081

THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme
Level 5 – FINAL EXAMINATION – 2023 / 2024
CYU 5308– INSTRUMENTAL METHODS IN CHEMICAL ANALYSIS

Duration: Two hours
Date and time: 25.03.2024, 9.30 a.m. – 11.30 a.m.

Instructions to students:

❖ **Answer all four (4) questions.**

1. The following is the indirect method carried out to analyze X^{2+}.
To the sample solution having the metal ion X^{2+} (50.0 mL), an excess amount of Y^{2-} (50.0 mL of 0.02M) was added to form the complex XY; stirred the solution and then, 100.0 mL of 0.02M Z^{2+} (in excess) was added. The absorbance of ZY formed was measured at 470nm and at a pathlength of 1cm (the linear range of absorbance of ZY is 0.1-0.6). The molar absorptivity coefficient of ZY is 6.66×10^3 $mol^{-1}cm^{-1}$. The stability constant of XY is higher than that of ZY. The results obtained were,
Absorbance of the blank solution = 0.15
Absorbance of the final mixture= 0.45

(i) What is the maximum concentration of the standard solution you can use if a calibration curve is drawn? (10 marks)

(ii) The standard solution of 2.00×10^{-5} M of ZY gave an absorbance of 0.550 under the same conditions. Results of the blank solution were also the same. Calculate the concentration of X^{2+} in the original sample solution. (20 marks)

(iii)Give reasons for not using UV visible spectroscopy directly to determine X^{2+}.(10 marks)

(iv) One suggested the following. Do you agree with the suggestions? Justify your answer.

(a) Atomic Absorption Spectroscopy (AAS) would have been a better method to determine X^{2+}. (15 marks)

(b) Standard addition method could have been used instead of a blank. (15 marks)

(v) Explain the following in brief.

(a) Although Raman spectroscopy is sometimes more advantageous compared to IR spectroscopy, it is not widely used. (10 marks)

(b) In Fluorometer, two monochromators are used in different settings of λ_{max} for different purposes. (10 marks)

(c) In Chemical Ionization Mass Spectroscopy, the mass of the molecular ion has an extra H atom. (10 marks)

2. (i) A polarographic analysis was carried out to determine the concertation of X^{2+} in an effluent sample. The diffusion current (I_d) obtained at the half wave potential $E_{1/2}$ (0.12 mV) for the effluent sample and the 4.00 ppm standard solution of X^{2+} was 0.130 mA and 0.548 mA respectively.

(a) Determine the concentration of X^{2+} in the sample. (10 marks)

(b) Sketch the Voltammogram relevant to the standard solution and indicate the I_d and $E_{1/2}$ on it. (10 marks)

(c) If the effluent sample contaminated with another compound Y^{3+} which shows $E_{1/2}$ at 0.25 mV, Comment on the results obtained for effluent sample in question (i). (10 marks)

(d) Briefly explain an advantage of using polarography than voltammetry. (10 marks)

(ii) A 250.0 mL of water sample was contaminated with N_2H_4. To determine the amount of N_2H_4 the water sample was acidified with HCl and a coulometric titration was carried out using KBr (to generate Br_2 electrochemically in acid medium).

$N_2H_4(aq) + 2Br_2(l) \rightarrow 4HBr(aq) + N_2(g)$

The sample required 5 mins at 193 mA to reach the endpoint.

(a) Calculate the charge supplied for the titration until the endpoint was reached. (08 marks)

(b) Write down balanced half-cell reactions related to generation of Br_2 taking place at the electrodes. (08 marks)

(c) Determine the concentration of N_2H_4 in the sample. (14 marks)

(iii) Electrogravimetry was used to analyze Ni^{2+} in a contaminated water sample. In this method, 250.0 mL of sample was electrolyzed, and the weight of the electrode was increased by 0.020 mg at the end of the electrolysis.

(a) Write down the reaction at the cathode. (05 marks)

(b) Find the concentration of Ni^{2+} in the contaminated water sample in ppm. (10 marks)

(c) How can you make sure all the Ni^{2+} in the water sample was deposited on the electrode? (05 marks)

(d) "Voltametric analysis also can be used to determine the concentration of Ni^{2+}". Do you agree with the above statement? Justify your answer. (10 marks)

3. (i) Gas chromatography was carried out to determine two organic compounds X and Y. An open tabular column with helium was used as the carrier gas for this analysis and the chromatogram signals recorded by the Flame Ionization Detector are given below.

Compound	Retention time (min)	Base width (min)
Air (unretained)	1.8	
X	10.0	0.76
Y	10.8	0.84

(a) Calculate the retention factor of X. (10 marks)

(b) Determine the selectivity factor of X. (08 marks)

(c) Resolution of the peaks of X and Y is not satisfactory" Justify the statement with proper calculations. (07 marks)

Hint: $R = \frac{2(t_Y - t_X)}{W_X + W_Y}$

(d) State one disadvantage of using Flame Ionization Detector? (05 marks)

(ii) An HPLC analysis was conducted for caffeine in a sports drink. A 5.00 mL of methanol was introduced to 300 ppm standard caffeine solution and the sports drink sample. The HPLC chromatograms were obtained with C_{18} (silica with C_{18} column having 0.45 μm particle diameter) and the mobile phase methanol: water in 95: 5 (v/v). It showed broad peaks at 8.4 min and the peak areas for the 300 ppm standard, and sample were 5840 and 3250 arbitrary units respectively.

(a) Find the concentration of caffeine in the sports drink. (15 marks)

(b) Comment on how particle diameter affects peak broadening. (10 marks)

(c) Suggest a method to reduce the peak broadening without changing the stationary and mobile phases. (05 marks)

(d) "This is reverse phase chromatography". Justify. (08 marks)

(iii) Briefly explained following. (08 marks each)

(a) Gradient elution in HPLC

(b) Guard column in HPLC

(c) Anion exchange resin

(d) Column bleeding in GC

4. The radioisotope $^{225}_{92}D$ is resulted by a neutron irradiation process. It undergoes decaying at a rate of 4.48 x 10^{13} disintegrations s^{-1} producing $^{201}_{82}M$ and the half-life is 70 hrs.

(i) What is meant by the underlined sentence? (10 marks)

(ii) Show that the decaying cannot be just with alpha emission only. (15 marks)

(iii) The $^{201}_{82}M$ is resulted only by this decay.

(a) Calculate the mass of $^{225}_{92}D$ at the time of measuring the decay rate. (15 marks)

(b) The present amounts of $^{201}_{82}M$ was found to be 0.7611mg. How long had it been decaying after measuring the activity? (10 marks)

(iv) The activities were measured using liquid scintillation counters having short deadtimes.

(a) Briefly explain the mechanism behind the liquid scintillation counters. (10 marks)

(b) Why a counter having a short deadtime is selected? (10 marks)

(v) UV/Visible spectroscopy and Fluorometry can be used to determine D. Explain in brief how $^{225}_{92}D$ can be used as a tracer to compare the accuracy of two methods to determine D. (15 marks)

(vi) State how Gamma rays can be used for qualitative and quantitative analysis. (15 marks)