MACHAKOS UNIVERSITY

University Examinations 2016/2017

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

FOURTH YEAR FIRST SEMESTER EXAMINATION FOR BACHELOR OF EDUCATION (SCIENCE)

SCH 404: INSTRUMENTAL METHODS

DATE: 4/8/2017 **TIME: 8:30 – 10:30 AM**

INSTRUCTIONS

- The paper consists of **two** sections.
- Section **A** is **compulsory**.
- Answer any **two** questions from section **B**.
- Find Periodic Table on the last Page.

Required Data/Information

- **Rydberg's constant (R) =** 10 973 731.6 m^{-1}
- **Planck's constant (h)=**$6.63x10^{-34}$ Js
- **Speed of light in a vacuum (C)** = $2.998x10^{8}$ m/s
- **Boltzmann Constant (K) = 1.38 x 10^{-23} $m^2kgS^{-2}K^{-1}$**

This Paper Consists of 8 Printed Pages. Please Turn Over.

SECTION A:COMPULSORY

QUESTION ONE (30 MARKS)

a) Define the following terms

i. Lambda max (1 mark)

ii. Stokes shift (1 mark)

iii. Mass Spectroscopy (1 mark)

b) Distinguish between the following terms as used in various spectroscopic techniques

i. Rayleigh scattering and tyndall scattering (2 marks)

ii. Fluorescence and phosphorescence (2 marks)

iii. Bending vibrations and stretching vibrations (2 marks)

c) With specific reference to the analysis of an aqueous $MgCl_2$ solution using Atomic Absorption Spectrometry (AAS), and describe the processes that are likely to occur. (5 marks)

d) H-Cl absorbs a photon of energy 5.94×10^{-20} J.

i. Determine the spectral region (2 marks)

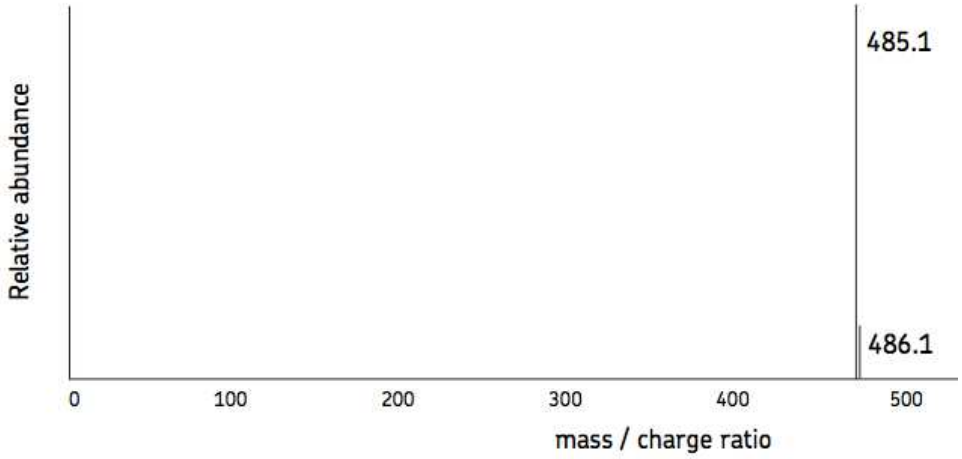
ii. If the quantum number of the initial state of the transition is n = 1. Determine the quantum number of the final state of the transition (3 marks)

e) Compare the UV absorption spectrum of 1-butene to that of 1,3-butadiene (2 marks)

f) Consider the analysis of Magnesium using a graphite furnace operated at 2600K. Determine the fraction of Mg atoms in the excited state that has a ΔE corresponding to light at 589 nm given that the degeneracies of the excited and ground states are 2 and 1 respectively (4 marks)

g) List three advantages of FT-IR spectrophotometers over conventional IR spectrophotometers that uses a monochromator. (3 marks)

h) The mass spectrum shown is of a protein that has been produced by electrospray ionization. Determine the relative molecular mass of this protein. (2 marks)



SECTION B:
ATTEMPT ANY TWO QUESTIONS (20 MARKS EACH)
QUESTION TWO (20 MARKS)

a) Using a relevant example, briefly describe the theory of molecular fluorescence spectroscopy (5 marks)

b) List the main advantage of fluorescence over UV-Vis spectroscopy (0.5 marks)

c) Discuss 5 factors that can affect quantitative accuracy in fluorescence spectroscopy (7.5 marks)

d) Briefly explain why:

i. Fluorescence spectrometers often use "double- beam optics" (2 marks)

ii. The radiation source for fluorescence spectrometry should be more powerful than for absorption spectroscopy (2 marks)

iii. Phosphorescence measurements are usually determined at a low temperature and not room temperatures (2 marks)

e) Explain how photo-decomposition can be reduced in fluorescence spectroscopic measurements (1 mark)

