

THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 – FINAL EXAMINATION – 2014 / 2015



CMU 3128/CME 5128/CHU 3129 – Instrumental methods in chemical analysis

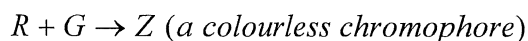
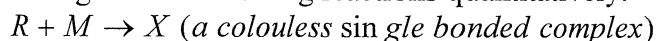
Duration: Two hours

Date and time: 23rd of October, 2015 from 9.30 a.m. to 11.30 a.m.

Instructions to students

This question paper consists of six pages and six questions. Answer any four questions only.

1. (a) The organic compound R does not absorb UV/Visible radiation but undergoes the following reactions quantitatively.

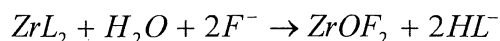


What is the most suitable compound having R from X, Y and Z for the determination of the concentration of R using UV/Visible spectroscopy? Justify your answer. **(24 marks)**

- (b) One student states that in the analysis of trace amounts of metal ions, even with the same stable high energy atomizers, Atomic Emission Spectroscopy gives more accurate results compared to Atomic Absorption Spectroscopy. Do you agree with him? Give reasons for your answer. **(10 marks)**
- (c) IR spectroscopy has been used to confirm the structure of a compound.
- (i) What is the principle behind IR spectroscopy with respect to qualitative analysis?
- (ii) Write two differences between the UV/Visible spectrophotometer and IR spectrophotometer.
- (iii) Draw and label a schematic diagram of an IR spectrum.

(36 marks)

- (d) The complex ZrL_2 is colored complex and it reacts with fluoride ion in aqueous medium and gives a colourless compound $ZrOF_2$.



When a 500.0 mL of F^- solution was added to a 1000.0 mL of ZrL_2 , the absorbance decreased from 0.600 to 0.200 at a path length of 1 cm. The molar absorptivity coefficient of ZrL_2 was $2.00 \times 10^5 \text{ Lcm}^{-1}\text{mol}^{-1}$. What is the concentration of the F^- solution added? **(30 marks)**

2. A compound which does not fluoresce was reacted with a fluorophore and the resultant compound M was determined quantitatively using Fluorescence Spectroscopy.

- (a) State three main characteristics of M that you would expect for it to be determined using Fluorescence Spectroscopy? **(15 marks)**
- (b) Why the detector is placed right- angled to the light source in the spectrofluorimeter? **(10 marks)**
- (c) State two important differences in the spectrum obtaining in Atomic fluorescence spectroscopy and Molecular fluorescence spectroscopy. **(10 marks)**
- (d) Do you agree with the following statements? Give reasons for your answer.
 (i) Only liquid samples can be analysed using Atomic Emission Spectroscopy.
 (ii) In Mass Spectroscopy if the chemical ionization done with excess of methane, the molecular ion resulted will have an extra H atom. **(20 marks)**
- (e) When a 25.0 mL of the compound E was titrated with Q having a high concentration, the compound D was resulted. Each substance absorbs the wavelengths given below. Sketch and label the expected photometric titration curve when the absorbance is measured at the wavelength of 500nm.

Substance	wave lengths (nm)
E	275 - 400
Q	300-450, 700-800
D	275-300, 475-700

(20 marks)

- (f) A 0.6538 g of a rock sample having trace amounts of Ni and Zn was digested, treated with excess of L and was diluted to 100.0 mL. This solution shows an absorbance of 0.244 and 0.700 at 553 nm and 637 nm respectively. Molar absorptivities (ϵ) of NiL_2 and ZnL_2 are given below. Calculate the percentage of Zn in the sample. ($Zn = 65.38$)

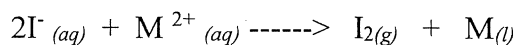
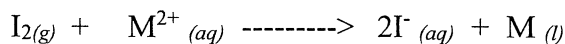
Compound	ϵ at $\lambda = 553 \text{ nm}$ ($\text{Lmol}^{-1}\text{cm}^{-1}$)	ϵ at $\lambda = 637 \text{ nm}$ ($\text{Lmol}^{-1}\text{cm}^{-1}$)
NiL_2	1.22×10^3	4.70×10^3
ZnL_2	0	6.00×10^3

(25 marks)



Write down the half-cell reactions at each electrode and hence, the balanced equation for the above cell reaction.

(ii) The following cell reactions are said to be not feasible. Explain.

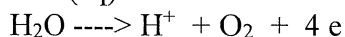
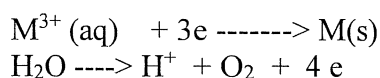


$$[M^{2+}_{(aq)} / M_{(l)} E^{\circ} = 0.45 \text{ V} ; I_{2(g)} / I^-_{(aq)} E^{\circ} = 0.54 \text{ V}]$$

(iii) Write down the correct cell reaction corresponding to the above half reactions and determine the standard cell potential.

(36 marks)

(b) The following half cell equations represent the changes taking place at the cathode and anode, respectively.



(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 a cation A^{2+} that undergoes reduction as in (i) above, it was found that a constant deposit of $A_{(s)}$ was obtained with a passage of 1930 C of electricity. Assuming that all of the A^{2+} were reduced and the initial volume of the solution was 50.0 mL (Faraday's Constant = $96,500 \text{ C mol}^{-1}$).

