

# 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 28 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.

## Physical constants and equations

In these tasks, we assume the activities of all aqueous species to be well approximated by their respective concentration in  $\text{mol L}^{-1}$ . 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: | $273.15 \text{ K}$   |
| 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

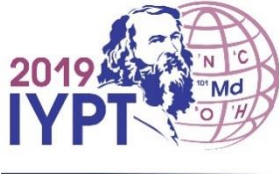
The unit of molar concentration is either “M” or “ $\text{mol L}^{-1}$ ” ( $\text{mol dm}^{-3}$ ):

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

# Periodic table

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

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



## 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:<br>- Wash bottle (bench)<br>- Plastic bottle (bench)<br>- Plastic canister (hood) | <b>Deionized Water</b> | Not hazardous         |
| Ethanol, in a wash bottle   | <b>Ethanol</b>         | H225, H319            |
| Sample of white wine, 300 mL in amber plastic bottle  | <b>Wine sample</b>     | H225, H319            |

## For problem P1

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

## For problem P2

| Chemicals   | Labeled as                        | GHS hazard statements |
|---|-----------------------------------|-----------------------|
| 1 M potassium thiocyanate solution, 20 mL in plastic bottle       | <b>KSCN 1 M</b>                   | H302+H312+H332, H412  |
| 0.00200 M potassium thiocyanate solution, 60 mL in plastic bottle | <b>KSCN 0.00200 M</b>             | Not hazardous         |
| 1 M perchloric acid solution, 10 mL in plastic bottle             | <b>HClO<sub>4</sub></b>           | H290, H315, H319      |
| 0.00200 M iron(III) solution, 80 mL in plastic bottle             | <b>Fe(III) 0.00200 M</b>          | Not hazardous         |
| 0.000200 M iron(III) solution, 80 mL in plastic bottle            | <b>Fe(III) 0.000200 M</b>         | Not hazardous         |
| 0.3% hydrogen peroxide solution, 3 mL in amber glass bottle       | <b>H<sub>2</sub>O<sub>2</sub></b> | Not hazardous         |

**For problem P3**

| <b>Chemicals</b>  | <b>Labeled as</b>                               | <b>GHS hazard statements</b> |
|---|---|------------------------------|
| 0.01 M iodine solution, 200 mL in amber glass bottle                            | <b>I<sub>2</sub></b>                            | H372                         |
| 0.03 M sodium thiosulfate solution, 200 mL in plastic bottle                    | <b>Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub></b> | Not hazardous                |
| 1 M NaOH solution, 55 mL in plastic bottle                                      | <b>NaOH</b>                                     | H290, H314                   |
| 2.5 M sulfuric acid solution, 80 mL in plastic bottle                           | <b>H<sub>2</sub>SO<sub>4</sub></b>              | H290, H315, H319             |
| 0.5 M potassium iodide solution, 25 mL in plastic bottle                        | <b>KI</b>                                       | H372                         |
| Potassium iodate, about 100 mg (exact mass written on the label), in glass vial | <b>KIO<sub>3</sub></b>                          | H272, H315, H319, H335       |
| Starch solution, 25 mL in plastic bottle  | <b>Starch</b>                                   | Not hazardous                |

**Equipment**  
**For all problems**

| Personal equipment   | Quantity  |
|--|-----------|
| Pipette filler bulb  | 1         |
| Safety goggles   | 1         |
| 1 L plastic bottle for organic waste, labeled “ <b>Organic waste</b> ” | 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:  | 1        |
| - Clamp holder with small clamp   | 2        |
| - Clamp holder with large clamp   | 1        |
| Conical flask with ground joint, 100 mL   | 1        |
| Conical 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 “ <b>TLC elution chamber</b> ”                           | 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 <b>C</b> and <b>R</b> | 2 |
| Pre-weighed amber glass vial, 10 mL, with stopper, labeled with <b>Student Code</b>   | 1 |
| Magnetic stirring bar retriever   | 1 |

**For problem P2**

| <b>Personal equipment</b>               | <b>Quantity</b> |
|---|-----------------|
| 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**

| <b>Personal equipment</b>              | <b>Quantity</b> |
|--|-----------------|
| Laboratory stand with burette clamp    | 1               |
| Burette, 25 mL                         | 1               |
| Glass transfer funnel                  | 1               |
| Conical flask, 100 mL                  | 3               |
| Conical 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<br>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 few decades, chemists have tried to replace harmful reagents in oxidation processes in order to reduce hazardous waste treatment. In this problem, potassium peroxomonosulfate (Oxone<sup>®</sup>) has been chosen because its products are non-toxic and non-polluting sulfate salts.

