THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 – FINAL EXAMINATION – 2012 / 2013

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

Duration: Two hours
Date and time: 04.12.2013 9.30 a.m. – 11.30 a.m.

Information 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
- Mobile phones are **NOT** allowed; switch them off and leave them outside.
- Faraday's constant (F) = 96500 C mol^{-1}
- Gas constant (R) = 8.314 J K^{-1} mol^{-1}

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

(i) In atomic fluorescence spectroscopy, the emitted wavelength is equal to absorbed wavelength, but it is not so in molecular fluorescence spectroscopy.
(ii) Structure determination of a symmetric molecule cannot be done by IR spectroscopy but can be done by Raman spectroscopy.
(iii)Chemical ionization is more advantageous compared to electron impact ionization in Mass Spectroscopy. (45 marks)

(B) Draw a schematic diagram of a fluorimeter. How does it differ from UV/ Visible spectrophotometer. (20 marks)

(C) A solution of 4.0 ppm $KMnO_4$ shows a transmittance of 25% at 520 nm and 52% at 480 nm.
(i) What is the best wavelength to measure absorbance (assume that there are no other interfering ions)? Justify your answer with proper calculations.
(ii) What is the advantage of your selection with respect to analysis?
(iii)Calculate the molar absorptivity coefficient for $KMnO_4$ at the best wavelength that you have selected (path length = 1cm, molar mass of $KMnO_4$ = 158.036 g).
(iii)Unlike most other coloured transition metal complexes, very low concentrations of $KMnO_4$ can be detected using UV/Visible spectroscopy. Why?
(35 marks)

2. (A) In a mass spectrum three important signals are the base peak, molecular ion peak and (M+1) peak. Explain the significance of these peaks and also how these peaks are used to identify the compound. (15 marks)

(B) Sketch the expected photometric titration curve of a titration of which only the reactant in the burette (titrant) absorbs light but neither the reactant in the flask nor the product absorbs light. (10 marks)

(C) (i) Draw a schematic diagram of a Atomic Emission Spectrophotometer. How does it differ from Atomic Absorption Spectrophotometer?

(ii) When tested for lithium using an emission technique, solution "X" of a sample of soil gave a meter reading of 25 in arbitrary units. Solution "Y" consisting of the same quantity of the unknown solution "X", but with 10 mg L^{-1} of added lithium, gave a meter reading of 62 in the same units. Calculate the concentration of lithium in solution "X".

(iii)Justify the following statement.

"When the absorption of light is compared, compounds with single bonds shows very low absorption compared to compounds with double bonds. Compounds with two or more double bonds conjugated even show better absorption compared to compounds with double bonds."

(45 marks)

(D) Explain the following in **brief**.

(i) IR spectra are band spectra and not line spectra.

(ii) The values of quantum efficiency of three organic compounds A,B and C are 0.15, 0.71, 0.42 respectively. The least fluorescent compound is A.

(30 marks)

3. (A) Write the physical state of the stationary phase and the mobile phase in each of the chromatographic types given below.

(i) Thin layer chromatography
(ii) Paper chromatography
(iii) Gas liquid chromatography
(iv) High performance liquid chromatography (24 marks)

(B) List three (**03**) basic requirements of a liquid phase used in GC. (15 marks)

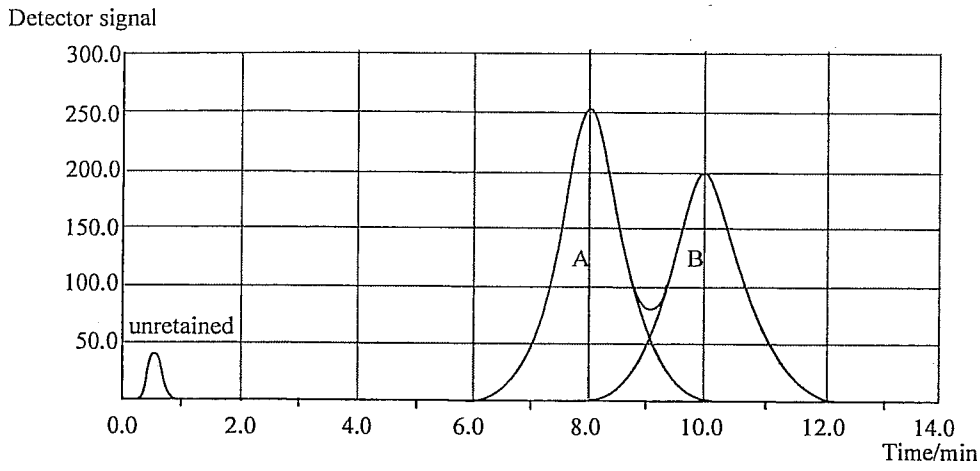
(C) Both the Flame Ionization Detector (FID) and Thermal Conductivity Detector (TCD) are good general purpose detectors.

(i) What would be your choice for an analysis of a mixture of large number of components with various concentration ranges? Justify your answer.

(ii) What would be your choice for a GC coupled to another analytical instrument? Justify your answer.

(25 marks)

(D) Given below is a part of a GC chromatogram which shows the elution of two components A and B. The length of the column packing is 2.0 m. Isocratic elution was carried out at a flow rate of 10 mL/min.



(i) Calculate the retention factors (k′) for A and B.
(ii) Calculate the selectivity factor (α) for separation of A and B.
(iii) Calculate the number of theoretical plates (N) for A and the height (H) of a theoretical plate for A.
(iv) Calculate the resolution (R) of the two peaks.
(v) What should N be for the peaks to be just resolved (R = 1.5)?

