UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE SPECIAL DEGREE LEVEL I (SEMESTER II) EXAMINATIONS- DECEMBER-2016

SUBJECT: Chemistry

COURSE UNIT: *CHE 4242* Advanced Analytical Chemistry II

TIME: Two (**02**) hours

Answer **ALL** questions.

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

01. Answer **all** parts

(a) Draw a block diagram of an atomic absorption spectrophotometer (AAS).

(20 marks)

(b) Draw a diagram of the hollow cathode lamp and briefly explain how it produces monochromatic wavelengths.

(20 marks)

(c) Sodium atoms absorb at a wavelength of 589 nm. What is the energy difference between the ground state and the excited state? At a temperature of 2500 K, what is the ratio of excited state to ground state population if the relative degeneracy is 2?

(15 marks)

(d) Draw a diagram of the inductively coupled plasma (ICP) torch and show the different regions of the plasma and the corresponding temperatures.

(15 marks)

(e) Using a suitable diagram, briefly describe the interface between the plasma torch and the mass spectrometer of the inductively coupled plasma–mass spectrometry (ICP-MS).

(15 marks)

(f) Calculate the mass resolution required to resolve Sn^{+} (atomic weight = 115.90219) and Th^{+2} (atomic weight = 232.03805) in an ICP-MS experiment.

(15 marks)

02. Answer all parts

(a) Consider the extraction of the carboxylic acid, HA, from water to ether.

(i) Write down the possible equilibria present in this system.

(10 marks)

(ii) Derive the relationship between the distribution ratio, D, and H_3O^+ concentration in the aqueous phase ($[H_3O^+]aq$) for the above system.

(20 marks)

(iii) 0.025 *mol* dm^{-3} HA in 50.00 mL of aqueous solution buffered to pH 3 was extracted into 50.00 mL of ether. Calculate the extraction efficiency. K_a of HA is 1.00×10^{-5} and K_D between H_2O and ether is 3.00

(15 marks)

(iv) If benzene is used as the organic solvent instead of ether for the extraction, would you expect any changes to the expression derived in part (ii)? Explain your answer.

(10 marks)

(b) The extraction efficiencies of metal ions show a marked pH dependency. Dithiozone is a chelating agent used to extract metal ions from aqueous phase to organic phase. The minimum pH values for 99% extraction of different aqueous metal ions into organic phase using 4.00 mM dithiozone is tabulated below. Explain how you would separate the metals ions in an aqueous mixture of metal ions containing Cu^{2+}, Cd^{2+}, and Ni^{2+} by extracting with an equal volume of CCl_4.

Metal ion	Minimum pH
Cu^{2+}	-0.8
Zn^{2+}	2.3
Cd^{2+}	3.6
Pb^{2+}	4.1
Ni^{2+}	6.0

(10 marks)

(c) (i) State the conditions that must be satisfied in order to use simple distillation to separate a mixture of two components

(10 marks)

(ii) Some distillation processes are carried out under vacuum. Explain the reason(s) of using vacuum.

(10 marks)

(iii) What is the composition of the vapor which is in equilibrium with a liquid containing 46 mole % of compound A and 54 mole % compound B at its boiling point? The mixture boils at 80 °C and the vapor pressures of pure A and pure B at this temperature are 1050 and 427 torr respectively.

(15 marks)

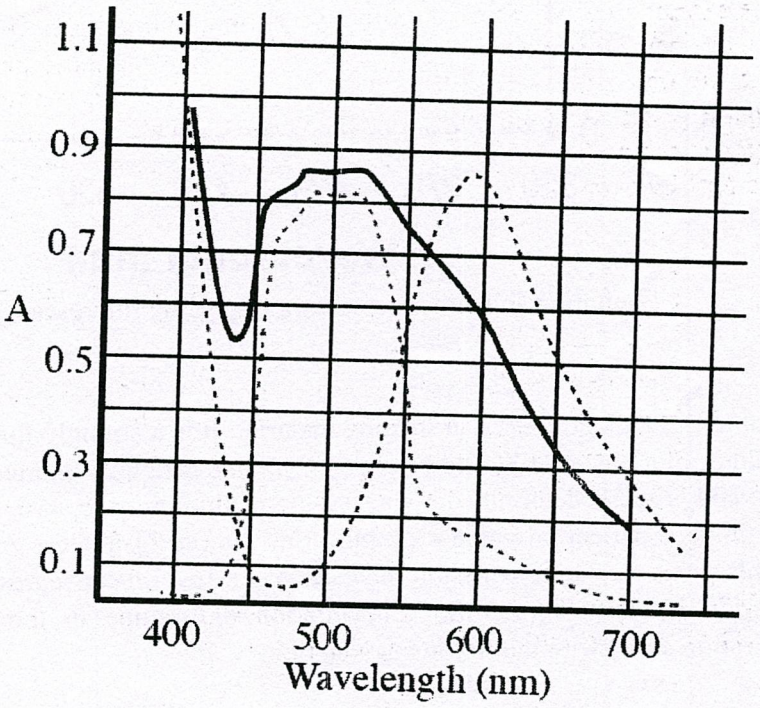
03. Answer **all** parts

(a) Molar absorptivity of acetone is 12 $dm^3\ mol^{-1}\ cm^{-1}$, and it has an absorption maximum at 270 nm in hexane, If the spectrometer in the laboratory can reliably measure transmittance between 10% and 90%. What is the range of acetone concentration that can be measured in a 1.00 cm cell under these circumstances?