Furthermore, the reaction is done in a mixture of water and ethanol, which are green solvents.

Your task is to

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

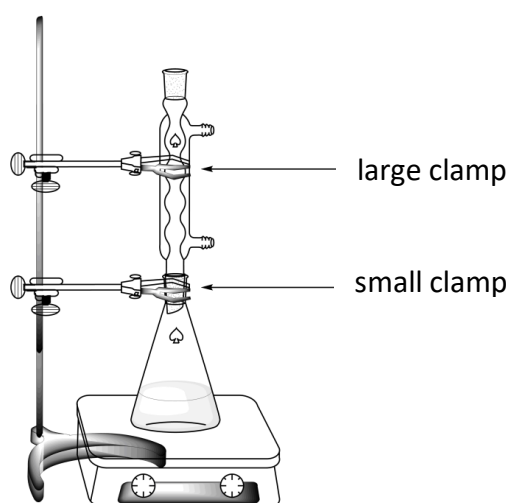
**Note:** Ethanol waste and eluent must be disposed of in the “Organic waste” bottle.

### Procedure

#### I. Oxidation of 4-nitrobenzaldehyde

1. **Mix** 20 mL of water and 5 mL of ethanol.
2. **Insert** the magnetic bar into the 100 mL **ground-joint** conical flask.
3. **Transfer** the pre-weighed 1.51 g of 4-nitrobenzaldehyde into the conical flask. **Add** all of the water/ethanol mixture prepared previously. **Clamp** the conical flask to the stand. **Start stirring** the mixture, then **add** the pre-weighed 7.87 g of Oxone<sup>®</sup>.
4. **Attach** the reflux condenser, first loosening the large clamp (see Figure 1). Then **raise** your HELP card. A lab assistant will come to turn on the water and set the hotplate.
5. **Heat** the reaction mixture to a gentle reflux (about 1 drip per second) for 45 minutes. The mark on the heater corresponds to the necessary setting to reach a gentle reflux.

Figure 1. Setup for heating the reaction mixture under reflux



6. Then **turn off** the heating on the hotplate stirrer. **Carefully slide** the hot plate away and let the reaction mixture cool down for 10 minutes.
7. **Place** the flask (clamped) in the crystallizing dish partially filled with an ice-water mixture (pack ice around it). **Let** it stand for another 10 minutes.
8. **Set up** a vacuum filtration apparatus (see Figure 2) using a Büchner funnel, a filter paper and a suction flask. This should be secured to the laboratory stand with a small clamp. Then **raise** your HELP card. A lab assistant will show you how to connect the suction flask to the vacuum source.