(β) determine the initial concentration of A^{2+} .

(λ) 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.

(40 marks)

(c) Technique of electro-gravimetry, involves the deposition of the substance of interest whose concentration is to be determined.

(i) Write down the important properties of the deposit in order for the above technique to be effective.

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

(24 marks)

4. (a) List down five factors on which the efficiency of a chromatographic separation depends on. **(10 marks)**

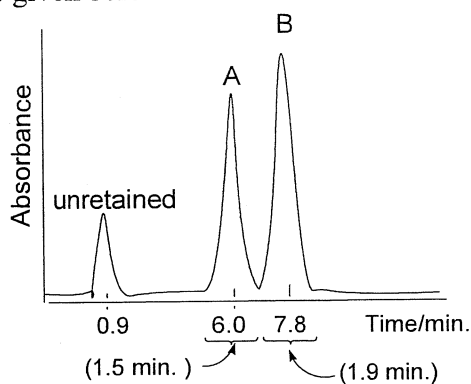
(b) In relation to chromatography, describe the following terms.

(i) Distribution coefficient (K)

(ii) Selectivity factor (α)

(20 marks)

(c) A chromatogram for the separation of two solutes (A and B) on a 25cm long HPLC column is given below.



Determine the following.

(i) Plate height (H) achieved under the operating conditions.

(ii) Retention volumes (V) for solutes A and B.

(iii) Resolution (R) achieved for solutes A and B.

(iv) Retention factors (k') for solutes A and B.

(v) Linear velocity (u) of the mobile phase in the column.

(50 marks)

(d) What is zone broadening in column chromatography? Give reasons for zone broadening.

(20 marks)

5. (a) Give a fully labeled diagram to illustrate the schematic layout of a gas chromatograph.

(20 marks)

(b) Briefly describe the two types of columns used in gas chromatography.

(20 marks)

- (c) Write short accounts on the following.
- (i) Gel permeation chromatography
 - (ii) Ion exchange chromatography **(30 marks)**
- (d) Describe the principle behind thermal conductivity detector. **(15 marks)**
- (e) What are the advantages and disadvantages of a thermal conductivity detector? **(15 marks)**

6. Answer either part I or II.

Part I

- (a) To a crude mixture of a plant extract is having cinnamaldehyde as a component, 20 mg of $^{14}_6\text{C}$ with a specific activity of $25.0 \text{ counts min}^{-1}\text{mg}^{-1}$ was added. After mixing, 40 mg of cinnamaldehyde was purified with an activity of $250 \text{ counts min}^{-1}$ which was measured using Scintillation counter. $^{14}_6\text{C}$ decays by beta emission.
- (i) Write down the equation to show decaying of $^{14}_6\text{C}$.
 - (ii) Give a possible reason for using the above method for analysis.
 - (iii) Give two advantages of scintillation counters over Geiger – Muller counter.
 - (iv) What was the weight of cinnamaldehyde in the plant extract?
 - (v) State two possible errors that would have taken place when activity measurements are taken. Suggest ways of minimizing the stated errors. **(56 marks)**
- (b) How does a Gamma Ray spectroscopy differ from UV/Visible spectroscopy with respect to measurement? **(10 marks)**
- (c) Briefly Describe the following related to radioactivity detectors.
- (i) Dead time
 - (ii) Scintillators **(14 marks)**
- (d) Comment on the following statement.
“In order to determine a trace amount of an element using radiochemical methods, it does not have to be radioactive. However, it does not mean that all the elements can be analyzed using radiochemical methods.” **(20 marks)**

Part II

- (a) A student performed a potentiometric titration using 25.0 mL of a solution of Fe^{2+} as the titrand and a standard solution of Ce^{4+} (0.02 M) as the titrant. The equivalence point, found graphically by plotting E vs Volume of titrant, was 22.0 mL.
- (i) Write down the balanced equation for the redox reaction between Fe^{2+} and Ce^{4+} .
 - (ii) Calculate the concentration of the titrand.
 - (iii) Sketch (with appropriate labels) the following graphs.
 - (α) Potential of cell vs Volume of titrant
 - (β) The first derivative curve (rate of change of potential vs volume of titrant). Comment on the two equivalence points.

(36 marks)
- (b)
 - (i) Compared to metallic electrodes, membrane electrodes work on a different principle. Explain the above statement.
 - (ii) List the three categories of membranes used to make ion-selective electrodes.
 - (iii) Consider a hypothetical ion-selective electrode for the ion A^- which obeys the equation,

$$E = 0.026 \ln \frac{B}{[\text{A}^-]}$$
 where B is a constant and E is the electrode potential.
 Suppose a $1.0 \times 10^{-2} \text{ mol L}^{-1}$ solution of A^- gave a value of -0.250 V for the electrode potential measured under standard conditions of temperature (25°C) and pressure. Calculate the expected value of the potential, measured under the same conditions when the concentration of A^- is $1.0 \times 10^{-3} \text{ mol L}^{-1}$.

(34 marks)
- (c)
 - (i) Name the 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.
 - (α) Benzaldehyde
 - (β) Ethyl bromide
 - (γ) Propyl cyanide

(30 marks)