THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme
Level 5 – FINAL EXAMINATION – 2017 / 2018

CYU 5308/CMU 3128 – INSTRUMENTAL METHODS IN CHEMICAL ANALYSIS

Duration: Two hours
Date and time: 02.04.2019, 9.30 a.m. – 11.30 a.m.

Instructions to students:

- **Answer any four (4) questions only.** If more than four questions are answered, only the **first four relevant answers** in the order written, will be considered for marking.
- The use of a non-programmable electronic calculator is permitted.

1. (A) The structure of the compound Z was qualitatively analyzed using an Electron Impact Mass Spectrophotometer and a IR spectrophotometer.

(i) Briefly explain how the mass spectrum of Electron impact Mass Spectroscopy (EIMS) is resulted. **(15 marks)**

(ii) Sketch and label the axes and main features of conventional IR spectrum. **(10 marks)**

(iii) A 0.0521 g of the compound Z was treated with the ligand L and the resultant product Z_2L was dissolved in 100.0 mL which gave a transmittance of 0.362 in 1.00 cm cell at 380 nm. Calculate the molecular weight of the compound Z.The molar absorptivity coefficient was 1.35×10^4 L cm^{-1} mol^{-1}. **(20 marks)**

(iv) Give one possible reason for measuring the transmittance and not the absorbance. **(10 marks)**

(B) The spectrophotometer manual had the following information. Decide whether the three samples A, B and C having approximate amounts of 3×10^{-4} M, 3×10^{-3} M and 3.1×10^{-4} M of Z_2L respectively can be analyzed accurately using this spectrophotometer. Justify your answer.
Minimum detection limit = 1×10^{-4} M
Linear range = 1×10^{-4} M to 8×10^{-4} M
Sensitivity = 0.5×10^{-4} M **(20 marks)**

(C) State two differences of the IR spectrophotometer and UV/Visible spectrophotometer. **(10 marks)**

(D) Explain the following in brief.
"Method of standard addition improves accuracy of the results."
(15 marks)

2. (A) Explain the following in **brief**.

(i) Atomic fluorescence spectroscopy and molecular fluorescence spectroscopy are different with respect to the emitted and absorbed wavelengths..

(ii) The values of quantum efficiency of three organic compounds M, Y and E are 0.11, 0.65, 0.32 respectively. The least fluorescent compound is M.

(20 marks)

(B) Draw a schematic diagram of a fluorimeter. Sate two differences of fluorimeter and flame photometer. **(20 marks)**

(C) NaX is a strong electrolyte. The anion X^- absorbs light having wavelength of 440 nm. An aqueous solution of 0.100 M of NaX showed 0. 276 absorbance at 440 nm. However, an aqueous solution of 0.200 M of the weak acid HX showed only 0.138 absorbance at 440 nm. Both the measurements were done using the same cell and the instrument. Calculate the dissociation constant of the acid HX.

(20 marks)

(D) A photometric titration was carried out at 440 nm to find the unknown concentration 25.0 mL of NaOH solution with HX solution (0.01 M).

(i) State two advantages of photometric titrations over classical titrations.

(10 marks)

(ii) Sketch and label the expected photometric titration curve. Justify.**(20 marks)**

(iii) How do you practically overcome the dilution error in this titration?

(10 marks)

3. (A) A radioactive isotope Q (mass = m, atomic no. = n) undergoes decaying by emitting alpha rays.

(i) Write the nuclear reaction equation to show the decay. The new element formed is R. **(10 marks)**

(ii) Suggest a suitable detector to measure the activity of Q and give a brief account of the mechanism, advantages and disadvantages of the detector suggested. **(20 marks)**

(iii)To a 1 mL of sample having Q, 4.0 mg of the labelled radioisotope of Q with a specific activity of 0.040 $\mu Ci\ mg^{-1}$ was added. From this mixture, 40 mg of pure sample of Q having an activity of 2.4×10^{-2} μCi was isolated. Calculate the weight of Q in the sample. **(16 marks)**

(B) Briefly explain the following.

(i) The daughter nucleus resulted by beta emission is different to that of positron emission.

(ii) Sometime even secondary scintillators are used in scintillation counters.
(24 marks)

(C) (i) Explain briefly the principle behind Neutron Activation Analysis.
(15 marks)

(ii)State two major differences in between Gamma ray spectroscopy compared to other spectroscopic methods. **(15 marks)**

4. (A) Explain the meanings of the following terms

(i) Retention factor (K')
(ii) Selectivity factor (α)
(iii) Dead time
(iv) Diffusion **(20 marks)**

(B) Given below is the van Deemter equation for column efficiency.

$$H = A + \frac{B}{u} + Cu$$

(i) Define all the terms in the equation.

(ii) Draw and label the van Deemter plot showing the three separate component graphs.

(iii) What is the significance of the terms A and B in gas liquid chromatography and in solid-liquid chromatography? **(60 marks)**

(C) Explain why Gel electrophoresis cannot be considered as a chromatographic technique. **(20 marks)**

5. (A) How do you reduce the zone broadening in the following techniques?
(i) GC separation
(ii) HPLC separation **(30 marks)**

(B) Compare the following pairs.
(i) Thin layer chromatography and paper chromatography

(ii) Normal phase chromatography and reverse phase chromatography

(iii) Isocratic elution and gradient elution in column chromatography
(45 marks)

(C) Explain why a GC with a thermal conductivity detector (TCD) can be coupled with a mass spectrometer while that with a flame ionization detector (FID) cannot be coupled. **(25 marks)**

5. (A) $M|M^{2+} \parallel Cl^-$ (saturated) $|Hg_2Cl_2, Hg|Pt$

(i) Write down the half cell reactions for the anode and cathode and hence, the overall spontaneous cell reaction

$E^0{}_{M^{2+}/M} = -1.10$ V $\qquad E^o{}_{Hg_2Cl_2|Hg} = 0.268$ V

(ii) Calculate the standard cell potential for this cell assuming that standard conditions exist for this cell

(24 marks)

(B) A student carried out the following experiment involving electrolysis to relate the mass deposited on the cathode to that of the known / expected amount from a standard solution of $CuSO_4$ (0.2 M). It was found that 1.35 g of Cu(s) was deposited on the cathode from a 100.0 ml of the standard solution. Assuming that all the copper ions have been reduced

[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) Calculate the expected amount of Cu and hence the yield

(24 marks)

(C) (i) Both the electro analytical techniques of Coulometry and Gravimetry do not require **calibration**. What is meant by calibration?

(ii) A coulometric titration (constant current) was carried out to determine the amount of dissolved phenol in a certain water sample. This based on the stoichiometric and fast reaction between phenol and electrochemically generated bromine to give tribromophenol. (C = 12.0; H=1.0; O = 16.0; Br = 80.0)

A water sample (50.0 ml) was acidified and an excess of KBr was added. Coulometric titration was then carried out at a constant current of 20 mA. The end point was reached in 500 seconds. With the aid of the relevant chemical equations, calculate the phenol content in the water sample in **mol m^{-3}**

(36 marks)

(D) (i) Name the two advantages of using a dropping mercury electrode (DME) in polarographic analysis

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

(16 marks)