SGP_1

PRACTICAL EXAM

51st — International Chemistry Olympiad France — Paris — 2019

Making science together!

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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; d**o 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. Aqueous solutions can be disposed in the sink. Organic waste must be disposed of in the marked capped container.

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):	$Q = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$
Henderson−Hasselbalch equation:	$pH = pK_a + \log\dfrac{[A^-]}{[AH]}$
Nernst–Peterson equation:	$E = E^o - \frac{RT}{zF}\ln Q$
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:	$A = \varepsilon l c$
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:	$M_n = \dfrac{\sum_i N_i M_i}{\sum_i N_i}$
Mass average molar mass M_w:	$M_w = \dfrac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$
Polydispersity index I_p:	$I_p = \dfrac{M_w}{M_n}$

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	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	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											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, *ca* 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	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	1
Pencil	1
Eraser	1
Black pen	1
Felt-tip pen for glassware	1
Ruler	1

Shared equipment	Quantity
UV lamp for TLC visualization	2 per lab
Colorimeter	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	1
Erlenmeyer flask with ground joint, 50 mL	1
Reflux condenser	1
Hotplate stirrer	1
Crystallizing dish	1
Magnetic stirring bar	1
Suction flask	1
Büchner funnel with rubber adapter	1
Zipped bag with 3 pieces of filter paper	1
Petri dish	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 the Petri dish)	4
Plastic tweezers	1
Glass rod	1
Graduated cylinder, 25 mL	1
Beaker, 150 mL	2
Plastic powder funnel	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 tube	15
Test tube stopper	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	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. Green 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. **Mix** 20 mL of water and 5 mL of ethanol.

2. **Insert** the magnetic bar in the 100 mL ground-joint Erlenmeyer (conical) flask.

3. **Transfer** the pre-weighed 1.51 g of 4-nitrobenzaldehyde into the Erlenmeyer flask. **Add** the water/ethanol mixture prepared previously. **Clamp** the Erlenmeyer flask to the stand. **Stir** the mixture, then **add** the pre-weighed 7.87 g of Oxone®.

4. **Attach** the reflux condenser by loosening the large clamp and adjusting the ground joints (see Figure 1). **Raise** your HELP card. A lab assistant will come to turn on the water and set the hotplate.

5. **Heat** the reaction mixture on gentle reflux (*approximately* 1 drop refluxing per second) for 45 minutes.

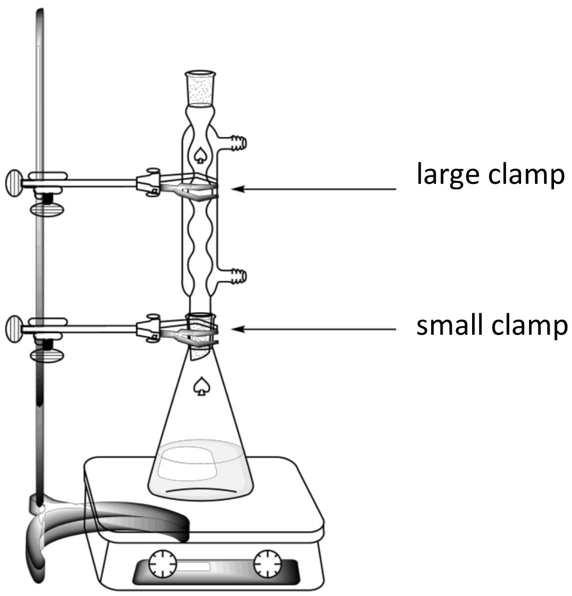


Figure 1. Setup for heating the reaction mixture under reflux

6. **Turn off** the heating on the hotplate stirrer. **Remove** the hotplate and **let** the reaction mixture cool down for 10 minutes. **Place** the reaction mixture in an ice-water bath (use a crystallizing dish). **Let** it stand for another 10 minutes.

7. **Set up** a vacuum filtration apparatus (see Figure 2) using a Büchner funnel, *one* filter paper and a suction flask. Clamp the suction flask 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.

