



PQ1

أولمبياد الكيمياء الدولي السابع والخمسون
الإمارات العربية المتحدة
57th ICHO - United Arab Emirates - 2025

1. A complex problem

10% of the total

1.1	1.2	1.3	1.4	1.5	1.6	1.7	Total
1	20	0	18	3	2	3	47

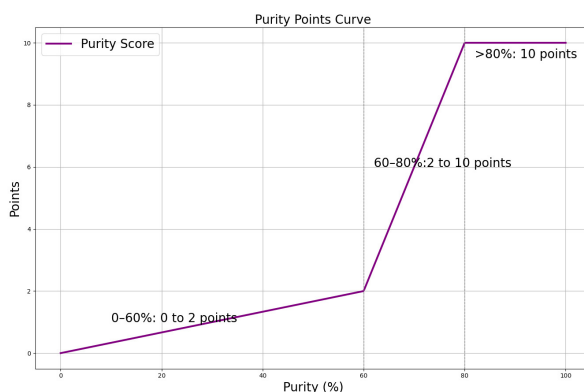
1.1

The compound **X** is H₂O. **1 pt**

1.2

The sample will be dried in oven and the mass of the dry sample will be determined. The purity of the sample will be determined by UV-Vis spectroscopy by comparison to standard samples of the complex and the free ligand. A purity percentage will be determined for the sample, with a maximum of **10 pt** for purity.

Purity, *p* (10 pt)



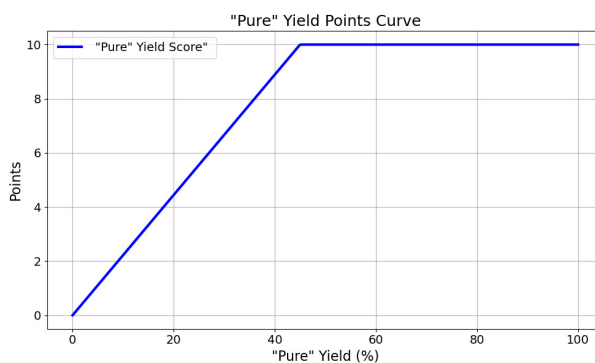


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- $p = 0\%$ **0 pt**
- $0\% \leq p \leq 60\%$ **$0.0333p$ pt**
- $60\% = p$ **2 pt**
- $60\% \leq p \leq 80\%$ pure **$(0.4p - 22)$ pt**
- $80\% \leq p \leq 100\%$ pure **10 pt**
- $100\% \leq p \leq 102\%$ **10 pt** Will be treated as 100% pure to allow for measurement error.
- $102\% < p$ A full UV-Vis absorption spectrum will be run. The science committee will determine whether this spectrum is the same as that of the iron salen complex, or contains contaminants. If no contaminants are detected will be treated as 100% pure and given **10 pt**. If contaminants are detected **0 pt**.
- Any samples of an obviously different colour will also be checked by a full spectrum.

The mass of the dry sample will be converted to a percentage yield, and this will be multiplied by the purity percentage to determine the "pure" percentage yield, which will be graded with a maximum of **10 pt**.

"Pure" Yield, y (10 pt)



- $0\% = y$ **0 pt**
- $0\% \leq y \leq 45\%$ **$0.222y$ pt**
- $45\% \leq y \leq 100\%$ **10 pt**

1.3 (0 pt)



1.4

There are **2 pt** available for each of the nine accepted absorption results. Values of accepted absorption results will be calculated from the row(s) selected by the students. Any wells crossed out by the students will be removed from this calculation. If the student has not ticked any rows, then an average will be taken from all wells containing solution.

An average value for background absorbance will be subtracted from the student's absorbance values and these corrected student values compared with the background corrected master values. The master values for each column also account for the time between when the student submitted the plate and the plate was analysed.

