CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

FOURTH YEAR EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

CHEM 452: ANALYTICAL CHEMISTRY II

STREAMS: B.ED (SC), B.Sc **TIME: 2 HOURS**

DAY/DATE: THURSDAY 7/12/2017 **8.30 A.M - 10.30 A.M**

INSTRUCTIONS:

- **Answer Question ONE and any other TWO Questions**
- **Do not write on the question paper**

QUESTION ONE: [30 MARKS]

(a) (i) Discuss the principles and practice of isotope dilution analysis. [5 Marks]

(ii) A crude sample of an organic compound x was analyzed by the technique of isotope dilution. Radiocarbon labeled pure organic compound x (50 mg) having a specific activity of 30,000 cpm g^{-1} was added to the crude sample and equilibrated. The organic compound was separated and 100 mg of the pure sample showed an activity of 25 cpm. Calculate the weight of the organic compound x in the crude sample. [2 Marks]

b (i) List two statistical procedures which should be applied to a calibration curve obtained using instrumental methods. [1 Marks]

(ii) Quinine may be determined by measuring the fluorescence intensity in $1\,MH_2SO_4$ solution. Standard solution of quinine gave the following fluorescence values. Calculate the correlation coefficient r. [5 Marks]

Concentration of quinine x_1(Mg ml^{-1}	0.00	0.10	0.20	0.30	0.40
Fluorescence Intensity Y_i (arb. units)	0.0	5.20	9.90	15.30	9.10

(b) (i) Proximate analysis of a coal sample was carried out using 22 mg and the following weight changes were observed at different temperatures: 105-115ºC (-0.5 mg), 500-800ºC in nitrogen atmosphere (-5 mg), and above 900º in air (-15 mg). Interpret the observed data. [4 Marks]

(c) (ii) Calculate the X-ray fluorescence emission wavelength which appears as strong peak at $2\theta = 46.82^{\circ}$ on being diffracted by the analyser crystal having a d spacing o$f\ 2.24\overset{o}{A}$ [1 Mark]

(iii) Derive any equation showing relationship between fluorescence intensity and concentration. [3 Marks]

(d) (i) Discuss the principles involved in Electron spin n Resonance Spectroscopy. [3 Marks]

(ii) State and explain two advantages of carbon - 13 NMR spectra over proton NMR spectra. [2 Marks]

(iii) Using the 208_{pb} peak in the figure below showing mass spectrum of natured isotopes of pb, find the resolving power.

(iv) State and explain four selection criteria of the Attenuated Total Reflectance (ATR) crystal material for a specific sample analysis. [2 Marks]

(e) Silica particle occupies 40% of the column volume and solvent occupies 60% of the column volume, regardless of the particle size. The column used in figure "a" has an inside diameter of 4.6 mm and was run at a volume flow rate (Uv) of 3.0 mL/mln with a sample size of 20 ml. the column used in Figure "b" has a diameter of dc=2.1 mm.

(i) Calculate the flow rate which should be used in trace "b" to achieve the same linear velocity (Uv) as in trace "a".

(ii) Calculate the sample volume which should be used

(a and b chromatograms of the same sample run at the same linear velocity on 5.0 cm long columns packed with C_{18}-Silica. [1 Mark]

QUESTION TWO

a (i) Explain how neutron activation analysis is carried out. [3Marks]

(ii) A 10 mg sample of steel containing 0.2% of Mn was irradiated for 60 min at a neutron flux of $2\ x\ 10^{12}$ neutrons $cm^{-2}S^{-1}$. The half-life period of 56_{mn} isotope is 2-6 h and the cross section for neutron absorption is $13.3x10^{-2}cm^{-1}$ for 55_{Mn}. Calculate the activity of the sample. [1 Mark]

(b) (i) With the help of a well labeled diagram, explain how thermogravimetry (TG)and differential thermogram (DTG) techniques can be used to follow the decomposition of copper (IT) sulphate pentahydrate. [3 Marks]

(ii) The decomposition of copper (IT) sulphate pentahydrate follows the course shown in Figure I (attached at the back).Analyze the graph and calculate the most likely reactions. [3 Marks]

(iii) Write short notes o a heat flux differential scanning calorimetry. [3 Marks]

(c) In the Bradford protein determination, the colour of a dye changes from brown to blue when it binds to protein. Absorbance of light nit is measured and the results obtained are shown in the table below.

