CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE AND BACHELOR OF EDUCATION (SCIENCE)

CHEM 304: ANALYTICAL CHEMISTRY

STREAMS: **TIME: 2 HOURS**

DAY/DATE: MONDAY 4/12/2017 **8.30 A.M – 10.30 A.M**

INSTRUCTIONS:

- **Answer question one and any other two questions**

QUESTION ONE

(a) Explain how the following chromatography methods address the general elution problem;

(i) Liquid chromatography. [1mark]

(ii) Gs chromatography. [1mark]

(iii) Super critical fluid chromatography. [1mark]

(b) List the types of samples applicable for the gas chromatographic detectors listed below: Flame ionization, thermal conductivity, electron capture, mass spectrometer (ms) thermionic, electrolytic conductivity (hall), photoiozation, fourier transform IR(FTIR). [4marks]

(c) Given the following electrochemical cell:

Ni (s)/$Niso_4$ (0.0025M) // $KI0_3$(0.10M) / Cu$(IO_3)_2$(s) / cu(s)

(i) If the cell potential is 0.512V, find KsP for Cu $(IO_3)_2$ (ignore activity coefficients)

$cu^{2+} + 2e^- \rightleftharpoons$ cu(s) E^0 = + 0.337V at 25°C

$Ni^{2+} + 2e^- \rightleftharpoons$ Ni(s) E^0 = - 0.250V at 25°C [2marks]

(ii)Identify potential sources of errors in the above calculation associated with measuring the cell potential. [4½ marks]

(d) A constant potential of -1.0v was applied to mixture containing cu^{2+} and cd^{2+}, causing both cadmium and copper ions to be reduced and deposited as metals . The voltage was then slowly reduced as shown by voltammogram given below.

(i)State with a reason the metal which is oxidized first. [1marks]

(ii) State with a reason the ion which had a higher concentration in the original mixture. [1mark]

(e) Explain the principle of operation of an ion selective electrode. [2marks]

(ii) How does a compound electrode differ from an ion selective electrode? [1mark]

(iii)A fluoride ion selective electrode has a selectivity coefficient $K_{f-}^{pot}\ OH^-$ =0.1 .Calculate the change in electrode potential when 1.0 x 10^{-4} MF^- at PH 5.5 is raised to p^H 10.5. [2½ marks]

(f) State the advantages of the inductivity coupled plasma compared with a flame in aatomic spectroscopy. [2marks]

(ii) Why is an internal standard most appropriate for quantitative analysis using atomic spectroscopic technique when unavoidable sample losses are expected during sample preparation? [1mark]

(iii) List four different excitation methods employed in emission spectroscopy. [2marks]

(g)(i) Outline the steps involved in the analytical process. [3marks]

(ii) Explain the terms precision and accuracy. [1mark]

QUESTION TWO

(a) (i) The following data was obtained in a set of replicate analysis of the nickel content of an alloy in percent as 7.72, 7.86, 7.54, 4.58, 7.62, 7.66 and 7.05. Assess the data by Q-test for a confidence limit or 95%. Rejection quotient at 95% are given in the table below.

Rejection quotient Q, at 95% confidence limits.

No of observation	3	4	5	6	7	8
Confidence level (Q_{95})	0.970	0.829	0.710	0.625	0.568	0.526

[3marks]

(ii) The protein content of a sample determined from five analysis using a new method of analysis are 46.2%, 45.8%, 46.4% ,45.9% and 46.3%. The protein content of the same sample was determined to be 46.4% by a standard method of analysis. Comment on the acceptability of the new method at 95% level. The value of t for confidence v degrees of freedom for 95% confidence level are given below.

V	1	2	3	4	5	6	7	8
Confidence level at 95%	12.706	4.303	3.182	2.776	2.571	2.447	2.365	2.306

(iii) A calibration exercise for an a tomic absorption method to be used in the determination of a metal yielded the following results.

