42nd International Chemistry Olympiad
Japan, 2010

Practical Problems

Chemistry : the key to our future

Instructions

Examination Procedures

- You have **5 hours** to complete **Tasks 1, 2, and 3**. You may perform the tasks in any order you choose.
- There will be an additional **15 minutes reading time** before the start.
- **DO NOT** begin working on the tasks until the **START command** is given.
- When the **STOP command** is given **at the end of the 5 hours,** you must **stop** your work on the tasks **immediately. A delay in doing so may lead to your disqualification from the examination.**
- After the **STOP command** has been given, **wait in your lab space**. A supervisor will check your lab space. The following items should be **left behind:**
  - ✓ The problem booklet (this booklet)
  - ✓ The answer booklet
  - ✓ Your chosen TLC plates in zipper storage bags A and B with your student code (from Task 1)
  - ✓ Your product and glass microfiber filter sheet in a crystallization dish with a lid in zipper storage bag C with your student code (from Task 1)
- **Do not leave** the examination hall until you are instructed to do so by the supervisors.

Safety

- **Safety** is the most important issue in the laboratory. You are expected to follow the safety rules given in the IChO regulations. **Safety glasses** and **lab coats** must be worn at **ALL TIMES**.
- If you behave in an unsafe manner, you will receive **one warning** before you are asked to leave the laboratory. If required to leave due to a second warning, you will receive a score of zero for the entire experimental examination.
- **NO eating or drinking** is allowed in the laboratory.
- In case of emergency, follow the instructions given by the supervisors.

Notes on the booklets and answer methods

- The **problem booklet** comprises 23 pages including cover page.
- The **answer booklet** comprises 6 pages. Do not attempt to separate the sheets.
- You should confirm **your student code** inscribed on the booklets and write **your name and student code on every answer sheet**.
- Use only the pen provided for filling in the **answer sheets.** You may also use the calculator and the ruler provided. Use the mechanical pencil provided only for experiments in Task 1. Do not use the mechanical pencil for filling in the **answer sheets.**
- All results must be written in the appropriate areas on the answer sheets. Results written elsewhere will not be graded. If you need to do **rough calculations, etc.**, use the back of the sheets.
- You should take care to report answers to an appropriate number of significant figures.
- Keep your answer booklet in the envelope provided. Take out the booklet only when you write the answers. Do not seal the envelope.

Notes on the Examination

- You may need to reuse some glassware during the examination. If this is the case, clean it carefully in the sink closest to you.
- Contact a supervisor near you if you have any **questions** regarding the tasks or if you need a **refreshment/toilet break**.
- Use the labeled **waste containers** under the hood or near the windows for disposal of liquids and solids. A waste container (plastic beaker) is also available on each bench for aqueous waste. Discard used glass capillaries into a labeled plastic tube .
- **Replacement of chemicals and laboratory ware** will be provided if necessary. Other than the first, for which you will be pardoned, each such incident will result in the **loss of 1 point** from your 40 practical points. Refilling of washbottle water is permitted with no loss of points.
- An official English version of this examination is available upon request if you require clarification.

Periodic table with relative atomic masses

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.01																	2 He 4.00
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 24.30											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 72.64	33 As 74.92	34 Se 78.96	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 95.96	43 Tc -	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	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 -							

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm -	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
89 Ac -	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

Apparatuses

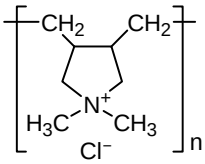
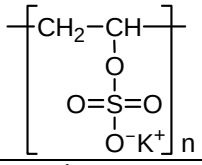
Apparatuses	Number
For multiple tasks (on the desk or in Box 1):	
20-mL beaker for taking a small portion of liquid to rinse inside of glassware	1
Paper	3
2-mL pipette bulb	1
5-mL pipette bulb	1
Pipette rack	1
200-mL plastic beaker for waste	1
Safety bulb	1
Spatula	1
Stand	1
100-mL washbottle	1
500-mL washbottle	1
For Task 1 (in Box 1, on the desk or on pipette rack):	
Büchner funnel with rubber adapter	1
Clamp with muff (clamp holder)	1
200-mL conical beaker	1
300-mL conical beaker	1
Diaphragm vacuum pump with tubing and connecter	1
Glass capillary tube (in a plastic tube)	8
Glass microfiber filter sheet in a crystallization dish with lid	1
2-mL graduated pipette	3
5-mL graduated pipette	1
Magnetic stirrer	1
10-mm magnetic stirring bar	1
22-mm magnetic stirring bar	1
10-mL measuring glass	1
pH test paper (in a zipper storage bag)	3
10-mL plastic graduated cylinder	1
Plastic tube for used glass capillary	1

