NAME:

STUDENT CODE:

Task 1 13% of the total

Reaction of Hantzsch Ester with Urea Hydrogen Peroxide

1a	1b	1c	1d	1e			Total
				i	ii	iii	
4	4	2	2	2	2	24	40

a) Copy (sketch) the TLC plate in bag "A" on your answer sheet.

Indicate the solvent front line and the base line.

1) If there are less than three spots loaded on the base line, 3 points will be subtracted.
2) If the spots are not separated on the TLC after development, 2 points will be subtracted.
3) If the solvent front line and/or the base line is missing, 1 point will be subtracted for each.

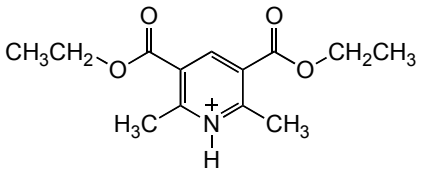
b) Determine and record the R_f values of the spots on the TLC plate in bag "A."

Spot	R_f value
1,4-DHP	0.32-0.42
Product	0.61-0.71

Two points each will be awarded for R_f values (to the 2nd decimal place) in the ranges shown above. No points will be awarded for values outside the ranges. A score of 1 will be given if the value is reported down to the 1st decimal place.

c) Draw the structural formula of the organic cation before adding sodium hydrogencarbonate.

If the correct structural formula is drawn as is shown below, 2 points will be awarded.



d) What is (are) the final product(s) derived from UHP? Give the chemical formula(e) of the product(s).

If correct chemical formulae are written as shown below, 1 point each will be awarded.

H_2O and CH_4N_2O

e) Submit the following:

i) TLC plate in bag "A"

If the outline to be drawn with a pencil around the UV-active spots is unclear or missing, 1 point will be subtracted.

ii) TLC plate in bag "B"

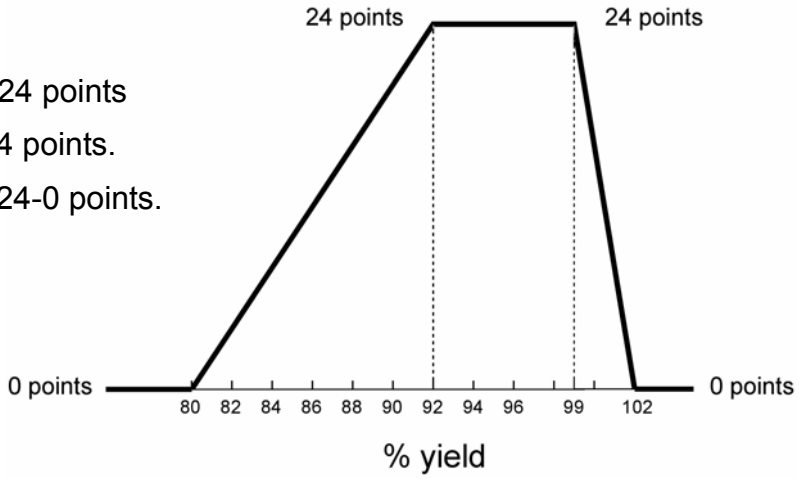
1) If the outline to be drawn with a pencil around the UV-active spots is unclear or missing, 1 point will be subtracted.

2) If the solvent front line and/or the base line is missing, minus 1 point for each will be subtracted.

iii) Your product and filter paper in the crystallization dish stored in bag "C"

1) The scientific committee will measure the percent yield after drying at 60 °C.
2) In most cases, the sample is pure and dissolved in $CDCl_3$ completely. The following calculation based on the percent yields obtained will be applied only if no 1,4-DHP or byproducts is observed in the ^1H NMR spectrum and the product is completely soluble in $CDCl_3$.

If 80.0 ≤ %yield <92.0, 0-24 points
If 92.0 ≤ %yield < 99.0, 24 points.
If 99.0 ≤ %yield < 102.0, 24-0 points.



3) If there are peaks of 1,4-DHP (ca δ 2.19 ppm) and the corresponding pyridine product (ca δ 2.85 ppm) in the ^1H NMR spectrum and the percent yield is 100% or less, the actual percent yield is calculated by the following equation:

$$\frac{\text{Sample mass (g)}}{\text{Theoretical yield (g)}} \times \frac{\text{(Integral at } \delta \text{ 2.85 ppm) x 251.3}}{\text{(integral at } \delta \text{ 2.19) x 253.3 + (integral at } \delta \text{ 2.85 ppm) x 251.3}} \times 100$$

4) If insoluble material remains after the addition of $CDCl_3$ for ^1H NMR measurement, 6 points will be subtracted.
5) If byproducts are detected evidently in the ^1H NMR spectrum, 6 points will be subtracted.