Reference mg/kg	0	2	4	6	8	10	12
absorbance	0.021	0.050	0.090	0.126	0.173	0.210	0.247

(I) Determine the equation of the least squares straight line through these points in the for m y = [m($\pm$Um] x+[b($\pm$Ub)] with a reasonable number of significant figure at 95% confidence limit. [9½ marks]

(II) An unknown metal sample gave absorbance of mean 0.157 for five replicate calculate the number of mg kg^{-1} of metal in the unknown and estimate its uncertainty at 95% confidence limit. The value of t for 95% confidence limit are given below. [2½ marks]

Degree of freedom	1	2	3	4	5	6	7	8
Confidence level 95%	12.7	4.30	3.18	2.78	2.57	2.45	2.36	2.31

(III) Calculate correlation coefficient. [1mark]

QUESTION THREE (20MARKS)

(a) (i)Chromatograms of compounds A and B were obtained at the same flow rate with two column of equal length. The value of t_m is 1.3 min in both cases.

For the separation of A and B by column 2(i) explain how the flow rate can be changed to improve resolution if broadening is mainly due to longitudinal diffusion.[½ mark]

(ii) If broadening is mainly due to the finite equilibrium time, how should the flow rate be changed to improve the resolution. [½ mark]

(ii)If broadening is mainly due to multiple flow paths, what effect will flow rate have on the resolution? [½ mark]

(b) (i) Why does plate weight depend on linear velocity, not volume flow rate?

(ii) Why is longitudinal diffusion a more serious problem in gas chromatography than in liquid chromatography? [1mark]

(iii)In chromatography, why is the optimal flow rate greater if the stationary phase particle size is smaller? [½ mark]

(iv)A mixture of benzene toluene and methane was injected into a gas chromatograph. Un retained methane gave a sharp spike in 42S, whereas benzene required 251S and toluene was eluated in 333s. Find the adjusted retention time and retention factor for each solute and the relative retention. [3½ mark]

(v)A band from a column eluted at a rate of 1.35 ml/min has a width at half height of 0.272 min. The sample was applied as a sharp plug with a volume of 0.30 ml, the detector volume is 0.20ml and the connecting tubing is 30cm long with a 0.050 cm diameter. Find the variance introduced by injection, detecting and connecting tubing assuming a solute diffusion coefficient of 1.0 x $10^{-9}m^2$/s. What would $w_{½}$ (in time units) be if broadening occurred only on the column? [6½ mark]

(c) (i) When would you use split, splitless or on column injection in gas chromatography? [2½ mark]

(ii) Explain how solvent trapping work in splitless. [1mark]

(iii)Why is splitless injection used with purge and trap sample preparation ? [½ mark]

(iv)Why does mobile phase strength increase as solvent becomes less polar in reversed phase chromatography whereas mobile phase strength increases as solvent becomes more polar in normal phase chromatography? [½ mark]

(II) Why are the relative eluent strengths of solvents in adsorption chromatography fairly independent or solute?

(v)(I) Why is high pressure needed in HPLC. [½ mark]

(II) For a given column why do smaller particles give a higher plate number. [½ mark]

(III)What is a bonded phase in liquid chromatography? [½ mark]

(vi) (I) Why are HPLC particles porous. [½ mark]

(II) Why are particles with 60- to 120 A° stationary phases used to separate polypeptides and proteins? [½ mark]

(vii) Why are silica stationary phases generally limited to operating in the p^H range 2-8? Why does the silica in figure below have improved stability at low p^H?

[½ mark]

QUESTION FOUR (20MARKS)

4.(a) Figure below shows a temperature profile for a furnance atomic absorption experiment. Explain the purpose of each different part of the neating profile.

(ii) Explain how the following background correction technique work in atomic spectroscopy.

(I) Beam chopping . [3½ marks]
(II) Deuterium lamp. [3marks]
(III) Zeeman [6marks]

(iii)State the advantage of Zeeman background correction compared with deuterium lamp background correction. [1½ marks]

(b)(i)Describe the main limitation of the normal dc polarography. [1½ marks]

(ii) List modern polagraphic techniques which has taken care of the above limitation (bcis). [3marks]
