PRACTICAL

EXAM

IChO

**51st — International
Chemistry Olympiad
France — Paris — 2019**

Making science together!

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

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RÉPUBLIQUE FRANÇAISE

MINISTÈRE
DE L'ÉDUCATION
NATIONALE ET
DE LA JEUNESSE

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

General instructions

- This practical booklet contains 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 scrap paper, use the back 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 toilet 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. If you break a rule again you will be dismissed from the laboratory and your practical examination will be nullified.
- 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 gum is not allowed.
- Work only in the designated area. Keep your work area and the common work areas tidy.
- No unauthorised 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 $c° = 1\,mol\,L^{-1}$ is omitted.

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

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

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

Henderson−Hasselbalch equation:

$$pH = pK_a + \log\frac{[A^-]}{[AH]}$$

Nernst–Peterson equation:

$$E = E° - \frac{RT}{zF}\ln Q$$

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

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

Beer–Lambert law:

$$A = \varepsilon l c$$

Rate laws in integrated form:
- Zero order: $\qquad\qquad\qquad\qquad [A] = [A]_0 - kt$
- First order: $\qquad\qquad\qquad\quad \ln[A] = \ln[A]_0 - kt$
- Second order: $\qquad\qquad\qquad 1/[A] = 1/[A]_0 + kt$

Half-life for a first order process: $\qquad t_{1/2} = \ln 2/k$

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 "$mol\,L^{-1}$":

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

Periodic table

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

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

2019 IYPT

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 vapour.
H226 Flammable liquid and vapour.
H228 Flammable solid.
H271 May cause fire or explosion; strong oxidiser.
H272 May intensify fire; oxidiser.
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	Labelled as	GHS hazard statements
Deionised water in: - Wash bottle (bench) - Plastic bottle (bench) - Plastic canister (hood)	**Deionised 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	Labelled as	GHS hazard statements
4-nitrobenzaldehyde, 1.51 g in amber glass vial	**4-nitrobenzaldehyde**	H317, H319
Solvent A, 20 mL in glass vial	**Eluent A**	H225, H290, H304, H314, H319, H336, H410
Solvent 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	Labelled 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	Labelled 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, approximately 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, labelled "**Organic waste**"	1
Large paper towels	15 sheets
Small tissues for cuvettes	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	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-glass joint, 100 mL	1
Conical flask with ground-glass joint, 50 mL	1
Reflux condenser	1
Hotplate stirrer	1
Crystallising dish	1
Magnetic stirring bar	1
Side arm flask	1
Büchner funnel with rubber adapter	1
Zipped bag with 3 pieces of filter paper	1
Petri dish	1
TLC chamber, labelled "**TLC elution chamber**"	1
Zipped bag with 3 TLC plates (with fluorescence indicator), labelled with Student Code	1
TLC spotters (in the Petri dish)	4
Plastic tweezers	1
Glass rod	1
Measuring 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, labelled **C** and **R**	2
Pre-weighed amber glass vial, 10 mL, with stopper, labelled 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
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
Measuring cylinder, 25 mL	1
Measuring cylinder, 10 mL	1
Measuring 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 used in oxidation reactions to reduce hazardous waste. In this problem, potassium peroxomonosulfate (Oxone®) has been chosen as the oxidising agent, because it only produces non-toxic and non-polluting sulfate salts.

This reaction 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 recrystallise the product, to compare TLC solvents and to check the purity of the product using TLC.

Note: Ethanol waste and solvent 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.   **Put** the magnetic bar into the 100 mL **ground-glass 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. **Clamp** the conical flask. **Start stirring** 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-glass joints (see Figure 1). **Raise** your HELP card. A lab assistant will turn on the water and the hotplate.

5.   **Heat** the reaction mixture with a gentle reflux (approximately 1 drop refluxing per second) for 45 minutes. The mark on the heater corresponds to the necessary power to get a gentle reflux.
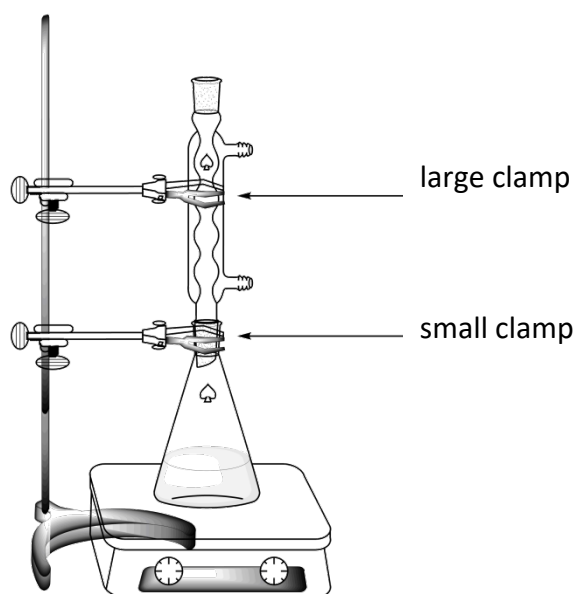

