

PRACTICAL EXAM



Making science together!

2019-07-24



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 designated areas** on the exam paper. 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 designated 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 noted, 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-minute 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. Footwear must completely cover the foot and 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 gum is 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.

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 $c^\circ = 1 \text{ mol L}^{-1}$ is omitted.

| | |
|----------------------------|--|
| Avogadro's constant: | $N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$ |
| Universal gas constant: | $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ |
| Standard pressure: | $p^\circ = 1 \text{ bar} = 10^5 \text{ Pa}$ |
| Atmospheric pressure: | $P_{\text{atm}} = 1 \text{ atm} = 1.013 \text{ bar} = 1.013 \cdot 10^5 \text{ Pa}$ |
| Zero of the Celsius scale: | 273.15 K |
| Faraday constant: | $F = 9.649 \cdot 10^4 \text{ C mol}^{-1}$ |
| Watt: | $1 \text{ W} = 1 \text{ J s}^{-1}$ |
| Kilowatt hour: | $1 \text{ kWh} = 3.6 \cdot 10^6 \text{ J}$ |
| Planck constant: | $h = 6.626 \cdot 10^{-34} \text{ J s}$ |
| Speed of light in vacuum: | $c = 2.998 \cdot 10^8 \text{ m s}^{-1}$ |
| Elementary charge: | $e = 1.6022 \cdot 10^{-19} \text{ C}$ |
| Electrical power: | $P = \Delta E \times I$ |
| Power efficiency: | $\eta = P_{\text{obtained}}/P_{\text{applied}}$ |
| Planck-Einstein relation: | $E = hc/\lambda$ |
| Ideal gas equation: | $pV = nRT$ |
| Gibbs free energy: | $G = H - TS$ |
| | $\Delta_r G^\circ = -RT \ln K^\circ$ |
| | $\Delta_r G^\circ = -n F E_{\text{cell}}^\circ$ |
| | $\Delta_r G = \Delta_r G^\circ + RT \ln Q$ |

Reaction quotient Q for a reaction
 $a \text{ A(aq)} + b \text{ B(aq)} = c \text{ C(aq)} + d \text{ D(aq)}$:

$$Q = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{AH}]}$$

Nernst–Peterson equation:

$$E = E^\circ - \frac{RT}{zF} \ln Q$$

where Q is the reaction quotient of the reduction half-reaction

$$\text{at } T = 298 \text{ K, } \frac{RT}{F} \ln 10 \approx 0.059 \text{ V}$$

Beer–Lambert law:

$$A = \epsilon l c$$

Rate laws in integrated form:

- Zero order:

$$[\text{A}] = [\text{A}]_0 - kt$$

- First order:

$$\ln[\text{A}] = \ln[\text{A}]_0 - kt$$

- Second order:

$$1/[\text{A}] = 1/[\text{A}]_0 + kt$$

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”:

$$1 \text{ M} = 1 \text{ mol L}^{-1} \quad 1 \text{ mM} = 10^{-3} \text{ mol L}^{-1} \quad 1 \text{ }\mu\text{M} = 10^{-6} \text{ mol L}^{-1}$$

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/Containers | Labeled as | GHS hazard statements |
|--|-----------------|-----------------------|
| Deionized water in: - Wash bottle (bench) - Plastic bottle (bench) | Deionized Water | Not hazardous |
| Clear plastic bin (hood) | | |
| 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 ₂ O 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 | 1 |
| Safety goggles | 1 |
| 1 L plastic bottle for organic waste, labeled “ Organic waste ” | 1 |
| Paper towels | 15 sheets |
| Precision wipers (Kimwipe-like tissue) | 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: | 1 |
| - Small clamps | 2 |
| - Large clamp | 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. Greening the oxidation of nitrobenzaldehyde

For decades, chemists have tried to replace harmful reagents in oxidation processes in order to reduce hazardous waste treatment. In this problem, potassium peroxomonosulfate is used as an 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