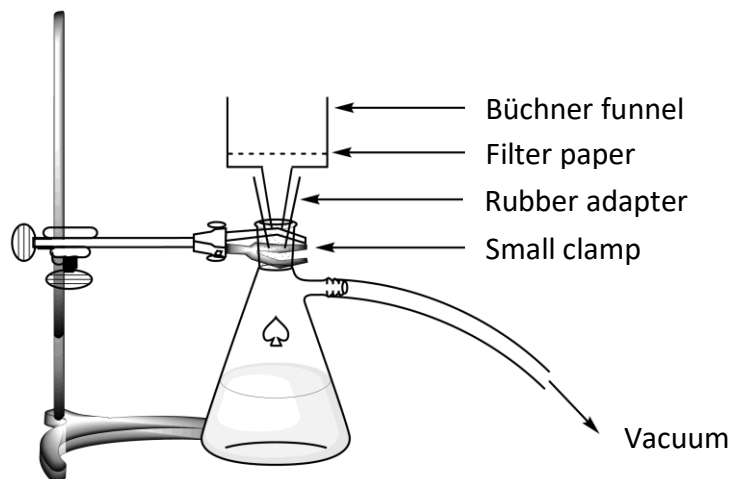


Figure 2. Setup for the vacuum filtration

9. **Wet** the filter paper with water and **ensure** that it covers all the holes of the Büchner funnel.
10. **Pour** the suspension of the crude product into the Büchner funnel and then **apply** a vacuum.
11. **Wash** the solid thoroughly with deionized water (at least 4×20 mL).
12. **Let** air suck through the precipitate for 5 minutes to pre-dry the product. **Disconnect** the vacuum source. **Use** the small spatula to transfer product (one tip of the spatula's worth) to the 1.5 mL amber glass vial, labelled **C**. **Close** the vial and **save** it for part III.
13. **Transfer** all remaining solid into the 50 mL ground-joint conical flask.
14. **Discard** the filtrate in the "Organic waste" bottle and **rinse** 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. **Mix** 9 mL of water and 21 mL of ethanol.
2. Recrystallize the crude product in the 50 mL ground-joint conical flask by first adding the minimum amount of the water/ethanol mixture. Use the same setup for heating as in Figure 1. Then **raise** your HELP card. A lab assistant will turn on the water and set the hotplate. **Add** any additional water/ethanol mixture through the top of the condenser.
3. **Use** the procedure as described previously (I.7 to I.10) to obtain the crystalline solid. Then use the small spatula to transfer (one tip of a spatula's worth) the recrystallized product to the 1.5 mL amber glass vial, labelled **R**. **Close** the vial and **save** it for part III.

4. **Transfer** the remaining recrystallized solid to the pre-weighed vial labelled with your Student Code. **Close** the vial.
5. **Discard** the filtrate in the “Organic waste” bottle. Then **raise** your HELP card. A lab assistant will turn off the water of the condenser.

### III. TLC analysis

1. **Prepare the elution chamber. Load** the elution chamber with eluent A to a height of about 0.5 cm. Cover the chamber with a Petri dish. **Wait** for the eluent to saturate the atmosphere in the elution chamber.
2. **Prepare your samples.** You are provided with a sample of 4-nitrobenzaldehyde in an amber glass vial labeled **TLC standard** (referred to 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 amber glass vials. **Add** about 1 mL of ethanol to each of the vials 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 to spot the 3 samples. Use the following labels: **S** (Starting material), **C** (Crude product) and **R** (Recrystallized product) (see Figure 3).
4. At the top left of the plate, **write** your **Student Code**. On the top right of the plate, **write** the eluent you used (for this experiment **Eluent A**, then later **Eluent B** see below). **Spot** the three samples on the plate, using capillary spotters.

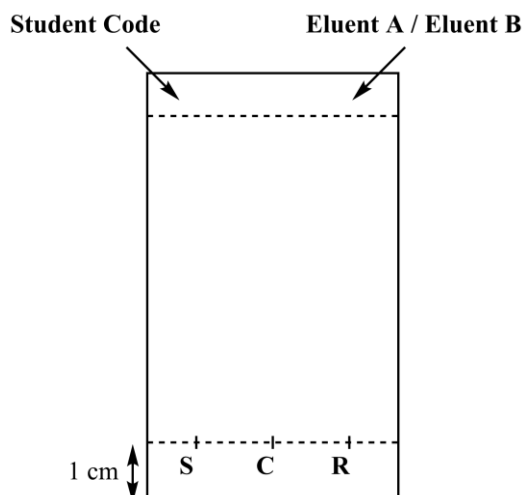


Figure 3. TLC plate preparation

5. **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** about 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.
6. **Visualize the TLC plate.** Place the TLC plate under the UV lamp (found on the common bench). With a pencil, **circle** all the visible spots.
7. **Discard eluent A into the “Organic waste” bottle.**
8. **Repeat** steps 1, 3, 4, 5, and 6 with eluent **B**.
9. **Place** your plates in the zipped bag with your Student Code.