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Task 2 11% of the total

Determination of Fe(II) and Fe(III) by visual colorimetry

2a	2b	2c	2d	2e	2f		Total
					i	ii	
2	2	15	15	3	3	5	45

a) Report your results for **measurement A** using the table provided on the answer sheet.

	h′ (height of standard solution 1) / mm	Lower limit of *h* /mm	Higher limit of *h* /mm	*h* (estimated height of test solution) / mm
Measurement A	Any value	Any value	Any value	Any value

Two points will be awarded, except when there is no answer.

b) Report your results for **measurement B** using the table provided on the answer sheet.

	h′ (height of standard solution 1) / mm	*h* (estimated height of test solution) / mm
Measurement B	Any value	Any value

Two points will be awarded, except when there is no answer.

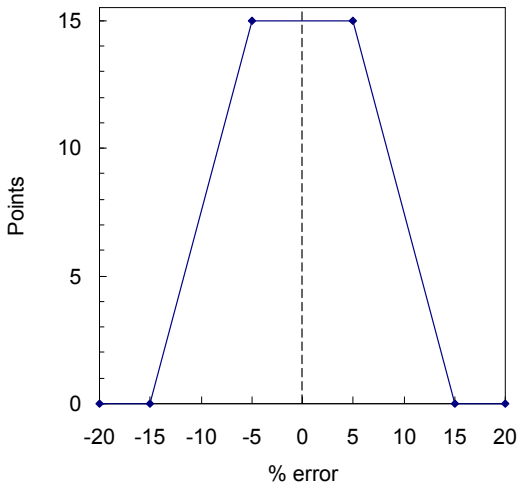
c) Report your results for **measurement C** using the table provided on the answer sheet.

	h′ (height of standard solution 1) / mm	*h* (estimated height of test solution) / mm
Measurement C	Experimental value of *h′*	sample 1: 1.23 *h′*
		sample 2: 1.16 *h′*
		sample 3: 1.10 *h′*

d) Report your results for **measurement D** using the table provided on the answer sheet.

	h′ (height of standard solution 1) / mm	*h* (estimated height of test solution) / mm
Measurement D	Experimental value of *h′*	sample 1: 0.763 *h′*
		sample 2: 0.725 *h′*
		sample 3: 0.749 *h′*

For 2c and 2d, a full score of 15 points will be awarded for values within a ±5% error range. A score of zero will be given if the absolute error is 15% or more. A linear point scale will be applied for scores from zero to 15; points will be calculated by the following equation:



$$P = 15\left[1 - \frac{|MV - h| - MV \cdot 0.05}{(MV \cdot 0.15) - (MV \cdot 0.05)}\right]$$

$$MV = \frac{h' \cdot 2.0\ (\text{mg L}^{-1})}{c}$$

P : Points (no negative value; zero if *P* < 0)

MV : Master value of *h* (mm)

h : Experimental height of liquid column of the test solution (mm)

h' : Experimental height of liquid column of reference solution (mm)

c : Concentration of Fe in correctly prepared test solutions (mg L^{-1})

for 2c, *c* = 1.63,1.72 and 1.82 for Sample 1, 2 and 3, respectively.

for 2d, *c* = 2.62, 2.76, and 2.67 for Sample 1, 2 and 3, respectively.

e) Express the concentration of the test solution, c, using the concentration of the reference solution, c', and the height of each liquid column, h and h'.

$$c = \frac{c'h'}{h}$$

3 points. Any equivalent formula is acceptable.

f) Calculate the concentrations of Fe(II) and Fe(III) in the sample solution in mg L^{-1}.

For Fe^{2+},

$$[Fe^{2+}] = \frac{2.0(\text{mg L}^{-1}) \times h_C^{'} \times 50(\text{mL})}{h_C \times 10(\text{mL})}$$

$[Fe^{2+}]$: concentration of Fe^{2+} in the sample solution (mg L^{-1})

h_C: experimental height (mm) of the liquid column of the test solution in the measurement C

h'_C: experimental height (mm) of the liquid column of the standard solution in the measurement C

If the concentrations are calculated correctly from the experimental data, full marks will be awarded 3 points.

