The Open University of Sri Lanka
Faculty of Natural Sciences
B.Sc/ B.Ed Degree Programme

Course Code	**: CMU3128**
Title	: Instrumental Methods of Chemical Analysis
Department	: Chemistry
Level	: 05
Name of the Examination	: Final Examination
Academic Year	: 2019/ 2020
Date	: 28.10.2020
Time	: 09.30 am- 11.30 am
Duration	: Two Hours

General Instructions

1 This question paper consists of 06**(Six)** questions in **06(Six)** pages

2. Read all instructions carefully before answering the questions

3. Answer **04(Four)** questions **only**. All questions carry equal marks. If more than four questions are answered, **only the first four relevant answers**, in the order they are written, will be marked.

4. Having any unauthorized documents/ mobile phones/any other electronic equipment in your possession is a punishable offence.

5. Use blue or black ink to answer the questions.

6. Clearly state your index number in all pages of your answer script.

7. The use of a non-programmable electronic calculator is permitted

1.(a) B^+ is an important ion which undergoes the following reaction with alcohol.

$CH_3CH_2OH + B^+ \longrightarrow BH + CH_3CHO + H^+$

Information with respect to absorption of light is shown in the figure and the Table below.

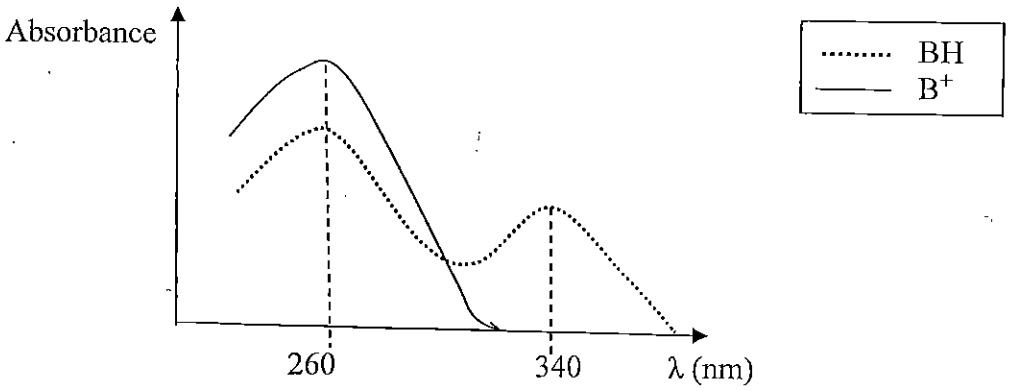


Table: Molar absorptivity coefficient values (ϵ) ($mol^{-1}Lcm^{-1}$)

Species	At λ = 260 nm	At λ = 340 nm
B^+	16,000	0
BH	14,000	8,000

A blood sample was brought to the laboratory to determine the amount of alcohol. After quantitative separation of the blood plasma from blood cells, a 0.50 mL of blood plasma was taken to a 25.0 mL volumetric flask. The solution was mixed well after adding 10.0 mL (an excess amount) of B^+ and topped up to the mark with distilled water. The transmittance of this solution was 59.7% at λ = 340 nm in a 2.00 cm cell. (molecular weight of the alcohol= 46.2 g)

(i) What is the significance of selecting a wavelength of high molar absorptivity coefficient when measuring absorbance?

(ii) However, in the above determination the absorbance was measured at λ = 340 nm. What may be the reason?

(iii) Draw and label a schematic diagram of a UV/Visible spectrophotometer. Name the light source and make of the sample cell that should have been used for the above determination.

(iv) Calculate the amount of alcohol in blood in units of ppm.

(v) If you have been asked to determine the amount of unreacted B^+ using UV/Visible spectroscopy using the above information, write in brief the experimental steps you would carry out and show how you would calculate the amount of unreacted B^+.

(vi) Both above determinations were affected by matrix effect. Briefly explain what is meant by the matrix effect and suggest a way to overcome it.

(75 marks)

(b) An unlabeled bottle was found in the laboratory store and the technical officer suspects it to be a known compound and decides to carry out an IR spectroscopic determination.

(i) State one important requirement that compound should satisfy to have an accurate IR spectroscopic determination.

(ii) Describe briefly how you would carry out an experiment to identify the compound using IR spectroscopy.