**Results of your TLC analysis.** Complete the diagrams below with your results. This may help you answer the following questions. The diagrams will not be graded.

| <b>Eluent A</b>  | <b>Eluent B</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;"> <span style="margin: 0 10px;">S</span> <span style="margin: 0 10px;">C</span> <span style="margin: 0 10px;">R</span> </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;"> <span style="margin: 0 10px;">S</span> <span style="margin: 0 10px;">C</span> <span style="margin: 0 10px;">R</span> </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**.
- Kia kaha

|  |                          |  |
|--|--------------------------|--|
| Submitted items  |                          |  |
| <b>Recrystallized product</b>  | <input type="checkbox"/> |  |
| <b>TLC plate A</b>   | <input type="checkbox"/> |  |
| <b>TLC plate B</b>   | <input type="checkbox"/> |  |
| <b>Signatures</b> <div style="display: flex; justify-content: space-between; margin-top: 10px;"> <div style="text-align: center; width: 45%;"> <hr style="border: 0; border-top: 1px solid black; margin: 0;"/>             Student           </div> <div style="text-align: center; width: 45%;"> <hr style="border: 0; border-top: 1px solid black; margin: 0;"/>             Lab Supervisor           </div> </div> |                          |  |

**Questions**

1. **Propose** a structure for the organic product of the reaction between 4-nitrobenzaldehyde and Oxone<sup>®</sup>.

2. Based on the results of your 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<br>P2<br>14% of<br>total | Question | Calibration | Iron<br>determination | P2.1 | P2.2 | P2.3 | Stoichiometry<br>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 is naturally found in wine. When its concentration exceeds 10 to 15 mg per liter, oxidation of iron(II) to iron(III) may lead to quality loss, through the formation of precipitates. It is therefore necessary to monitor the iron content during wine production.

Given the very low concentration of iron species, a coloured complex of iron(III) with thiocyanate  $\text{SCN}^-$  is used to spectrophotometrically measure the amount of iron.

**Your task is to use spectrophotometry to**

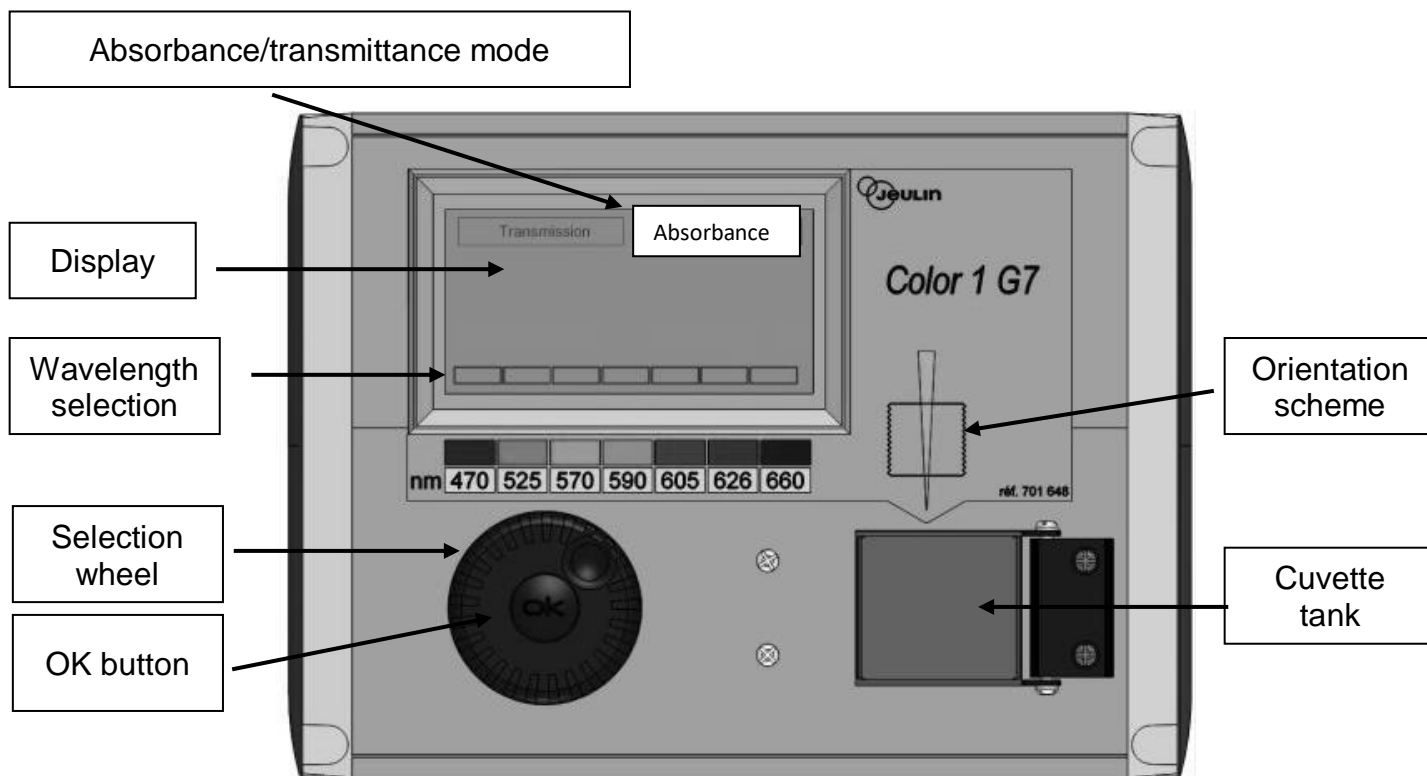
- **determine the iron(III) concentration of the white wine provided,**
- **determine the stoichiometry of the thiocyanate – iron(III) complex.**