The scoring for each absorbance value will be determined as follows:

Values within $\pm 5\%$ of master value **2 pt**

Values more than $\pm 15\%$ of master value **0 pt**

Between $+5\%$ and $+15\%$, and between -5% and -15% , there will be a linear decrease from **2 pt** to **0 pt**

However, any student value that falls within two "machine standard deviations" of the master value will be given **2 pt** to account for random error on the machine. The machine standard deviation is calculated from the background readings.

These two criteria are used as depending on the column, the relative size of these two factors is different.

Absorbance values decrease slightly over time, due to a presumed slow decomposition of the complex. To account for this, master values will be analysed covering up to and over the maximum time period that the student samples had to wait for analysis. This decrease differs for each point, but is linear over the time period. This analysis will be used to determine the time-dependent master values.

(18 pt)



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1.5

1:1 Fe:Ligand **3 pt**

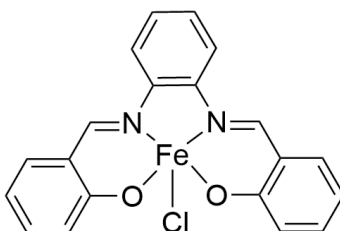
Answers will be marked if they are consistent with student data. Alternative answers will be accepted if they are consistent with student data. If no plate has been submitted then **0 pts** for this part.

1.6

$n = 5$ (1 pt) $z = +3$ (1 pt)

(2 pt)

1.7



Correct: **3 pt**

Deductions. Chloride not coordinated (-1.5 pt); No chloride (- 2pt); Solvent coordinated (-2 pt); Iron oxidation state not consistent with their answer to 1.6 (-1.5 pt); Trivial error in drawing salen ligand (-0.5 pt per error). Correct four atoms of salen ligand not coordinated (-1 pt). OH groups of salen are not deprotonated (-1 pt).

Alternative structures that are not 1:1 but consistent with earlier student data will be credited according to the scheme above.



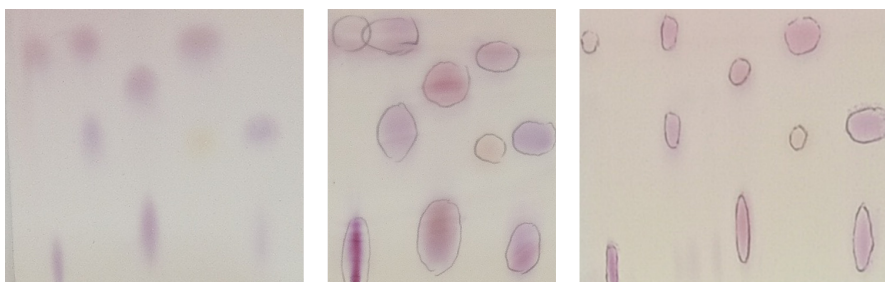
2. Exploring the AminOasis

15% of the total

2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	2.10	Total
14	11.5	6.5	0	10	3	0	15	1	4	65

2.1

Examples of TLC plates from one of the variants given in the Mock Exam (starting and finish line were cut out not to disclose R_f values before the practical examination):



2 pt: 0.5 pt for starting line, 1 pt for finish line, 0.5 pt for labels **1–5**, 0.5 pt deduction if the finish line is not parallel to the starting line.

2 pt: 0.2 pt per clearly circled spot of each amino acid, 0.2 pt deduction per additional spot in a **Mix**.

10 pt: 1 pt per amino acid for R_f within 2SD of the master value, 1 pt deduction per tilting of a lane, 1 pt deduction per overlap between spots from 2 adjacent lanes.

Grading is based on the photos of the TLC plates taken during the exam.

2.2, 2.3

One of the variants for **Mix 1-Mix 5**. The combination of amino acids in each **Mix** is the same in all variants.