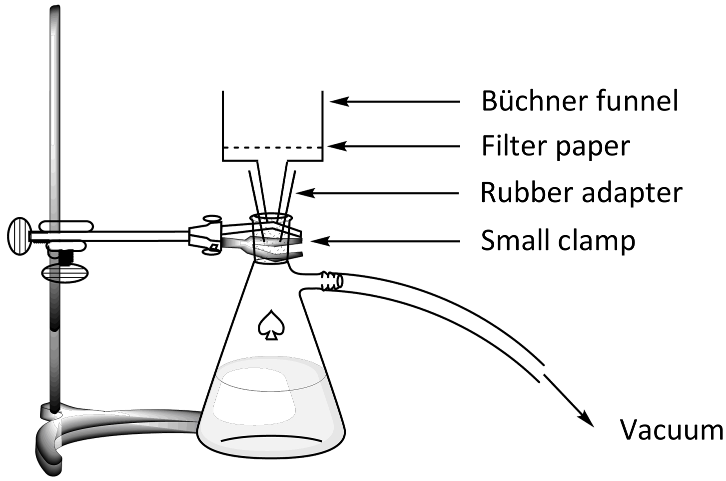


Figure 2. Setup for the vacuum filtration

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

9. **Transfer** 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. Leave the crude product on the vacuum for 5 minutes. **Disconnect** the vacuum source. **Use** the small spatula to transfer one tip of spatula of the product in the 1.5 mL amber glass vial, **labeled C**. **Close** the vial and **keep** it for part III.

11. **Transfer** the remaining solid into the 50 mL ground-joint Erlenmeyer flask.

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 mixture containing 9 mL of water and 21 mL of ethanol.

2. **Perform** the recrystallization of the crude product using the above prepared water/ethanol mixture and the same reflux heating setup (see Figure 1) on the 50 mL ground-joint Erlenmeyer flask. **Raise** your HELP card. A lab assistant will come to turn on the water and set the hotplate. The solvent mixture can be added from the top of the condenser.

3. Once the product has crystallized, perform vacuum filtration using the procedure described previously (I.7 to I.10) and collect the solid product. **Use** the small spatula to transfer one tip of spatula of the recrystallized product in the 1.5 mL amber glass vial, **labeled R**. **Close** the vial and **keep** it for part III.

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

5. **Discard** the filtrate in 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 TLC elution chamber: Load** the elution chamber with *approximately* 0.5 cm in height of eluent A. Cover it with a Petri dish. **Allow** 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 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** *approximately* 1 mL of ethanol in 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 shown 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.

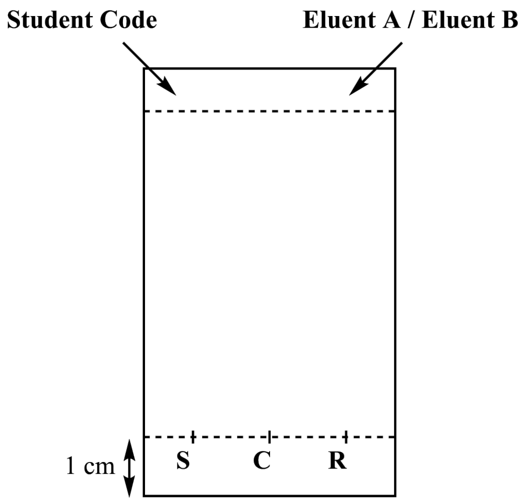


Figure 3. TLC plate preparation

4. **Perform the TLC analysis**. Using tweezers, **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 air-dry the plate.

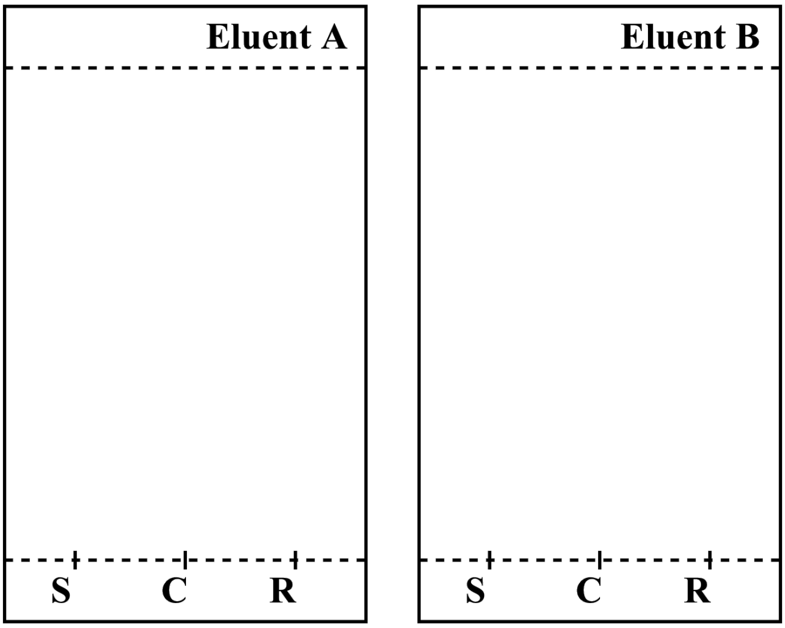
5. **Place** the TLC plate under the UV lamp kept on the common bench. **Circle** all the visible spots with a pencil.