- Mix** 20 mL of water and 5 mL of ethanol.
- Place** the stir bar into the 100-mL Erlenmeyer flask having a **ground-glass joint**.
- Transfer** the pre-weighed 1.51 g of 4-nitrobenzaldehyde into the Erlenmeyer flask. **Add** all of the water/ethanol mixture previously prepared. **Clamp** the Erlenmeyer flask to the stand. **Begin stirring** the mixture, then **add** the pre-weighed 7.87 g of Oxone[®].
- To assemble the reflux setup, **loosen** the large clamp, **fit** the reflux condenser into the ground-glass joint of the Erlenmeyer, and **re-tighten** the large clamp (see Figure 1). **Raise** your HELP card. A lab assistant will come to turn on and set the hotplate as well as the water.
- Reflux** the reaction mixture gently at a rate of approximately 1 drop per second for 45 minutes. Note: The mark on the hot plate corresponds to the necessary power to get a gentle reflux.

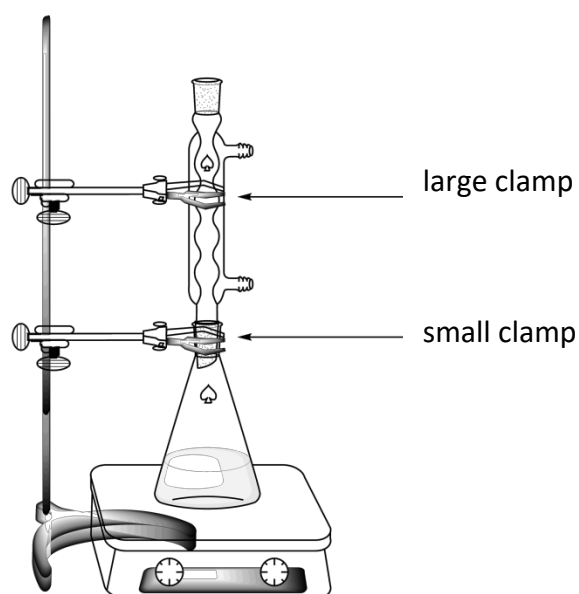


Figure 1. Setup for heating the reaction mixture under reflux

6. **Turn off** the heat and stirring. **Remove** the reaction from the hotplate and **allow** it to cool for 10 minutes. Fill a crystallizing dish with an ice/water mixture and **set** the already-cooled reaction mixture in it. **Let** it cool 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 to the laboratory stand with a small clamp. **Raise** your HELP card. A lab assistant will come and show you how to connect the suction flask to the vacuum source.

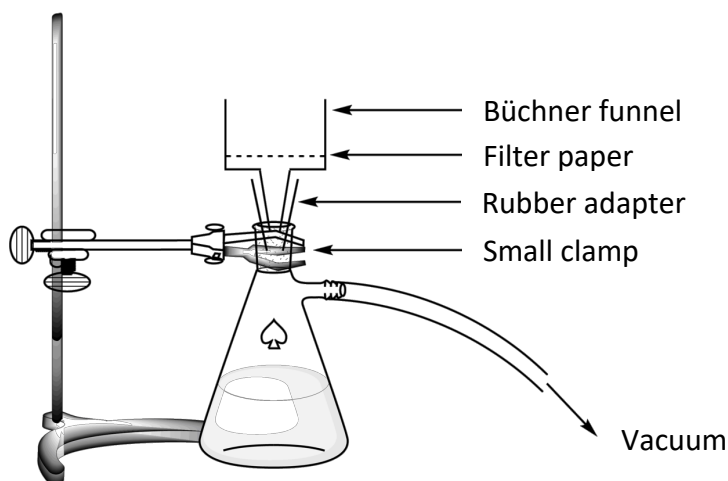


Figure 2. Setup for the vacuum filtration

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 pass through the precipitate for 5 minutes to pre-dry the product. **Disconnect** the vacuum source. Use the small spatula to **transfer** a small amount (one tip of the spatula) of the product into 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 Erlenmeyer flask with a ground-glass joint.
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 the ethanol waste.