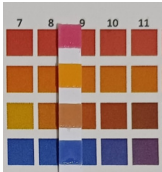
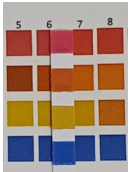
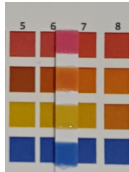
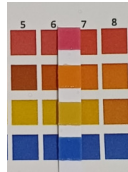
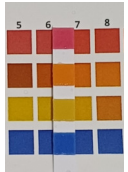


PQ2

	Mix 1		Mix 2		Mix 3		Mix 4		Mix 5	
pH	8–10 (or 8, 8.5, 9, 9.5, 10)		6–7 (or 6, 6.5, 7)		6–7 (or 6, 6.5, 7)		6–7 (or 6, 6.5, 7)		6–7 (or 6, 6.5, 7)	
Ehrlich	-		+		-		-		-	
Nitroprusside	-		-		+		-		-	
Sakaguchi	-		-		-		-		+	
Pauly	+		-		+		-		-	
Gerngross	+		-		-		-		-	
AA	Tyr	Lys	Trp	Ser	Cys	His	Phe	Pro	Glu	Arg
Higher R_f	☒	☐	☒	☐	☒	☐	☒	☐	☒	☐

Possible way of solving:

1) Analysis of pH reveals that one of the basic amino acids (Lys or Arg) must be in **Mix 1**:

	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
pH					
Conclusion	Lys or Arg				

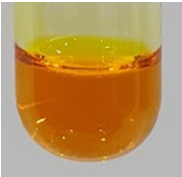
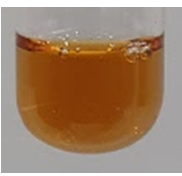
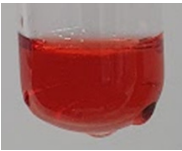
There is no other basic or highly acidic solution. Therefore, Glu and Lys/Arg must be together in **Mix 2/Mix 3/Mix 4/Mix 5**.

2) Individual tests – if successfully performed, 5 amino acids (Tyr, Trp, Cys, His, Arg) can be identified:



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	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
Ehrlich					
Nitroprusside					
Sakaguchi					
Pauly					
Gerngross					
Conclusion	Tyr	Trp	Cys + His		Arg

3) Yellow spot on the TLC – clear identification of Pro:

	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
TLC (R_f)	0.XXX 0.XXX	0.XXX 0.XXX	0.XXX 0.XXX	0.XXX 0.XXX (yellow) – Pro	0.XXX 0.XXX
Conclusion	Tyr	Trp	Cys + His	Pro	Arg

4) Combining the identification of Arg in **Mix 5**, the conclusion that Glu and Lys/Arg must be together and that Lys or Arg must be in **Mix 1**, one identifies Glu in **Mix 5** and Lys in **Mix 1**:



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	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
Conclusion	Tyr + Lys	Trp	Cys + His	Pro	Glu + Arg

5) Assignment of R_f values to already identified amino acids based on polarity:

	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
TLC (R_f)	0.XXX – Tyr 0.XXX – Lys	0.XXX – Trp? 0.XXX – Trp?	0.XXX – Cys 0.XXX – His	0.XXX 0.XXX (yellow) – Pro	0.XXX – Glu 0.XXX – Arg
Conclusion	Tyr + Lys	Trp	Cys + His	Pro	Glu + Arg

6) Only 2 amino acids are left: Ser and Phe. The polarity order is as follows: Ser < Trp $\approx$ Phe. Therefore, $R_f(\text{Ser}) < R_f(\text{Trp}) \approx R_f(\text{Phe})$. This allows us to finalise the identification:

	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
TLC (R_f)	0.XXX – Tyr 0.XXX – Lys	0.XXX – Trp 0.XXX – Ser	0.XXX – Cys 0.XXX – His	0.XXX – Phe 0.XXX (yellow) – Pro	0.XXX – Glu 0.XXX – Arg
Conclusion	Tyr + Lys	Trp + Ser	Cys + His	Pro + Phe	Glu + Arg

Overall, the chemical tests allow us to identify 5/10 amino acids. Observing the yellow spot on the TLC reveals 1 additional amino acid. Using the pH data reveals 2 more amino acids. Further analysis of the TLC allows us to identify the last 2 amino acids.



