P1. Synthesise and analyse (A new complex problem)

Equipment

Item	Quantity	Label
Part A		
Magnetic stirrer bar	1	
Steel spatula	1	
Sintered funnel	1	
Round bottom flask with ground-glass joint	1	
Vacuum pump with hose connected to a bubbler at the back	1	
Glass beaker, 100 mL	1	
Pre-weighed glass vial with cap for product	1	**A + student code**
Measuring cylinder, 10 mL	1	
Magnetic rod	1	
Yellow paper for product transfer	1	
Part B		
Graduated pipette, 10.0 mL	1	
Glass beaker, 50 mL	2	
Erlenmeyer flask, 100 mL	2	
Measuring cylinder, 10 mL	1	
Part C		
Plastic Pasteur pipette, 3 mL	12	
Eppendorf tube, 0.5 mL	15	

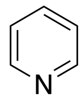
Chemicals

Name	State	Concentration	Quantity	Placed in	Label
Part A					
Solution **R1** (synthesis)	aq	To be determined	10.0 mL	Glass vial with cap, 30 mL	**R1-syn**
Solution **R2**	aq	1.03 M	10.0 mL	Glass vial with cap, 30 mL	**R2**
Pyridine in ethanol (synthesis)	sol	8.4 % v/v	10 mL	Plastic tube (15 mL) in plastic cup	**Py**
Part B					
Solution **R1** (analysis)	aq	To be determined	10.0 mL	Volumetric flask, 100 mL	**R1-an**
Ethylenediamine-tetraacetic acid disodium salt	aq	0.0770 M	50 mL	Bottle, 50 mL	**EDTA**
Ammonia buffer	aq	-	40 mL	Bottle, 50 mL	**NH_3 buffer**
Eriochrome Black T	s	1% in NaCl	0.2 g	Sample container	**Eriochrome**

Part C					
Complex **A**	s	-	10 mg	Eppendorf tube, 0.5 mL	**A**
Iron(III) nitrate	aq	0.4 %	0.5 mL	Eppendorf tube, 0.5 mL	**Fe^{3+}**
Copper(II) sulphate	aq	5%	0.5 mL	Eppendorf tube, 0.5 mL	**Cu^{2+}**
Pyridine in ethanol (analysis)	sol	8.4 % v/v	0.5 mL	Eppendorf tube, 0.5 mL	**Py-qual**
X^-	aq	0.1 M	0.5 mL	Eppendorf tube, 0.5 mL	**X^- – qual**
Unknown solvent	l	-	1 mL	Eppendorf tube, 1.5 mL	**Solvent**
Dithizone	s	-	1 mg	Eppendorf tube, 0.5 mL	**Dithiz.**
Dichloromethane	l	-	0.75 mL	Eppendorf tube, 1.5 mL	**CH_2Cl_2**

14% of total											
Question	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	1.10	**Total**
Total	10	0	10	1	3	1	4	2	1	1	33

In this problem, you will synthesise and analyse complex **A** with molecular formula $[M(Py)_m X_n]$ where:

- M^{k+} is an unknown metal cation; - Py (pyridine); - X^- is either OCN^- or SCN^-; - m = 0, 1, 2, 3, ...; - n = 1, 2, 3, ...	*Py* = 

Part A. Synthesis

To synthesise complex **A**, solutions **R1-syn** and **R2** are used:

- Solution **R1-syn** contains 10.0 mL of an aqueous solution of a M^{k+} salt with unknown concentration.
- Solution **R2** contains 10.0 mL of an aqueous solution of potassium salt of X^- with a concentration of 1.03 M.