(20 marks)

(b) In the following graph the two **dotted curves** are absorbance spectra for pure Co(II) and Ni(II) EDTA complexes. The **solid curve** is obtained from a mixture of the two ions and EDTA in a 1.00 cm cuvette. From the spectra of the pure complexes, the molar absorptivities have been determined at two wavelengths and are summarized in the following table. What is the concentration of Ni(II) and Co(II) in the mixture?

	ε_{500} ($dm^3\ mol^{-1}\ cm^{-1}$)	ε_{590} ($dm^3\ mol^{-1}\ cm^{-1}$)
Ni(II)	1.0	8.7
Co(II)	13.0	2.7



(25 marks)

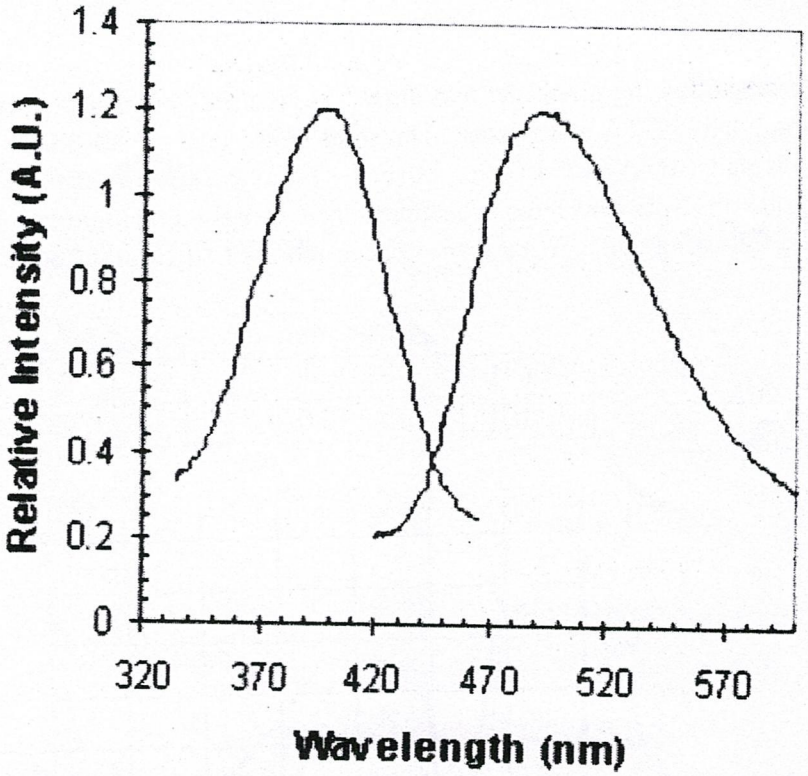
(c) (i) Why is spectrofluorometry potentially more sensitive than spectrophotometry?

(10 marks)

(ii) Differentiate between the terms "excitation spectrum" and "emission spectrum" in fluorescence spectroscopy.

(10 marks)

(iii) During the development of a procedure for the fluorometric assay for the amino acid glycine, the follwing spectra were acquired. The glycine was reacted with a reagent, fluorescamine, which forms a fluorescent product with amines. In order to optimize the assay for sensitivity to glycine, to which wavelength should the excitation monochromator be tuned and to which wavelength should the emission monochromator be tuned?
Comment about self-absorption which may affect the analysis.



Excitation and emission spectra of glycine fluorescamine fluorophore.

(20 marks)

(d) Quinine is an alkaloid used in treating malaria. It is a strongly fluorescent compound in dilute solutions of H_2SO_4 ($\Phi f = 0.55$). Quinine is rapidly excreted from the body in urine and is easily determined by measuring its fluorescence. After ingesting 10.0 mg of quinine, a patient provided a 2.0 mL urine sample 24-h later. Analysis of the urine sample gives a relative emission intensity of 28.16. Linear regression of the relative emission intensity versus the concentration of quinine in the standards gives a calibration curve with the following equation.

$$I_f = 0.124 + 9.978 \times \frac{\text{g quinine}}{\text{mL}}$$

Calculate the concentration of quinine in the urine sample in mg/L and the percent recovery for the ingested quinine.

(15 marks)

04. Answer **all** parts.

(a) Answer the following questions pertaining to IR spectroscopy.

(i) Although most simple quantitative infrared methods of analysis use the intensities of the C=O, N–H or O–H groups, explain why the C=O stretching band is the most commonly used one.

(05 marks)

(ii) Quantitative infrared analysis is based on Beer's law. It is usual to use a baseline method to obtain absorbance of a desired peak. Using an appropriate illustration show how absorbance of an IR peak is determined in this method.

(10 marks)

(iii) What would be the effect of an increase in temperature on the infrared spectrum of a hydrogen-bonded compound?

(05 marks)

(iv) A bromotoluene, C_7H_7Br has a single band at 801 cm^{-1}. What is the correct structure and which vibration is responsible for this band?

(05 marks)

(b) Describe briefly the following terms.

(i) Linearly polarized light
(ii) Circularly polarized light
(iii) Circular dichroism
(iv) Circular dichroism (CD) spectroscopy.

(20 marks)

(c) (i) Give the two criteria that a molecule should fulfil in order to obtain its CD spectrum.

(08 marks)

(ii) What are the major uses of CD spectroscopy?

(12 marks)

(d) The Circular dichroism bands of proteins occur in two distinct regions in the Electro Magnetic Spectrum.

(i) Give the names and the wavelength ranges of the above two regions.

(08 marks)

(ii) Specify the dominated groups which absorb in each region and the use of them.

(12 marks)

(e) Explain briefly how you would use CD spectroscopy in order to identify the conformation of proteins.

(15 marks)