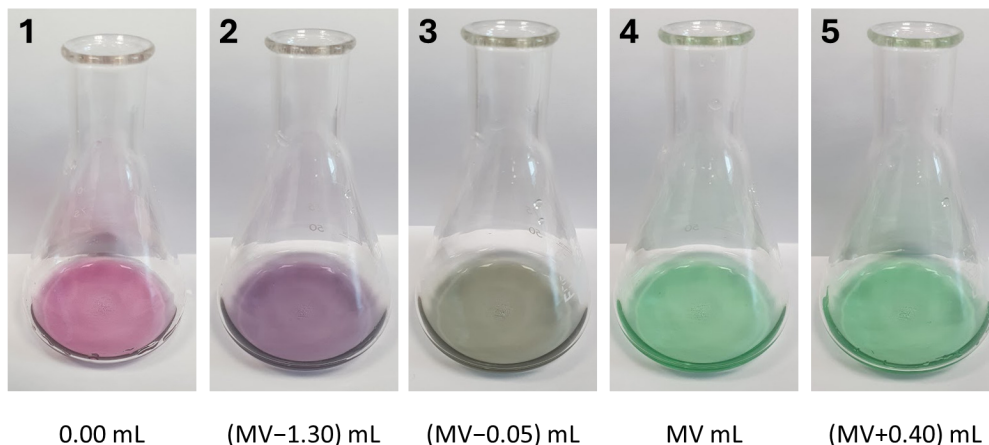
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pH measurement: 0.3 pt per correct value.
Ehrlich test: 2 pt if "+" is only for Mix 2 , 1 pt if one additional "+".
Nitroprusside test: 2 pt if "+" is only for Mix 3 , 1 pt if one additional "+".
Sakaguchi test: 2 pt if "+" is only for Mix 5 , 1 pt if one additional "+".
Pauly test: 2 pt if "+" is only for Mix 1 and Mix 3 , 1 pt if one additional "+" or one missing "+".
Gerngross test: 2 pt if "+" is only for Mix 1 , 1 pt if one additional "+".
Amino acid codes: 0.5 pt per amino acid if in agreement with test results and TLC.
Choice of amino acid with a higher R_f : 0.3 pt per given pair.

2.4

0 pt (not graded)

2.5



Master value (MV): $V_{\text{Na}_2\text{H}_2\text{EDTA}} = \text{XX.XX mL}$

10 pt for $(\text{MV} - 0.05) \leq V \leq (\text{MV} + 0.05)$, 0 pt if $V \leq (\text{MV} - 0.25)$ or $V \geq (\text{MV} + 0.25)$, linear in-between.
Penalty 2 pt if the reported value is missing. In this case, the average value of all reported titration values from 2.4 is used for further grading.



PQ2

2.6

$\text{Cu}(\text{CH}_3\text{COO})_2$ reacts with $\text{Na}_2\text{H}_2\text{EDTA}$ in a 1:1 ratio (1 pt). Therefore:

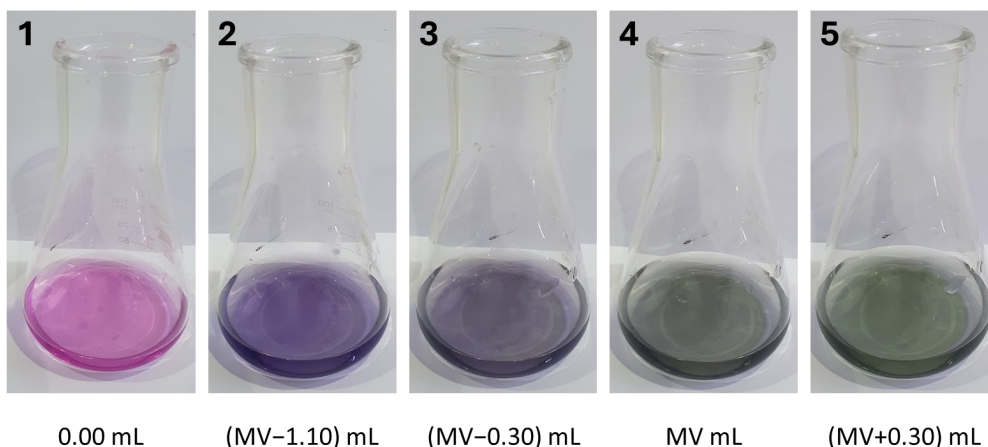
$$n(\text{Cu}^{2+}) = 1 \cdot c(\text{Na}_2\text{H}_2\text{EDTA}) \cdot V(\text{Na}_2\text{H}_2\text{EDTA}) = 0.0200 \cdot V_1 \text{ (1 pt)}$$

