

UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE SPECIAL DEGREE LEVEL I (SEMESTER II)
EXAMINATIONS- DECEMBER-2017

SUBJECT: Chemistry

COURSE UNIT: CHE 4242 Advanced Analytical Chemistry II

TIME: Two (02) hours

Answer **ALL** questions.

Velocity of light, c	=	$3 \times 10^8 \text{ m s}^{-1}$
Avogadro's number, N_A	=	$6.022 \times 10^{23} \text{ mol}^{-1}$
Universal gas constant, R	=	$8.314 \text{ J} \cdot \text{K}^{-1} \text{ mol}^{-1}$
Boltzmann constant, k	=	$1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$
Planck's constant, h	=	$6.626 \times 10^{-34} \text{ J} \cdot \text{s}$

01. Answer **all** parts

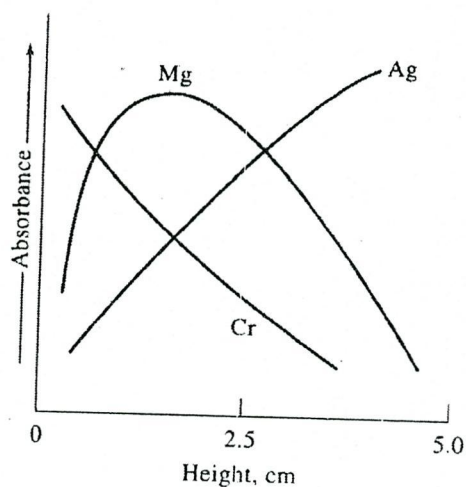
(a) Explain the theoretical basis of atomic absorption, emission and fluorescence spectroscopy.

(15 marks)

(b) Describe the process by which a solution of PbCl_2 in a flask is converted into an atomic vapour in a flame-based atomic spectrophotometer.

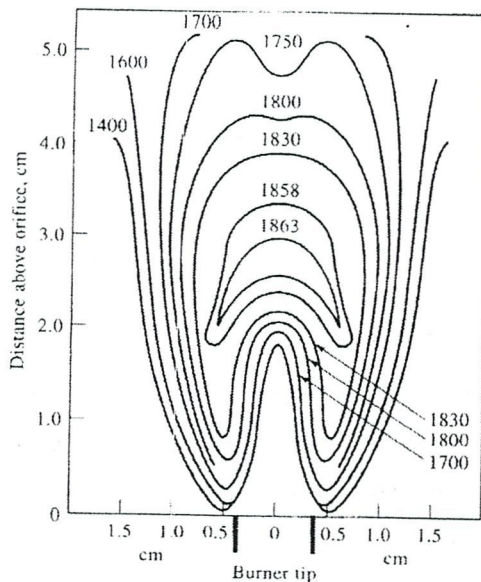
(24 marks)

(c) Describe the effects that are responsible for the three different absorbance profiles in the figure below.



(12 marks)

- (d) Potassium shows an emission line at 766.5 nm in emission spectroscopy. The ground state and excited state degeneracies of potassium is 2 and 6 respectively. For the flame shown below,



- I. Calculate the electron distribution between ground and excited states of potassium at 2.0 cm, 3.0 cm, 4.0 cm and 5.0 cm heights above the flame (assume no ionization).
 - II. Calculate the relative intensities of the emission line at each height compared to 2.0 cm height.
- (34 marks)
- (e) Calculate the mass resolution required to resolve Rh^+ (atomic weight = 102.905503) and Pb^{+2} (^{206}Pb atomic weight = 205.974455) in an ICP-MS experiment.
- (15 marks)

02. Answer **all** parts

(a) Define following terms.

- (i) Liquid-liquid extraction.
- (ii) Extractant.

(10 x 2 marks)

(b) Identify the characteristics of a solvent which should be considered to be used as a solvent in liquid-liquid extraction.

(15 marks)

(c) Chelate type complexes are formed through the reaction between a metal cation (M^{z+}) and anions of organic acids (HA). The complex formation between M^{z+} and A^- proceeds until a neutral complex is formed. If it is assumed that the only extractable metal species is MA_z , the *distribution ratio* of the metal (D_M) can be given by the following equation.

$$D_M = \frac{K_{DC} \beta_z [A]^z}{\sum_0^N \beta_n [A]^n}$$

(i) Name the terms K_{DC} and β in the above equation.

(ii) Acetyl acetone (HA) reacts with Cu(II) ions in aqueous solutions to form a complex CuA^+ and CuA_2 .

(I) Write down an expression for D_{Cu} , the distribution ratio of Cu(II) between the organic phase and water.