Suction flask	1
10-mL test tube	1
100-mL test tube	1
TLC developing chamber with lid	1
TLC plate (in a zipper storage bag)	4
Tweezers	1
Zipper storage bags A and B for submission of TLC plates	1 for each
Zipper storage bag C for submission of glass microfiber filter sheet in a crystallization dish	1
For Task 2 (in Box 2, on the desk or on pipette rack):	
2-mL graduated pipette	1
5-mL graduated pipette	1
Label (in a zipper storage bag)	4
LED light box (in a zipper storage bag: do not remove from the bag at any time.)	1
Nessler tube	5
Nessler tube rack	1
50-mL volumetric flask	2
5-mL volumetric pipette	1
10-mL volumetric pipette	1
For Task 3.1 (in Box 2 or on pipette rack):	
Burette	1
Burette clamp	1
100-mL conical beaker	6
Glass funnel (for transferring chemicals to a burette)	1
1-mL graduated pipette	2
5-mL volumetric pipette	1
20-mL volumetric pipette	1
For Task 3.2 (in Box 2):	
10-mL vial (in a zipper storage bag)	10
Plastic Pasteur pipette	1
Shared equipment:	
Gloves of various sizes	

UV lamp	
Cleaning tissue	

Chemicals on Each Desk

Chemical	Quantity	Container	R phrases	S phrases
For multiple tasks (in Box 1):				
0.5 mol L^{-1} hydrochloric acid (**0.5 mol L^{-1} HCl**)	50 mL	Plastic bottle	None listed	None listed
For Task 1 (in Box 1):				
1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylic acid diethyl ester (**$C_{13}H_{19}NO_4$; 1,4-DHP_powder**)	1 g	Vial	36/37/38	26
1,4-DHP for TLC (**1,4-DHP_TLC**)	3 mg	Vial	36/37/38	26
Ethanol (**C_2H_5OH**)	10 mL	Glass bottle	11	7-16
Ethyl acetate (**$CH_3COOC_2H_5$**)	25 mL	Glass bottle	11-36-66-67	16-26-33
Heptane (C_7H_{16})	20 mL	Glass bottle	11-38-50/53-65-67	9-16-29-33-60-61-62
Potassium iodide (**KI**)	150 mg	Glass bottle	None listed	None listed
Sodium metabisulfite (**$Na_2S_2O_5$**)	1 g	Glass bottle	22-31-41	26-39-46
Saturated sodium hydrogencarbonate solution (**Sat. $NaHCO_3$ solution**)	25 mL	Glass bottle	None listed	None listed
Urea hydrogen peroxide (**$CH_4N_2O•H_2O_2$; UHP**)	1 g	Vial	8-34	17-26-36/37/39-45
For Task 2 (in Box 2):				
Sample solution (labeled as "**Sample solution**")	30 mL	Plastic bottle	None listed	None listed
Standard $Fe(bpy)_3^{2+}$ solution 1 (containing 2.0 mg of iron in 1 L solution) (labeled as "**Standard $Fe(bpy)_3^{2+}$ solution 1**")	50 mL	Plastic bottle	None listed	None listed
Standard $Fe(bpy)_3^{2+}$ solution 2 (containing 3.0 mg of iron in 1 L solution) (labeled as "**Standard $Fe(bpy)_3^{2+}$ solution 2**")	50 mL	Plastic bottle	None listed	None listed
Acetate buffer solution (pH 4.6, 1:1 mixture of acetic acid and sodium acetate; **CH_3COOH-CH_3COONa solution**)	50 mL	Plastic bottle	None listed	None listed