$$c(\text{Cu}^{2+}) = \frac{n(\text{Cu}^{2+})}{V(\text{Cu}^{2+})} = \frac{0.0200 \cdot V_1}{5.00} \text{ (1 pt)}$$

2.7

0 pt (not graded)

2.8



Master value (MV): $V_{\text{Cu}(\text{CH}_3\text{COO})_2} = \text{XX.XX mL}$

15 pt for $(\text{MV} - 0.05) \leq V \leq (\text{MV} + 0.15)$, 0 pt if $V \leq (\text{MV} - 0.25)$ or $V \geq (\text{MV} + 0.95)$, linear in-between.

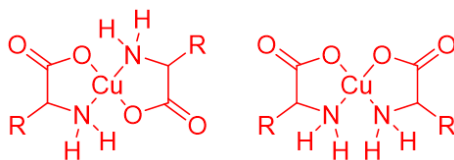
Penalty 2 pt if the reported value is missing. In this case, the average value of all reported titration values from **2.7** is used for further grading.



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2.9



Both *cis*- and *trans*-complexes are accepted. It can also be 5- or 6-coordinated with H₂O as an additional ligand. (1 pt)

2.10

Cu(CH₃COO)₂ reacts with the amino acid X in a 1:2 ratio (1 pt). Therefore:

$$n_{\text{aliq.}}(X) = 2 \cdot c(\text{Cu}^{2+}) \cdot V(\text{Cu}^{2+}) = 2 \cdot c(\text{Cu}^{2+}) \cdot V_2 \quad (1 \text{ pt})$$

$$n(X) = n_{\text{aliq.}}(X) \cdot \frac{V(X)}{V_{\text{aliq.}}(X)} = 2 \cdot \frac{100.0}{10.00} \cdot c(\text{Cu}^{2+}) \cdot V_2 \quad (1 \text{ pt})$$

$$M_r(X) = \frac{m(X)}{n(X)} = \frac{m(X)}{2 \cdot \frac{100.0}{10.00} \cdot c(\text{Cu}^{2+}) \cdot V_2} \quad (1 \text{ pt})$$



3. R_f you ready to spot the answers?

15% of the total

3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	3.9	3.10	3.11	3.12
+	+	+	+	+	+	+	+	+	+	5.8	2

3.13	3.14	3.15	3.16	3.17	3.18	3.19	3.20	3.21	3.22	3.23	Total
1.2	4	1	2	1	0	6	15	6	1	18	73

3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	3.9	3.10	3.11	3.12
1	1	1	1	1	1	1	1	1	1	5.8	2

3.13	3.14	3.15	3.16	3.17	3.18	3.19	3.20	3.21	3.22	Total
1.2	4	1	2	1	0	4	15	4	12	62

Part A

The total mark for each question is indicated and represents the maximum score. Each question has a minimum score of 0 points, so it is not possible to receive a negative mark.