II. Recrystallization of the product

1. **Mix** 9 mL of water and 21 mL of ethanol.
2. For safety reasons, **use** the same setup as for the reflux (see Figure 1) to **recrystallize** the crude product in the 50-mL Erlenmeyer flask. **Raise** your HELP card. A lab assistant will come to turn on the water and set the hotplate. **Add** the appropriate amount of water/ethanol mixture (step II.1) through the top of the condenser.
3. Once the product has crystallized, **use** the same procedure as described previously (I.7 to I.10, except use the 1.5 mL amber glass vial **labeled R**) to collect the solid. **Close** the vial and **save** it for part III.
4. **Transfer** the purified solid into 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. **Fill** the elution chamber with approximately 0.5 cm (in height) of eluent A. 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 labeled **TLC standard** (referred to as **S** on the TLC plate in Figure 3). 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 in each of the vials in order to dissolve the samples.
3. Prepare your TLC plate: Use a pencil to carefully **draw** the start line (1 cm above the bottom of the plate) and **mark** the positions for 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.

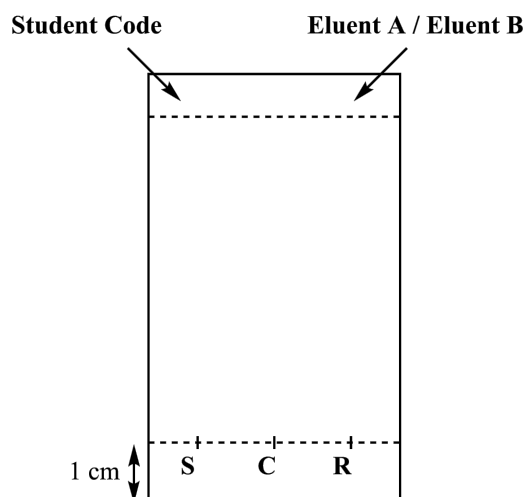


Figure 3. TLC plate preparation

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/solvent front with a pencil and **let** the plate air-dry.
5. Visualize the TLC plate: **Place** the TLC plate under the UV lamp kept on the common bench. With a pencil, **circle** all the visible spots.
6. **Discard the eluent into the “Organic waste” bottle.**
7. **Repeat** steps 1, 3, 4, 5, and 6 with eluent B.
8. **Place** your plates in the zipped bag with your Student Code.

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

| Eluent A | Eluent B |
|--|--|
| <div style="border-top: 1px dashed black; margin-bottom: 10px;"></div> <div style="display: flex; justify-content: space-around; border-top: 1px dashed black; padding-top: 5px;"> + S + C + R </div> | <div style="border-top: 1px dashed black; margin-bottom: 10px;"></div> <div style="display: flex; justify-content: space-around; border-top: 1px dashed black; padding-top: 5px;"> + S + C + R </div> |

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 | <input type="checkbox"/> | |
| TLC plate A | <input type="checkbox"/> | |
| TLC plate B | <input type="checkbox"/> | |
| Signatures <div style="display: flex; justify-content: space-between; margin-top: 20px;"> <div style="width: 45%; text-align: center;"> <hr style="border: 0; border-top: 1px solid black; margin-bottom: 5px;"/> Student </div> <div style="width: 45%; text-align: center;"> <hr style="border: 0; border-top: 1px solid black; margin-bottom: 5px;"/> Lab Supervisor </div> </div> | | |

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 naturally found in wine. When its concentration exceeds 10-15 mg per liter, the oxidation of iron(II) to iron(III) may lead to the formation of precipitates. Therefore, it is necessary to assess the iron content of the wine during its production.

