THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme
Level 5 – FINAL EXAMINATION – 2020 / 2021

CYU 5308 – INSTRUMENTAL METHODS IN CHEMICAL ANALYSIS

Duration: Two hours
Date and time: 20th March, 2022 from 9.30 a.m. to 11.30 a.m.

Instructions to students

This question paper consists of four pages and four questions. Answer all the questions.

1. (a) Explain the following in brief.

(i) Principle of Raman Spectroscopy in structure determination.
(ii) Instrumentation of a fluorimeter is different to that of Atomic Emission spectrophotometer.
(iii) Resolution in mass analyzer in Mass Spectrophotometer is extremely important in detecting the exact molecular formula. **(10x3 = 30 marks)**

(b) An acid base indicator was available in the laboratory but of no use since the dissociation constant (K_a) was not known. The following procedure was followed to determine the dissociation constant.
In strong basic medium, the acid base indicator showed λ_{max} at 610 nm with a molar with molar absorptivity coefficient (ε) of 500 mol^{-1} dm^3 cm^{-1}. When the medium was strongly acidic the λ_{max} was at 440 nm with ε of 250 mol^{-1} dm^3 cm^{-1}. The absorbance was zero at 440 nm when the indicator was in strongly basic medium and also at 610 nm when the indicator was in strongly acidic medium. A small quantity of the indicator was added to water and the absorbance at 610 nm is 0.240 and at 440 nm it is 0.360 (path length =1 cm). Calculate the K_a of the indicator showing all the steps.
(30 marks)

(c) A photometric titration was carried at 460 nm with a standard EDTA solution to determine trace amount of X^{2+} and X^{3+} separately, in a sample solution of 20.0 mL.
The following information are given:
X^{2+} and X^{3+} form coloured complexes with EDTA at pH 7 (λ_{max} of X^{2+} and X^{3+} EDTA complexes are 460 nm and 590 nm respectively). The stability constants of EDTA complexes of X^{2+} and X^{3+} are 3.2×10^{20} mol L^{-1} and 8.7×10^{14} mol L^{-1} respectively. EDTA is colourless.

(i) Had the titration been successful to determine trace amount of X^{2+} and X^{3+} separately? Justify your answer with a labelled titration curve and explanation. Assume that there is no dilution error. **(20 marks)**

(ii) What changes in the procedure will you be suggesting in order to determine the concentrations of both ions, if you are allowed to carry out just one single photometric titration due to limited amount of EDTA? Justify your answer with a suitable titration curve.

(20 marks)

2. (a) Define
   (i) Faraday Law
   (ii) Faraday constant
   (iii) Coulometry **(18 marks)**

(b) 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

(12 marks)

(c) Consider the following half-cell reactions that represent the changes taking place at the cathode and anode, respectively.

$$M^{3+}(aq) + 3e \rightarrow M(s) \quad \text{----(1)}$$
$$2H_2O \rightarrow 4H^+ + O_2 + 4e \quad \text{-----(2)}$$

(i) With the aid of the balanced half cell equations, **derive** the overall balanced cell reaction.

(ii) In an experiment involving electrolysis to determine the concentration of M^{3+} in an aqueous solution, a constant deposit of M(s) was obtained with a passage of 4825 coulombs (C) of electricity through 100.0 cm^3 of this solution. Assuming that all of the M^{3+} were reduced,

(α) Determine the initial concentration of M^{3+}
(Faraday's Constant, F = 96,500 C mol^{-1})

(β) Calculate the pH of the solution at the end of the experiment assuming that all the H^+ ions formed are due to the above electrolysis only.

(36 marks)

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

(ii) Write down the balanced equation with respect to the reduction of the following compounds that take place at a DME, when subjected to a polarographic analysis under mild acidic conditions.

(22 marks)

(e) Concentration polarization, is a transfer process that is useful in electro analytical methods. **Name and outline** the three factors that contribute to the above ***transfer*** process.

(12 marks)

3. (a) Explain the principle of separation of different components in a mixture.

(20 marks)

(b) HPLC and GC are two important chromatographic analysis techniques.

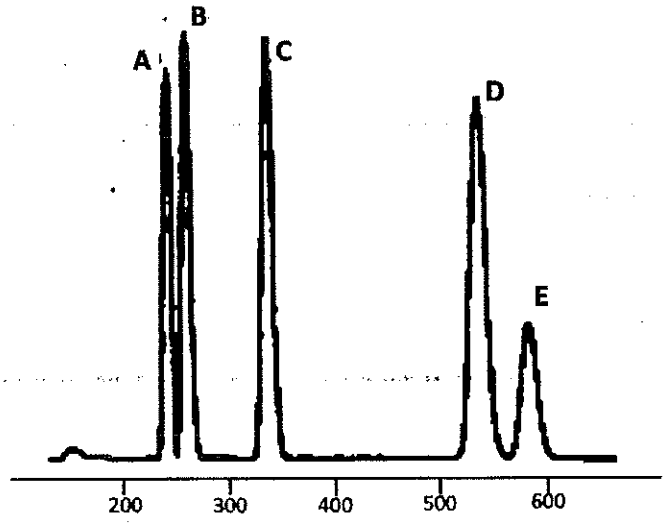
(i) Give three characteristics of compounds suitable to be determined by GC.

(12 marks)

(ii) How can the life span of an analytical column in HPLC be prolonged?

(12 marks)

(c) The following HPLC chromatogram and data were obtained from the separation of five pharmaceutical drugs using an HPLC equipped with C_{18} column. The compounds were eluted with a mixture of 55% v/v methanol and 45% v/v water.



Retention time (s)

Peak	Retention time, t_r, (s)
A	225
B	280
C	330
D	530
E	585

(i) Is this a reverse phase or normal phase chromatography? briefly explain your answer. **(10 marks)**

(ii) What kind of elution is this? **(10 marks)**

(iii) Compound C has width of at the base of 0.5 min on a column of 150 mm long. Calculate the number of plates and plate height. **(24 marks)**

(iv) The width at the base of peaks A and B were 40 s and 50 s, respectively. Calculate the resolution between these two peaks

(12 marks)

4. (a) A radioactive element $^{15}_{7}Z$ (solid) emits positrons followed by gamma radiation and has a half-life of 200 years.

(i) Write the balanced equation to show the positron emission. **(10 marks)**

(ii) What will be the detector suitable to measure the activity of this sample? Briefly state the mechanism behind counting of the detector you have chosen.

(15 marks)

(iii) State two possible errors during an activity measurement and suggest suitable methods to minimize/correct the errors.

(14 marks)

(iv) A fossil was containing 0. 150 g of $^{15}{}_{7}Z$ and 0.450g of the new product. What is the age of the fossil? **(16 marks)**

(b) A non- radioactive element D was irradiated by neutron activation to determine D quantitatively in a rock sample.

(i) What is the principle behind the analysis? **(10 marks)**

(ii) What are the properties that D should have in order to make the activation successful? **(10 marks)**

(iii) It was decided to use **fast neutrons** produced by **nuclear reactors for the activation**. Give a brief account of the type of neutron and the source.

(15 marks)

(iv) In another alloy sample D was analyzed following isotope dilution method using this radioactive D as a tracer.

The mass of non-radioactive D in the sample using Isotope Dilution Method was 4.8 g. Radioactive D added had an activity of 15000 cpm and the purified D (100 mg) isolated had an activity of 300 cpm. What is the amount of radioactive D that has used for this?

(10 marks)