### WARNING

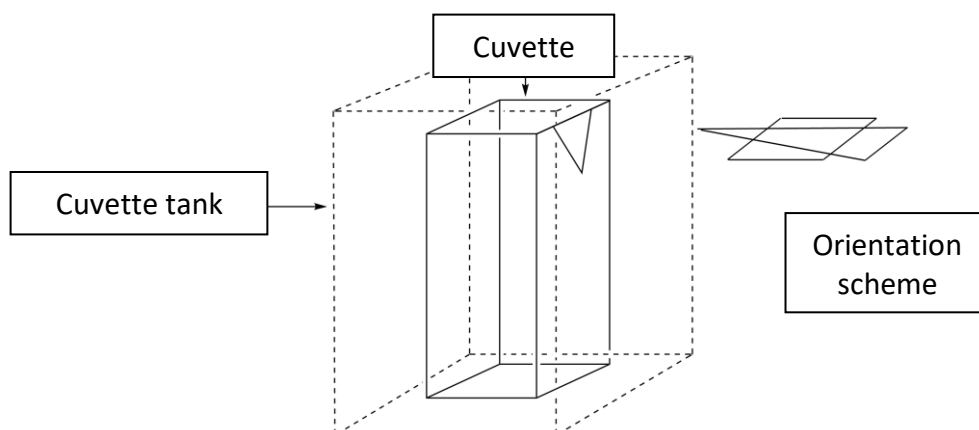
- In this task, you are provided with two iron(III) solutions and two potassium thiocyanate solutions of different concentrations. **Be very careful** not to confuse them.
- Once the mixtures are ready for spectrophotometric measurements. Record the absorbance **no later** than one hour after the addition of thiocyanate.
- When you need a colorimeter, raise your HELP card. A lab assistant will give you a labelled colorimeter. 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, you will be added to a waiting-list.
- You can call for the colorimeter only **three** times for this problem.

Instructions for using colorimeter are presented on the following page.

# 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 at the desired wavelength (470 nm). Press the OK button.
- Place the cuvette containing 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). Push the cuvette down to 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