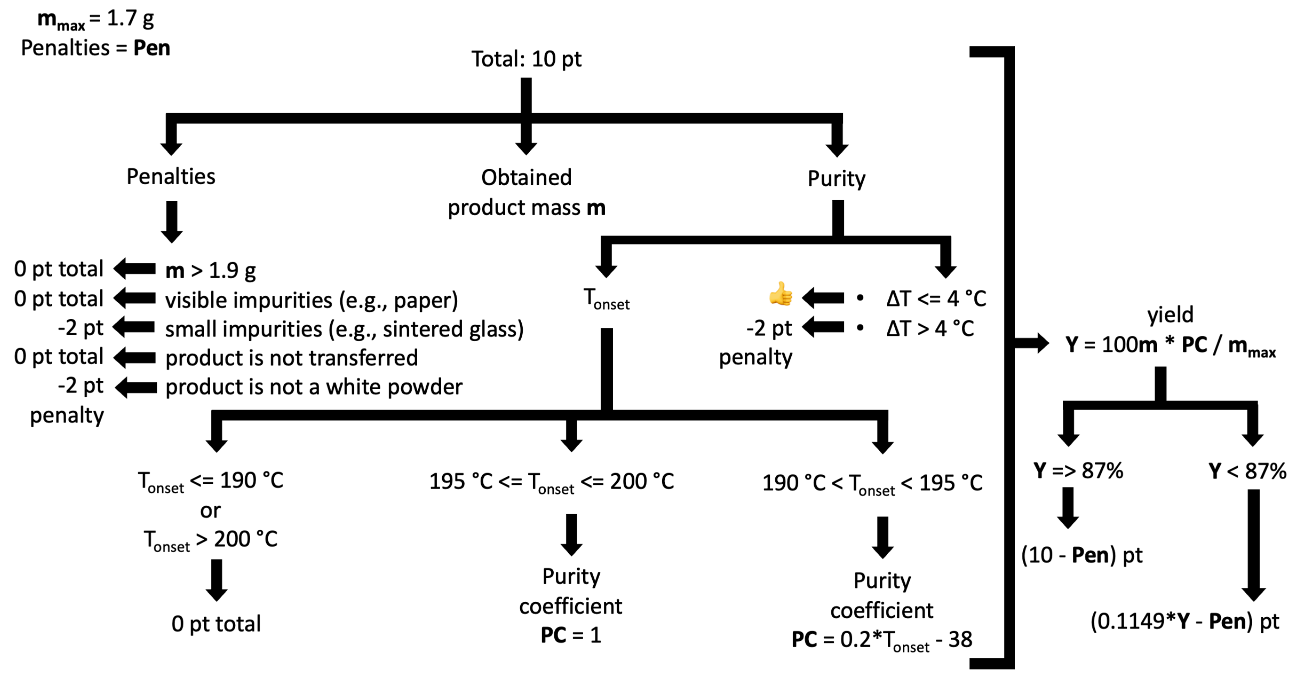
1. **Put** the stirrer bar in the 100 mL beaker.
2. **Transfer** the whole solution **R1-syn** to the same beaker.
3. **Rinse** the vial **R1-syn** with 1 mL of water using a Pasteur pipette and **transfer** the remains to the beaker.
4. **Add dropwise** the whole solution **R2** using a Pasteur pipette while stirring on the magnetic stirrer.
5. **Rinse** the vial **R2** with 1 mL of water using a Pasteur pipette and **transfer** the remains to the beaker.
6. **Add dropwise** the whole pyridine solution (**Py**) using a Pasteur pipette while stirring.
7. **Continue** stirring for 5 minutes.
8. **Connect** sintered funnel to a round bottom flask to assemble the vacuum filtration apparatus.
9. **Filter** the product using vacuum filtration and **wash** it three times with 10 mL portions of water.
10. Once you have finished washing, **ask** the lab assistant to collect the filtrate to avoid spills. For this, **raise** the green card with a question mark, **turn off** the pump and **disconnect** the vacuum hose. **Remove** the filter and **hand** the flask to the lab assistant. The lab assistant will discard the filtrate and **return** the empty flask.
11. **Reassemble** the filtration setup and **let** your product dry for **1 hour** with the vacuum turned on. During the drying, **it is important** to **use** your spatula **to break up** any aggregates of the product formed on the filter.
12. After complete drying, carefully **transfer** your product to the vial labelled "**A + Student Code**". For this you can use the yellow paper provided.

Q1.1 The lab assistant **will collect** your product at the end of the exam. Both you and the lab assistant should **sign** your answer sheet. 10 pt

The organisers will further dry your product in an oven before measuring the mass, however **it is important you have vacuum dried the product for 1 hour and broken up any aggregates** to remove the vast majority of the water before putting it in the vial.
(If the product is **not transferred** to the vial, it will **not be collected** and **ZERO points** will be awarded for the synthesis.)