Figure 1. Setup for heating the reaction mixture under reflux

6. **Turn off** the heating. **Remove** the flask from the hot plate and **let** the reaction mixture cool down for 10 minutes, then **place** it in the crystallising dish filled with an ice-water mixture. **Let** it stand for another 10 minutes.

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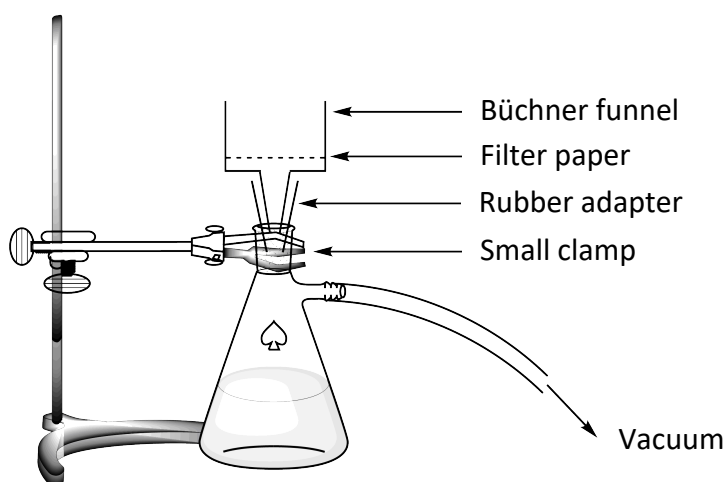
Figure 2. Setup for the vacuum filtration

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 deionised water (at least 4 × 20 mL).

10. **Let** air suck through the precipitate for 5 minutes to pre-dry the product. **Disconnect** the vacuum. **Use** the small spatula to transfer one spatula tip of the product into the 1.5 mL amber glass vial, **labelled C**. **Stopper** the vial and **save** it for part III.

11. **Transfer** all of the remaining solid into the 50 mL ground-glass joint conical flask.

12. **Discard** the filtrate into the "Organic waste" bottle and **wash** both the side-arm flask and the Büchner funnel with ethanol and water. **Use** the "Organic waste" bottle to dispose of the ethanol waste.

II.   Recrystallisation of the product

1.   **Mix** 9 mL of water and 21 mL of ethanol.

2.   **Recrystallise** the crude product using the appropriate amount of the water/ethanol mixture, using the same setup as for the reflux heating (see Figure 1). **Raise** your HELP card. A lab assistant will turn on the water and set the hotplate. More solvent can be added through the top of the condenser.

3.   Once the product has crystallised, **use** the same procedure as described previously (I.7 to I.10) to collect the solid. **Use** the small spatula to transfer one spatula tip of the recrystallised product into the 1.5 mL amber glass vial, **labelled R**. **Stopper** the vial and **save** it for part III.

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

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

III.   TLC analysis

1.   **Prepare the TLC chamber.** **Load** the chamber with a depth of approximately 0.5 cm of solvent A. Cover with a Petri dish. **Wait** for the solvent to saturate the atmosphere in the chamber.