For Fe^{3+}

$$[Fe^{3+}] = \frac{2.0(\text{mg L}^{-1}) \times h_D^{'} \times 50(\text{mL})}{h_D \times 5(\text{mL})} - [Fe^{2+}]$$

$[Fe^{3+}]$: concentration of Fe^{3+} in the sample solution (mg L^{-1})

h_D : experimental height (mm) of the liquid column of the test solution in the measurement D

h'_D : experimental height (mm) of the liquid column of the standard solution in the measurement D

If the concentrations are calculated correctly from the experimental data, full marks will be awarded 5 points.

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Concentrations of Fe^{2+} and Fe^{3+} in each *original* sample solution

	$[Fe^{2+}]$ / mg L^{-1}	$[Fe^{3+}]$ / mg L^{-1}
Sample 1	8.16	18.0
Sample 2	8.60	19.0
Sample 3	9.08	17.7

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Task 3 16% of the total

Polymers in Analysis

3.1a	3.1b	3.1c	3.1d	3.1e	3.1f	3.2	Total
4	10	1	10	1	4	20	50

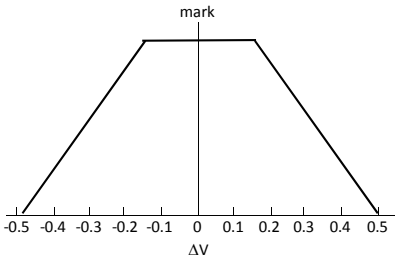
3.1

1a) Report the PVSK solution volume (in mL) consumed in the standardization of PDAC.

PVSK solution volume consumed in the standardization of PDAC:
z mL

MV(z) = 20.06 mL

A full score of 4 points will be awarded if the answer is *MV(z)* ± 0.15 mL. (*MV*: Master Value)
A score of zero will be given if the answer is less than (*MV(z)* – 0.5) mL or greater than (*MV(z)* + 0.5) mL. A linear point scale will be applied for answers in between.
Two points will be subtracted if the value is not reported down to the 2nd decimal place (in mL).



1b) Report the PVSK solution volume (in mL) consumed in the titration of the polysaccharide under basic conditions.

PVSK solution volume consumed under basic conditions:
x mL

Sample A: *MV(x)* = 13.14 mL
Sample B: *MV(x)* = 12.07 mL
Sample C: *MV(x)* = 10.91 mL

A full score of 10 points will be awarded if the answer is *MV(x)* ± 0.25 mL.
A score of zero will be given if the answer is less than (*MV(x)* – 0.6) mL or greater than (*MV(x)* + 0.6) mL. A linear point scale will be applied for answers in between.
Two points will be subtracted if the value is not reported down to the 2nd decimal place (in mL). A score of zero will be applied if the value becomes negative after the subtraction.

1c) Mark the acid group(s) ionized under basic conditions on the answer sheet.

conditions	acid group	
basic	☒ $-SO_3H$	☒ –COOH

Total 1 point.

1d) Report the PVSK solution volume (in mL) consumed in the titration of the polysaccharide under acidic conditions.

PVSK solution volume consumed under the acidic conditions:
y mL

Sample A: $MV(y)$ = 15.26 mL
Sample B: $MV(y)$ = 14.61 mL
Sample C: $MV(y)$ = 13.59 mL

A full score of 10 points will be awarded if the answer is $MV(y) \pm 0.25$ mL.
A score of zero will be given if the answer is less than ($MV(y)$ – 0.6) mL or greater than ($MV(y)$ + 0.6) mL. A linear point scale will be applied for answers in between.
Two points will be subtracted if the value is not reported down to the 2nd place of decimals (in mL). A score of zero will be applied if the value becomes negative after the subtraction.

1e) Mark the acid group(s) ionized under acidic conditions on the answer sheet.

conditions	acid group	
acidic	☒ $-SO_3H$	☐ –COOH

Total 1 point.

1f) Calculate the concentrations of the $-SO_3^-$ (or $-SO_3H$) groups and the $-COO^-$ (or –COOH) groups (in mol L^{-1}) in the given polysaccharide solution.