0.1 mol L^{-1} disodium hydrogenphosphate solution (**0.1 mol L^{-1} Na_2HPO_4**)	25 mL	Plastic bottle	None listed	None listed
0.2 %(w/v) 2,2'-bipyridine aqueous solution (**0.2 %(w/v) $C_{10}N_2H_8$**)	25 mL	Plastic bottle	None listed	None listed
Sodium thioglycolate (**$C_2H_3NaO_2S$**)	20 mg	Vial	22-38	36
For Task 3.1 (in Box 2 or on the desk):				
Polysaccharide solution (labeled as "**Polysaccharide solution**")	50 mL	Plastic bottle	None listed	None listed
Poly(diallyldimethylammonium chloride) aqueous solution (**PDAC**) 	240 mL	Glass bottle	None listed	None listed
Potassium poly(vinyl sulfate) aqueous solution (0.0025 mol L^{-1}; monomer unit concentration) (**0.0025 mol L^{-1} PVSK**) 	240 mL	Glass bottle	36/37/38	26-36
0.5 mol L^{-1} sodium hydroxide aqueous solution (**0.5 mol L^{-1} NaOH**)	50 mL	Plastic bottle	34	26-37/39-45
1 g L^{-1} toluidine blue (TB) aqueous solution (**1 g L^{-1} $C_{15}H_{16}N_3SCl$**)	6 mL	Dropper bottle	None listed	None listed

For Task 3.2 (in Box 2):				
Solution X-1 (X: A-H)	10 mL	Dropper bottle	36/37/38	26-36
Solution X-2 (X: A-H)	10 mL	Dropper bottle		
Solution X-3 (X: A-H)	10 mL	Dropper bottle		
Solution X-4 (X: A-H)	10 mL	Dropper bottle		
Solution X-5 (X: A-H)	10 mL	Dropper bottle		

Risk Phrases

Number	Special Risks
8	Contact with combustible material may cause fire.
11	Highly flammable
22	Harmful if swallowed
31	Contact with acids liberates toxic gas.
34	Causes burns
36	Irritating to eyes
38	Irritating to skin
41	Risk of serious damage to eyes
65	Harmful: may cause lung damage if swallowed.
66	Repeated exposure may cause skin dryness or cracking.
67	Vapors may cause drowsiness and dizziness.
36/37/38	Irritating to eyes, respiratory system and skin
50/53	Very toxic to aquatic organisms, may cause long term adverse effects in the aquatic environment.

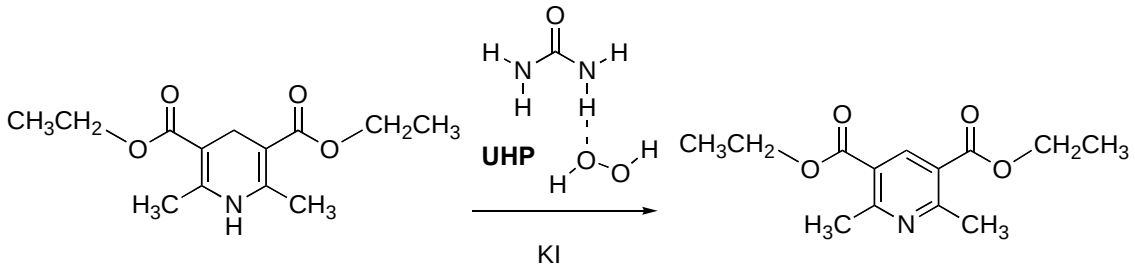
Safety Phrases

Number	Safety Recommendations
7	Keep container tightly closed.
9	Keep container in a well ventilated place.
16	Keep away from sources of ignition - No Smoking.
17	Keep away from combustible material.
26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
29	Do not empty into drains.
33	Take precautionary measures against static discharges.
36	Wear suitable protective clothing.
37	Wear suitable gloves.
39	Wear eye/face protection.
45	In case of accident or if you feel unwell, seek medical advice immediately. (Show the label where possible.)
46	If swallowed, seek medical advice immediately and show the container or label.
60	This material and its container must be disposed of as hazardous waste.
61	Avoid release to the environment. Refer to special instructions/ material safety data sheet.
62	If swallowed, do not induce vomiting: seek medical advice immediately and show the container or label
24/25	Avoid contact with skin and eyes.
36/37/39	Wear suitable protective clothing, gloves and eye/face protection.
37/39	Wear suitable gloves and eye/face protection

Task 1

Reaction of Hantzsch Ester with Urea Hydrogen Peroxide

In this experiment, you are required to synthesize a pyridinedicarboxylate derivative from 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylic acid diethyl ester (1,4-DHP or Hantzsch ester) by oxidation with urea hydrogen peroxide (UHP), an environmentally-friendly oxidant.



