CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS.

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

CHEM 304: ANALYTICAL CHEMISTRY

STREAMS: BSC (CHEM) Y3S2 **TIME: 2 HOURS**

DAY/DATE: WEDNESDAY 10/04/2019 **2.30 P.M 4.30 P.M.**

INSTRUCTIONS

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

QUESTION ONE: [30 MARKS]

(a) (i) Distinguish between electrolytic cells and electrochemical (Galvanic) cells. [3 Marks]

(ii) Give the half-cell and the overall cell reactions of the following cells and calculate their standard e.m.f of (E^o) at 25°C given that:

$$-¿ \rightleftharpoons Pb(s) + SO_4^{2-} \quad E^O = -0.30\,V$$
$$PbSO_4(s) + 2e^-$$

$$-¿ - \rightleftharpoons Cu(s) \quad E^O = +0.337\,V$$
$$2+¿ + 2e^-$$
$$Cu^{2+}$$

$$-¿ \rightleftharpoons Zn(s) \quad E^O = -0.763\,V$$
$$2+¿ + 2e^-$$
$$Zn^{2+}$$

$$-¿ \rightleftharpoons H_2(g) \quad E^O = 0.000\,v$$
$$+¿ + 2e^-$$
$$2H^+$$

(i) $Pb/PbSo_4(s), \quad \begin{matrix} 2+¿/Cu \\ 2-¿/¿Cu^{¿} \\ So_4^{¿} \end{matrix}$ [1 Mark]

(ii) $\begin{matrix} +¿¿H_2(Pt) \\ 2+¿/¿H^{¿} \\ Zn/Zn^{¿} \end{matrix}$ [1 Mark]

(iii) Draw an electrochemistry cell for the following reaction and then find out the standard free energy and enthalpy change from e.m.f at 25°C given that;

$\begin{matrix} -¿ \\ -¿ \rightleftharpoons 2Br^{¿} \\ Br_2(l)+2e^{¿} \end{matrix} \qquad E^O = 1.0652V$

$\begin{matrix} -¿ \\ -¿ \rightleftharpoons 2Cl^{¿} \\ Cl_2+2e^{¿} \end{matrix} \qquad E^0 = 1.359\,V$

Temperature coefficient of e.m.f = 5.4 x 10^{-4}

$\begin{matrix} -¿ \\ -¿ \rightleftharpoons ½Br_2+Cl^{¿} \\ ½Cl_2+Br^{¿} \end{matrix}$

(F = 96500C) [4 Marks]

(b) (i) Distinguish between reversible cell and irreversible cell. [3 Marks]

(ii) Calculate the activity of chloride ions in the following electrochemical cell.

$\begin{matrix} 3+¿(a=0.075/pt) \\ 2+¿(a=0.15),Fe^{¿} \\ -¿(a=x)/Fe^{¿} \\ Ag/Agcl/cl^{¿} \end{matrix}$

The measured cell potential at 25°C is is 0.440V and

$\begin{matrix} -¿=+0.222 \\ E^O\ Ag, Agcl, Cl^{¿} \end{matrix}$

$\begin{matrix} 2+¿=+0.771 \\ 3+¿, Fe^{¿} \\ E^O\ Fe^{¿} \end{matrix}$ [2 Marks]

(c) (i) Describe the principle of operation of ion-selective electrode. [1½ Marks]

(ii) Briefly explain the difference between ion-selective electrode and compound electrode. [1 Mark]

(iii) A cation-sensitive electrode is used to determine the activity of calcium in the presence of sodium. The potential of the electrode in 0.01M $cacl_2$ measured against an SCE is 195.5 mV. In a solution containing 0.01M C_aCl_2 and 0.01M Nacl, the potential is 201.8 mV. Calculate the activity of calcium ion in an unknown solution if the potential of the electrode in this 215.6 mV versus SCE and the sodium ions activity has been determined with a sodium ion-selective electrode to be 0.012M. Assume Nernstian response.

(The effective diameter of the hydrated ion in nanometers are $\propto_{Na}=0.4, \propto_{Ca}=0.6$)

(d) (i) Write short notes on qualitative analysis by polarography. [1½ Marks]
(ii) State two used of cyclic voltammetry. [1 Mark]
(iii) Compare and contrast the cyclic voltammetry and ordinary polarography. [2 Marks]
(iv) Outline seven advantages of electroanalytical methods. [3 Marks]

(e) Describe sample breaking method in flame Emission and atomic absorption spectroscopy. [1 Mark]

QUESTION TWO: [20 MARKS]

(a) (i) Write short notes on detection of interferences in Emission and atomic spectroscopy. [3 Marks]

(ii) Explain the causes of upward curvature of the calibration plot in the emission and absorption spectroscopy and suggest ways of overcoming these effects.

[1½ Marks]

(b) Comment on each of the following statement:
(i) Increase in sensitivity while using laminar flow burner can be obtained by placing an impact bead directly in the path of the droplets. [1 Marks]

(ii) Atomic absorption spectroscopy uses laminar flow system with a long narrow burner. [½ Mark]

(iii) Atomic emission spectroscopy employs total consumption burner instead of laminar flow burner. [2 Marks]

(iv) Explosion sometimes is observed when using premix burner in atomic absorption spectroscopy. [3½ Marks]

(c) A serum sample is analyzed for potassium by flame emission spectrometry using the method of standard addition. Two 0.500 ml aliquots are added to 5.0 ml portions of water.