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

3.   **Prepare your TLC plate**. Use a pencil to **draw** carefully the start line (1 cm from the bottom of the plate) and **mark** the positions of the 3 samples. **Label** them **S** (Starting material), **C** (Crude product) and **R** (Recrystallised 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 solvent you use (first **Eluent A**, then **Eluent B**). **Spot** the three samples on the plate, using the capillary spotters.
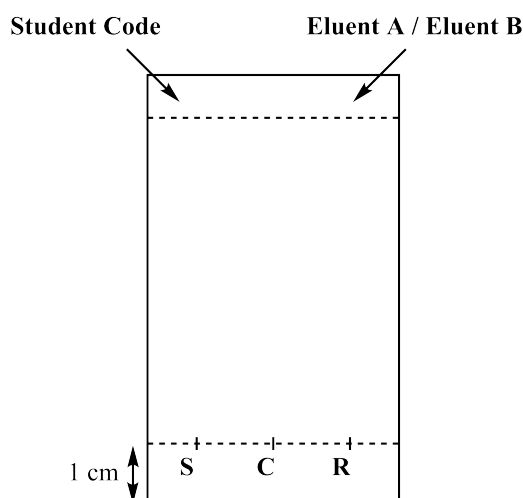

Figure 3. TLC plate preparation

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

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

6.   **Discard the solvent 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 (**complete** the diagrams with your results).

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

Eluent A	Eluent B
S C R	S C R

At the end of the examination, your lab supervisor will pick up the following items:
- Glass vial labelled with your **Student Code** containing your recrystallised product;
- TLC plates A and B in zipped bag labelled with your **Student Code**.

Submitted items	
Recrystallised 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 from the TLC analysis, **answer** the following questions.

●   Which TLC solvent is better to follow the reaction progress?

□ A	□ B

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

□ True	□ False

