00129

THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme
Level 5 – FINAL EXAMINATION – 2024 / 2025
CYU 5308– INSTRUMENTAL METHODS IN CHEMICAL ANALYSIS

Duration: Two hours
Date and time: 27.04.2025, 9.30 a.m. – 11.30 a.m.

Instructions to students:

❖ **Answer all four (4) questions.**

1. To determine the concentration of element X (absorptivity coefficient = 1.40×10^4 L mol^{-1} cm^{-1}) in an unknown sample solution using Atomic Absorption Spectroscopy (AAS) having flame as the atomizer, the sample solution was prepared as follows: Sample solution- To a 25.0 mL of the unknown solution of X^+, 10.0 mL of Sr^+(1.00 M) was added before topping up to 100.0 mL. The absorbance was 0.420.

   (i) Give possible reasons for adding Sr^+ to the sample solution. (07 marks)

   (ii) One student commented that it is always better to use a calibration curve using standard solutions in this analysis. Do you agree with the comment? Justify your answer. (08 marks)

   (iii) Describe briefly how you should prepare 100.0 mL of 5.00 ppm standard solution using 50 ppm standard solution with matching matrix for the above analysis. (10 marks)

   (iv) If the standard solution prepared correctly as above had given an absorbance of 0.630, calculate the % error of the concentration of X if standard solution result is not used. (molar mass of X = 75 g) (20 marks)

   (v) Suggest two ways of increasing the absorbance measurement for the same solutions prepared with the same instrument used. (10 marks)

   (vi) One suggested that if Arc Emission Spectroscopy was used for the above determination, the sensitivity can be increased. Comment briefly. (10 marks)

   (vii) Comment on the following statements.

   (a) Qualitative analysis using IR spectroscopy and Raman spectroscopy complement each other but the principles are different. (15 marks)

   (b) In Atomic Fluorescence Spectroscopy the wavelength of the absorbed radiation is as same as the wavelength of the emitted radiation, but it is different in Molecular Fluorescence Spectroscopy. (10 marks)

   (c) It is always better to have a mass analyzer with high resolution in Mass Spectrophotometer. (10 marks)

2. (i) A voltammetry analysis was carried out to determine the concentration of two metal ions (X^{2+} and Y^{3+}) in a contaminated water sample. In this analysis, 2.00 mL of 1 M KCl was added to the sample and 1.00 ppm standard solutions of X^{2+} and Y^{3+}. The half wave potentials ($E_{1/2}$) and the diffusion current obtained for the sample and 1.00 ppm of standards are given below.

Ion	$E_{1/2}$ (V)	I_d (Sample) (mA)	I_d (1 ppm standard) (mA)
X^{2+}	0.22	0.440	0.220
Y^{3+}	0.48	0.210	0.420

(a) What is the reason to add 1 M KCl? (10 marks)

(b) Can the two metal ions X^{2+} and Y^{3+} be analyzed selectively using normal voltammetry analysis? Justify your answer. (10 marks)

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

(d) If the student performs stripping volumetry analysis for the sample, Sketch the graph to show the relationship between current and the potential. (10 marks)

(ii) A sample of **ascorbic acid ($C_6H_8O_6$)** dissolved in 200.0 mL of water is titrated with a coulometric technique, using a silver electrode. The relevant reactions are:

$Ag^{+}(aq) + e \rightarrow Ag(s)$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e$$

$$C_6H_8O_6(aq) + 2Ag^+(aq) \rightarrow C_6H_6O_6(aq) + 2Ag + 2H^+$$

In this titration, endpoint was achieved after 10 minutes at constant current 150 mA.