(iii) They did not have an IR spectrophotometer in the laboratory, but the basic design of UV/Visible spectrophotometer and IR spectrophotometer are the same. Therefore, they decided to use the UV/Visible spectrophotometer to measure IR absorption. Do you agree with the decision? If not, why?

(25 marks)

2. (a) Both X^{2+} and Z^{2+} forms coloured complexes with the ligand L at the optimal pH 8. At pH 8 the formation constant of XL = 3.0×10^{19} and λ_{max} = 560 nm. At the same pH, the formation constant of ZL= 7.5×10^{10} and λ_{max} = 660 nm. A photometric titration of a sample solution (25.0 mL) having both X^{2+} and Z^{2+} only was carried out with a solution L at λ = 660 nm.

(i) What may be the reasons for selecting photometric titration but not classical titration?

(ii) Giving reasons for the shape of the curve, sketch and label the expected titration curve.

(iii) State one important assumption that you made when sketching the curve and suggest the changes required in the experimental procedure to make that assumption valid.

(45 marks)

(b) It was decided to analyse X^{2+} in the above sample solution in (a) using Atomic Emission Spectroscopy and Z^{2+} using Molecular Fluorescence Spectroscopy.

(i) Name two differences in Atomic Emission Spectrophotometer and Molecular Fluorescence Spectrophotometer.

(ii) What is meant by sensitivity in an instrument? Suggest two ways of increasing the sensitivity of the Flame photometer.

(iii) To analyse Z^{2+} using Fluorescence Spectroscopy a fluorophore was added to form the compound P. State two main characteristics that P should satisfy to analyse using Fluorescence Spectroscopy.

(25 marks)

(c) The λ_{max} of the ion B^- is 420 nm. A weak acid solution HB (0.02 M) gave an absorbance of 0.450 at λ = 420 nm. An aqueous solution of NaB (0.01 M), a strong electrolyte gave an absorbance of 0.600 in same experimental conditions. Calculate the dissociation constant of the weak acid. State the assumptions clearly.

(20 marks)

(d) "When Mass Spectroscopy is used to determine the molecular weight to identify a compound, a mass analyser with a high resolution is always recommended".
Comment on the above statement. (10 marks)

3. (a)(i) Write nuclear equations for the following radioactive decays:

(I) β^- decay by $^{131}_{53}I$

(II) positron emission by carbon-11

(III) K electron capture by beryllium-7

(ii) (I) Define the term, 'half-life'.

(II) Given that the half-life of ^{99}Mo is 67.0 hrs, how long will it take for 1.000 g sample of pure ^{99}Mo sample to become 0.032 g?

(III) How much of ^{99}Mo will be left behind after 402 hrs?

(25 marks)

(b)(i) Briefly explain the principle behind Liquid scintillation detectors for measuring radiation.

(ii) How does the Liquid scintillation (LS) detector differ from the Geiger- Müller (GM) counter?

(iii) Write one advantage of LS detector over GM counter.

(20 marks)

(c) To 1.00 g of a crude mixture of amino acids containing alanine, 40.0 mg of ^{14}C-labelled alanine with an activity of 1500 counts min^{-1} (cpm) was added. After equilibration, 20.0 mg of alanine isolated gave a count rate of 500 cpm.

(i) Briefly explain the principle behind isotope dilution analysis.

(ii) What was the weight of alanine in the original amino acid mixture?

(20 marks)

(d) (i) Briefly explaining the basic principle underlying neutron activation analysis, describe how it is used in both qualitative and quantitative analyses.

(ii) Write the type of neutrons used in neutron activation analysis.

(iii) List the sources of neutrons used in activation analysis.

(35 marks)

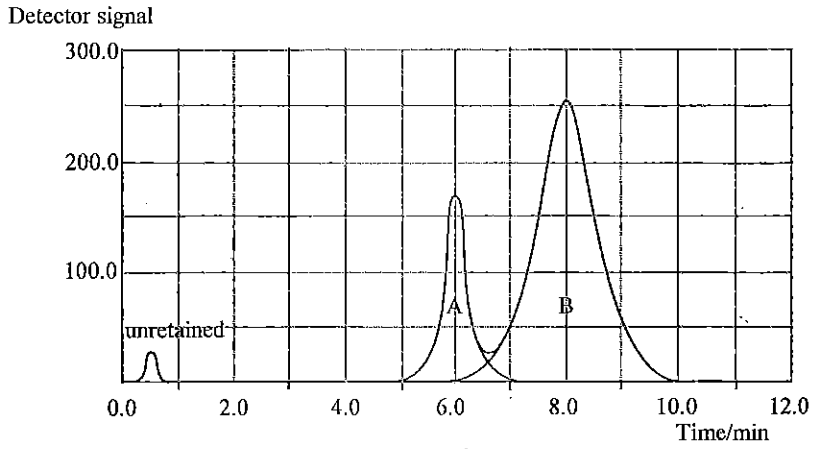
4. (a) What is meant by planar chromatography?
List down the advantages and disadvantages of planar chromatography.