●   The recrystallised 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 found naturally in wine. When its concentration exceeds 10 to 15 mg per litre, oxidation of iron(II) into iron(III) may lead to loss of quality, through precipitates forming. It is therefore necessary to measure the iron content of the wine during its production.

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

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

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 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.
- Instructions for the colorimeter are on the following page.
- You can request the colorimeter at most three times for this problem.

Instructions for the use of the colorimeter
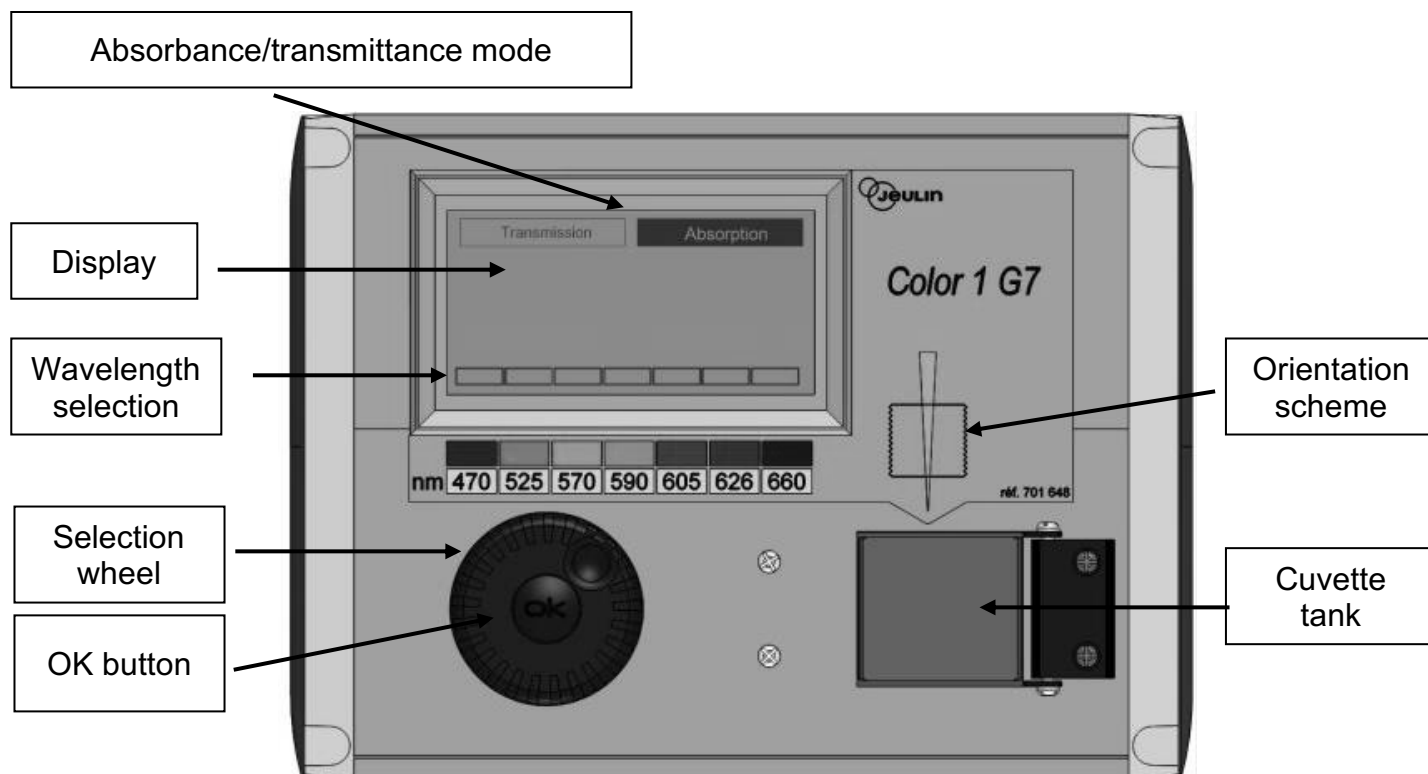
- Plug in the colorimeter.
- Check that "Absorbance" is highlighted. If not, turn the selection wheel until a dashed line appears around "Absorbance" and then press the OK button.
- Turn the selection wheel until a dashed line appears around the desired wavelength (470 nm). Press the OK button.
- Place the cuvette with a depth of approximately 3 cm of the blank solution in the tank. Be careful to choose the correct orientation (check 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 to the bottom. 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 a depth of approximately 3 cm of the solution to be analysed in the tank. Close the lid.
- Read the absorbance value.
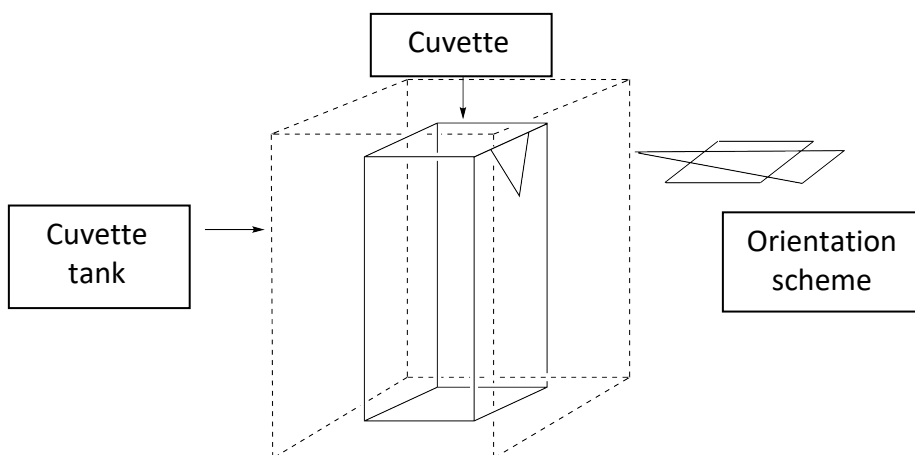
I.   Determination of the iron content in the wine

