



THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 – FINAL EXAMINATION – 2013 / 2014

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

Duration: Two hours

Date and time: 20th of November, 2014 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 water sample contains the following compounds-A, X,Y, M and D. These compounds are to be analysed using UV/Visible spectroscopy and the important information are given below.

| Compound | $\lambda_{\max}(\text{nm})$ | Molar absorptivity coefficient ($\text{L mol}^{-1}\text{cm}^{-1}$) |
|----------|-----------------------------|--|
| A | 200 | 10,000 |
| X | 560 | 21,000 |
| Y | 590 | 5,000 |
| M | 615 | 85,000 |
| D | 260 | 65,000 |

- (i) What is the most sensitive compound with respect to UV/Visible spectroscopy? Give reasons for your answer. **(15 marks)**
- (ii) X was analysed after A. What was the light source for the analysis of A and what are the changes in the operation of the instrument you should do when analysing X? (Assume that the molar absorptivity coefficient values are available) **(10 marks)**
- (iii) Of A and D, one is having a chromophore.
 - (a) What is a chromophore?
 - (b) What would you expect to have a chromophore out of A and D? Give reasons for your answer. **(20 marks)**
- (iv) X and Y are metal complexes and their absorption spectra are overlapping. Describe briefly how the analysis should be carried out with the calculations in order to find the concentrations of X and Y separately. **(20 marks)**

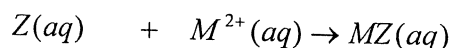
- (v) Compound A can be analysed using molecular fluorescence spectroscopy too.
- If a spectrofluorometer is also available, what is the method that you will select to analyse A? Give reasons for your answer.
 - Write two differences between the UV/Visible spectrophotometer and spectrofluorometer.
 - What can you say about the λ of emitted radiation if A is analysed using molecular fluorescence spectroscopy? Give reasons for your answer.
- (35 marks)**

2. The structure of the compound Z was qualitatively analysed using Electron impact Mass spectrophotometer.

- Briefly explain how the mass spectrum of Electron impact Mass Spectroscopy (EIMS) is resulted.
- (15 marks)**
- Information on the significant peaks of the mass spectrum of Z which has an isotope is given below. Identify the main peaks and briefly describe the important information you can get from them.
- (12 marks)**

| Mass | Relative abundance (%) |
|------|------------------------|
| 43 | 100 |
| 56 | 30 |
| 72 | 40 |
| 116 | 25 |
| 117 | 10 |

- Z (aq)(colourless) undergoes the following reaction with the metal ion M^{2+} (aq) (colourless) and form MZ which is coloured. Z was quantitatively analysed by carrying out a photometric titration between Z(aq) and M^{2+} (aq).



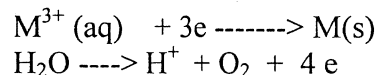
- Draw and label a schematic diagram of the photometric titration curve of the titration between aqueous solutions of Z and M.
 - Give two possible reasons why a classical titration was not carried out between Z and M.
- (20 marks)**

- (iv) The concentration of Ca^{2+} in a water sample (100.0 ml) was quantitatively analysed by Flame photometry.
- What is the principle behind the quantitative analysis of Atomic Emission Spectroscopy? **(10 marks)**
 - To a 10.0 ml of the sample, 5.0 ml of 50 ppm Ca^{2+} standard solution and 10.0 ml of 0.02 M EDTA were added (pH= 10) before diluting to 100.0 ml and the emission resulted was 90. To another 10.0 ml of the sample, 10.0 ml of 0.02 M EDTA was added (pH= 10) before diluting to 100.0 ml and the emission of this solution was 40. If the emission measurements were done under similar conditions, calculate the concentration of Ca in the water sample. **(16 marks)**
 - Write a brief account on advantages of Inductive Coupled Plasma Emission Spectroscopy over other emission methods. **(15 marks)**
 - Give two main differences between Atomic Emission Spectrophotometer and Atomic Absorption Spectrophotometer. **(12 marks)**
3. (i) Consider the following electrodes and their standard reduction potentials.
- $$\text{AgCl(s)} + \text{e} \longrightarrow \text{Ag(s)} + \text{Cl}^{\text{-(aq)}} \quad E^{\circ} = -0.20 \text{ V}$$
- $$\text{Cd}^{2+}(\text{aq}) + 2\text{e} \longrightarrow \text{Cd(s)} \quad E^{\circ} = -0.40 \text{ V}$$
- [E° , standard reduction potentials]
- Write down the half cell reactions and the overall spontaneous cell reaction.
 - Identify the cathode and the anode; explain your choices. **(22 marks)**
- (ii)
- $$\text{Hg}^{2+}(\text{aq}) + 2\text{e} \longrightarrow \text{Hg(l)} \quad E^{\circ} = 0.85 \text{ V}$$
- $$\text{I}_2(\text{g}) + 2\text{e} \longrightarrow 2\text{I}^{\text{-(aq)}} \quad E^{\circ} = 0.54 \text{ V}$$
- The following cell reactions are said to be **not feasible**. Explain.

$$\text{I}_2(\text{g}) + \text{Hg}^{2+}(\text{aq}) \longrightarrow 2\text{I}^{\text{-(aq)}} + \text{Hg(l)}$$

$$\text{I}_2(\text{g}) + \text{Hg(l)} \longrightarrow 2\text{I}^{\text{-(aq)}} + \text{Hg}^{2+}(\text{aq})$$
 - Write down the correct cell reaction and determine the standard cell potential. **(22 marks)**

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



- (a) With the aid of the balanced half cell equations, **derive** the overall balanced cell reaction.
- (b) In an experiment involving electrolysis to determine the concentration of X^{3+} it was found that 1.50 g of $\text{X}(\text{s})$ (Rel. atomic mass = 100) was deposited on the cathode. Assuming that all the X^{3+} have been reduced and that a volume of 100.00 ml of this solution was used for electrolysis,
 - (α) calculate the quantity of electricity that was passed through this solution (Faraday's Constant = $96,500 \text{ C mol}^{-1}$).
 - (β) determine the initial concentration of X^{3+} .
 - (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.