QUESTION THREE (20 MARKS)

a) Describe the process by which a solution of a metal salt in a flask is converted into an atomic vapor in a flame-based atomic spectrophotometer (5 marks)

b) Draw a block diagram showing the components of a typical single beam flame atomic absorption spectrophotometer (4 marks)

c) Explain why a continuous source like D_2 lamp or tungsten lamp can not be used in

atomic absorption spectroscopy (2 marks)

d) In higher-temperature sources, sodium atoms emit a doublet with an average wavelength of 1139 nm. The transition responsible is from the 4s to 3p state. Calculate the ratio of the number of excited atoms in the 4s to the number in the ground 3s state in

i. An acetylene-oxygen flame (3000 ^{o}C) (3 marks)

ii. The hottest part of an ICP source (9000 ^{o}C) (3 marks)

e) Briefly provide a solution for the following types of flame atomic Absorbance interferences

i. Non-vaporization of high- melting compounds, such as phosphates and oxides (1 mark)

ii. Formation of stable oxides in the flame (1 mark)

iii. Ionization of atomic species, producing ions which do not absorb at the same wavelength as the atomic species (1 mark)

QUESTION FOUR (20 MARKS)

a) Atomic Absorption Spectroscopy (AAS) can be used to determine elemental concentrations. A student prepared standard arsenic solutions and the absorbance of each solution was measured. A Garden soil sample was also prepared. 10 mL of this prepared soil sample was placed in a 100 mL volumetric flask and enough water was added to make it up to the mark. The absorbance of this diluted soil sample and the standard solutions were recorded as shown below.

Sample	**Concentration (ppm)**	**Absorbance**
Blank	0.00	0.00
Standard 1	1.00	0.17
Standard 2	2.00	0.34
Standard 3	3.00	0.48
Standard 4	4.00	0.65
Standard 5	5.00	0.83
Sample	?	0.26

i. Explain the purpose of carrying out the blank analysis (1 mark)

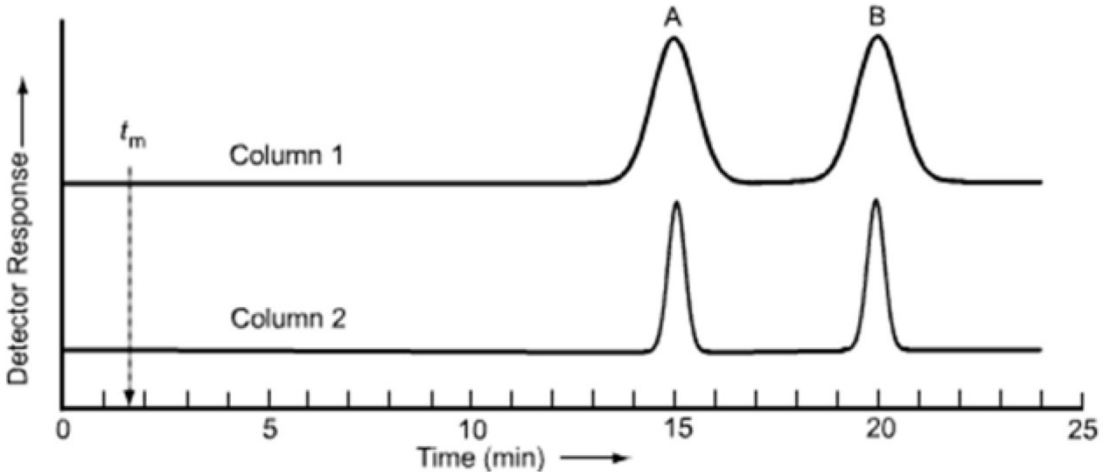
ii. Calculate the concentration of arsenic (Ar) in the original (undiluted) soil sample. Show your working (5 marks)

b) High performance liquid chromatography is basically a highlyimproved version of Column chromatography

i. Differentiate between normal phase HPLC and reversed phase HPLC (2 marks)

ii. Briefly describe how you can use HPLC to carry out both qualitative and quantitative analysis of a given compound (4 marks)

c) Chromatograms of A and B shown below were obtained at the same flow rate with two HPLC columns of equal length. State and explain the



i. Column with more theoretical plates (1 mark)

ii. Column that gave a higher resolution and calculate the resolution in each case (3 marks)

iii. Column that gave a greater relative retention (1 mark)