3.1 Ticking PS TLC before heating 1 pt

- +0.5: A is chosen
- +0.25: B is chosen
- +0.5: C is chosen
- 1.0: D is chosen
- 1.0: N is chosen

3.2 Sketch PS TLC before heating 1 pt



PQ3

0 pt: TLC is absent or uninformative

-1 pt: the sketch conflicts with the real TLC

+1 pt: the sketch does not conflict with the real TLC after heating (compare with TLC in **3.11**)

Since there is no photo of the TLC before heating, it is necessary to imagine what it might have looked like. This means that the number of spots on the sketch should be equal to the number of spots on the real TLC, or be less, but not more.

The most common situation is that there is no spot of B on the sketch, but there is one on the real TLC.

3.3 Ticking PS TLC after heating 1 pt

0 pt: TLC is absent or uninformative

-1.0: A is chosen

+1.0: B is chosen

-1.0: C is chosen

-1.0: D is chosen

-1.0: N is chosen because no additional spots (compare **3.2** and **3.4**)

3.4 Sketch PS TLC after heating 1pt

0 pt: TLC is absent or uninformative

-1.0: the sketch conflicts with the real TLC

+1.0: sketch conforms to real TLC after heating (compare with **3.11**)

3.5 Ticking AS TLC before heating 1 pt

0 pt: TLC is absent or uninformative

-1.0: A is chosen

-1.0: B is chosen

-1.0: C is chosen

-1.0: D is chosen

+1.0: N is chosen

3.6 Sketch AS TLC before heating 1 pt

0 pt: TLC is absent or uninformative

-1 pt: the sketch conflicts with the real TLC

+1 pt: "N" is chosen and no spots on the sketch (compare with **3.5**)



PQ3

3.7 Ticking AS TLC after heating 1 pt

0 pt: TLC is absent or uninformative

+0.4: A is chosen

+0.2: B is chosen

+0.2: C is chosen

+0.4: D is chosen

-1.0: N is chosen

3.8 Sketch AS TLC after heating 1 pt

0 pt: TLC is absent or uninformative

-1 pt: the sketch conflicts with the real TLC

+1 pt: sketch conforms to real TLC after heating (compare with **3.11**)

3.9 Ticking UV TLC after heating 1 pt

0 pt: TLC is absent or uninformative

-1: A is chosen

+1: B is chosen

-1: C is chosen

-1: D is chosen

-1: N is chosen

3.10 Sketch UV TLC 1 pt

0 pt: TLC is absent or uninformative

-1 pt: the sketch conflicts with the real TLC

+1 pt: sketch corresponds to spots circled on real UV TLC (compare with **3.11**)

In case the spots on the UV TLC are not circled, but a sketch is given, the number and location of spots on the sketch must match the real PS and AS TLC photos (**3.11**).

3.11

Real PC or AS TLC after heating 2 pt (the same grading applies to all the following TLC plates visualised by the stain)



PQ3

- +0.4 TLC preparation: plate is labelled as PS and compounds are abbreviated correctly and start line is present and it is straight
- +0.4 TLC loading: the spots at the start line are distributed evenly and at equal distance and all spots have acceptable size (width is below 9 mm) and spots do not overlap or touch the edge of the TLC plate
- +0.4 TLC development solvent front line is present and it is horizontal and the distance between the start and finish lines is greater than half the length of the TLC plate
- +0.4 TLC staining: all spots are circled and stain reaches solvent front line
- +0.4 acceptable R_f values: for B, C $R_f = 0.09 - 0.17$; for A, D $R_f = 0.33 - 0.53$
- 0.5: before the solvent front line, there is an additional major spot on any of the lines (e.g. 1 major spot on the D line, 2 major spots on the A line) or inappropriate impurities (fingerprints, solvent drops etc.)
- 0.5: plate is overheated (can be determined by the appearance of beige lines and spots in different locations, flaking of silica gel, uneven colouring of the TLC plate) and/or a spot is affected due to diffusion during stain (incorrect spot shape)