1,4-DHP

Procedures

(1) Place a 22-mm magnetic stirring bar in a 100-mL test tube. Fix the test tube on a magnetic stirrer using a clamp. Add 1,4-DHP (1 g) (labeled as 1,4-DHP_powder), and potassium iodide (150 mg) to the test tube, followed by ethanol (5 mL), with a 5-mL graduated pipette.

(2) Add 1 g UHP (wear gloves) and stir the mixture. (**Caution: this reaction is exothermic.**)

(3) For thin layer chromatography (TLC) analysis, prepare a mixture of ethyl acetate:heptane (1:2 in volume) with a measuring glass and place an appropriate amount of the mixture in a TLC developing chamber. Add 1 mL of ethyl acetate to the vial (labeled as 1,4-DHP_TLC) to dissolve 1,4-DHP (3 mg).

(4) Check your TLC plates before using. If they are damaged, they can be replaced without penalty. Draw a start line on the lower portion of a TLC plate with a pencil (see Fig. 1.1).

(5) During the reaction, the reaction mixture becomes clear (usually within 20 min). When the reaction mixture becomes clear (the precipitates may form when it cools, but precipitates will not affect the TLC analysis), take a small portion of the mixture using a

glass capillary and load it to make two spots in the center and right positions on the TLC plate. Load an appropriate amount of the 1,4-DHP solution prepared in procedure (3) in the center and left positions, so that there are three spots on the plate, with the center spot containing both the reaction mixture and 1,4-DHP (see Fig. 1.1). Develop the TLC plate in the TLC chamber (see Figs. 1.1 and 1.2). Mark the solvent front with the pencil. Visualize the spots using a UV lamp (254 nm) and draw a line around the UV-active spots on the TLC clearly with the pencil. Assess the completion of the reaction based on the TLC results. Repeat the TLC analysis after ten minutes, if you find significant amounts of 1,4-DHP in the reaction mixture. [Note that you will perform TLC analysis again in procedure (8).] Place the last TLC plate in a zipper storage bag marked “A.”

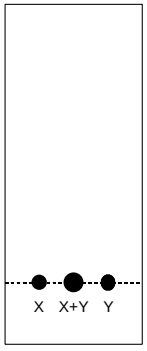


Fig. 1.1 Spots on the TLC plate before development; X: 1,4-DHP, Y: Reaction mixture.

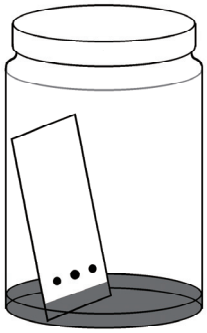


Fig. 1.2 TLC plate placed in the TLC developing chamber.

(6) Set up the suction filtration equipment (see Fig. 1.3). Connect the suction flask to the diaphragm vacuum pump. Place a Büchner funnel fitted with a rubber adapter onto the suction flask. Place a glass microfiber filter sheet on the funnel.

(7) Add water (5 mL) to the reaction mixture using a 10-mL plastic graduated cylinder. Add sodium metabisulfite (1 g), transfer the contents of the tube (including the stirring bar) into a 200-mL conical beaker and wash the

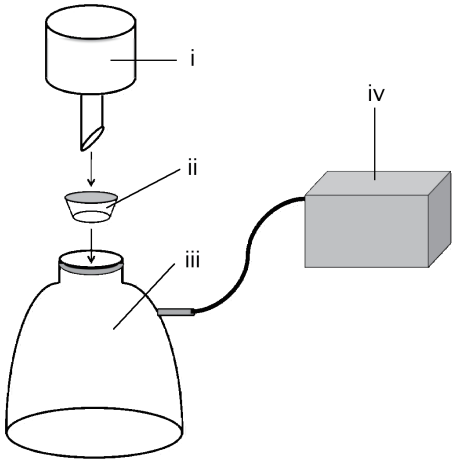


Fig. 1.3 Suction filtration equipment: i, Büchner funnel; ii, rubber adopter; iii, suction flask; iv, diaphragm vacuum pump.

