THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 –CYU 5302–ANALYTICAL CHEMISTRY
FINAL EXAMINATION PAPER 2023/24

Date: 2023.10.22 Duration: Two hours
Time: 1.30 p.m.- 3.30 p.m.

Instructions to students
Answer all four questions.

1. (A) A water sample (100.0 cm^3) containing equal amounts of metal ions X^+ and Y^+ was given to analyze using gravimetry. The stable precipitates expected to form by adding NaOH were XOH and YOH.

K_{sp} of XOH = 2.4 x 10^{-8} mol^2 dm^{-6}
K_{sp} of YOH = 4.0 x 10^{-6} mol^2 dm^{-6}

(i) Is selective precipitation of XOH and YOH possible? Justify your answer. (10 marks)

(ii) The precipitation started when the solution pH was 9. Calculate the concentration of the metal ion which starts precipitation first. (15 marks)

(iii) After completion of precipitation, the precipitate was filtered, washed with cold distilled water and dried at 110° C. Give three possible reasons for selecting cold distilled water as the washing solvent. (06 marks)

(iv) Another person suggested that it is better if you had heated the precipitate with the solution before filtering to get the precipitate in pure form. Do you agree? Give reasons for your answer. (12 marks)

(v) The weight of the precipitate obtained was 1.2400g. Calculate the percentage of X in the precipitate. (X= 53.00g, Y= 63.00g, O= 16.00g, H= 1.00g) (12 marks)

(B) A solution of the acid H_2D is contaminated with HCl. A 25.0 mL of this solution was titrated with 0.100 M NaOH solution to findout the amount of contamination.
(Of H_2D, K_{a1}= 6.0 x 10^{-2}, K_{a2}= 3.0 x 10^{-8})

(i) Draw and label all the important points in the expected titration curve. Justify the shape of the curve giving reasons. (20 marks)

(ii) If the first end point and the second end pont obtained were 25.00 mL and 40.00mL respectively, calculate the concentration of HCl in the intial sample solution. (10 marks)

(iii) During the titration, buffers were made. What was the buffer formed after the first end point? Predict the burette reading giving reasons when this buffer had shown the highest capacity. (15 marks)

2. (A) A 25.0 cm^3 sample of a factory effluent containing the metal ions M^{2+} was titrated with 0.02 M EDTA. The formation constant of MY^{2-} is 2×10^8.

	α_{Y4-}	α_{M2+}
pH= 7	0.85	0.73
pH= 5	0.35	0.73

(i) What is the most suitable pH to carry out the titration? Justify your answer. (10 marks)

(ii) If the end point obtained was 25.0 mL, calculate the $[M^{2+}]$ in equilibrium, after 10.0 mL of EDTA was added. (30 marks)

(iii) Comment on the statement below.
"The interference in EDTA titrations is very high but can be avoided." (10 marks)

(iv) If you are being asked to make the buffer of pH=7 with a high capacity, on what basis will you select the required solutions? (10 marks)

(B) A 20.0 mL of a sample solution having equal amounts of R^{2+}, Z^{+} and Q^{3+} was titrated with 0.02 M E^{3+} solution.

$E^o_{R^{3+}/R^{2+}} = +1.08\ V$ $\quad$ $E^o_{Z^{2+}/Z^{+}} = -1.38\ V$

$E^o_{Q^{3+}/Q^{2+}} = +1.24\ V$ $\quad$ $E^o_{E^{3+}/E^{2+}} = +2.00\ V$

(i) Sketch and label all the important points of the expected titration curve. Justify the shape of the curve. (30 marks)

(ii) When 30.00 mL of 0.02 M E^{3+} solution was added the potential reading of the solution in the flask was 1.08 V. Calculate the concentration of R^{2+} in the sample, showing all the steps clearly. (10 marks)

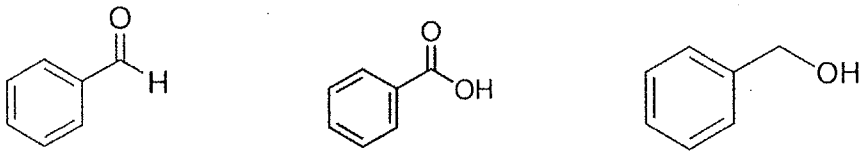
3.(A) Organic compound X in 25.0 mL of aqueous solution was extracted to 75.00 mL of organic solvent using a separatory funnel. After the extraction, the solvent in the organic layer was evaporated and recorded the weight of X. It was 1.200 g. The molecular weight of X and the distribution coefficient between the two layers are 80 g mol^{-1} and 20 respectively.

(i) Determine the concentration of X extracted to the organic layer. (08 marks)

(ii) What is the concentration of X remaining in the aqueous layer after the extraction? (10 marks)

(iii) Calculate the extraction efficiency (%) and suggest a method to increase it. (22 marks)

(B) Following three compounds were separated by thin-layer chromatography using silica as the stationary phase and hexane: methanol (2:1) as the mobile phase. The retardation factors (R_f) of three compounds are 1.0, 0.82, 0.70.