(a) Calculate the charge supplied during the titration. (10 marks)

(b) Determine the concentration of ascorbic acid in the sample (mg/L).
(Faraday constant = 96,500 $C\ mol^{-1}$, C-12, H-1, O-16) (20 marks)

(iii) The data obtained in the thermogravimetry analysis is given below when the Sample is heated from room temperature 25 °C to 600 °C

Temperature (°C)	25	100	200	450	600
Mass of sample (mg)	200	196	188	180	180

(a) Calculate the percentage weight loss when the sample reach to 100 °C (06 marks)

(b) Sketch the fully labeled thermogram using the weight percentages. (14 marks)

(c) How can you improve the thermogram for better accuracy? (10 marks)

3. (i) In a gas chromatography experiment, a mixture containing two organic compounds A and B only, with similar boiling points were analyzed using an open tubular silica column with nitrogen as the carrier gas. The retention times and peak heights for the mixture and a 2.00 ppm standard of compound A are provided below:

Peak	Retention time (min)	Peak Height (arbitrary unit)	
		Sample	2.00 ppm standard A
1	2.0	50	48
2	8.5	420	-
3	9.2	600	240

(a) Calculate the retention factor (k') of compound A. (10 marks)

(b) Based on the retention times of compounds A and B, comment on their relative polarities. (12 marks)

(c) Determine the concentration of compound A in the mixture. (08 marks)

(d) Using the Van Deemter equation, briefly explain how longitudinal diffusion affects plate height (H) in gas chromatography compared to liquid chromatography. (10 marks)

(ii) An HPLC analysis was conducted to determine the nicotine concentration in an energy drink labeled as **Sample B**. A 5.00 mL portion of a 300 ppm nicotine standard solution was added to 10.00 mL of Sample B to prepare the spiked sample. The peak areas for the standard and the spiked sample were recorded at 254 nm with the following data:

Sample Label	**Peak area (arbitrary units)**
300 ppm standard nicotine solution	4200
spiked sample (Sample B + nicotine standard)	6300

The Chromatographic Conditions are

- Column: C18 with 0.45 μm particle diameter.
- Mobile phase: Methanol: Water (95:5, v/v).
- Retention time for nicotine: 6.2 minutes.

(a) Determine the concentration of nicotine in sports drink (sample B). (15 marks)

(b) "Isocratic elution applied in this analysis". Justify. (10 marks)

(c) How you can adjust the mobile phase to increase the peak resolution in this analysis. (05 marks)

(d) "This is a normal phase chromatography" Justify this statement. (10 marks)

(iii) Briefly explain how the following factors influence peak separation in HPLC. (10 marks)

(∞) Larger column length
(λ) Faster flow rate

(iv) Provide a brief explanation of the functions of the following components in High-Performance Liquid Chromatography (HPLC): (10 marks)

(a) UV-visible Detector
(b) Guard column

4. To find the mass of the element Z of an ore sample, 5.00 mg of the radioisotope $^{200}_{92}Z$ having a specific activity of 2.00 x 10^8 counts min^{-1} mol^{-1} was added. After mixing, 0.050 mg of Z was separated followed by purification and had an activity of 30 counts min^{-1}.

(i) What is the name of this method? What may be the reasons for using this method? (10 marks)

(ii) What was the specific activity of the purified sample in SI units of radioactivity? (08 marks)

(iii) Calculate the mass of Z in the sample showing all the steps. (15 marks)

(iv) The radioisotope $^{200}_{92}Z$ decays producing $^{160}_{84}Y$ and the activity was measured using liquid scintillation counters with secondary scintillators but not with gas ionization counters.

(a) Give one reason for selecting scintillation counters instead of gas ionization counters? (5 marks)

(b) What is the role of the secondary scintillator? (10 marks)

(c) The activity measurements taken were found to be having the errors introduced by the background as well as the random errors. Describe them briefly and suggest how they could have minimized them. (16 marks)

(v) From the ore, another sample was taken, and it was having only $^{200}_{92}Z$ (0.140 g) and $^{160}_{84}Y$ (0.336 g). Half-life of $^{200}_{92}Z$ was found to be 400 years.

(a) Explain briefly how half-life can be found experimentally. (20 marks)

(b) Calculate the age of the ore. (10 marks)

(c) Calculate the decay constant of $^{200}_{92}Z$. (6 marks)