THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 – FINAL EXAMINATION – 2011 / 2012

CMU 3128/CHU 3129/CHE 3129 – INSTRUMENTAL METHODS IN CHEMICAL ANALYSIS

Duration: Two hours
Date and time: 21.11.2012, 9.30 a.m. – 11.30 a.m.

Instructions to students:

- This question paper consists of six(6) questions and six (6) pages
- **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
- Logarithm tables and graph paper will be provided on request
- Mobile phones are **NOT** allowed; switch them off and leave them outside.

1. (A) State the specific function of the following components/features in different types of spectrophotometers.
   (i) Two light sources of Deuterium and Tungsten lamps
   (ii) Double beams
   (iii)Excitation and emission monochromators
   (iv)Plasma atomizer
   (v) Double focusing mass analyzer (30 marks)

   (B) Explain the principles behind Infra Red (IR) spectroscopy and Raman spectroscopy as qualitative analytical methods. Sketch and label the axes and main features of conventional Raman spectrum and an IR spectrum.
   (40 marks)

   (C) A 1.00 g of a steel sample was dissolved in H_2SO_4 acid and the Mn in the sample was oxidized to $KMnO_4$ and the volume was made up to 100.0 cm^3. The absorbance of this solution was 0.700 at 530 nm. Another $KMnO_4$ solution having a concentration of 1.52×10^{-4} M gave an absorbance of 0.350 at similar conditions. Calculate the percentage of Mn in the steel sample. (Mn= 54.94 g)
   (30 marks)

2. (A) (i) Explain **briefly** the principle behind photometric titrations.
(ii) Sketch the expected photometric titration curve of a titration of which only the product absorbs light.
(iii)Give three situations where photometric titrations can be applied but not classical titrations.

(30 marks)

(B) Draw a schematic diagram of a mass spectrophotometer and identify the main components.

(10 marks)

(C) Explain the following in **brief**.
(i) Method of standard addition improves accuracy of the results.
(ii)Atomic emission spectroscopy is more sensitive than atomic absorption spectroscopy.

(20 marks)

(D) The absorbance of three solutions of methyl orange (having the same concentration but at different pH conditions) were measured at 510 nm using 1.00 cm cell. The results are as follows.

Condition	**Absorbance**
Strongly acidic	0.470
At pH of 4.5	0.176
Strongly basic	0.129

Find the value of the dissociation constant (K_a) of methyl orange.

Hint: Only one form of indicator is available either in strongly acidic or strongly basic conditions.

(40 marks)

3. (A) (i) Write down the primary/basic difference in the two quantitative techniques, Coulometry and Electrogravimetry.
(ii) Both the above techniques do not require calibration. Explain this statement starting with a reference to the process of calibration itself.

(26 marks)

(B) (i) Define the term (a) Buffer
(b) Overpotential
(ii) A dropping mercury electrode (DME) is a micro electrode used in a polarography.
(a)What are its advantages?
(b)Sketch a typical polarogram.
(c)What is meant by "half-wave potential'?

(iii) Identify all the symbols in the Ilkovic Equation $I_D(max) = 607\ n D^{\frac{1}{2}} m^{\frac{2}{3}} t^{\frac{1}{6}} c$

(iv) Write down the balanced equation and the expected product for the following reactions taking place at a DME when subjected to a polarographic analysis.

$C_2H_5Br + H^+$ ------>

$C_2H_5NO_2 + H^+$ ------>

$C_2H_5CN + H^+$ ------>

(54 marks)

(C) In carrying out a polarographic method of analysis, a student was asked to add 25.0 cm^3 of a 0.5 M KCl solution.
What is the purpose of adding KCl solution?
What is the special term used for such a solution?

(20 marks)

4. (A) The selectivity factor α and resolution R, in relation to chromatography can be expressed as follows.

$$\alpha = \frac{t_B - t_M}{t_A - t_M} \qquad R = \frac{2(t_B - t_A)}{W_A + W_B}$$

Define the terms t_A, t_B, t_M, W_A, and W_B in words.

(10 marks)

(B) Chromatographic separations become difficult if α is close to one (01). Give three measures that can be taken to overcome this problem.

(15 marks)

(C) Liquid chromatography was done on a two component mixture using a column length of 24.7 cm. V_S/V_M ratio for the packing is 0.12. Following data were obtained from the chromatogram. Flow rate is recorded as 0.32 mL/min.

