

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

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

CHEM 342: ATOMIC SPECTROSCOPY

STREAMS: BSC

TIME: 2 HOURS

DAY/DATE: MONDAY 22/03/2021

11.30 A.M. – 1.30 P.M.

INSTRUCTIONS:

- **Answer question ONE and any other TWO questions.**

QUESTION ONE

- (a) (i) Summarize the instrument operation characteristics. (5 marks)
- (ii) Compare atomic emission and atomic absorption methods in terms of their main advantages and disadvantages. (5 marks)
- (b) (i) Write short notes on self-absorption as applied in atomic emission spectroscopy. (5 marks)
- (ii) Outline the advantages and the difficulties of operating direct current arc when used as excitation devices in emission spectroscopy. (4 marks)
- (c) (i) Discuss Zeeman effect in atomic spectroscopy. (5 marks)
- (ii) List the four effects which causes spectral lines to be broader than predicted by uncertainty principle. (2 marks)

- (iii) Demonstrate the wavelength dependence of lifetime broadening by calculating the minimum theoretical bandwidth at 200nm, 400nm and 700 nm assuming a lifetime of ions $\{\hbar = 1.0546 \times 10^{-34} \text{ J} \cdot \text{s}\}$
 $C = 2.99 \times 10^8 \text{ m/s}$, $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}\}$ (3 marks)

- (d) Explain the following statement:

“The emission spectrum of a HCl of Mo has a sharp line at 313.3 nm as long as the lamp current is less than 50 mA. At higher current the emission line develops a cup like crater at its maximum.

(1 mark)

QUESTION TWO (20 MARKS)

- (a) (i) Explain why an internal standard can be used for ICP-OES but is not used for AAS. (1 mark)

- (ii) Discuss the various consideration which must be taken into account while choosing internal standard to be used in inductively coupled plasma atomic emission spectrometry. (5 marks)

- (iii) Strontium was being determined by flame emission spectrophotometry. A set of strontium standards was prepared to each of the standards and the samples of a fixed amount of scandium (as an internal standard) was also added. The emission intensities for each of the solutions were measured and the results (data) obtained are given in the table below:

Sr (mg/v)	0.00	1.00	2.00	3.00	4.00	5.00
Sr (Emission)	0.0	16.6	37.8	43.2	68.7	95.2
Sc Emission	19.4	21.5	24.7	18.6	22.3	24.6
Sample emission	A				45.6	20.2
	B				102.7	4.6

- (I) Determine the strontium concentration (mg/v) in each of the samples. (5 marks)

- (II) Explain why you do not need the concentration of scandium to answer Q(iii) (I) above. (1 mark)

- (b) Write short notes on hyperfine structure in spectroscopy. (5 marks)

- (c) Explain why NH_4NO_3 is rarely used nowadays as a modifier in electro thermal atomic absorption spectrometry. (3 marks)

QUESTION THREE (20 MARKS)

- (a) The complex that is formed between zinc (II) and the chelating reagent X was studied at $25^\circ C$ by measuring the absorbance of solutions in which the analytical concentration of zn (II) was held constant at $1.38 \times 10^{-4} mol/L$, while the concentration of X was varied measurement were made in 1.00 cm cell at 645 nm and results obtained are given in the table below

Concentration of X mol/L	Absorbance A	Concentration of x mol/L	Absorbance A
2.0×10^{-5}	0.058	3.5×10^{-4}	0.720
5.0×10^{-5}	0.134	4.50×10^{-4}	0.765
9.0×10^{-5}	0.245	5.50×10^{-4}	0.781
1.5×10^{-4}	0.405	7.0×10^{-4}	0.779
2.5×10^{-4}	0.612	9.0×10^{-4}	0.780

- (I) Evaluate the composition of the complex. (3 marks)
- (II) Calculate a value for the formation constant (stability constant) ($2\frac{1}{2}$ marks)
- (III) Determine the change in Gibb's free energy (ΔG). (1 mark)

- (b) 2-naphthylamine has the following absorbance

β -naphthol	3.49	0
β -naphthol anion	3.70	3.47
	$\log \epsilon (285 \text{ nm})$	$\log \epsilon (346 \text{ nm})$