SOLUTION:
Maximum mass (m_{max}) of the product is 1.7 g calculated for 100% theoretical yield. Points will be awarded based on the mass of the synthesised product (m) and purity of the complex (calculated from the melting point).
The melting point is measured twice for each sample and the onset point and clear point are recorded. An average value is taken for the start and end of the melting and then the average melting range is calculated ($\Delta T = T_{onset}^{aver} - T_{clear}^{aver}$).
If the start of the melting is above 200 °C, 0 pt are awarded for the synthesis. If the start of the melting is below 190 °C, 0 pt are awarded for the synthesis.
If the start of the melting is in range 195-200 °C, the sample is treated as pure and the purity coefficient (*PC*) is considered as $PC = 1$.
If the start of the melting is in range 190-195 °C, the sample is treated as impure and the purity coefficient (*PC*) is calculated as: $PC = 0.2 * T_{onset}^{aver} - 38$.
Yield of the pure product is calculated as: $Y = 100m * PC/m_{max}$
If $87 \leq Y < 105$, 10 pt are awarded for the synthesis.
If $Y < 87$, points are calculated $points = 0.1149 * Y$.
If $Y \geq 105$, 0 pt are awarded.
If the obtained product mass is greater than 1.9 g, 0 pt mark will be awarded for the synthesis.
-2 pt penalty is awarded if the melting range is above 4 °C.
-10 pt penalty if a residue of a major impropper impurity (e.g. paper, piece of plastic, pieces of gloves) is detected in the product by the naked eye.
-2 pt penalty is awarded if small impurities are detected during the melting point determination which does not melt (e.g. pieces of scraped sintered funnel).
-2 pt penalty if the product is not a white powder.
If the product is not transferred to the vial, it will not be collected and 0 pt mark will be awarded for the synthesis.

SOLUTION:



Part B. Quantitative Analysis

You will use a complexometric titration to determine the concentration of M^{k+} in solution **R1-an**. The volumetric flask **R1-an** contains 10.0 mL of M^{k+} solution with the same concentration as in **R1-syn** in **Part A**.

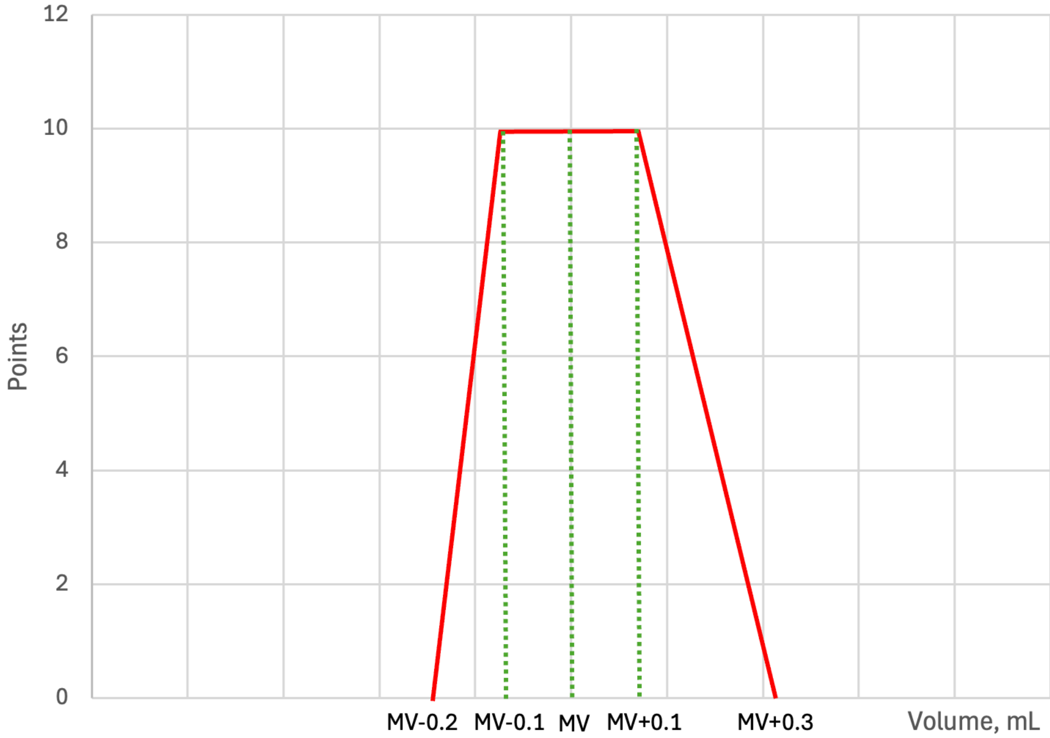
1. **Dilute** the **R1-an** solution in the volumetric flask with H_2O up to the mark and **mix** thoroughly.
2. **Fill** the burette with 0.0770 M **EDTA**.
3. **Add** a 10.0 mL aliquot of the diluted solution **R1-an** using a graduated pipette, 5 mL of ammonia buffer solution (**NH_3 buffer**), and a tip of the plastic spatula of indicator (**Eriochrome**; the spatula is inside the sample container) to an Erlenmeyer flask. **Close** the bottle of **NH_3 buffer** after using it.
4. **Titrate** the mixture with 0.0770 M **EDTA** solution until the colour turns a stable blue.
5. **Repeat** steps 3-4 if necessary.