6. **Discard the eluent into the "Organic waste" bottle.**

7. **Repeat** steps 1, 3, 4, 5, and 6 with eluent B.

8. **Place** your TLC plates in the zipped bag with your Student Code.

Draw the results of your TLC analysis in the figure below. You may use these drawings to help you answer the following questions. The figure 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 into 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.

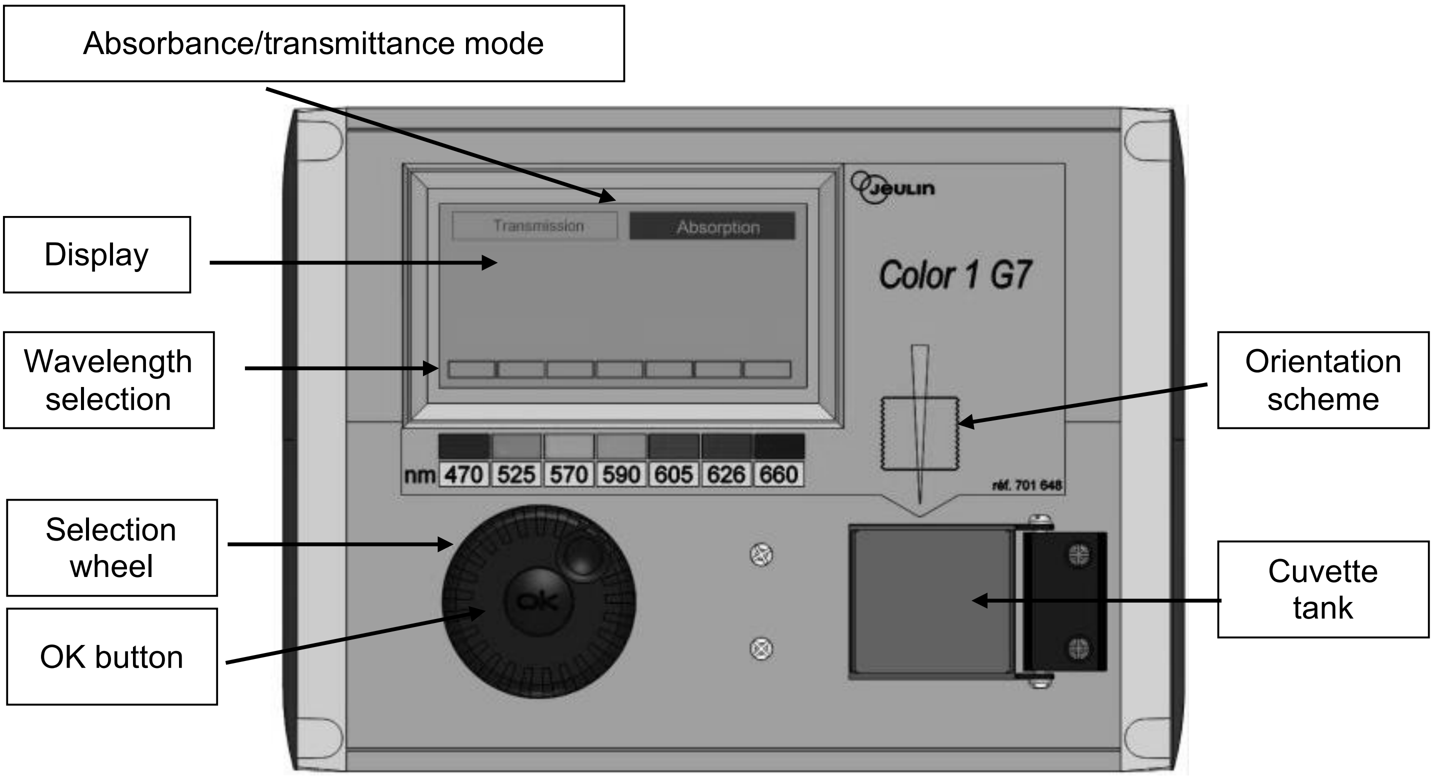
Given the very low concentration of iron species, a colored complex of iron(III) with thiocyanate SCN^- as a ligand is used to quantify the iron amount, through spectrophotometric measurements.