To one portion is added 10.0 μl of 0.0500M Kcl solution. The net emission signals in arbitrary units are 32.1 and 58.6. Calculate the concentration of potassium in the serum. [2 Marks]

(d) (i) Explain why air should not be used as a shear flow when using the induction coupled plasma (ICP) as excitation source in atomic emission spectrometry instead argon or nitrogen is used. [½ Mark]

(ii) Give reason as to why two-dimensioanl (2-D) imaging detectors are exclusively used currently in the induction coupled plasma-Atomic Emission spectrometry OR optical Emission Spectrometry. (ICP - AED OR ICP - OES) [1½ Marks]

(iii) Nakahara and Wasa determined germanium in meteorites by ICP-AES using microwave digestion and hydride generation. Consider the following data table from the referenced paper, which compares results of the work with accepted values for germanium in various meteorites.

Determination of Germanium in iron meteorites

Meteorites	Germanium content Mg-g	
	This work	Reported value
Gibeon	+¿0.01 −¿¿ 0.079¿	0.111
Henbury	+¿1.3 −¿¿ 30.1¿	34
Mundrabilla	200. +¿11.7 −¿¿ 5¿	208
Toluca	250. +¿15.6 −¿¿ 1¿	246
Odessa	285. +¿11.3 −¿¿ 2¿	285

The mean $\overset{+¿}{\underset{-¿¿}{❑_¿}}$ Standard deviation of the ten replicate determination.

Assume that the reported values are the true values of the concentration of germanium in the meteorites, hence determine whether the values determined by the workers are equal to or different from the reported values at the 95% confidence level. [4½ Marks]

QUESTION THREE: [20 MARKS]

(a) (i) List four critical requirements for coupling gas chromatography with either mass spectrometer OR infrared spectrometer. [3 Marks]

(ii) Briefly discuss split-splitless injector used in Gas Chromatography. [4½ Marks]
(iii) Write short notes on septum bleed in Gas Chromatography. [2½ Marks]
(iv) State three (3) advantages of low bleed column in Gas Chromatography. [1½ Marks]

(b) (i) When a mixture containing 1.21 mmol of 1-butanol and 0.95 mmol of 1-pentanol was chromatographed the ratio of peak areas of butanol to pentanol was found to be 1.02. Calculate the response factor for butanol. [1 Mark]

(ii) The mixture in Q b (i) above contained 0.57 mmol of 1-pentanol was added as an internal standard at the end of the reaction. The peak areas of butanol and pentanol were found to be 785 and 1331 respectively. Calculate millimoles of 1-butanol present in the mixture. [1 Mark]

(c) A chromatogram of a mixture of species A and B provided the following data: -
The length of packing = 32.6

	Retention, Time min	Width of peak Base (W), min
Non retained	2.5	-
A	8.5	0.75
B	27.4	2.23

Calculate for species A and B

(i) The resolution. [1 Mark]

(ii) The selectivity factor [1 Mark]

(iii) The length of column necessary to separate the two species on the column with a resolution of 2.5 [3 Marks]

(iv) The time required to separate the two species in the column in part (iii)

[1½ Marks]

QUESTION FOUR: [20 MARKS]

(a) (i) Explain some of the constraints affecting UV/Visible detectors used for testing of drug molecules while using reverse-phase high performance liquid chromatography (RP-HPLC). [1 Mark]

(ii) Discuss the advantages and disadvantages of pre-column off line and post-column on line derivatisation in liquid chromatography. [4 Marks]

(b) With the help of a flow diagram, suggest the process for validating chromatographic methods. [5 Marks]

(c) (i) Analyses of a sample of iron ore gave the following percentage values for the iron content:
7.08, 7.21, 7.12, 7.09, 7.16, 7.14, 7.07, 7.14, 7.18, 7.11.

Calculate the mean, standard deviation, coefficient of variation for the values, the standard error of the mean. [4½ Marks]

(ii) The following values were obtained for the determination of cadmium in a sample of dust: 4.3, 4.1, 4.0, 3.2 $\mu g\, g^{-1}$. Should the value of 3.2 be rejected?
[1½ Mark]

(iii) The mean $\acute{x}$ of four determination of the copper content of a sample of any alloy was 8.27% with a standard deviation s = 0.17%. Calculate the 95% confidence limit for the true value. [1½ Marks]

(iv) If the mean of the 12 determination is $\acute{x}=8.37$, and the true value is $\mu=7.91,$ state or explain whether or not the result is significant if the standard deviation is 0.7. (Take $t_{tab}\, at\, 95$ confidence level = 2.20) [1½ Marks]

(v) The standard deviation from one set of 11 determinations was $S_A=0.210$ and the standard deviation from another 13 determinations was $S_B=0.64.$ Is there any significant difference between the precision of these two sets of results? [1 Mark]
(Take F_{tab} at 95% confidence level = 2.91]

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