Protein (Mg)	0.00	9.36	18.72	28.08	37.44
Absorbance at 595 nm	0.466	0.676	0.883	1.086	1.280

(i) Deduce the equation of the least squares straight line through these points in the form $Y = [m(\pm U_m)]x + [_b(\pm(U_b)]$ with a reasonable number of significance figures at 95% confidence limit. [4 Marks]

(ii) An unknown protein sample gave an absorbance of 0.973. Calculate the number of micrograms of protein in the unknown and estimate its uncertainty at 95%. Confidence limit values of t for 95% levels of probability are given below. [3 Marks]

Degree of Freedom	1	2	3	4	5	6
Confidence level 95%	12.7	4.30	3.18	2.78	2.57	2.45

QUESTION THREE [20 MARKS]

a (i) A known mixture of compound A and B gave the following HPLC results.

Compound	**Centralization (mg/mL in mixture**	**Peak area (arbitrary units)**
A	1.03	10.86
B	1.16	4.37

A solution was prepared by mixing 12.49 mg of B plus 10.00 mL of unknown containing A and diluting to 25.00 mL. Peak areas of 5.97 and 6.38 were observed for A and B. Find the concentration of A (mg/mL) in the unknown. [3 Marks]

(ii) Two peaks emerge from a reversed phase chromatography column as sketched in the illustration.

Resolution is given by

Resolution $=\frac{\sqrt{N}}{4}\left(\frac{\propto-1}{\propto}\right)\left(\frac{K_2}{1+K_2}\right)$

Where N is plate number $\propto$ is relative resolution and K_2 is the retention factor for the more retained component.

(I) If you decrease the amount of organic solvent in the mobile phase, you will increase retention. Sketch the chromatogram if retention factors increase but N and $\propto$ are constant. [1 Mark]

(II) If you change the solvent type of the stationary phase, you will change the relative retention. Sketch the chromatogram if $\propto$ increases but N and K_1 are constant. [½ Mark]

(III) If you decrease particle size or increase column length, you can increase the plate number. Sketch the chromatogram if N increases by; (i) Decreasing particle size (ii) increasing column length. Assume $\propto$ and K_2 are constant. [½ Mark]

3 b (i) Calculate the volume of 0.0231 M NaoH needed to titrate the eluate when 10.00 mL of 0.0458 M K NO_3 have been loaded on a cation exchange column in the H^+ for m. [1½ Marks]

(ii) A 0.2692 g sample of unknown salt is dissolved in deionized water and loaded into a cation exchange column in the H^+ for m. The column is rinsed with deionized water and the combined loading and rinse solutions are titrated with 0.1396 M KOH. A volume of 30.64 mL is required to reach the end point. Calculate the number of equivalents of cation in the sample. Find the milliequivalents of cation per gram of sample (meq/g) [1½ Marks]

(iii) Calculate the equivalent mass of the sample in 3b (ii) [1 Mark]

3 c (i) In ion-exclusion chromatography, ions are separated from nonelectrolytes by an inon-exchange column. Nonelectrolytes penetrate the stationary phase, whereas ion of the same charge as the resin are repelled by the fixed charges. Because co-ions have access to less of the column volume, electrolytes are eluted before nonelectrolyltes. The chromatogram shows the separation of trichloroacetic acid (TCA, PKg=-0.5), dichloroacetic acid (DCA, PKa=1.1), and monochloroacetic acid (MCA. PKa=2.86) by passage through a cation exchange resin eluted with 0.01 M itcl. Explain why the three acids are separated and why they emerge in the order shown.

3 c (ii) Describe the fundamental differences between ion exchange chromatography and size Exclusion chromatography. [5 Marks]

3 d (i) State and explain seven advantages of applying the sample solutions on the HPTLC plate as sharp bands of 7 mm width with the help of camaglinomat iv sample applicator. [3 Marks]

(ii) Describe the function of filters and monochromators in X-ray spectroscopic instruments. [1 Mark]

QUESTION FOUR [20 MARKS]

(a) A Chemistry attempted to synthesize benzoic acid by the oxidation of benzyl/alcohol. However, a mixture of products was obtained and when chromatography was used to separate them, three organic compounds were obtained. The compounds gave the spectra given in Figure 2 (at the back). Identify the compounds.
[6½ Marks]

(b) Identify the main peaks for a mass specrum of ethyla mine in the Figure below.

c (i) Calculate the chemical shift, δ, in the PPm of a proton (1_H), whose NMR signal is displaced by 220 MHZ with respect to TMS (the field of the spectrometer is 1.879T)
[2 Marks]

(ii) The resonance signal for a proton is displaced by 90MHZ with respect to TMS when measured on 60MHZ spectrometer. What would happen to this displacement if an apparatus of 200 MHZ was employed? [½ Mark]

(iii) What would be the corresponding chemical shift of the same proton with both of these spectrometers? (I_H has a value of Y=2.6752x1010^8 $rad\ s^{-1}T - 1 - y$ [½ Mark]

(d) Describe the differences between fluorescence and phosphorescence [7½ Marks]

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