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

(36 marks)

4. (A) The standard reduction potentials of four (4) half cells are given below.

$I_3^-(aq) + 2e \text{ ---------> } 3\,I^-(aq)$ $\quad E^o = 0.54$ V

$Ag^+(aq) + e \text{ -------> } Ag(s)$ $\quad E^o = 0.80$ V

$AgCl(s) + e \text{ --------> } Ag(s) + Cl^-(aq)$ $\quad E^o = -0.20$ V

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

Explain, giving reasons, whether the following two (2) cell reactions, as written, are feasible or not.

(α) $I_3^-(aq) + 2Ag(s) \text{ ---------> } 3\,I^-(aq) + 2Ag^+(aq)$
(Assume that AgI do not precipitate out.)

(β) $Cd(s) + 2AgCl(s) \text{ -------> } Cd^{2+}(aq) + 2Ag(s) + 2Cl^-(aq)$

(20 marks)

(B) (i) Distinguish between coulometry and electrogravimetry.

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

M^{2+} (aq) + 2e -------> M(s)
$2H_2O$ ----> 4 H^+ + O_2 + 4 e

In an experiment involving electrolysis to determine the concentration of M^{2+}, it was found that 3.00 g of M (Rel. atomic mass = 150) was deposited on the cathode. Assuming that all the M^{2+} ions have been reduced and that a volume of 25.00 mL of this solution was used for electrolysis,

(a) calculate the quantity of electricity that was passed through this solution.
(b) determine the concentration of M^{2+}
(c) calculate the pH of the solution at the end of the experiment.

(36 marks)

(C) The following questions refer to Polarography, an electrochemical analytical technique (**quantitative** as well as **qualitative**)

(i) Sketch a clearly labeled polarogram.
(ii) What feature in this technique allows you to identify a species, quantitatively and qualitatively?
(iii) What is meant by overpotential? Name the two main causes for this.
(iv) Name and explain the four factors that give rise to polarization.
(v) How do you minimize the process of "Migration"? Explain
(vi) Write down the expected product and the balanced equation for the following reaction taking place at a DME when subjected to a polarograhic analysis.

C_6H_5CHO + H^+ + e - -----> (44 marks)

5. (A) A mixture separated by thin layer chromatography (TLC) on silica gel plates using hexane as the mobile phase was visualized under UV illumination.

(i) In terms of polarity, what components move up fast? Give reasons.
(ii) Explain why some components on TLC can be observed as coloured spots under UV illumination.
(iii) How can TLC be used to detect the presence of a known compound in the mixture?
(iv) What is meant by reverse phase chromatography?

(30 marks)

(B) Explain why electrophoresis is not considered as a chromatographic technique. (20 marks)

(C) Describe in brief how separation in gel permeation chromatography takes place. (20 marks)

(D) Explain why capillary columns are more efficient than packed columns. (20 marks)

(E) Describe the following terms in brief.
(i) molecular sieves
(ii) eddy diffusion
(10 marks)

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

Part I

(A) (i) What are the main advantage of Isotope dilution method ?
(ii) Explain briefly the principle behind Isotope dilution method.
(iii) What are the conditions that should be satisfied in order to carry out Isotope dilution method? (30 marks)

(B) (i) A sample of a radioactive element (molar mass = 238) decays at a rate of 2.3×10^{6} disintegrations s^{-1} and if the decay constant $K = 1.6 \times 10^{-10}\ s^{-1}$, what is the weight of the sample?
(ii) The above decay showed decrease in mass number by 4 units and atomic number by 2 units.
(a) What type of particles had emitted in decaying? State two properties of these particles.
(b) In order to measure the radioactivity of the above radioisotope, what would you select out of Geiger Muller counter and Gas proportional counter? Give reasons for your selection and also why the other counter was not selected. (45 marks)

(C) Explain the following in brief.
(i) Briefly explain the principle behind activation analysis.
(ii) Suggest a suitable method to detect gamma rays giving reasons. (25 marks)

Part II

(A) (i) Write down the relevant half reactions and hence, the spontaneous cell reaction of the following pair of electrodes (standard reduction potential values given in parenthesis)

Co^{2+}/Co (s) (-0.28) and $O_2/H^+/H_2O$ (1.23)

(ii) Determine the standard cell potential of this cell. (20 marks)

(B) (i) Name the three principle types of metallic electrodes

(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 $E = B - \frac{RT}{F}\ln[A^-]$ where B is a constant and E is the electrode potential.

Suppose a 2.5×10^{-2} $molL^{-1}$ solution of A^- gave a value of - 0.250 V for the electrode potential measured under standard conditions of temperature (25 ^{0}C) and pressure. Calculate the expected value of the potential, measured under the same conditions when the concentration of A^- is 1.5×10^{-3} mol L^{-1}

(40 marks)

(C) (i) Write down the half cell reaction corresponding to the calomel electrode

(ii) A cell was prepared by dipping a metal (M) wire in a solution of an electrolyte, 0.05 M solution of $M_2(SO_4)_3$ along side a standard calomel electrode (whose E^o is 0.25 V). Both the calomel electrode and the metal wire are connected to a potentiometer.

Write down the Nernst equation for the Metal electrode and calculate its half cell potential. Assume that the standard reduction potential for this electrode is 0.40 V

(iii) Write down the overall spontaneous cell reaction and hence, calculate the cell potential

(40 marks)