(II) Clearly indicating the assumptions you have made and, show that $D_{Cu} = K_{DC} \beta_2 [A^-]^2$ at the lowest concentration of A^- .

(III) Derive an expression for D_{Cu} which you would expect for the highest concentration of A^- .

(35 marks)

(d) Describe the term "distillation".

(10 marks)

(e) Giving reasons explain the situation where vacuum distillation is appropriate.

(06 marks)

(f) Calculate the total pressure of the system and the mole fraction of A in the vapour of a mixture of A and B at a temperature where the vapour pressure of pure A is 700 Torr and that of pure B is 300 Torr. Mole fraction of B in the liquid mixture is 0.3.

(14 marks)

03. Answer all parts

(a) (i) There are many causes of Beer's Law deviations. List causes of nonlinearity.
(10 marks)

(ii) One instrumental limitation to Beer's law is the effect of polychromatic radiation. Consider a line source that emits radiation at two wavelengths, λ' and λ'' . The molar absorptivity at λ' and λ'' are ϵ' and ϵ'' respectively.

(I) Assume that the radiant power of incident radiation is P_0' and P_0'' while transmitted power is P' and P'' . Write an equation for the absorbance A of solution if both wavelengths are measured simultaneously.

(II) Show that if the molar absorptivity at λ' and λ'' are the same ($\epsilon' = \epsilon'' = \epsilon$), the absorbance is equivalent to $A = \epsilon bc$ where b is the path length and c is the concentration.

(III) Construct Beer's law calibration curves over the concentration range of zero to 1×10^{-4} M using $\epsilon' = 1000$ and $\epsilon'' = 1000$, and $\epsilon' = 1500$ and $\epsilon'' = 500$. Assume a value of 1.00 cm for the path-length. Explain the difference between the two curves.

(30 marks)

(b) (i) Why are luminescence methods less widely applicable for quantitative analysis than absorption methods?

(ii) How do you compare luminescence methods with absorption spectrometry?

(iii) Why is a 90-degree instrument geometry employed in a fluorescence spectrometer?

(iv) Show that the intensity of emitted light, F , of a fluorophore is described by the relationship

$$F = \Phi I_0 (1 - e^{-2.303 \epsilon b c})$$

where Φ is the quantum efficiency, I_0 is the incident radiant power, ϵ is the molar absorptivity, b is the path length of the cell, and c is the molar concentration of the fluorophore.

(v) Show how the above equation reduces to a simple linear form for dilute concentrations of the fluorophore.

(vi) At high concentrations fluorescence intensity decreases. What is the reason for the decrease in the fluorescence emission intensity on increasing the concentration?

(vii) What is the concentration of an unknown drug that yielded a fluorescence intensity of 250, if a standard sample at a concentration of $18.73 \mu\text{M}$ produced an intensity of 750 (intensity units are arbitrary)?

(60marks)

04. Answer **all** parts.

- (a) (i) Explain why quantitative infrared absorption methods differ somewhat from ultraviolet/visible molecular spectroscopic methods. (10 marks)
- (ii) The percentage of mixtures of three compounds aspirin, phenacetin and caffeine in a drug is to be determined. Each of these components show distinct carbonyl bands in its IR spectrum and calibration data for known concentrations are listed below in Table 1. Each of the standards was studied by using a 0.1 mm pathlength NaCl transmission cell. IR data obtained for an unknown tablet under the same conditions are given below in Table 2. Estimate the concentrations of aspirin, phenacetin and caffeine in the unknown tablet.

Table 1 Calibration data for the analysis of pure samples.

Component	Concentration (mg ml ⁻¹)	C=O stretching wavenumber (cm ⁻¹)	%T
Aspirin	90	1764	60.67
Phenacetin	65	1511	65.31
Caffeine	15	1656	75.34

Table 2. Percent transmittance values for an unknown drug mixture.

Wavenumber (cm ⁻¹)	%T
1764	62.09
1511	62.81
1656	66.07

(15 marks)

(b) Write short notes on following.

- (i) Plane polarized light
- (ii) Circular birefringence
- (iii) Circular dichroism

(20 marks)

(c) Sketch a simple diagram to show how the light passes through the different components of a CD spectrophotometer starting from the Xenon lamp. Explain briefly.

(15 marks)

(d) Circular dichroism spectroscopy is widely used for the study of biological macromolecules.

- (i) List five applications of CD spectroscopy.
- (ii) List five advantages of using CD spectroscopy over the other techniques.
- (iii) Draw the standard CD curves obtained for alpha-helix, beta-sheet and random coil conformations of a protein. Specify the respective bands used in the identification of each conformer.

(40 marks)