A solution of buffer containing $1 \times 10^{-4} M$ β -naphthylamine with pH 9.20 showed an absorbance of 0.373 and 0.098 at 285 and 346 nm. Calculate the pK value of β -naphthylamine (5 marks)

- (c) Titanium (iv) and vanadium (v) form coloured complexes when treated with hydrogen peroxide in 1m sulphuric acid. The titanium complex has an absorption maximum at 415 nm and the vanadium complex has an absorption maximum at 455 nm. A $1.00 \times 10^{-3} M$ solution of the titanium complex exhibits an absorbance of 0.805 at 415 nm and of 0.465 at 455 nm, while a $1.00 \times 10^{-2} M$ solution of the vanadium complex exhibits absorbance of 0.400 and 0.600 at 415 and 455 nm respectively. A 1.00 g sample of an alloy containing titanium and vanadium was dissolved treated with excess hydrogen

peroxide and diluted to a final volume of 100 ml. The absorbance of the solution was 0.685 at 415 nm and 0.513 at 455 nm. Calculate the percentage of titanium and vanadium in the alloy

$$\{\text{Ti}=47.867, \text{v}=50.9415\} \quad (6 \text{ marks})$$

- (d) Explain why is it that, for the same concentration of nickel the absorbance at 352.4 nm was found to be about 30% greater for a solution containing 50% ethanol than for an aqueous solution when using atomic absorption spectrophotometer as a technique for analysis
(2 marks)

QUESTION FOUR (20 MARKS)

- (a) (i) Explain why is it necessary to have the mass spectrometer chamber under vacuum (very low pressure) for it to work. (1 mark)
- (ii) Outline the advantages and disadvantages of matrix-assisted laser desorption/ionization. (MALDI) (4 marks)
- (iii) Describe the working principles of time of flight mass spectrometer. (5 marks)
- (iv) A ${}^{35}_{17}\text{Cl}^{+6}$ ion travels through the flight tube of a TOF mass spectrometer with a kinetic energy of $3.65 \times 10^{-16} \text{ J}$. This ion takes $1.04 \times 10^{-5} \text{ s}$ to reach the detector. A vogadrols constant (L)= $6.022 \times 10^{23} \text{ mol}^{-1}$. Calculate the length in meters.
- (b) Explain why is the CaOH spectrum in figure 1 below is much broader than the barium emission line. (2 marks)

- (c) Sodium in tap water was analysed by flame emission spectroscopy using a simple flame photometer utilizing a butane/air flame. The following calibration graph was obtained

- (i) Why does the graph slope down at high concentrations? ($\frac{1}{2}$ mark)
- (ii) What can be done if anything to get a straight line for the calibration? ($\frac{1}{2}$ marks)
- (iii) The insert shows a zoom of the low concentrations why does this show a negative deviation from a straight line calibration? ($\frac{1}{2}$ mark)
- (iv) What can be done to remedy this part of the calibration graph? ($\frac{1}{2}$ marks)
- (v) Spectral interference can be a real problem in emission techniques. However in this scenario we don't have to worry about spectra interference. Explain. (1 mark)
- (d) Use the Boltzmann distribution equation to calculate the percentage of magnesium atoms that are in the excited state (electronic transition from 3 s to 3 P, $\lambda = 285.2 \text{ nm}$) under the conditions of
- (i) Air-acetylene flame at 2,955k. (2 marks)
- (ii) A plasma at 6,955k. Assume that $g_e/g_a = 3$ ($h = 6.626 \times 10^{-34} \text{ JS}$,
 $C = 2.99 \times 10^8 \text{ M/S}$ $1 \text{ NM} = 1 \times 10^{-9} \text{ M}$, Boltz many constant
 $(k) = 1.38065 \times 10^{-23} \text{ J K}^{-1}$) (1 mark)
- (e) In AES one of the concerns of using too hot of a source is the generation of atomic ions instead of atomic atoms. The plasma source used in AES is much hotter than the atomizer's used in AAS, yet we do not observe an overwhelming abundance of atomic ions in the sample spectrum. Explain. (1 mark)
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