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

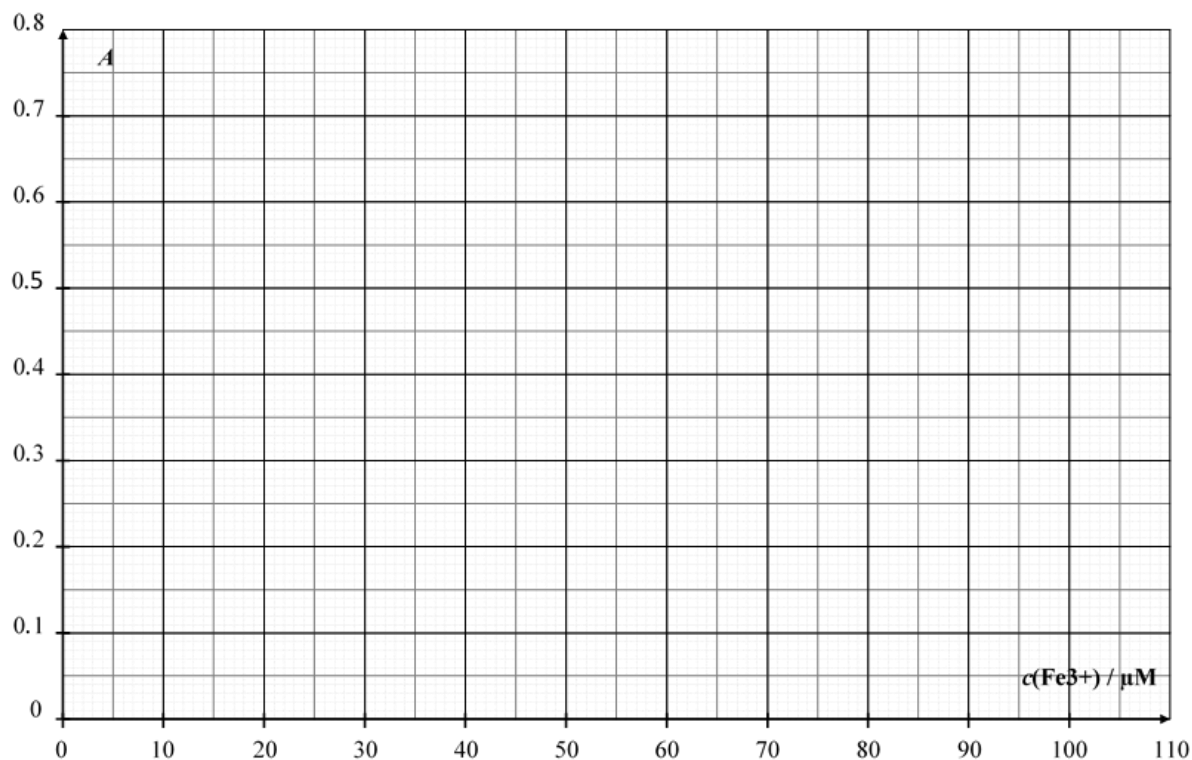
| Tube #               | 1      | 2      | 3      | 4      | 5       | 6       |
|----------------------|--------|--------|--------|--------|---------|---------|
| 0.000200 M iron(III) | 1.0 mL | 2.0 mL | 4.0 mL | 6.0 mL |         |         |
| 1 M perchloric acid  | 1.0 mL | 1.0 mL | 1.0 mL | 1.0 mL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

4. **Stopper** the tubes and mix the solutions by shaking (not you but the tube ☺).
5. **Add** 1.0 mL of 1 M potassium thiocyanate solution in tubes **1, 2, 3, 4** and **5**. (not to tube **6**). **Stopper** and **mix** the solutions in tubes **1** to **5**.
6. When all the tubes are ready, **raise** your HELP card to get a colorimeter from a lab assistant.
7. **Prepare** the colorimeter using the procedure described previously (see page 16). **Set** the wavelength at 470 nm. **Use** deionized water for the blank.
8. **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)   |    |    |    |    |   |   |
| Concentration of $\text{Fe}^{3+}$<br>$c(\text{Fe}^{3+}) / \mu\text{M}$ | 16 | 32 | 64 | 96 |   |   |
| Colorimeter code   |    |    |    |    |   |   |

## Questions

1. Show the data points for tubes **1** to **4** on the graph.



- Check the tube numbers you will use for your calibration curve.

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

2. Using the data you have chosen, **draw** the calibration straight line on the graph. **Determine** the concentration (in  $\mu\text{mol L}^{-1}$ ) of  $\text{Fe}^{3+}$  in tube **5**.