Real UV TLC 1.8 pt

- +0.4 TLC preparation: plate is labelled as UV and compounds are abbreviated correctly and start line is present and it is straight
- +0.4 TLC loading: the spots at the start line are distributed evenly and at equal distance and all spots have acceptable size (width is below 9 mm) and spots do not overlap or touch the edge of the TLC plate
- +0.4 TLC development: solvent front line is present and it is horizontal and the distance between the start and finish lines is greater than half the length of the TLC plate
- +0.2 TLC visualisation: all spots are circled
- +0.4 acceptable R_f values: for B, C $R_f \sim 0.1$; for A, D $R_f \sim 0.4$
- 0.5: before the solvent front line, there is an additional major spot on any of the lines (e.g. 1 major spot on the D line, 2 major spots on the A line) or inappropriate impurities (fingerprints, solvent drops etc.)

3.12 (a) Most polar compound(s) 1 pt

- 0 pt: not assessed if TLCs are absent or uninformative
- +1.0: C is chosen
- +0.5: B is chosen
- 1.0: A or D are chosen.



PQ3

3.12 (b) least polar compound(s) 1 pt

0 pt: not assessed if TLCs are absent or uninformative

+1.0: A is chosen

+0.5: D is chosen

-1.0: B or C are chosen.

3.13 (a-i) Statements about PS, AS and UV 1.2 pt

-0.4: a is selected

+0.4: b is selected

-0.4: c is selected

-0.4: d is selected

-0.4: e is selected

-0.4: f is selected

+0.4: g is selected

-0.4: h is selected

+0.4: i is selected

3.14 Compounds assignments 4 pt

+1.0: 1 = B

+1.0: 2 = D

+1.0: 3 = A

+1.0: 4 = C

+1.0: if 2 = A, 4 = D (0.5 pt each)

Part B

3.15 Solubility/miscibility test 1 pt

+0.25: E = Y

+0.25: F = Y

+0.25: G = N

+0.25: H = Y

3.16 Real TLC of unknowns 4*2 pt

Graded in the same way as **3.11** (see above)

acceptable R_f values: for E, H R_f ~ 0.5; for F R_f ~ 0.25



3.17 TLC analysis of pure unknowns 1 pt

+0.25: E = Y

+0.25: F = Y

+0.25: G = N

+0.25: H = Y

3.18 0 pt

3.19-3.21 and **3.23** are graded jointly

3.19 4*1 pt

1 pt for each pairwise reaction:

0 pt: not assessed if TLCs are absent or uninformative

+1.0 observations correctly characterise the real TLC (compare with **3.23**)

TLC analysis is not performed for the between E+H and F+G, so it will not be graded.

3.20 4*3 + 3*1 pt

5	6	7	8	9	10	11
F	H	-	E	-	G	-
3 pt	3 pt	1 pt	3 pt	1 pt	3 pt	1 pt

If a compound from F-G is assigned incorrectly, it will be graded according to the number of conflicting observation(s) with the chosen structure (3 pt are given at the beginning, first conflicting observation is -0.5 pt, second conflicting observation is -1 pt, third conflicting observation is -1.5 pt).

3.21 4*1 pt

1 pt for each chemically correct product that can be obtained from the corresponding pair of chemicals. The grading scheme (see the additional grading scheme for **3.19-3.21** uploaded).

There is no reaction between E+H and F+G as stated in the exam paper (the products for these reactions are not graded).

3.22 4*3 pt



PQ3

Each TLC of the reaction mixture has two main parts:

Quality of the TLC (graded with the same criteria as **3.11**): 2 pt

Desired reaction outcome 1 pt: the TLC shows that the possible reaction proceeds (see the table below)

E+F	E+G	E+H	F+G	F+H	G+H
2 starting materials and no products on R line including start	1 starting material and 1 product on R line	no reaction as stated in the exam paper (not graded)	no reaction as stated in the exam paper (not graded)	2 starting materials and 1 product on R line	2 starting materials and 2 products on R line*

* Only one reaction product may be formed in the reaction if the reaction vessel is heated longer than 10 minutes. This reaction outcome graded as a correct one.