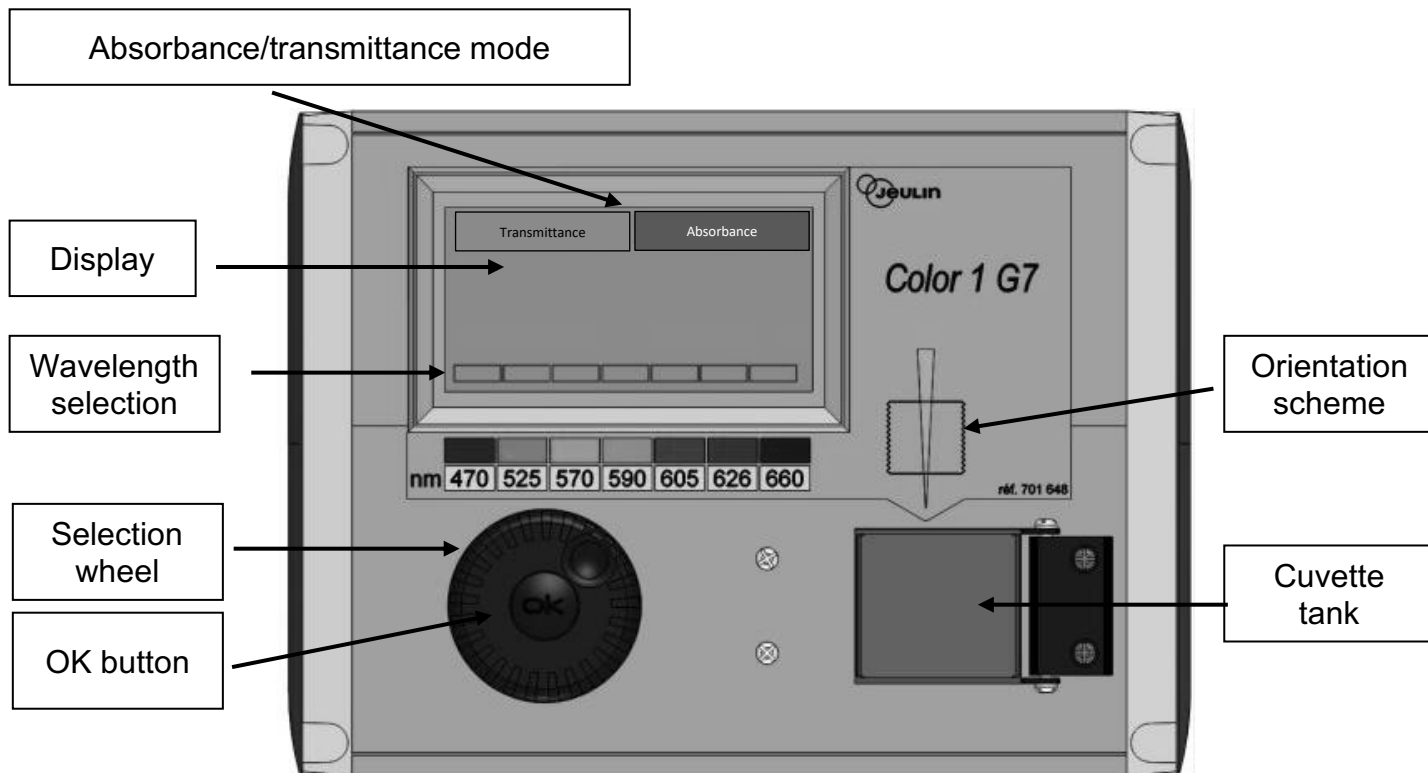
Given the very low concentration of iron species, a colored complex of iron(III) with thiocyanate SCN^- as a ligand is used to quantify the iron amount through spectrophotometric measurements.

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

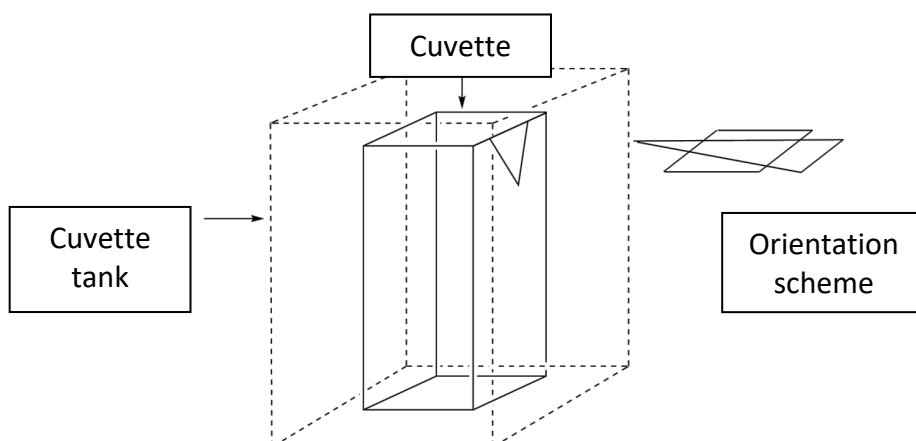
WARNING

- 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 call for 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 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.
- 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 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 # | 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. **Stopper** the tubes and **mix**.