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

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

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

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

## 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, the colour of the iron(III)-thiocyanate complex was used to determine the concentration of iron in the sample of wine. Part II of this problem will investigate the stoichiometry of the  $[\text{Fe}_a(\text{SCN})_b]^{(3a-b)+}$  complex (coordination of water to iron 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 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.* **Calculate** the mole fraction of iron(III) in each tube, using the following formula.

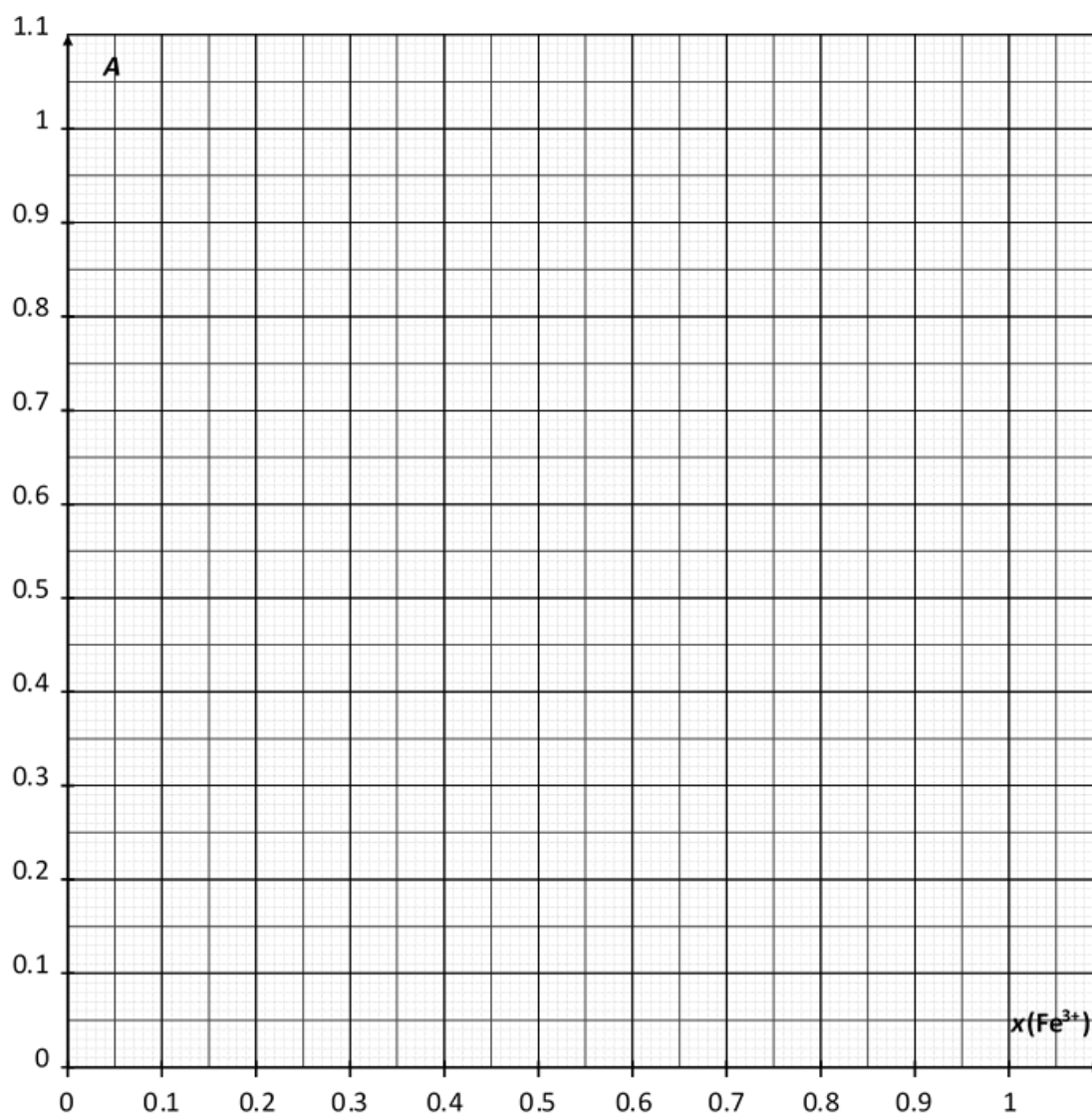
$$x(\text{Fe}^{3+}) = \frac{V_{\text{Fe(III)}}}{V_{\text{Fe(III)}} + V_{\text{SCN}^-}}$$

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

2. **Prepare** the tubes. 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 mole 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  $[(\text{Fe})_a(\text{SCN})_b]^{(3a-b)+}$ .

