THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 – FINAL EXAMINATION – 2007 / 2008

CHU 3129/CHE 5129 – INSTRUMENTAL METHODS IN CHEMICAL ANALYSIS

Duration: Two and half hours
Date and time: 17th of June, 2008 from 1.30 p.m. to 4.00 p.m.

Physical constants
Plank constant: $h = 6.626 \times 10^{-34}$ Js
Speed of light in a vacuum: $c = 2.998 \times 10^{8}$ m s^{-1}
Avogadro's constant: $L = 6.023 \times 10^{23}$ mol^{-1}
At 25°C, $\frac{RT}{F} \ln X = 0.0592 \log X$

Instructions to students

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

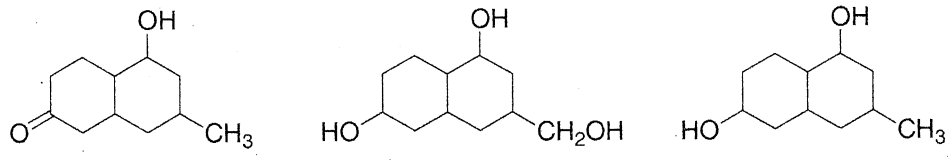
1. (a) What is the force (adsorption or partition) which operates in paper chromatography and also in reverse phase TLC?

(10 Marks)

(b) Describe the materials used for stationary phase in *normal phase* and in reverse phase TLC.

(20 Marks)

(c) Consider the mixture of following three organic compounds, **A**, **B** and **C**.



A **B** **C**

(i) The mixture was applied to a TLC plate (*stationary phase - silica gel*) and developed using ethyl acetate and visualized with an appropriate spray reagent.
Sketch the TLC plate that you would expect to observe in this experiment.

(15 Marks)

(ii) What would be the appropriate solvent system if this mixture to be separated on reverse phase TLC? (10 Marks)

(iii) Sketch the TLC plate if the above mixture was applied to reverse phase TLC and developed in appropriate solvent system.

(10 Marks)

(d) Identify the symbols of the following equations which are applicable to column chromatography.

$$N = \frac{16t_A^2}{W^2}$$

$$L = NH$$

(15 Marks)

(e) The length of the packing of a column used for liquid chromatography is 30 cm. Chromatogram of a mixture containing **X** and **Y** provided the following data.

	Retention time (min)	Width of peak base (min)
Non retained	3.5	
X	6.3	0.40
Y	12.8	0.80

Calculate the following:

(i) The number of theoretical plates from each peak.

(ii) The average number of theoretical plates for the column.

(iii) The average plate height.

(20 Marks)

2. (a) Briefly describe the two types of columns used in Gas chromatography.

(20 Marks)

(b) (i) A mixture containing equal masses of two silylated sugars **P** and **Q** was injected to a gas chromatograph and the areas under peaks were found to be 585 and 380 respectively in the resultant chromatogram. Calculate the response factor of **Q** relative to **P**.

(10 Marks)

(ii) An unknown mixture containing the above two silylated sugars **P** and **Q** was analyzed using GC and the areas under peaks were found to be 265 and 1660 respectively. Calculate the percentage of **Q** in the mixture.

(10 Marks)

(c) A sample of essential oil suspected to contain geraniol. How would you attempt to confirm its presence or absence in the essential oil using GC?

(20 Marks)

(d) Compare refractive index detectors and UV absorbance detectors used in HPLC.

(20 Marks)

(e) Write a short account on **one** of the following.

(i) Ion exchange chromatography

(ii) Gel permeation chromatography

(20 Marks)

3. (a) Comment briefly on the following statements.

(i) Information that could not be obtained using IR spectrum could be obtained using Raman spectrum.

(ii) Alkali and alkaline earth metals are more suitable to be analysed using Flame Emission Spectroscopy (FES) than Flame Atomic Absorption Spectroscopy (FAAS).

(iii) HCN molecule is expected to have four vibration modes.

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

(v) The values of quantum efficiency of three organic compounds A,B and C are 0.55, 0.91, 0.12 respectively. The most strongly fluorescent compound is B.

(08 x 5 = 40 Marks)

(b) (i) Draw and label a schematic diagram of the instrument used in Molecular Fluorescence Specrtoscopy.

(20 Marks)

(ii) How does it differ from the Atomic Absorption Spectrophotometer?

(06 Marks)

(iii) What is the difference in Atomic Fluorescence Specroscopy and Molecular Fluorescence Specrtoscopy with respect to light absorbed and emitted?

(05 Marks)

(c) A substance "X" with a concentration of 2.00×10^{-5} mol dm^{-3} showed an absorbance of 0.655 at 205 nm when measured in a quartz cell using a UV/ Visible Spectrophotometer.

(i) What may be the reason for using a quartz cell? (04 marks)

(ii) Calculate the molar absorptivity coefficient of the substance "X" at 205 nm. Give the answer in correct number of significant figures.