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.

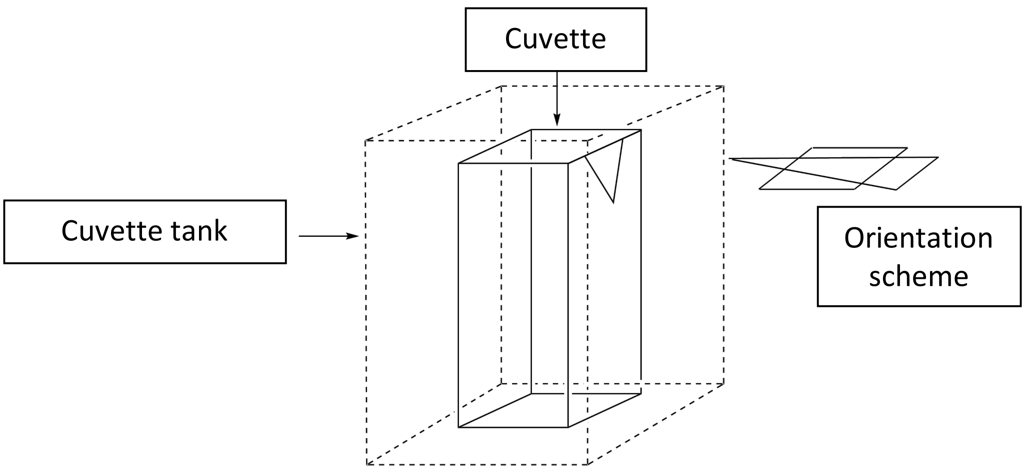
WARNING

- 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, 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.
- Instructions for the colorimeter are presented on the following page.
- You can use the colorimeter only **three times** for this problem.

Instructions for the use of the colorimeter



- Plug in the colorimeter.
- Check that "Absorbance" is highlighted. If not, turn the selection wheel until a dashed line 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 *approximately* 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 shown on the colorimeter, see figure below), and to push the cuvette down until the final position. Close the lid.
- 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 the analyzed solution in the tank. Close the lid.
- Record the absorbance value.



I. Determination of the iron content in the wine

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

Procedure

1. **Prepare** 6 tubes by adding to each tube the required volumes of the provided solutions, as described in the table below.

Tube number	**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. **Cap** the tubes with test tube stoppers and **homogenize**.

3. **Add** 1.0 mL of 1 M potassium thiocyanate solution in tubes **1**, **2** **3**, **4** and **5**. Do **not** add in tube **6**. **Cap** the tubes with test tube stoppers and **homogenize**.

