UNIVERSITY
OF
JOHANNESBURG

DEPARTMENT OF CHEMISTRY

MODULE   **CEM8X03**
                    ATOMIC SPECTROSCOPY

CAMPUS   **APK**

EXAM   **JUNE 2019**

DATE: 04 JUNE 2019   **SESSION: 08:30**

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EXTERNAL MODERATOR: **PROF. KL MANDIWANA**

DURATION: **3 HOURS**   **MARKS:**   **100**
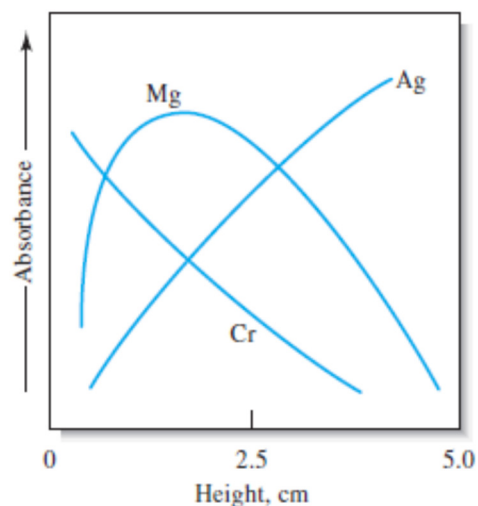
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NUMBER OF PAGES: 7

GENERAL INSTRUCTIONS

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There are a total of 3 questions in this examination booklet. Attempt ALL QUESTIONS. For full credit you must write adequate reasoning and show all steps involved in calculations.

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QUESTION ONE

1.1   Briefly explain robustness and ruggedness of a method.   (4)

1.2   A new lab technician has been given a task to analyse copper (Cu) in urine samples collected from mine workers. The technician would like to start with making a set of standards to make a calibration curve. He is not sure about a few things and needs your assistance. Here are a few questions he has:

(a) He was advised by his manager to be cautious of the matrix effect. What calibration method can he use to account for the matrix, and briefly explain how the standards and samples are prepared?   (4)

(b) The technician decides to prepare 100 ppm Cu^{2+} standard solution from $CuSO_4.5H_2O$ (249.5 g mol^{-1}) by dissolving it in de-ionised water and diluting to a 50.00 mL volumetric flask. With aid of calculations, describe the preparation of standard solution.   (3)

1.3   Discuss the role of matrix modifiers in GF-AAS. Give at least two examples of matrix modifiers.   (6)

1.4   Distinguish between collisional broadening and Doppler broadening.   (6)

1.5   The temperature of a flame depends on the position of the radiation beam emanating from the lamp above the burner tip, making it is necessary to adjust the height of the flame to get best signal. The figure below shows the effect of flame temperature on absorbance of analytes. Explain why the sensitivity varies with the type of element.   (8)

1.6 Why is atomic emission more sensitive to flame instability than atomic absorption? (4)

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QUESTION TWO

2.1 The following calibration data were obtained for the determination of iron (Fe) in an unknown sample. A 2.0 g aliquot of a solid sample containing iron was dissolved in deionized water and diluted to 100 mL. The sample solutions were prepared in triplicate and the signal corresponding to each solution was recorded using flame atomic absorption spectrometry. The following replicate data were then obtained:

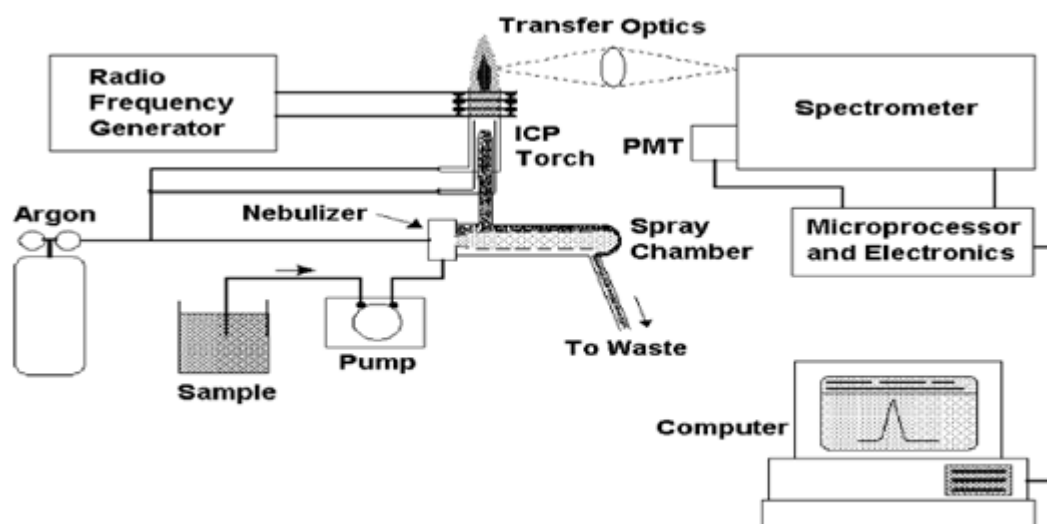| Concentration (ppm)	Number of replicates	Mean absorbance	Standard deviation
0	25	0.031	0.0075
2	4	0.173	0.0094
6	5	0.422	0.0084
10	5	0.702	0.0084
14	5	0.956	0.0085
Unknown 1	1	0.622	
Unknown 2	1	0.597	
Unknown 3	1	0.611	

A least-squares analysis of calibration data for the quantification of iron based on its absorbance yielded the following regression equation:

$$A = 0.066C_{Fe} + 0.0341$$

where C_{Fe} is the iron concentration in ppm and A is the absorbance. Answer questions (a) to (d) based on the information provided.

