CHUKA   **UNIVERSITY**

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF

CHEM 342: ATOMIC SPECTROSCOPY

STREAMS: BCHM Y3S1   **TIME: 2 HOURS**

DAY/DATE: WEDNESDAY 4/12/2019   **2.30 P.M – 4.30 P.M**

MAAGIZO:
Answer question one and any other two questions

QUESTION ONE

1.   (a) (i) Write short notes on the following

              (I) Limit of detection (LOD)

              (II)Limit of quantitation (LOQ)   [2 marks]

        (iii) You have measured the blank for a determination of arsenic in food samples by

        hydride generation atomic fluorescence spectrometry. The blank values are 0.23 ppb,

        0.14ppb, 0.16ppb, 0.28ppb,0.18 ppb, 0.09 ppb, 0.10 ppb, 0.20 ppb As calculate.

        (I)   LOD at 95% and 99% confidence levels.   [4 marks]

        (II)   Based on your answer in

                 (iii) (I) Calculate the respective LOQ's for arsenic at the two levels . [1 mark]

        (b) (i) Briefly discuss the internal standard calibration method.   [5 marks]

        (ii) Spectrophotometric method for the quantitative analysis of in blood uses   as an

internal standard. A standard containing 1.75 pp b and 2.25 ppb yields a   ratio of (SA/sis of

2.37. A sample of blood is spiked with the same concentration of   giving a signal ratio of 1.80.

Determine the concentration of   in the sample.

        [2 marks]

        (c) (i) Explain why at higher concentration deviations from Beer Lambert's law is

        expected.   [3 marks]

(ii) Explain the major causes of broadening of a spectral line in AAS.   [2 marks]

(d) (i) Why are arc sources often blanketed with a stream of an inert gas.   [1 mark]

(ii) Why is argon widely used for producing plasmas?   [1½ marks]

(iii) State how the varous classifications of the plasma based on the kind of electrical field used to create and sustain it are formed.   [1 ½ marks]

(iv) State four factors which are responsible for decreasing the resolution of the mass spectrometer.

QUESTION TWO (20 MARKS)

2.   (a) (i) A simultaneous determination for cobalt and nickel can be based on absorption by their respective 8 hydroxyquinolmol complexes. Molar absorption corresponding to their absorption maxima are as follows.

Molar absorptivity ,		
	365nm	700nm
Co	3529	428.9
Ni	3228	10.2

Calculate the molar concentration of nickel and cobalt in each of the following solutions using the following data.   [5 marks]

Absorbance A (1.00 cm cell)		
Solution	365nm	700nm
a	0.426	0.026
b	0.792	0.081

2.   (a) (ii) The accompanying data were obtained in a slope ratio investigation of the complex formed between and 1 –cyclopentene -1 di thiocarboxylic acid (CDA). T he measurements were made at 530nm in 1.0 cm cells.

CCDA = 1.00 x M		= 1.00 x M	
,M		CCDA,M	
5.00 x	0.051	9.00 x	0.031

1.20 x	0.123	1.50 x	0.051
3.50 x	0.359	2.70 x	0.092
5.00 x	0.514	4.00 x	0.137
6.00 x	0.616	6.00 x	0.205
7.00 x	0.719	7.00 x	0.240

(I)   Determine the regression equations and hence find the formula of the complex.

[9½ marks]

(II)   Find the molar absorptivity of the complex.   [½ mark]

(b)   (i) Calculate the ration of sodium atoms in the 3p excited to the number in the ground state at 2500 and 2600k { h= 6.6261 x JS, C = 2.998 x m/s, 1 nm = m, the statistical weights for the 3s and 3p quantum states are 2 and 6 respectively. Boltzmann's constant k = 1.38 x .   [2 ½ marks]

(ii) The mean lifetime of the excited state produced by irradiating mercury vapour with a pulse of 253.7nm radiation is 2 x S. Calculate the approximate value for the width the fluorescence line produced in A { 1nm = m, C = 3 x m/s.   [2½ marks]

QUESTION THREE (20 MARKS)

3.   (a) (i) Give reasons to why source modulation is employed in AAS.   [1 mark]

(ii) Explain how light chopper (circular rotating metal disk) can be used as a source modulator.   [2 ½ marks]

(iii) When a sample is introduced into a flames of atomic emission spectroscopy, what processes occur that lead to the emission of radiant energy.   [3½ marks]

(b) Describe the effects that are responsible for the three different absorbance profiles in the figure below and select three additional elements you would expect to have similar profiles.

(ii) Describe how a denterium lamp can be used to provide back ground correction for an atomic absorption spectrum. [2 marks]

(iii) In a hydrogen –oxygen flame, the atomic absorption signal for iron was found to increase in the presence of large concentration of sulphate.

(I)   Suggest an explanation for this observation. [½ mark]

(II)   Suggest three possible methods for overcoming the potential interference of sulphate in a quantitative determination of iron. [1½ marks]

(c)   (i) Why is it that a continuous source like lamp or tungsten lamp can not be used in atomic absorption spectroscopy? [2 marks]

(ii) What are the advantages of plasma sources compared with flame sources for emission spectrometry. [3 marks]

(iii) Why do ion lines predominate in spark spectra while atomic lines predominate in arc and icp spectra? [1 mark]

QUESTION FOUR (20 MARKS)

4.   (a)What are the advantages and disadvantages of atomic emission spectroscopy based on arcs and plasma.   [6 marks]

(b) State with reason the type of ionization technique which would be appropriate for analyzing each of the following;

(i) Gasoline fractions   [1 mark]

(ii) Pesticide residue   [1½ marks]

(iii) I buprofen and acetaminophen.   [½ mark]

(iv) Insuline   [½ mark]

(v) Tripeptides   [½ mark]

(vi) Heavy metals in water.   [½ mark]

(c) Suggest with reason which mass analyzer would be appropriate for the following analysis;

(i) Routine analysis of drug testing samples   [1 mark]

(ii) Analysis of small, 2000 dalton, protein.   [1 mark]

(iii) Analysis of polymers upto 50,000 dalton.   [1 mark]

(iv) High sensitivity testing for chemical warfare agents.   [1 mark]

(v) High resolution analysis.   [1 mark]

(d) (i) A confiscated sample is suspected to be heroin (MW 369.41, structure   below)

Discuss how forensic scientist could confirm the sample as heroin by using different mass spectrometry techniques.   [1 mark]

(ii) Calculate the difference in arrival time at the detector for two singly charged ions in a time of flight mass analyzer, one with m/z = 1252.054 and another with m/z = 1253. 138 accelerated by a potential of 20kv in a 1.750m flight tube.

{IV = 1 , IJ = 1kg
IC = IAS, e = 1.602 x C
IU = 1 amu = 1.6605 x kg
IT = 1 kg   = 1 kg }
Give your answer in nanosecond.   [4 marks]