4. When all the tubes are ready, **raise** your HELP card to get a colorimeter from a lab assistant.

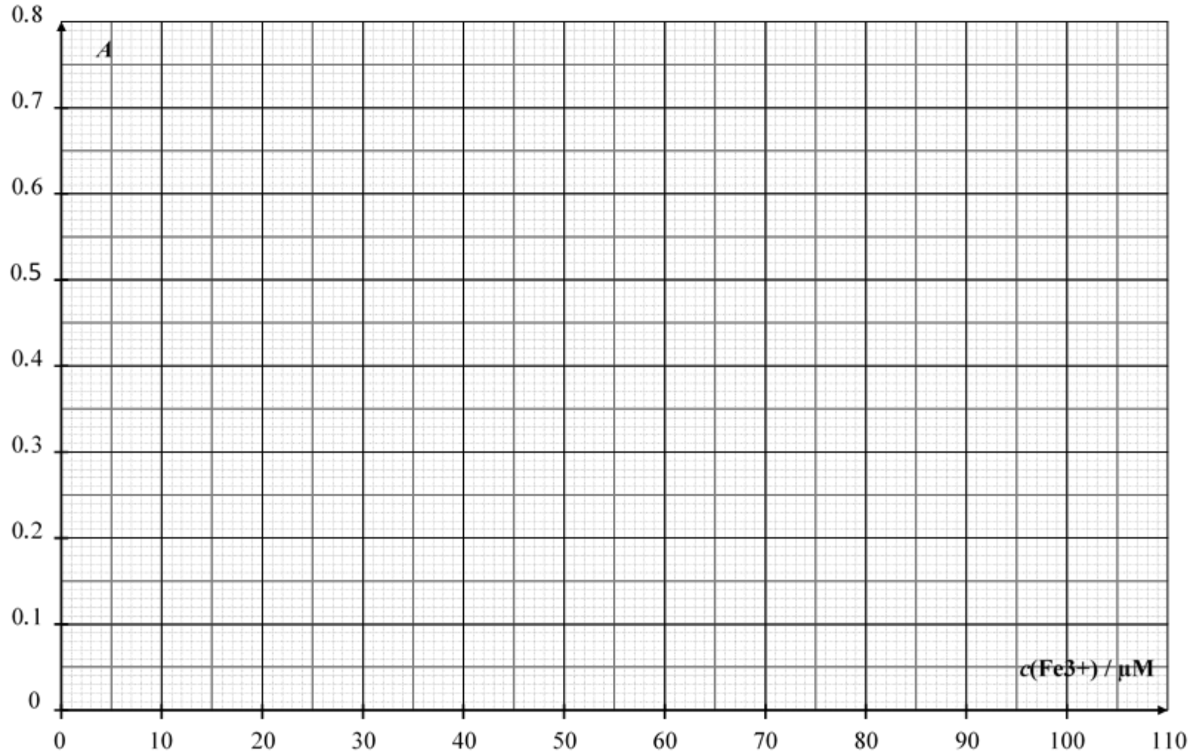
5. **Use** the colorimeter by following the instructions described previously (see page 16). **Set** the wavelength at 470 nm. **Use** deionized water as the blank solution.

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

Tube number	**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		
Code of the colorimeter used						

Questions

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



- In the following table, put a **X** in the boxes for the values you used for your calibration curve.

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

2. Using 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 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 0.00200 M iron(III) solution and the 0.00200 M potassium thiocyanate solution.

Procedure

In part I of this problem, we use 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, a spectrophotometer cuvette, a colorimeter (upon request), and any other labware on your bench that you think useful.

1. **Fill** the first three rows of the following table with volumes that will allow you to determine the stoichiometry of the complex, by spectrophotometric measurements. *You don't have to fill all the columns*. **Calculate** 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 number	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Volume of 0.00200 M iron(III) solution $V_{\mathrm{Fe(III)}}$ / mL									
Volume of 0.00200 M potassium thiocyanate solution $V_{\mathrm{SCN^-}}$ / mL									
Molar fraction in iron(III) $x(Fe^{3+})$									
Absorbance (at 470 nm)									
Code of the colorimeter									