$-SO_3^-$ (or $-SO_3H$) group: $0.0005(z - y)$ mol L^{-1}
$-COO^-$ (or –COOH) group: $0.0005(y - x)$ mol L^{-1}

Total 4 points, 2 points for each.
A score of 2 is given to the values within (calculated value) ± 0.2. A score of 1 is given to the values which were outside the above allowance (± 0.2 mol L^{-1}) and within (calculated value) ± 0.5 mol L^{-1}.

3. 2

Identify the compound in each solution based on the experimental results. For each solution, mark one of the five boxes to indicate your identification. You are also asked to fill in the blanks with one of the letters in the Roman alphabet, from A to H, to indicate your sample code.

Sample code	
☐ -1	☐ TEG ☐ PEO ☐ PMANa ☐ PSSNa ☐ PDAC
☐ -2	☐ TEG ☐ PEO ☐ PMANa ☐ PSSNa ☐ PDAC
☐ -3	☐ TEG ☐ PEO ☐ PMANa ☐ PSSNa ☐ PDAC
☐ -4	☐ TEG ☐ PEO ☐ PMANa ☐ PSSNa ☐ PDAC
☐ -5	☐ TEG ☐ PEO ☐ PMANa ☐ PSSNa ☐ PDAC

Before (upper rows) and after (lower rows) the addition of HCl

	TEG	PEO	PMANa	PSSNa	PDAC
TEG					
PEO	- -				
PMANa	- -	- +			
PSSNa	- -	- -	- -		
PDAC	- -	- -	+ -	+ +	

+: Precipitation, -: No precipitation (or the precipitate disappears)

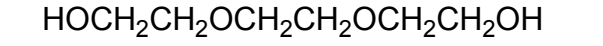
PMANa and PSSNa are polyanions, and they interact with a polycation (PDAC) to form a precipitate. Under acidic conditions, the carboxylate ($-COO^-$) groups in PMANa undergo protonation, and PMANa changes to protonated poly(methacrylic acid) (PMA). The resulting carboxy (-COOH) groups interact with the ether oxygen atoms in PEO through hydrogen bonding to form a precipitate. Since protonated PMA is no longer a polyanion, the precipitate (the complex between PMANa and PDAC) disappears after the addition of HCl.

On the other hand, PSSNa does not exist as the protonated form, even under acidic conditions, and no precipitate is observed with PEO at a lower pH. Since TEG is a small molecule, its interaction with PMA is not strong enough to form a precipitate.

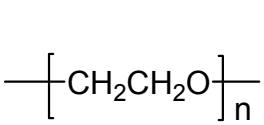
1) For each correct answer, 4 points will be awarded.
2) If two or more boxes are marked for one sample, 0 points will be given for that sample even if the correct answer is included in the marked compounds.
3) If the same box is marked for more than two samples, 0 points will be given for these samples even if the correct answer is included in the marked samples.

Table List of samples in Task 3.2

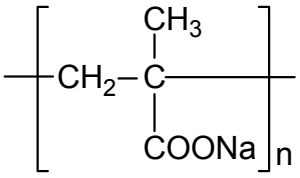
TEG	PEO	PMANa	PSSNa	PDAC
A-3	A-2	A-1	A-4	A-5
B-2	B-1	B-5	B-3	B-4
C-1	C-5	C-4	C-2	C-3
D-5	D-4	D-3	D-1	D-2
E-3	E-2	E-1	E-4	E-5
F-2	F-1	F-5	F-3	F-4
G-1	G-5	G-4	G-2	G-3
H-5	H-4	H-3	H-1	H-2



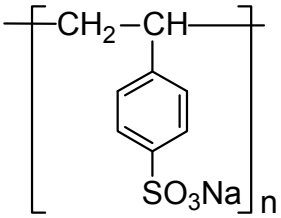
(TEG)



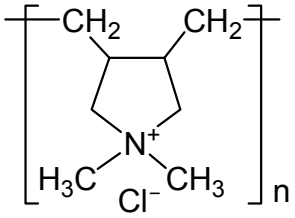
(PEO)



(PMANa)



(PSSNa)



(PDAC)

[Abbreviations: **TEG**, triethylene glycol; **PEO**, poly(ethylene oxide); **PMANa**, poly(sodium methacrylate); **PSSNa**, poly(sodium 4-styrenesulfonate); **PDAC**, poly(diallyldimethylammonium chloride)