test tube with water (30 mL). Place the 200-mL conical beaker on the magnetic stirrer and stir the solution. Add saturated sodium hydrogencarbonate solution in small portions using a 2-mL graduated pipette until the pH of the aqueous phase becomes just over 7 (check the pH with pH test paper). Filter the precipitate formed through the Büchner funnel with suction using the diaphragm vacuum pump, and wash the precipitate with a small portion of water. Suck air through the precipitates for a minute to dry the product.

(8) Transfer the filtrate from the suction flask to a 300-mL conical beaker. Transfer the filtrate (2 mL) to a 10-mL test tube using a 2-mL graduated pipette. Place a 10-mm magnetic stirring bar in the test tube and fix it securely with the clamp. Add 1 mL of ethyl acetate to the test tube using a 2-mL graduated pipette and stir the solution vigorously for 30 seconds on the magnetic stirrer. Stop stirring and wait for the solution to separate into two layers. Analyze the upper layer by TLC to see if there is any product remaining in the filtrates. Spot the filtrates on the plate in the same way as procedure (5). Mark the solvent front and the spot(s), if any. Place the TLC plate in a zipper storage bag marked “B.” If you detect the product on the TLC plate, add more saturated sodium hydrogencarbonate solution.

(9) At this stage, if you find a precipitate formed, filter and wash it. If you find no precipitate, skip this filtration process.

(10) Suck air through the precipitate for 10 minutes to dry the product. Place your product and the glass microfiber filter sheet in the crystallization dish. Cover the dish with the lid marked with your code. Avoid placing the stirring bar in the dish. Place the crystallization dish with the lid in a zipper storage bag marked “C.”

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

b) Determine and record the R_f values (to the 2nd decimal place) of the spots on the TLC plate in bag “A.”

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

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

e) Submit the following:

i) TLC plate in bag “A”

ii) TLC plate in bag “B”

iii) Your product and filter paper in the crystallization dish placed in bag “C”

Task 2

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

In this experiment, you are required to determine Fe(II) and Fe(III) in a given sample solution which simulates a dissolved magnetite ore by visual colorimetric analysis involving a color reaction between Fe(II) and 2,2'-bipyridine (bpy) to form an intensely red complex, $Fe(bpy)_3^{2+}$.

The amount of $Fe(bpy)_3^{2+}$ complex can be quantified by visual colorimetric measurement using Nessler tubes. This is a quite simple technique that was employed before photoelectric instruments were generally available, but an accuracy of less than ±5% can be achieved. In this technique, a pair of Nessler tubes is used; one is filled with a reference solution, and the other is filled with a solution to be tested. The depths of colors of the two solutions are balanced by adjusting the heights of liquid columns of the solutions.

When the colors look the same, the concentration can be calculated from that of the reference solution with a known concentration and the height of the column of each solution based on the Lambert-Beer law:

$$A = \varepsilon c l$$

where A is the absorbance, c is the concentration, l is the pass length and ε is the molar absorption coefficient. First, you will learn to employ this technique by conducting **measurements A** and **B**, and then you will determine the concentrations of Fe(II) and Fe(III) with **measurements C** and **D**.

Procedures

(1) Add 5 mL of acetate buffer solution, 5 mL of disodium hydrogenphosphate solution (to mask Fe(III)), 5 mL of 2,2'-bipyridine solution and 10.00 mL of sample solution into a 50-mL volumetric flask using appropriate pipettes for each and dilute the resulting solution with water to the 50-mL mark. Then stopper the flask and mix the solution well. Allow it to stand for at least **20 min** to fully develop color. This solution is named "**sample 1**."