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

Procedure

1.   **Prepare** 6 test tubes 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
Deionised water	9.5 mL	8.5 mL	6.5 mL	4.5 mL		1.0 mL

2.   **Stopper** the tubes and **shake to mix**.

3.   **Add** 1.0 mL of 1 M potassium thiocyanate solution to tubes **1**, **2 3**, **4** and **5**. Do **not** add to tube **6**. **Stopper** and **shake to 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 17). **Set** the wavelength at 470 nm. **Use** deionised 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 $c(Fe^{3+})$ / µM	16	32	64	96		
Colorimeter code						

Questions

1.   **Plot** the absorbance A of tubes **1** to **4** against the analytical concentration of Fe^{3+} in the tube.
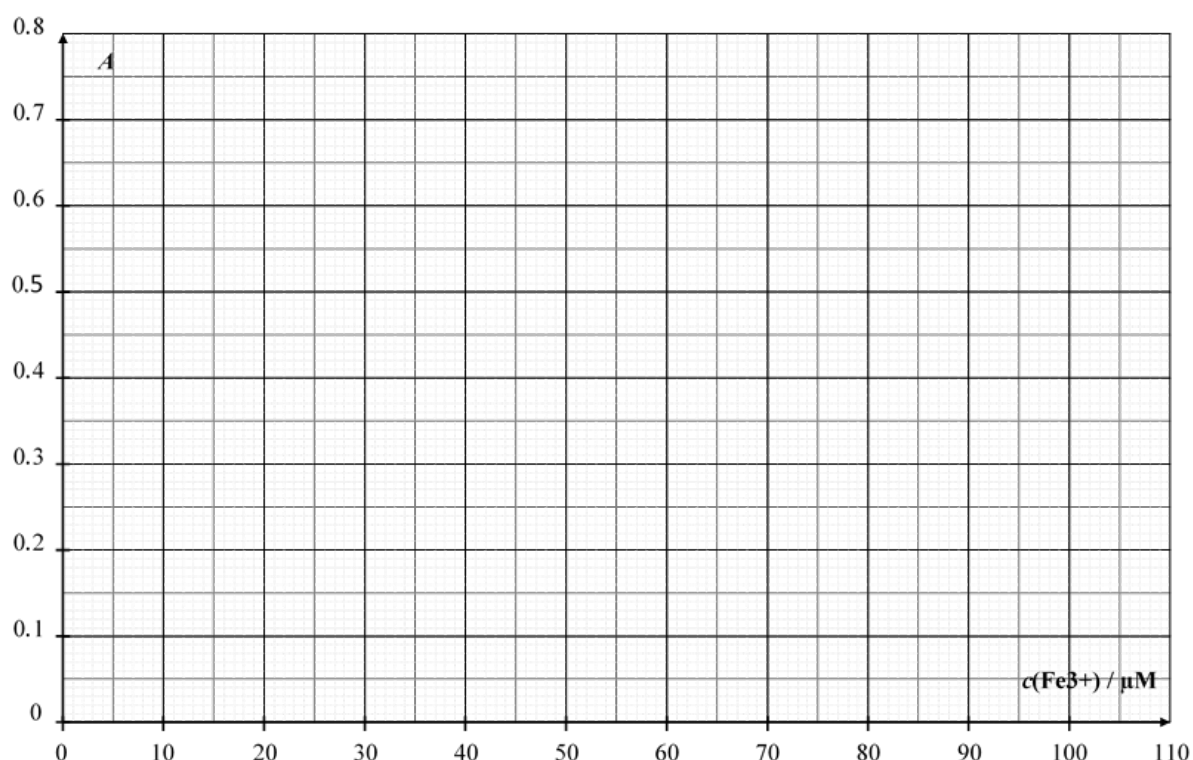
- In the following table, tick the boxes of the data you are using for your calibration curve.

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

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

$c(Fe^{3+})_{TUBE\ 5} = $ _____ $\mu mol\ L^{-1}$

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

3.   **Calculate** the concentration, in mg per litre, of iron in the 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 colour of the iron(III)-thiocyanate complex to determine the concentration of iron in the sample of wine. Part II of this problem aims to determine the stoichiometry of the $[Fe_a(SCN)_b]^{(3a-b)+}$ complex (the 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. **Complete** the first three rows of the table with 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.

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

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

2.   **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 17). **Set** the wavelength at 470 nm. **Use** deionised water for the blank.