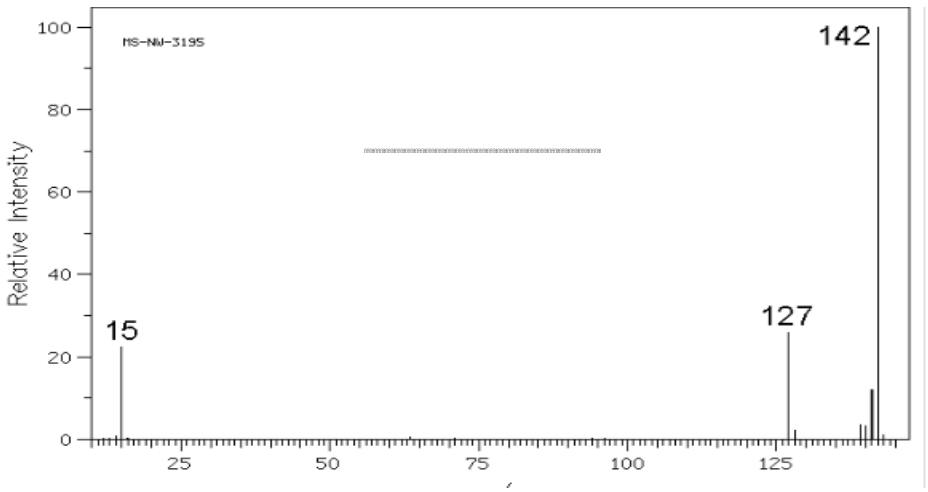
iv. Compound that has a higher retention factor (1 mark)

d) Suggest two detectors that can be used with HPLC instrument (2 marks)

QUESTION FIVE (20 MARKS)

a) Briefly explain the principle of mass spectrometry (3 marks)

b) Shown below is the mass spectrum of a halo alkane A



i. What is the m/z value for the base peak (1 mark)

ii. Determine the fragments that are responsible for the peaks at m/z = 127 and m/z = 15 (2 marks)

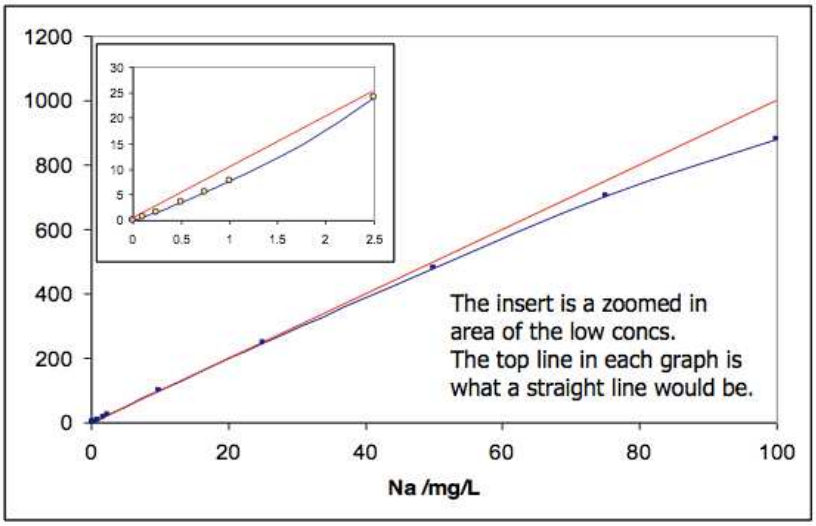
iii. Using the information in the mass spectrum, determine the molecular formula of compound A (2 marks)

c) Briefly explain

a) The principle of flame emission spectrometry (4 marks)

b) Four advantages of emission methods based on plasma excitation sources (4 marks)

d) Sodium in tap water was analyzed by flame emission spectroscopy using a simple flame photometer utilizing a butane/air flame. The following calibration graph was produced. The insert is a zoomed in area of the low concentrations. The top line in each graph is what a straight line would be.



a) Why does the graph slope down at high concentrations? (1 mark)

b) What can be done to get a straight line for the calibration? (1 mark)

c) The insert shows a zoom of the low concentrations. Why does this show a negative deviation from a straight-line calibration? (1 mark)

d) What can be done to remedy, if anything, this part of the calibration graph? (1 mark)

-END-

1																	18
1 **H** 1.0079	2											13	14	15	16	17	2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.180
11 **Na** 22.990	12 **Mg** 24.305	3	4	5	6	7	8	9	10	11	12	13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.065	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.098	20 **Ca** 40.078	21 **Sc** 44.956	22 **Ti** 47.867	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.845	27 **Co** 58.933	28 **Ni** 58.693	29 **Cu** 63.546	30 **Zn** 65.409	31 **Ga** 69.723	32 **Ge** 72.64	33 **As** 74.922	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.798
37 **Rb** 85.468	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57-71 *	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89-103 #	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (270)	109 **Mt** (268)	110 **Ds** (281)	111 **Rg** (272)	112 **Uub** (285)	113 **Uut** (284)	114 **Uuq** (289)	115 **Uup** (288)	116 **Uuh** (291)		118 **Uuo** (294)

* Lanthanide series	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
# Actinide series	89 **Ac** (227)	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)