(2) Add 5 mL of acetate buffer solution, 5 mL of 2,2'-bipyridine solution and 5.00 mL of sample solution into a 50-mL volumetric flask. Then add 20 mg of sodium thioglycolate powder (in excess) to reduce Fe(III) to Fe(II). Dilute the solution with water to the

50-mL mark, stopper the flask and mix the solution well. Allow it to stand for at least **20 min**. This solution is named "**sample 2**."

(3) Perform visual colorimetric measurements A – D based on the "Instructions for visual colorimetric measurement" shown below.

Instructions for visual colorimetric measurement

Set a pair of Nessler tubes on a Nessler tube rack placed on an LED light box (do not remove it from the bag at any time) and turn on the light (see Fig. 2.1). Pour the provided "**standard $Fe(bpy)_3^{2+}$ solution 1**" into one tube to an appropriate height (70 – 90 mm is recommended) from the bottom (etched marks on the tube indicate fixed heights from the bottom in mm) and use this as a reference for **measurements A - D**. Pour the solution to be measured into the other tube, and then compare its depth of color with that of the reference solution by looking downward through the solutions toward the LED light box.

Adjust the height of the liquid column of the test solution by adding or removing the solution with a graduated pipette until the depth of color in the two tubes is identical. Estimate your reading to at least 1 mm.

Note that the depths of color in a certain range may be recognized as identical to human eyes. The appropriate value for the height of the test solution, *h*, should be determined by taking the range into the consideration. For example, if you adjust the height of the liquid column of the test solution only by increasing (or decreasing) the volume, you could reach a lower (or higher) value than the true one. A possible way to estimate the true value is to take an average between the values of lower and higher limits.

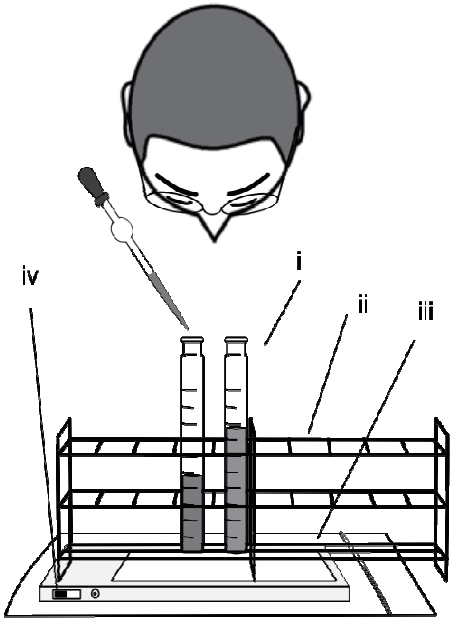


Fig. 2.1 Visual colorimetric measurement: i, Nessler tube; ii, Nessler tube rack; iii, LED light box in a zipper storage bag; iv, power switch.

Measurement A: Perform a measurement using "**standard $Fe(bpy)_3^{2+}$ solution 1**" as both the reference and the test solutions. In this measurement, pour the reference solution into a Nessler tube to achieve an appropriate height, and then pour the test solution into the other Nessler tube until the colors of the two solutions match each other. (When the colors match, the heights should IDEALLY be the same.) Then add more test solution until you recognize that the colors have become different from each other. Report both the lower and higher limits of the height of the liquid column of test solution with the same depth of color as the reference solution.

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

Measurement B: Perform a measurement of "**standard $Fe(bpy)_3^{2+}$ solution 2**" as a test solution using "**standard $Fe(bpy)_3^{2+}$ solution 1**" as a reference.

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

Measurement C: Perform measurement of **sample 1.**

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

Measurement D: Perform measurement of **sample 2.**

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

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'.

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

Task 3

Polymers in Analysis

Polymers can be used in various analyses. In this task, you are first required to analyze a polysaccharide using a polymer-polymer interaction, which will then be utilized to identify polymers in the second part.

3.1 Analysis of Polysaccharide by Colloid Titration

You are provided with a solution of a polysaccharide containing sulfonate ($-SO_3^-$) and carboxylate ($-COO^-$) groups. You are asked to determine the concentrations of these two groups by colloid titration under the basic and acidic conditions based on the differences in the protonation behavior of these acid groups. A back-titration technique is utilized.