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**. **Stopper** and **mix**.

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

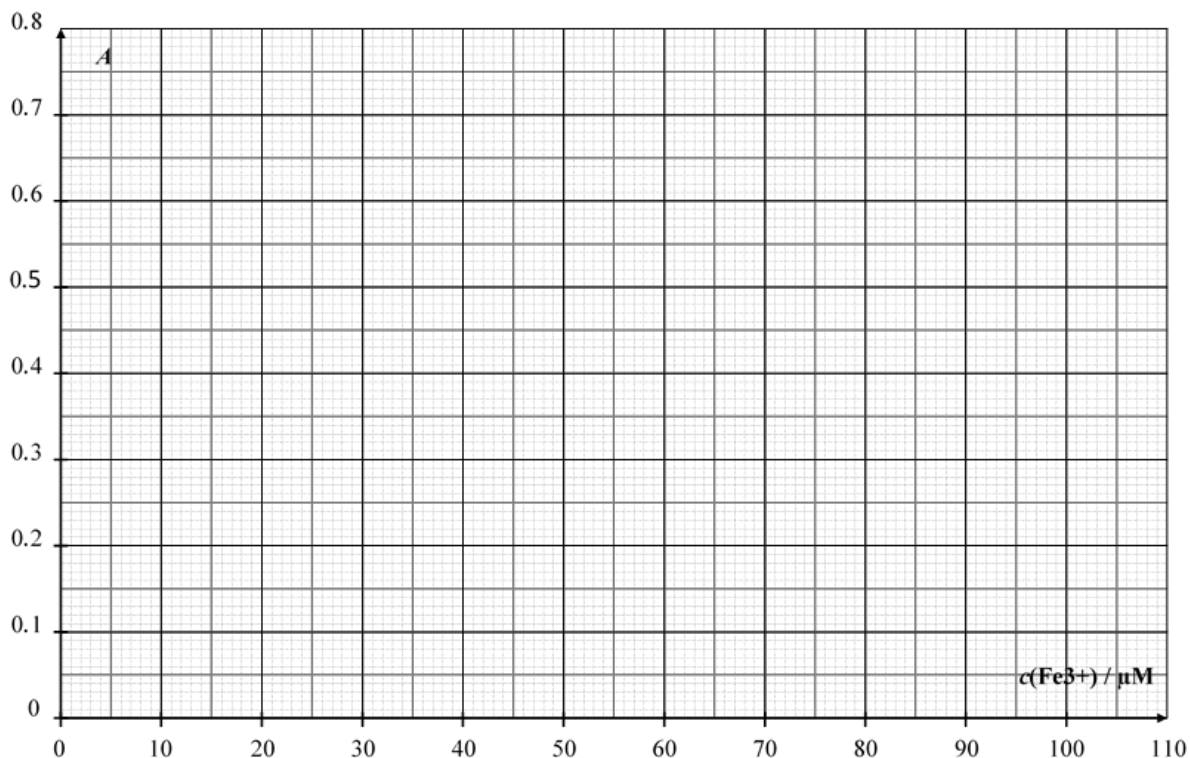
5. **Prepare** the colorimeter using the procedure described previously (see page 16). **Set** the wavelength at 470 nm. **Use** deionized water for the blank.