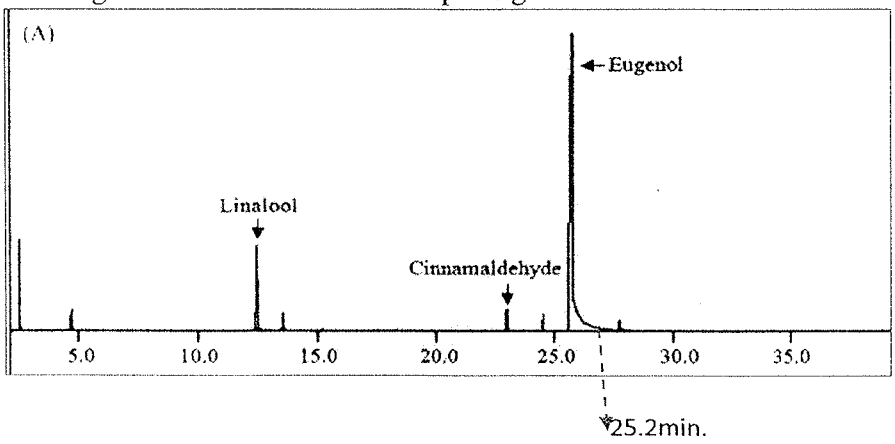
P **Q** **R**

(i) Identify the three compounds with their retention factors. Justify your answer. (20 marks)

(ii) According to the Rf values, one compound travels with solvent. How would you modify the mobile phase, to overcome this problem? Justify your answer. (10 marks)

(iii) If you use a silica column using with the same mobile phase for separation, which compound will eluate first from the column? (05 marks)

(C) The amount of Eugenol present in an oil sample was determined by the Gas chromatography. The peak areas obtained for the standard solution of 2.00 ppm Eugenol and Eugenol in the sample are 20.0 and 60.0 arbitrary units respectively. The chromatogram obtained for the oil sample is given below.



(i) Find the Retention Factor of eugenol. Dead time is 1.0 min. (8 marks)

(ii) Find the concentration of Eugenol present in the sample. (7 marks)

(iii) Then briefly explain how you can qualitatively confirm this unknown oil sample is cinnamon oil using chromatography. (10 marks)

4. (A) A student determined the concentration of total iron (Fe^{2+} and Fe^{3+}) in an effluent using a UV/visible spectrometer after complexing it with 1,10- phenanthroline.

$Fe^{2+}(aq) + 3\ Phen\ (aq) \rightarrow [Fe(phen)_3]^{2+}(aq)$

First, he transferred 10.00 mL of sample into the 100.0 mL volumetric flask containing 10.00 mL of hydroxylamine hydrochloride. Next, he added 10.00 mL 1,10-phenanthroline and diluted up to the mark. Similarly, he repeated this for the 10.00 mL of 5.00 ppm Fe^{2+} standard solution. After that, he adjusted the instrument to zero at 508 nm using the blank solution and measured absorbance of the sample and standard solutions using a 1.0 cm glass cell which were 0.310 and 0.620 respectively.

(i) What is the reason to add hydroxylamine hydrochloride? (5 marks)

(ii) What is the concentration of total iron (ppm) present in your sample? (15 marks)

(iii) Write down two assumptions that you made during the above calculation. (10 marks)

(iv) Briefly explain how he should prepare the blank solution. (10 marks)

(B) Another student decided to determine the concentration of 1,10-phenanthroline used in the above analysis in 4. (A). He performed a photometric titration for 20.00 mL of 1,10-phenanthroline solution with 0.2 mmol L^{-1} Fe^{2+} solution at 508 nm. The endpoint he obtained was 10.00 mL.

Species	$\varepsilon\ (at\ 508\ \ nm)$ (L mol^{-1} cm^{-1})
Fe^{2+}	100
$[Fe(phen)_3]^{2+}$	1.11×10^4

(i) Briefly explain the variation of absorbance value before starting, during and after the end point in the above titration. (10 marks)

(ii) Determine the concentration of 1,10-phenanthrolen in ppm. The molecular weight of 1,10-phenanthrolen is 180 g mol^{-1}. (10 marks)

(iii) During the titration, the total volume in the flask increases and it affects the absorbance reading. Suggest a method to overcome this when plotting the titration curve. (10 marks)

(C) A 20.00 mL of 0.01 M NH_4OH was titrated with 0.01 M H_2A (a strong acid). The pH meter readings were taken after each addition of 2.50 mL of H_2A up to 30.00 mL to draw the titration curve of this titration.

(i) What is the expected end point reading? Sketch the titration curve for the above titration and show the endpoint value in the expected pH range. (15 marks)

(ii) Two students drew the titration curves separately with the actual readings obtained in this experiment, but the end points obtained from the curves were not the same. What may be the reason? How do you correct it? (05 marks)

(iii) Give two major advantages of using a pH meter other than the accuracy, compared to classical acid-base titrations. (10 marks)