When these acid groups are ionized, the polysaccharide becomes a polyanion. Upon addition of polycation, poly(diallyldimethylammonium) (provided as its chloride salt, PDAC), it forms a polyion complex. PDAC solution is standardized using the standard solution of potassium poly(vinyl sulfate) (PVSK). At the endpoint of colloid titration, the number of anionic groups becomes equal to that of cationic groups.

Procedures

(1) Take precisely 20 mL of the PDAC solution using a volumetric pipette into a 100-mL conical beaker. Add 2 drops of toluidine blue (TB) into the conical beaker. Titrate the resulting blue solution with the 0.0025 mol L^{-1} PVSK (monomer unit concentration) standard solution. At the endpoint, the color turns purple. Note that the solution becomes gradually turbid as the endpoint approaches. The endpoint is determined when the color remains purple for 15-20 seconds. Repeat if necessary.

1a) Report the PVSK solution volume (in mL) consumed in the standardization of PDAC. Record your reading to 0.05 mL.

(2) Take precisely 5 mL of the polysaccharide solution and 20 mL of the PDAC solution using volumetric pipettes into another conical beaker. Add 0.4 mL of 0.5 mol L^{-1} NaOH and 2 drops of TB to the solution. Titrate the resulting blue solution with the PVSK standard solution in a similar manner. Repeat if necessary. (The appearance of

coagulation may be different, depending on the pH of the solution.)

1b) Report the PVSK solution volume (in mL) consumed in the titration under basic conditions. Record your reading to 0.05 mL.

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

(3) Repeat procedure 2 above with the addition of 0.5 mL of 0.5 mol L^{-1} HCl instead of 0.5 mol L^{-1} NaOH.

1d) Report the PVSK solution volume (in mL) consumed in the titration under acidic conditions. Record your reading to 0.05 mL.

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

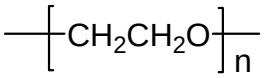
1f) Calculate the concentrations of the $-SO_3^-$ (or $-SO_3H$) groups and the $-COO^-$ (or -COOH) groups (in mol L^{-1}) in the given polysaccharide solution.

3.2 Identification of compounds

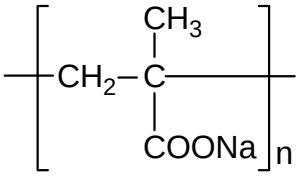
You are provided with five solutions **(X-1~5, "X" designates your sample code, which is a letter in the Roman alphabet from A to H)**, and each solution contains one of the compounds below (all of which are used). The concentration is 0.05 mol L^{-1} (for polymers, monomer unit concentration). Your task is to identify all the compounds by carrying out the following procedures.

$HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$

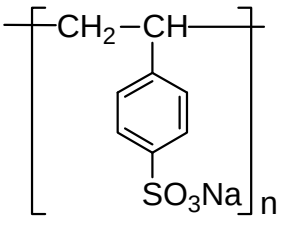
(TEG)



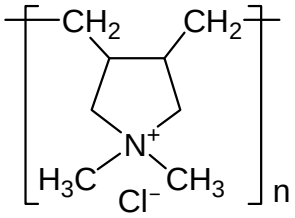
(PEO)



(PMANa)



(PSSNa)



(PDAC)

[Abbreviations: **TEG**, triethylene glycol; **PEO**, poly(ethylene oxide); **PMANa**, poly(sodium methacrylate); **PSSNa**, poly(sodium 4-styrenesulfonate); **PDAC**, poly(diallyldimethylammonium chloride) MW. stands for molecular weight.]

Helpful comments

1) Aggregates observed in **Task 3.1** could be observed when mixing two polymer solutions in an appropriate combination, in which an interaction takes place between the two polymers. They can be utilized to identify polymer samples.
2) The volume of a solution measuring 5 mm in height from the bottom of the vial is approximately 1 mL. Remind that you have only 10 mL of each solution.

Procedures

(1) Mix similar volumes of two solutions together in a vial.

(2) If necessary, you can acidify the resulting mixture. Ten drops of hydrochloric acid (0.5 mol L^{-1} HCl) from a plastic Pasteur pipette are sufficient for this purpose.

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.

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(22,575 characters without spaces)