(a)   Calculate the individual concentrations and the mean concentration for iron in the original solid sample. (7)

(b)   What is the calibration sensitivity? (1)

(c)   Calculate limit of detection for this method. (2)

(d)   Calculate the limit of quantitation for this method. (2)

2.2   The figure below shows the most common components of an ICP-OES system. Answer questions (a) through (d) based on this figure.

Major components and layout of a typical ICP-OES instrument.

a)   What are two functions of a spray chamber? (2)

b)   Discuss the importance of drain in ICP-OES.   (4)

c)   Is a vacuum system required for the detection of elements by this system? Explain.   (3)

d)   The argon gas is split into three lines. Name and explain the function of each flow of argon gas.   (7)

2.3   Why is an arc excitation often done in a controlled gas atmosphere?   (4)
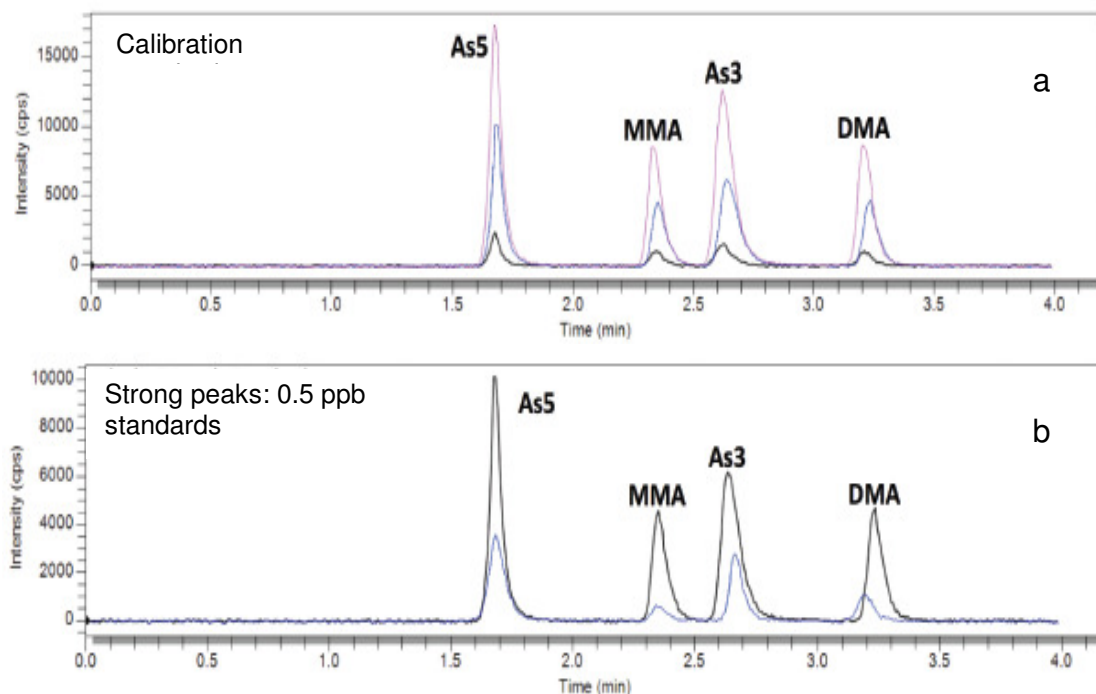
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QUESTION THREE

3.1   Interferences are commonly encountered in chemical analysis. Answer questions (a) through (d) based on types of interferences encountered in ICP-MS analysis.

(a) Briefly explain non-spectroscopic interferences in ICP-MS.   (2)

(b) Briefly explain spectroscopic interferences in ICP-MS.   (4)

(c) What is the limitation of quadrupole mass analyzer?   (2)

(d) Briefly explain how collision/reaction cell technology is applied to eliminate interferences in ICP-MS analysis.   (6)

3.2   ICP-MS is a very powerful tool for detecting and analysing trace and ultra-trace elements, however, coupling the ICP torch with the mass spectrometer is often compared to "Placing of the Earth about half a mile away from the Sun". Briefly describe the role and nature of the interface between the ICP torch and the mass spectrometer in an ICP-MS.   (5)

3.3 Chromatograms of (a) calibration standards of four arsenic species (As^{5+}, MMA, As^{3+}, and DMA) and (b) a mixture of arsenic standards, 0.5 ppb each, and apple juice sample determined using HPLC hyphenated to ICP-MS are shown below.

Answer questions (a) to (c).

(a) A mixture of arsenic standards, 0.5 ppb each, and an apple juice sample were separately injected into the column and provided the chromatograms shown in figure (b). Why is the tracing of a chromatogram of a standard over that of a sample important? (3)

(b) Outline the procedure you would follow to prepare an apple juice sample for the determination of arsenic species by HPLC hyphenated to ICP-MS. (3)

(c) How would you determine the concentration of the arsenic species in the apple juice sample based on the information in figures (a) and (b)? (4)

3.5 Explain how XRF works. (4)

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The Periodic Table

Period	1	2											13/III	14/IV	15/V	16/VI	17/VII	18/VIII
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.30	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	La- Lu	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 210.0	85 At 210.0	86 Rn 222.0
7	87 Fr 223.0	88 Ra 226.0	Ac- Lr	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	......								

s block | d block | | p block

Lanthanides

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 144.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 239.1	95 Am 243.1	96 Cm 247.1	97 Bk 247.1	98 Cf 252.1	99 Es 252.1	100 Fm 257.1	101 Md 256.1	102 No 259.1	103 Lr 260.1

Actinides

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