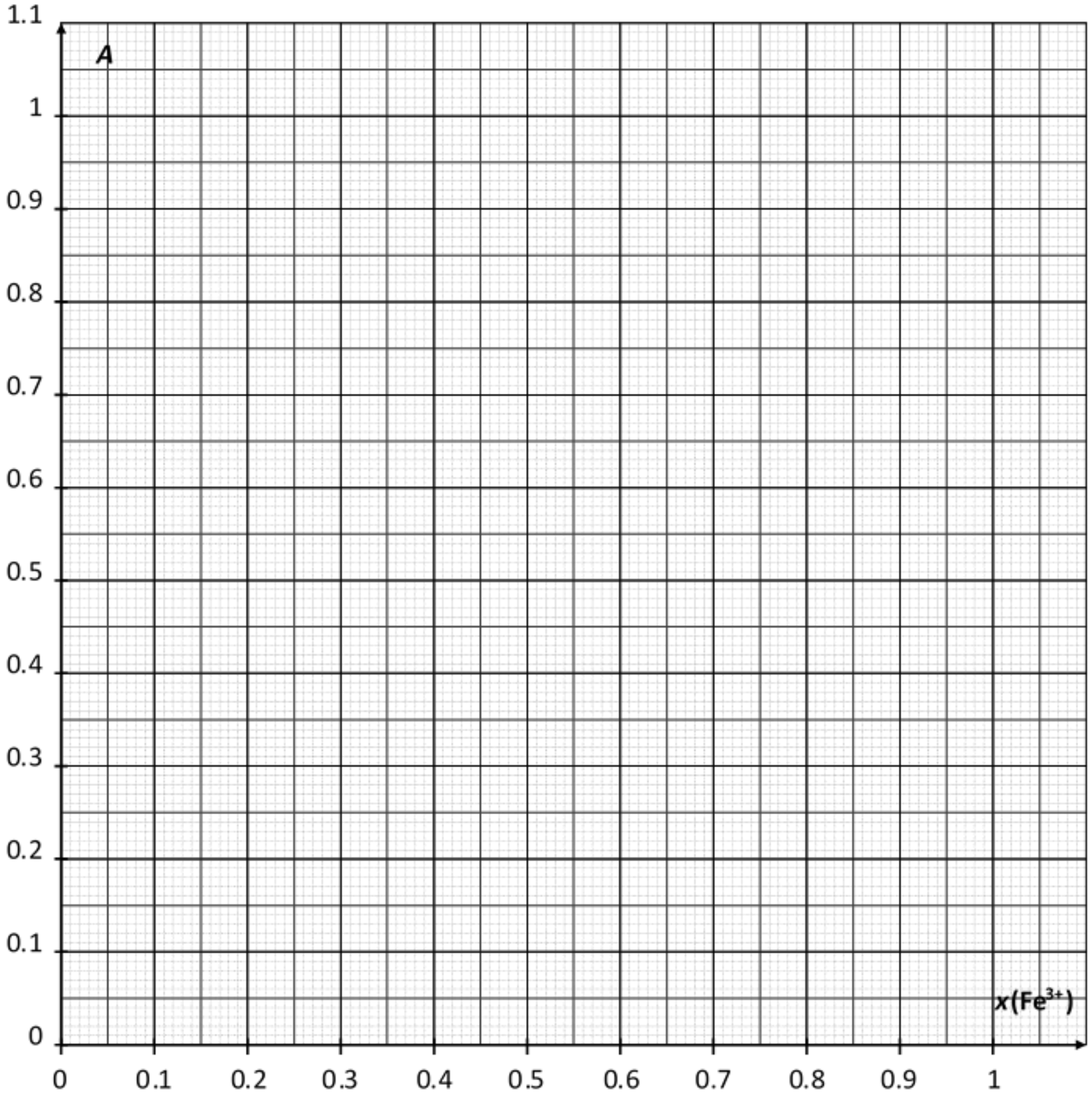
2. **Prepare** the tubes. When all the tubes are ready, **raise** your HELP card to get a colorimeter from a lab assistant.

3. **Use** the colorimeter by following the instructions described previously (see page 16). **Set** the wavelength at 470 nm. **Use** deionized water for the blank.

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

Questions

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



6. 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 *approximately* 100 mg of pure potassium iodate KIO_3. The exact mass is written on the label of the vial. **Record** the mass in the table below.

2. **Prepare** a standard solution of potassium iodate using the 100 mL volumetric flask with all the solid provided. This solution is called **S**.

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

4. **Swirl** the Erlenmeyer flask, **cover** it with Parafilm and **keep** the solution in the cupboard for at least five minutes.

5. **Fill** the burette with the provided thiosulfate solution. **Titrate** the content of the Erlenmeyer flask with constant swirling. When the liquid turns pale yellow, **add** ten drops of the starch solution and **continue to titrate** until the solution becomes colorless. **Record** the titration volume V_1.

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

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

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

II. Standardization of the iodine solution

1. Using 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 **continue to titrate** until the solution becomes colorless. **Record** the titration volume V_2.

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

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

III. Determination of total sulfur dioxide

1. Using 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. **Cover** the flask with Parafilm, **swirl** the content then let it stand for at least 20 minutes.

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

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

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

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

Questions

1. **Write** the balanced equations of all the reactions occurring during the standardization of the sodium thiosulfate solution.

2. **Calculate** the molar concentration of the sodium thiosulfate solution. The molar mass of potassium iodate is $M(KIO_3) = 214.0$ 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** the balanced 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 $M(SO_2)$ = 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		