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

Questions

4.   **Plot** the absorbance A of the tubes against the molar fraction of iron(III), $x(Fe^{3+})$.
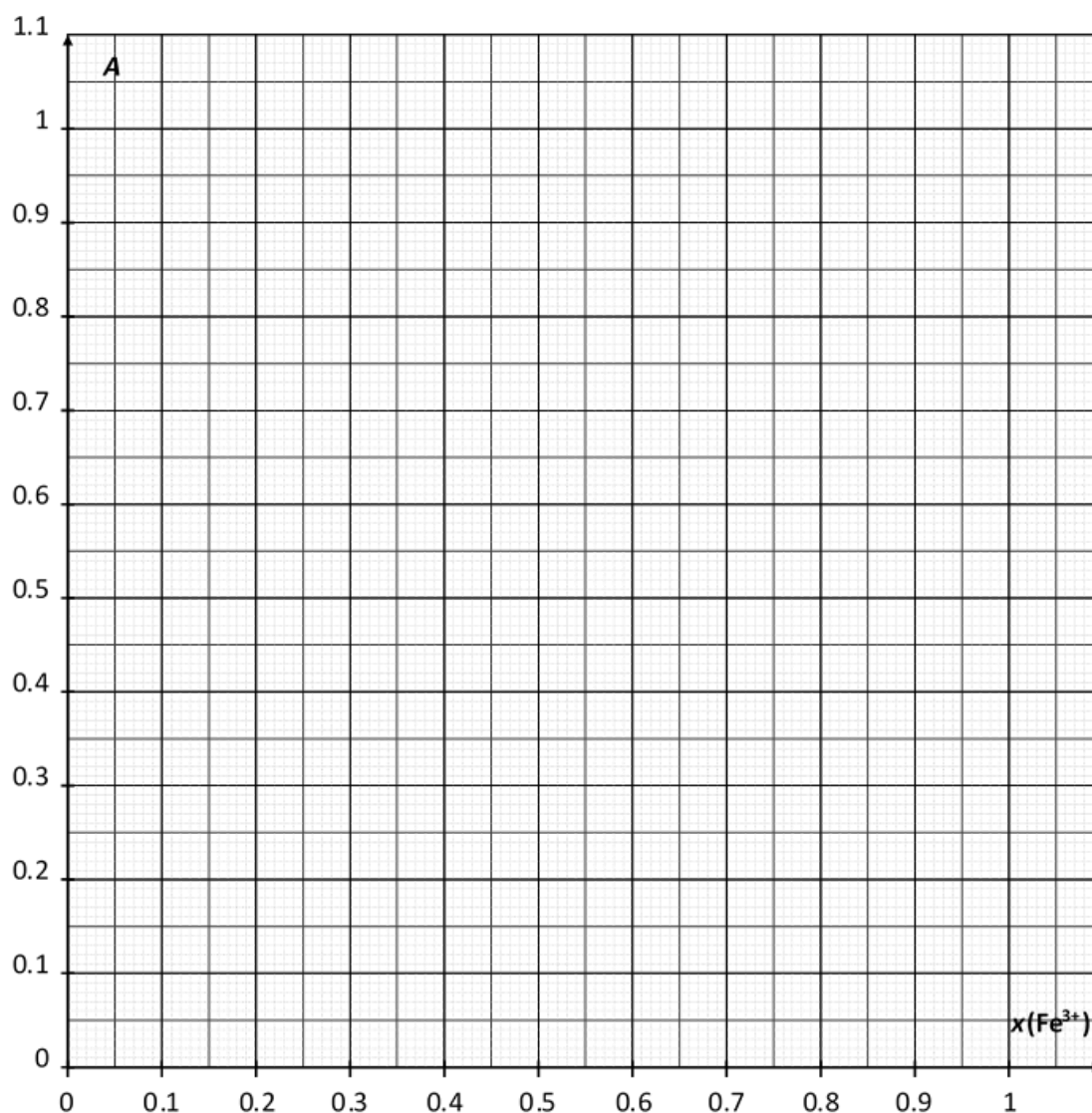
5.   Based on the results of the experiments you carried out, **determine** the stoichiometry of the complex $[(Fe)_a(SCN)_b]^{(3a-b)+}$.

$a = $ _____ $b = $ _____

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

Problem P3. Wine for keeping

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

$$SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^-$$
$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$$
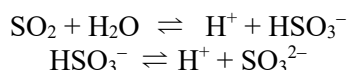
These three different forms of sulfur dioxide in water can react with chemicals in wine such as acetaldehyde, pigments and sugars, forming products P. The total concentration of sulfur dioxide is the sum of the concentration of the "free" forms (SO_2, HSO_3^- and SO_3^{2-}) and P.

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.   Standardisation 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** it in the table.

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

3.   To a 100 mL conical 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 measuring cylinder;
*   10 mL of the sulfuric acid solution (2.5 M) with a 10 mL measuring cylinder.

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

5.   **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 **continue to titrate** until the solution becomes colourless. **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.   Standardisation of the iodine solution

1.   **Transfer** 25 mL of the iodine solution labelled **I₂** with a volumetric pipette into a 100 mL conical flask.

2.   **Titrate** the content of the conical 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 colourless. **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. **Transfer** 50 mL of wine using a volumetric pipette into a 250 mL conical flask.

2. **Add** 12 mL of the sodium hydroxide solution (1 M), using a 25 mL measuring cylinder.

   Cover the flask with Parafilm, **swirl** the content and 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 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.

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

Questions

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

2.   **Calculate** the 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 concentration of the iodine solution.

$c(\mathbf{I_2}) = $ _____ **mol L^{-1}**

If you could not calculate c(I$_2$), the value c(I$_2$) = 0.00700 mol L^{-1} can be used in the rest of the problem.

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

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

$c_\mathbf{m}(\mathbf{SO_2}) = $ _____ **mg L^{-1}**

PENALTIES

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