Component	Retention time/min.	Peak width/ min.
Non retained	2.7	0.01
A	12.9	1.05
B	13.7	1.14

(i) Calculate N, the average number of theoretical plates.
(ii) Calculate the plate height for the column.
(iii) Calculate the retention factors (k_A' and k_B') and find out the distribution coefficients K_A and K_B for both components.
(iv) Calculate the selectivity factor (α) and the resolution (R) of the two peaks.

(v) What should be the length of the column required to separate the two components with a resolution of 1.5. The relationship between resolution and the number of theoretical plates is given by the equation,

$$R = \frac{1}{4}\left(\frac{\propto -1}{\propto}\right)\left(\frac{k'}{1+k'}\right)\sqrt{N}$$

(75 marks)

5. (A) Draw and label the main components in a schematic diagram of a gas chromatograph.

(20 marks)

(B) Give three desirable properties that a sample should possess in order to be analyzed by GC.

(15 marks)

(C) List the advantages and disadvantages in using an electron capture detector.

(15 marks)

(D) What do you understand by 'gradient elution'? Explain why gradient elution is carried out.

(20 marks)

(E) Discuss the factors underlying separations in gel electrophoresis and gel permeation chromatography.

(20 marks)

(F) Describe what 'channelling' means in relation to column chromatography and explain how it could be avoided.

(10 marks)

6. **Answer either Part I or Part II**

Part I

(A) Explain the following related to radiochemical methods.
(i) Dead time of detectors
(ii) Measurement of random errors
(iii) K electron capture

(15 marks)

(B) Give a brief account of the mechanism, advantages and disadvantages of Geiger Muller Counter. What are the modifications introduced in the Gas Flow counter in order to overcome the disadvantages in the Geiger Muller Counter?

(45 marks)

(C) (i) Explain briefly the principle behind isotope dilution analysis.
(ii) To a sample (0.7 g) having mercury,10 mg of Hg^{203} with a specific activity of 2400 cpm/g was added. After equilibration, mercury was separated and 0.100 g of mercury showed 30 cpm of activity. What is the percentage of mercury in the sample?

(40 marks)

Part II

(A) Consider the following electrodes and their standard reduction potentials

$A^{2+}{}_{aq}/A_s$ $\quad E^o = 0.54$ V
$B^{+}{}_{aq}/B_s$ $\quad E^o = -0.40$ V

(i) Write down the half cell reactions and the overall spontaneous cell reaction.
(ii) Identify the cathode and the anode.
(iii) Determine the standard cell potential.

(22 marks)

(B) 50.00 ml portion of a solution containing an ion, M^{3+} (relative atomic mass = 80.0) was subjected to electrolysis in order to determine its concentration. At the end of this process, it was found that 2.00 g of the solid, M was deposited on the cathode. Assuming that all the M^{3+}ions have been reduced, calculate the initial concentration of M^{3+} and the quantity of electricity that was passed through this solution.

(22 marks)

(C) Consider the half reaction of the form

$A^{p+} + qe \rightleftharpoons A^{r+}$

Write down the Nernst equation for this reaction in terms of activity and identify, clearly, the symbols used.

(10 marks)

(D) Consider the following electrolysis reactions occurring at 25 °C whose standard reduction potentials (E^o values) are given below.

$M^{2+}(aq) + 2e \text{ ---> } M(s)$ $\quad E^o = 0.40$ V
$2X^{-}(aq) - e \text{ -----> } X_2$ $\quad E^o = 0.80$ V

Assuming the current flow to be negligible, calculate the voltage needed to drive the overall reaction. The initial concentrations are $M^{2+} = 0.2$ M and $X^{-} = 0.4$ M

(20 marks)

(E) A student performed a potentiometric titration using 25.0 cm^3 of a solution of Fe^{2+} as the titrand and a standard solution of Ce^{4+} (0.05 M) as the titrant. The equivalence point of 20.0 cm^3 was found graphically by plotting E vs volume of titrant.

(i) Write down the balanced equation for the redox reaction between Fe^{2+} and Ce^{4+}
(ii) Sketch the above plot and label the axes. Indicate the equivalence point on your sketch.
(iii) Calculate the concentration of the titrand.

(26 marks)