, is used as a preservative in wine. When SO_2 is added to wine, it can react with water leading to bisulfite ions, HSO_3^-, and protons, H^+. Bisulfite can also be converted to sulfite, SO_3^{2-}, by the loss of a second proton.

$$SO_2 + H_2O = H^+ + HSO_3^-$$
$$HSO_3^- = H^+ + SO_3^{2-}$$

These three different forms of sulfur dioxide in water can react with chemicals in wine such as acetaldehyde, pigments, sugars, etc. forming products P. The total concentration of sulfur dioxide is the sum of the concentration of the “free” forms (SO_2, HSO_3^- and SO_3^{2-}) and P.

The preservative concentration is regulated because sulfites and sulfur dioxide can be harmful to some people. In the EU, the maximum total sulfur dioxide content is set at 100 mg L^{-1} for red wine and 150 mg L^{-1} for white or rosé.

Your task is to determine the total sulfur dioxide concentration of the provided white wine by iodometric titration.

Procedure

I. Standardization of the sodium thiosulfate solution

1. You are given a sample of about 100 mg of pure potassium iodate KIO_3. The exact mass is written on the label of the vial. **Report** it in the table in the next page.

2. **Prepare** 100 mL of potassium iodate solution in the 100 mL volumetric flask (בקבוק כיול), using the whole sample of solid potassium iodate and deionized water. This solution is called **S**.

3. In a 100 mL Erlenmeyer flask, **add**:
- 20 mL of solution **S** with a volumetric pipette;
- 5 mL of the potassium iodide solution (0.5 M), using a 5 mL graduated cylinder (משורה);
- 10 mL of the sulfuric acid solution (2.5 M) with a 10 mL graduated cylinder.

4. **Swirl** (ערבבו ידנית) the Erlenmeyer flask, **cover** it with Parafilm and **keep** it in the cupboard (ארונית) for at least five minutes.

5. **Fill** the burette with the provided thiosulfate solution using a beaker (כוס כימית). **Titrate** the content of the Erlenmeyer flask with constant swirling (ערבוב ידני). When the liquid turns pale yellow (צהוב בהיר), **add** ten drops of the starch solution and **keep titrating** until the solution becomes colorless. **Record** the titration volume V_1 in the table in the next page.

6. **Repeat** the procedure (steps 3-5) as needed.

Mass of potassium iodate (report the value on the label)	

Analysis Number	V_1 / mL
1	
2	
3	
Reported value V_1 / mL	

II. Standardization of the iodine solution

1. With a volumetric pipette, **transfer** 25 mL of the iodine solution labeled **I_2** into a 100 mL Erlenmeyer flask.

2. **Titrate** the content of the Erlenmeyer flask with the sodium thiosulfate solution. When the liquid turns pale yellow, **add** ten drops of the starch solution and **keep titrating** until the solution becomes colorless. **Record** the titration volume V_2.

3. **Repeat** the procedure (steps 1-2) as needed.

Analysis Number	V_2 / mL
1	
2	
3	
Reported value V_2 / mL	

III. Determination of total sulfur dioxide

1. With a volumetric pipette, **transfer** 50 mL of wine into a 250 mL Erlenmeyer flask.

2. **Add** 12 mL of the sodium hydroxide solution (1 M), with a 25 mL graduated cylinder (משורה). **Cover** the flask with Parafilm, **swirl** (ערבב ידנית) the content then let it stand for at least 20 minutes.

3. **Add** 5 mL of the sulfuric acid solution (2.5 M), and about 2 mL of starch solution using a graduated disposable plastic pipette (פיפטת פסטר מפלסטיק).

4. **Titrate** the content of the Erlenmeyer flask with the iodine solution in the burette, until a dark color appears and persists (לא נעלם) for at least 15 seconds. **Record** the titration volume V_3.

5. **Repeat** the procedure (steps 1-4) as needed.

Analysis Number	V_3 / mL
1	
2	
3	
Reported value V_3 / mL	

Questions

1. **Write down** the balanced equations of all the reactions occurring during the standardization of the sodium thiosulfate solution (in part I).

2. **Calculate** the molar concentration of the sodium thiosulfate solution. The molar mass of potassium iodate is $Mw(KIO_3)$ = 214.0 g mol^{-1}.

$c(S_2O_3^{2-})$ = ________________ mol L^{-1}

If you could not calculate $c(S_2O_3^{2-})$, the value $c(S_2O_3^{2-})$ = 0.0500 mol L^{-1} can be used in the rest of the problem.

3. **Calculate** the molar concentration of the iodine solution.

$c(I_2)$ = _______________ mol L^{-1}

If you could not calculate $c(I_2)$, the value $c(I_2)$ = 0.00700 mol L^{-1} can be used in the rest of the problem.

4. **Write down** the equation of the reaction between iodine I_2 and sulfur dioxide SO_2, assuming that sulfur dioxide is oxidized into sulfate ions SO_4^{2-}.

5. **Calculate** the mass concentration, in mg per liter, of total sulfur dioxide in the wine. The molar mass of sulfur dioxide is $Mw(SO_2)$ = 64.1 g mol^{-1}.

$c_m(SO_2)$ = ________________ mg L^{-1}

PENALTIES

Incident #	Student signature	Lab supervisor signature
1 (no penalty)		
2		
3		
4		
5		