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 # | 1 | 2 | 3 | 4 | 5 | 6 |
|--|----|----|----|----|---|---|
| Absorbance (at 470 nm) | | | | | | |
| Analytical concentration of Fe^{3+} in the tube $c(\text{Fe}^{3+}) / \mu\text{M}$ | 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 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 curve on the previous plot and **determine** the analytical concentration (in $\mu\text{mol L}^{-1}$) of Fe^{3+} in tube **5**.

$$c(\text{Fe}^{3+})_{\text{TUBE 5}} = \underline{\hspace{2cm}} \mu\text{mol L}^{-1}$$

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

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

$$c_{\text{m}}(\text{iron}) = \underline{\hspace{2cm}} \text{mg L}^{-1}$$

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 used the color of the iron(III)-thiocyanate complex to determine the concentration of iron in a sample of wine. Part II of this problem aims at investigating the stoichiometry of the $[\text{Fe}_a(\text{SCN})_b]^{(3a-b)+}$ 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 is useful.

1. **Fill** the first two 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.* **Calculate** the molar fraction of iron(III) in each tube, using the following formula:

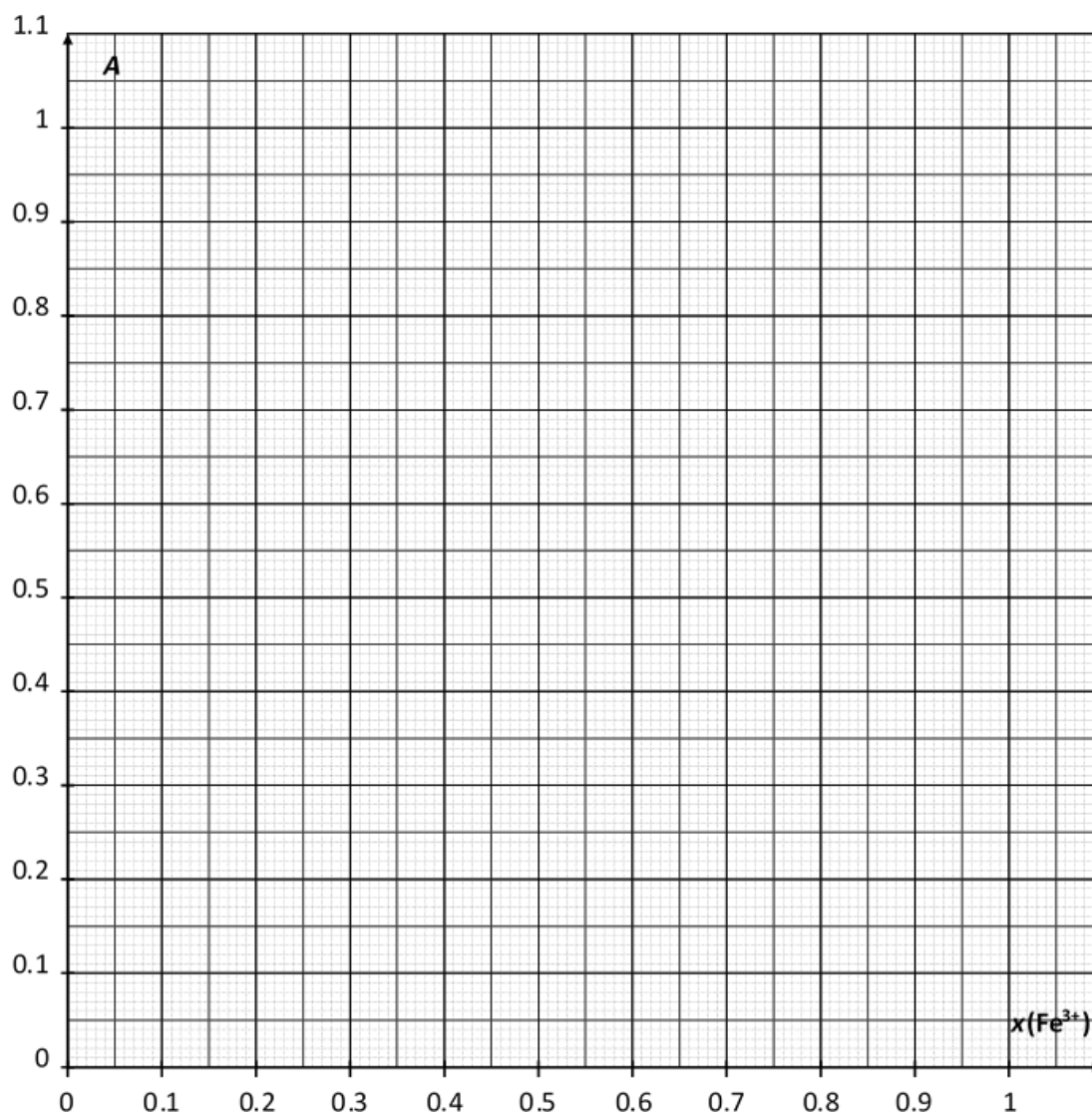
$$x(\text{Fe}^{3+}) = \frac{V_{\text{Fe(III)}}}{V_{\text{Fe(III)}} + V_{\text{SCN}^-}}$$