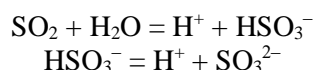
$a =$  \_\_\_\_\_

$b =$  \_\_\_\_\_

| Problem P3<br>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,  $\text{SO}_2$ , is used as a preservative in wine. When  $\text{SO}_2$  is added to wine, it can react with water leading to hydrogensulfite ions,  $\text{HSO}_3^-$ , and protons,  $\text{H}^+$ . Hydrogensulfite can also be converted to sulfite,  $\text{SO}_3^{2-}$ , by the loss of a second proton.



These three different forms of sulfur dioxide in water can react with chemicals in wine such as acetaldehyde, pigments, sugars, forming products P. The total concentration of sulfur dioxide is the sum of the concentrations of the “free” forms ( $\text{SO}_2$ ,  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$ ) 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  $\text{mg L}^{-1}$  for red wine and 150  $\text{mg L}^{-1}$  for white wine 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  $\text{KIO}_3$ . 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 conical 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.
- Swirl** the conical 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 contents of the conical flask with constant swirling. When the liquid turns pale yellow, **add** ten drops of the starch solution and **keep titrating** until the solution becomes colourless. **Record** the titration volume  $V_1$ .
- Repeat** the procedure (steps 3-6) as needed.

| Mass of potassium iodate<br>(report the value on the label) |            |
|---|------------|
|   |            |
| Titration number  | $V_1$ / mL |
| 1   |            |
| 2   |            |
| 3   |            |
|   |            |
|   |            |
| Reported value $V_1$ / mL                                   |            |

## II. Standardization of the iodine solution

- Using a volumetric pipette, **transfer** 25 mL of the iodine solution labeled **I<sub>2</sub>** into a 100 mL conical flask.
- Titrate** the contents of the conical 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 colourless. **Record** the titration volume  $V_2$ .
- Repeat** the procedure (steps 1-2) as needed.

| Titration number          | $V_2$ / 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 conical flask.
2. **Add** 12 mL of the sodium hydroxide solution (1 M), using a 25 mL graduated cylinder. **Cover** the flask with Parafilm, **swirl** the contents. 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. **Titrate** the contents of the conical flask with the iodine solution in the burette, until a dark colour appears and persists for at least 15 seconds. **Record** the titration volume  $V_3$ .
5. **Repeat** the procedure (steps 1-4) as needed.

| Titration number                            | $V_3$ / mL |
|---|------------|
| 1   |            |
| 2   |            |
| 3   |            |
|   |            |
|   |            |
| <b>Reported value <math>V_3</math> / mL</b> |            |



**Questions**

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

**Calculate** the concentration in  $\text{mol L}^{-1}$  of sodium thiosulfate.  $M(\text{KIO}_3) = 214.0 \text{ g mol}^{-1}$ .

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

*If you could not calculate  $c(\text{S}_2\text{O}_3^{2-})$ , use  $c(\text{S}_2\text{O}_3^{2-}) = 0.0500 \text{ mol L}^{-1}$  for the rest of the problem.*

2. **Calculate** the concentration in  $\text{mol L}^{-1}$  of the iodine solution.

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

*If you could not calculate  $c(\text{I}_2)$ , use  $c(\text{I}_2) = 0.00700 \text{ mol L}^{-1}$  for the rest of the problem.*

3. **Write** the equation for the reaction between iodine  $\text{I}_2$  and sulfur dioxide  $\text{SO}_2$ , assuming that sulfur dioxide is oxidized to sulfate ions  $\text{SO}_4^{2-}$ .

4. **Calculate** the concentration, in mg per liter, of total sulfur dioxide in the wine.

$$M(\text{SO}_2) = 64.1 \text{ g mol}^{-1}.$$

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

**PENALTIES**

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