(30 marks)

(b) Describe the mechanism of analyte separation that takes place in paper chromatography when a thick sheet of filter paper is used.

(20 marks)

(c) The chromatogram given below shows peaks of the two components **A** and **B**. They were eluted through a column of length 10.0 cm.



(i) Calculate the number of theoretical plates (N) for **A** and the height (H) of a theoretical plate for **A**.

(ii) Calculate the retention factors (k′) for **A** and **B**.

(iii) Calculate the selectivity factor (α) for separation of **A** and **B**.

(iv) Calculate the resolution of the two peaks **A** and **B**.

(v) Estimate the length (L) of the column needed for the peaks to be just resolved *i.e.* R = 1.5.

$$\left[\quad R = \frac{1}{4}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k'}{1 + k'}\right)\sqrt{N} \quad \right]$$

* *Define all the terms in equations used for the calculations.*

(40 marks)

(d) Explain what 'channelling' is in relation to column chromatography?

Describe the measures that can be taken to avoid channelling.

(10 marks)

5. (a) (i) Define all the terms in van Deemter equation.

$$H = A + \frac{B}{u} + C\,u$$

(ii) Illustrate the van Deemter equation graphically showing all the component graphs clearly labelled.

(25 marks)

(b) Describe the effect of larger particle size of stationary phase on separations in column chromatography.

(25 marks)

(c) Discuss the advantages and disadvantages of a Thermal Conductivity Detector (TCD) over a Flame Ionization Detector (FID).

(20 marks)

(d) Justify the following statements
(i) Capillary columns are more efficient than packed columns.
(ii) Gel electrophoresis is not a chromatographic method.

(30 arks)

6. (a) (i) Write down the two half-cell reactions occurring in a Daniel Cell.

(ii) What is the function of the salt bridge in the above cell?

(iii) Based on the half-cell equations given below, **derive** the overall balanced cell reaction and its standard cell potential. Identify the anode and cathode.

$M^+(aq) + e$ ------> $M(s)$ $\quad E^o = -1.25$ V

$Hg_2Cl_2(s) + 2e$ ------> $2Hg + 2Cl^-(aq)$ $\quad E^o = 0.268$ V

(iv) Write down the short hand representation for the above cell.

(30 marks)

(b) The following represent the two half-cell reactions of a cell

$M^{2+}(aq) + 2^e$ -------> $M(s)$ $\quad E^o = 0.75$ V

$X_2(g) + 2^e$ -------> $2X^-(aq)$ $\quad E^o = 0.45$ V

Consider the following cell reactions as written. They are said to be **NOT FEASIBLE.** Explain.

(i) $X_2(g) + M^{2+}(aq)$ ---------> $2X^-(aq) + M(s)$

(ii) $X_2(g) + M(s)$ -------> $2X^-(aq) + M^{2+}(aq)$

(18 marks)

(c) (i) Define Coulometry

(ii) A student carried out an electro gravimetric experiment to relate the mass deposited on the cathode to that of the expected amount from a standard solution of $CuSO_4$ (1.0 M). It was found that 10.50 g of Cu(s) was deposited on the cathode from a 200.0 ml of the standard solution. (Faraday's Constant = 96,500 C mol^{-1}) [Cu : 63.5; S = 32: O = 16].

(I) Calculate the quantity of electricity passed to complete the above deposition.

(II) Assuming that all the copper ions have been reduced, calculate the expected amount of Cu (theoretical yield) and hence, determine the percentage yield.

(30 marks)

(d) (i) The technique of electro-gravimetry, involves the deposition of the substance of interest whose concentration is to be determined. **Write down** the important properties of the deposit in order for the above technique to be effective.

(ii) Name any three (3) factors that affect the properties of such a deposit.

(iii) What is the purpose for adding a supporting electrolyte such as KCl in a polarographic analysis?

(22 marks)