(32 marks)

- (iv) (a) Outline the **principle** involving Coulometry and Electro-gravimetry, two quantitative electro-analytical techniques (experimental details NOT necessary)
- (b) Name the three major components of the instruments associated with constant potential coulometry

(24 marks)

4. (i) van Deemter equation gives the relationship between various column parameters to the effective plate height for a solute in that particular column.

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

- (a) Define all the terms in the van Deemter equation.
- (b) Construct the overall curve, H vs. u giving individual graphs for the separate components in the equation.
- (c) Which term is independent of flow rate? Give reasons.

- (d) Which term is negligible in open (unpacked) columns? Give reasons.
- (e) Plot in the same graph, the two curves you expect when the particle size of the column material is $10.0\mu\text{m}$. and $3.0\mu\text{m}$. (*Label the curves clearly.*)
- (f) Justify your answer given in above (e). (50 marks)
- (ii) Describe the separation technique involved in gel filtration chromatography. (25 marks)
- (iii) Tabulate the differences between HPLC and GC. (25 marks)
5. (i) Describe the terms distribution coefficient (K) and retention factor (k') of a component **A** in relation to chromatography. (20 marks)
- (ii) A two component mixture was analyzed by GC. Linear flow rate of the mobile phase was 25 cm/min . Air elutes 3.0 minutes after injection. Table below gives the information obtained from its chromatogram.

| Compound | Retention time/min. | Peak width/min. |
|----------|---------------------|-----------------|
| P | 21.2 | 0.75 |
| Q | 20.0 | 0.95 |

Calculate the following.

- (a) Length of the column L .
- (b) Average number of plates for the column.
- (c) Selectivity factor (α) for **P** and **Q**.
- (d) Resolution (R) between **P** and **Q**.
- (e) Comment on the separation between **P** and **Q** with respect to the values you have got for α and R . (40 marks)

(iii) A mixture containing non polar aromatic compounds and a polar organic acid is analyzed by HPLC using a reverse phase silica gel column with a guard column attached to the instrument.

- (a) If 60% aqueous methanol solution is used as the eluent, what do you expect to move out fast? Give reasons.
- (b) How does reverse phase silica gel structurally differ from normal phase silica gel?
- (c) What is the function of the guard column and the advantage of using a guard column?

(30 marks)

(iv) How does an electron capture detector (ECD) work?

(10 marks)

6. Answer either part I or Part II

Part I

(i) $M|M^{3+} \parallel Cl^- \text{ (saturated)} |Hg_2Cl_2, Hg|Pt ;$

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

(18 marks)

(ii) A coulometric titration (constant current) was carried out to determine the amount of dissolved phenol in a certain water sample. The basis of this determination was the stoichiometric and fast reaction between phenol and electrochemically generated bromine to give tribromophenol.

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} ($C = 12.0$; $H = 1.0$; $O = 16.0$; $Br = 80.0$)

(24 marks)

(iii) Sketch (with appropriate labels) the following with respect to potentiometric titrations.

- (a) Potential of cell vs Volume of titrant
- (b) The first derivative curve (rate of change of potential vs volume of titrant). Comment on the two equivalence points. **(20 marks)**

- (iv) (a) Identify all the symbols (including units where relevant) in the Ilkovic Equation
- $$I_D(\text{max}) = 607 n D^{\frac{1}{2}} m^{\frac{2}{3}} t^{\frac{1}{6}} c$$
- (b) Name the two advantages of using a dropping mercury electrode (DME)
- (c) A student carried out a polarographic method of analysis to determine the concentration of a metal ion (A^{n+}) in an unknown sample present in the form of a solution.

To a 20.00 ml of the sample, 25.00 ml of 0.5 M KCl (as an inert supporting electrolyte) was added and the total volume was made up to 75.0 ml with distilled water. The limiting current (after correcting for residual current) was found to be 0.70 A. The analysis was then repeated using the same amount of sample and KCl and including 10.00 ml of a 10.0 ppm standard solution of A^{n+} ion before diluting to a final volume of 75.0 ml ; the limiting current now was found to be 0.95 A.

Determine the concentration of A in the original sample in ppm.
(38 marks)

Part II

- (i) Briefly describe how neutron activation analysis is used for qualitative analysis.
(15 marks)
- (ii) How does a gamma ray spectroscopy differ from UV/Visible spectroscopy with respect to measurement?
(10 marks)
- (iii) To a fertilizer sample having arsenic, 40 mg of $^{76}_{33}\text{As}$ with an activity of 1200 cpm was added. After mixing, 20 mg of arsenic having an activity 400 cpm was purified and separated. Activities were measured using Gas Ionization detector.
- (a) What is the **mechanism** behind Gas Ionization detectors?
(10 marks)
- (b) Give **one advantage** and **one disadvantages** of Geiger Muller Counter.
(10 marks)

- (c) What are the modifications introduced in the Gas Flow counter in order to overcome the disadvantages in the Geiger Muller Counter?
(10 marks)
- (d) What is the weight of As in the original sample?
(15 marks)
- (e) Give a possible reason for using the above method for analysis.
(10 marks)
- (iv) Describe the following related to radioactive measurements in brief.
- (a) Random errors
- (b) K electron capture
(20 marks)