Q1.2	**Record** the observed volumes (V_0, mL – initial burette reading; V_f, mL– final burette reading; T, mL - titre). This table is for your convenience and will not be graded. **SOLUTION:** The table in **Q1.2** will not be graded.	0 pt

Q1.3 **Record** your accepted final titre of **EDTA** (V_{EDTA}, mL). 10 pt

SOLUTION:

If **Q1.3** is empty, 0pt are given and **Q1.2** is not graded.



Q1.4 **Calculate** the ratio of X^- and M^{k+} ($n_{X^-}/n_{M^{k+}}$) used in the synthesis according to your result. **Round** your answer to two decimal places. 1 pt

SOLUTION:

n_{X^-} can be calculated from the concentration given in the task.

$n_{M^{k+}}$ in sample **R1-syn** is calculated from the accepted titre (concentration of M^{k+} in **R1-syn** is the same as in **R1-an**):

$n_{M^{k+}} = V(EDTA) * c(EDTA) * V(flask)/V(aliquot)$

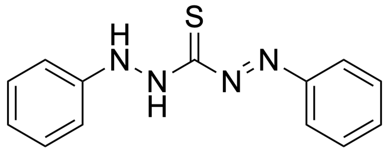
Error carried from **Q1.3** is not penalised. Full marks are given for correct ratio calculation with wrong volume. 0.5pt points are given if rounded incorrectly (e.g., the calculated value was 3.1234, but the student wrote 3.1 or 3.123; this student will be given 0.5 pt only).

Part C. Qualitative Analysis

In this part, you need to perform different chemical tests to identify the components of complex **A**.

1. **Prepare** a 0.4 mL solution of complex **A** in the Eppendorf tube by adding the solvent with a Pasteur pipette from the Eppendorf tube labelled **Solvent** until the 0.4 mL mark. If the sample has not dissolved completely, shake the tube and use the supernatant for the tests below.

2. **Prepare** a 0.4 mL solution of the indicator Dithizone (**Dithiz.**) in the Eppendorf tube by adding the solvent with a Pasteur pipette from the Eppendorf tube labelled **Solvent** until the 0.4 mL mark. The structure of the indicator is given below.



3. **Take** four empty Eppendorf tubes and **transfer** 1 drop of the solution of **A** obtained to each.
4. **Perform** the individual tests **T1–T4** by **adding** the following reagents to each of the four Eppendorf tubes:

- **T1**: 2 drops of **Fe^{3+}**(acidified $Fe(NO_3)_3$)
- **T2**: 2 drops of the prepared **Dithizone** solution
- **T3**: 2 drops of **Cu^{2+}**($CuSO_4$)
- **T4**: 2 drops of **Cu^{2+}**($CuSO_4$) followed by 3 drops of **CH_2Cl_2** and **shake**

You may perform additional tests; for this you are provided with extra equipment and chemicals (e.g., solutions of Py and X^-). *Additional information:* $\rho(CH_2Cl_2) = 1.32$ g/cm^3

Q1.5 **Tick** the correct box(es) corresponding to your observation(s) in **T1 - T3**. 3 pt

(a) No visible change
(b) Formation of precipitate
(c) Solution became colourless
(d) Solution became red or pink

SOLUTION:
T1: 1 pt for (d); 0 pt for any other option.
T2: 1 pt for (d); 0 pt for any other option.
T3: 1 pt for (b), option (c) can be chosen (does not affect the final point); 0 pt if (a) or (d) is chosen.
1 pt for each correct answer.
0 pt for each incorrect answer.
Each of the tests T1-T3 is graded separately.

Q1.6 **Tick** the correct box(es) corresponding to your observation(s) in **T4**. 1 pt

(a) The aqueous phase changed colour
(b) The aqueous phase did not change colour
(c) The CH_2Cl_2 phase changed colour
(d) The CH_2Cl_2 phase did not change colour

SOLUTION:

	T4
a	☒
b	☐
c	☒
d	☐

1 pt for choosing both (c) and (a) or both (c) and (b).
(a) or (b) should be chosen (the result depends on the concentration), but (a) and (b) can not be chosen together (0 pt for this question in this case).
0 pt if (d) is chosen.