(05 marks)

(iii) Calculate the percentage of transmittance of this sample. (10 marks)

(iv) Calculate the energy required for the excitation of one mole of "X" at 205 nm.

(10 marks)

4. (a) Explain the following in brief.

(i) Rayleigh scattering in Raman Spectroscopy

(ii) Molecular ion peak in a mass spectrum

(iii) A singlet excited state

(iv) A plasma used in plasma atomizers

(v) Phosphorescence

(06 x 5 = 30 marks)

(b) An unknown organic compound containing C,H and may be O showed a molecular ion peak in Chemical Ionization Mass Spectrum (CIMS) at m/z = 91.

(i) What is the actual molecular weight of the compound?

(ii) Give three possible molecular formulae of this compound.

(20 marks)

(c) An acid base indicator in acid medium had maximum absorption at 410nm with a molar absorptivity coefficient of 347 mol^{-1} dm^3 cm^{-1}. When the medium was basic it showed maximum absorption at 640 nm with a molar absorptivity coefficient of 100 mol^{-1} dm^3 cm^{-1}. The absorbance was zero at 640 nm when the indicator was in acid medium and also at 410 nm when the indicator was in basic medium. A small quantity of indicator was added to water and the absorbance at 410nm is 0.118 and at 640 nm it is 0.267. What is the pH of the aqueous solution? (pK_a of the indicator is 3.90)

(40 marks)

(d) When tested for sodium using an emission technique, a solution "A" of a sample of mineral ash gave a meter reading of 56 in arbitrary units. Solution "B" consisting of the same quantity of the unknown solution "A", but with 23 mg cm^{-3} of added sodium, gave a meter reading of 72 in the same units. Calculate the concentration of sodium in solution "A".

(10 marks)

5. (a) Standard reduction potentials corresponding to a number of half reactions at 25°C are given below.

	E°/V
$PbSO_4(s) + 2e \rightarrow Pb(s) + SO_4^{2-}(aq)$	−0.35
$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6e \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$	+0.268
$Pb^{2+}(aq) + 2e \rightarrow Pb(s)$	−0.126
$O_2(g) + 2H_2O(l) + 4e \rightarrow 2H_2O(l)$	+1.23
$2IO_3^-(aq) + 12\,H^+(aq) + 10e \rightarrow I_2(s) + 6H_2O(l)$	+1.196

(i) Giving reasons, indicate which one of the chemicals that appear above will be the

(α) strongest oxidizing agent

(β) strongest reducing agent

(12 Marks)

(ii) Using the Nernst equation calculate the reduction potential of the following half cell (1M = 1 mol dm^{-3}).

$$IO_3^-(0.5\ M), I_2(5\times10^{-4}\ M), H^+\ (2\times10^{-3}\ M) \mid Pt$$

(24 Marks)

(iii) If you were to construct an electro chemical cell using the half cell indicated in (ii) above and a standard calomel electrode as the other half cell,

(α) deduce the EMF of the electro chemical cell.

(β) write down the overall cell reaction.

(14 Marks)

(b) Explain the most essential difference that exists between

(i) Voltammetry in general and Polaragraphy.

(ii) Coulometry and Electrogravimetry when used as analytical techniques.

(15 Marks)

(c) A 1 dm^3 sample of water containing phenol as an impurity was acidified and 25 g of KBr (in excess) was added. A coulometric titration of the sample required 500 seconds at 30 mA to reach the end point. The relative molecular mass of phenol is 94.

(i) Write down balanced chemical equations for the essential processes that occur and are necessary for the satisfactoery conduct of the coulometric titration for phenol.

(ii) Calculate the phenol content in the water in mg dm^{-3}.

(35 Marks)

6. (a) Write complete nuclear equation for the following:

(i) α decay by $^{238}_{92}U$

(ii) Positron decay by $^{19}_{10}Ne$

(iii) Electron capture by $^{40}_{19}K$ (15 Marks)

(b) (i) Define the terms 'half- life' and 'activity' of a radioactive nuclide.

(ii) Iodine- 129 is a product of nuclear fission from a nuclear power plant. It is a β- emitter with a half- life of 1.7×10^7 year. Calculate the activity (in disintegrations per second- dps) of a sample containing 1.00 mg ^{129}I ?

(25 Marks)

(c) (i) Explain the principles behind radiocarbon dating.

(ii) A wooden object found in an Indian burial site shows a ^{14}C decay rate of 5.5 counts per minute per gram of C. The decay rate for freshly cut wood is 13.6 counts per minute per gram of C. Estimate the age of the wooden

item. Write any assumption(s) you make. The half- life of ^{14}C is 5730 years.

(25 marks)

(d) (i) Briefly explain, using a labeled diagram, how radiation can be detected using Geiger- Müller counter.

(ii) Write the conditions that must be fulfilled for an element to be capable of being determined by Neutron Activation Analysis (NAA).

(35 marks)