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

2. **Prepare** the tubes as in the table above. When all the tubes are ready, **raise** your HELP card to get a colorimeter from a lab assistant.
3. **Prepare** the colorimeter using the procedure 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) $x(\text{Fe}^{3+})$.



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

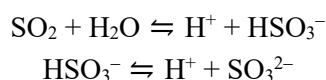
$a =$ _____

$b =$ _____

| 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 producing bisulfite ions, HSO_3^- , and protons, H^+ . Bisulfite can also be converted to sulfite, SO_3^{2-} , by the loss of the proton.



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

- 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 below.
- Prepare** 100 mL of potassium iodate solution in the 100-mL volumetric flask, using the entire sample of solid potassium iodate and deionized water. This solution is called S.
- 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;
 - 10 mL of the sulfuric acid solution (2.5 M) with a 10 mL graduated cylinder.
- Swirl** the Erlenmeyer flask, **cover** it with Parafilm and **keep** it in the cupboard for at least five minutes.
- Fill** the burette with the provided thiosulfate solution using a beaker. **Titrate** the content of the Erlenmeyer flask with constant swirling. When the liquid turns a pale yellow, **add** ten drops of the starch solution and **keep titrating** until the solution becomes colorless. **Record** the titration volume, V_1 , in the table on the following page.
- Repeat** the procedure (steps 3-5) as needed.

| Mass of potassium iodate (report the value on the label) | |
|---|------------|
| | |
| Trial # | V_1 / mL |
| 1 | |
| 2 | |
| 3 | |
| | |
| | |
| Reported value V_1 / mL | |

II. Standardization of the iodine solution

- With a volumetric pipette, **transfer** 25 mL of the iodine solution labeled I_2 into a 100 mL Erlenmeyer flask.
- 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 , in the table below.
- Repeat** the procedure (steps 1-2) as needed.

| Trial # | 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 sample into a 250 mL Erlenmeyer flask.
2. **Add** 12 mL of 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 about 2 mL of starch solution using a graduated disposable plastic pipette.
4. **Prepare** the buret with the iodine solution. Then, **titrate** the content of the Erlenmeyer flask with the iodine solution from the buret, until a dark color appears and persists for at least 15 seconds. **Record** the titration volume, V_3 , in the table below.
5. **Repeat** the procedure (steps 1-4) as needed.

| Trial # | 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 $M(\text{KIO}_3) = 214.0 \text{ g mol}^{-1}$.

$$c(\text{S}_2\text{O}_3^{2-}) = \underline{\hspace{2cm}} \text{ mol L}^{-1}$$

If you could not calculate $c(\text{S}_2\text{O}_3^{2-})$, the value $c(\text{S}_2\text{O}_3^{2-}) = 0.0500 \text{ mol L}^{-1}$ can be used in the rest of the problem.

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

$$c(\text{I}_2) = \underline{\hspace{2cm}} \text{ mol L}^{-1}$$

If you could not calculate $c(\text{I}_2)$, the value $c(\text{I}_2) = 0.00700 \text{ mol L}^{-1}$ 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 $M(\text{SO}_2) = 64.1 \text{ g mol}^{-1}$.

$$c_{\text{m}}(\text{SO}_2) = \underline{\hspace{2cm}} \text{ mg L}^{-1}$$

PENALTIES

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