Q1.7 The above tests **T1–T4** are designed to identify the components of the complex **A**. <u>**Tick**</u> the box(es) that correctly describe(s) the result(s) of each test. 4 pt

(a) Identifies presence of metal M^{k+}
(b) Identifies presence of ligand X^-
(c) Identifies presence of ligand Py
(d) Identifies absence of ligand Py

SOLUTION:

	T1	**T2**	**T3**	**T4**
a	☐	☒	☐	☐
b	☒	☐	☒	☒
c	☐	☐	☒	☒
d	☐	☐	☐	☐

T1 is the ferric thiocyanate test.
T2 gives a positive result with different metals, but dithizone-zinc complex yields a characteristic pink colour.
T3 and T4 give such a result only with Py and SCN^- together which can be checked by additional tests with:
1) Cu^{2+} with Py,
2) Cu^{2+} with SCN^-,
3) Cu^{2+} with Py and SCN^- together.
As a result of the test, the organic phase gets coloured due to formation of $Cu(Py)_2(SCN)_2$ and its extraction.
T1-T2: 1 pt for each correct answer.
T3-T4: 0.5 pt for each correct answer, 1 pt in total.

Q1.8 **Identify** ligand X^- and metal M^{k+} with its charge in complex **A**. 2 pt

SOLUTION:

X^-: ☐ OCN^- ☒ SCN^-	M^{k+}: Zn^{2+}

$X^- = SCN^-$ can be identified by test **T1** (ferric thiocyanate test).
$M^{k+} = Zn^{2+}$ can be identified by test **T2** (dithizone-zinc complex yields a pink colour) and by additional tests with NH_3-buffer or NaOH.

The student might suggest another metal/ligand pair that fits the results of the tests and described observations.
For instance, test **T1** was performed incorrectly and the specific colour change was not observed; thus, option (a) was chosen in **Q1.5 T1**; as such the student reports $X^- = OCN^-$ which is graded fully in the question **Q1.8**, however, the test result in **Q1.5 T1** is graded with zero points.

0.5 pt for correct ligand that corresponds to the test results.
1.5 pt for correct metal that corresponds to the test results. If one observation of the student does not match the metal suggested, 1 pt is given for metal determination; if two observations do not match the metal suggested, 0 pt are given for metal determination.
-0.5 pt penalty if the metal is specified without a charge.

Q1.9 From the list below, **choose** the correct description of M^{k+}/X^- stoichiometry in the synthesis based on your reported results. Consider as little as an additional 1 mol% as an excess of the reagent. 1 pt

(a) M^{k+} and X^- were used in a stoichiometric amount
(b) M^{k+} was used in excess
(c) X^- was used in excess

SOLUTION:
The answer should correspond to the answer in **Q1.4** and to metal/ligand ratio from **Q1.8** and **Q1.10**.
If the ratio $n_{X^-}/n_{M^{k+}} = 2.09$ is reported in **Q1.4** and the metal complex formula is reported as MX_2, answer **(c)** should be graded fully.
If the ratio $n_{X^-}/n_{M^{k+}} = 2.00$ is reported in **Q1.4** and the metal complex formula is reported as MX_2, answer **(a)** should be graded fully.
If the ratio $n_{X^-}/n_{M^{k+}} = 1.95$ is reported in **Q1.4** and the metal complex formula is reported as MX_2, answer **(b)** should be graded fully.
1 pt for correct answer that corresponds to **Q1.3** and **Q1.4**.
0 pt here if the titration result is not reported in **Q1.3**.
0 pt here if the ratio $n_{X^-}/n_{M^{k+}}$ is not reported in **Q1.4**.

Q1.10 **Write** the molecular formula of complex **A** assuming it follows the 18-electron rule. 1 pt

SOLUTION:

$Zn(Py)_2X_2$

If the 18-electron rule is applied correctly on the wrong metal atom and/or ligand X^-, full marks are awarded.

For example, $In(Py)(SCN)_3$ can be graded fully if the tests in **Q1.4-Q1.6** are reported with the following results:

- **Q1.8**, $X^- = SCN^-$ and $M^{k+} = In^{3+}$;
- **Q1.9**, b (as 3 eq. of SCN^- is required for it to be in stoichiometric amount with In^{3+});
- **Q1.10**, $In(Py)X_3$ which corresponds to hypothetically possible complex that fits 18-electron rule.

Both options $Zn(Py)_2(SCN)_2$ and $Zn(Py)_2(NCS)_2$ are graded as correct ones (connectivity of Zn-X is not graded).

1 pt if the answer corresponds to correct ligand/metal ratio and to the tests in **Q1.5-Q1.6**.
0pt if the answer does not follow 18-electron rule.