UNIVERSITY OF SWAZILAND
FIRST SEMESTER EXAMINATION, 2014/2015

TITLE OF PAPER	**:**	**Special Analytical Techniques**
COURSE CODE	**:**	**c614**
TIME ALLOWED	**:**	**Three (3) Hours.**
INSTRUCTIONS	**:**	**Answer any <u>Four</u> (4) Questions. Each Question Carries 25 Marks**

DO NOT OPEN THIS QUESTION PAPER UNTIL PERMISSION TO DO SO HAS BEEN GRANTED BY THE CHIEF INVIGILATOR.

Question 1 (25 marks)

(a) Briefly, discuss the interactions of the following radiations with matter

(i) β-rays [10]

(ii) γ-rays [15]

Question 2 (25 marks)

(a) A commonly employed activation method is the 'Neutron Activation Analysis', (NAA). For this method (i.e NAA) :

(i) Distinguish between the two types i.e RNAA and INAA. [2]

(ii) Discuss the general principles of this method and the general steps usually taken when employing this method. [5]

(iii) Identify the main sources of neutrons for this method. [3]

(iv) Give three advantages and two limitations of this method [5]

(v) Summarize the procedure for the INAA (instrumentation neutron activation analysis). [4]

(b) A 0.500-g sample of newly developed Ni alloy and 1.00-g of a standard alloy were set up in a nuclear reactor for irradiation with neutrons. On completion of irradiation, both the sample and the standard were allowed to cool. Their activities were found to be 1020 counts/min for the sample and 3540 counts/min for the standard. If the standard was known to contain 5.93% w/w Ni, calculate the % w/w Ni in the new alloy, using the method of external standards. [6]

Question 3 (25 marks)

(a) For the 'Isotope Dilution Analysis' :

(i) Summarize the usual general procedure for the method. [2]

(ii) Enumerate the requirements for a successful application of this method. [3]

(iii) Discuss the specific procedural steps involved when employing the Direct Isotope Dilution analysis for the particular analysis. [4]

(b) Summarize the advantages and limitations of the following isotope dilution analytical methods:

(i) Direct Isotope dilution analysis, (DIDA).

(ii) Indirect isotope dilution analysis, (IIDA).

(iii) Radiorelease method of analysis. [9]

(c) During an isotope dilution experiment for the determination of the concentration of insulin in a sample, a 1.00-mg sample of insulin labeled with ^{14}C, with an activity of 549 counts/min was added to a 10.00mL sample. After an adequate sample homogenization, a portion of the insulin was separated and purified, producing 18.30mg of pure insulin. The measured activity of the isolated insulin was 148 counts/min. Calculate the amount of insulin (in mg), present in the original sample. [7]

QUESTION 4 [25]

(a) State the difference between "batch extraction" and "continuous extraction" in analytical chemistry. (2)

(b) Metal chloro complex MCl_3 is extremely soluble in ether, with the distribution coefficient for a water/ether system being 50. Calculate the concentration of MCl_3 left in 50ml of aqueous 0.01M$FeCl_3$ solution after extraction

(i) once with a 10-mL portion of ether (1)

(ii) once with a 20--mL portion of ether (1)

(iii) twice with 10mL portions of ether (1)

(c) Describe two ways of recovering analytes from an organic solvent during the stripping stage of solvent extraction. (4)

(d) Flow injection analysis with atomic absorption detection is a hyphenated analytical technique used to measure hexavalent chromium in waste water sludges.

(i) Draw and label an FIA system. (4)

(ii) Use diagrams to describe the concept of the "Nernst Diffusion Layer" in flow injection analysis. (4)

(iii) Use drawings to explain how a phase separator works in flow injection analysis. (4)

(iv) How is quantification of Cr (VI) carried out in an FIA-AAS instrument? (4)

QUESTION 5 [25]

a. The inductively coupled plasma, coupled to a mass spectrometer, is one of the most useful hyphenated techniques in use today.

(i) Use diagrams to explain how the excitation temperatures of the ICP are measured. (4)

(ii) What excellent characteristics make the ICP an ideal source for analytical mass spectrometry? (2)

b. There are certain operational difficulties associated with coupling a quadrupole unit to an ICP.

(i) Draw a schematic diagram of an ICP-MS instrument that uses a quadrupole unit, and explain how ions from the ICP are separated in the quadrupole unit. (4)

(ii) Use diagrams to explain how the interface in an ICP-MS instrument works. (3)

(iii) How are the ions coming out of the quadrupole detected? (3)

c. Discuss each of the following interferences in ICP-MS

i) Isobaric interferences (3)

ii) Polyatomic interferences (3)

iii) Doubly charged ion interferences (3)

QUESTION 6 [25]

(a) Use a diagram to explain why a double focusing magnetic analyzer is superior over a single focusing instrument in GC-MS. (3)

(b) The interface is very important in coupling a GC to a mass spectrometer.

(i) Use a diagram to explain how direct coupling works, and describe the most appropriate columns for this type of interfacing. (4)

(ii) Use a diagram to explain how a jet separator works in GC-MS. (3)

(iii) Use a diagram to explain how an effusion separator works in GC-MS (3)

(c) Ionization of analytes from a gas chromatograph is one of the most essential steps prior to introduction into a mass analyzer.

(i) Use a diagram to explain how electron ionization is achieved in GC-MS. (3)

(ii) Use a diagram to explain how chemical ionization is achieved in GC-MS. (3)

(d) In HPLC-MS,

(i) Explain how flow splitting is achieved. (3)

(ii) Use a diagram to explain how electrospray ionization is achieved.(3)

General data and fundamental constants

Quantity	Symbol	Value
Speed of light†	c	$2.997\,924\,58 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
Faraday constant	$F = eN_A$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = kN_A$	$8.314\,51$ J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^{3} atm K^{-1} mol^{-1}
		62.364 L Torr K^{-1} mol^{-1}
Planck constant	h	$6.626\,08 \times 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}$ J s
Avogadro constant	N_A	$6.022\,14 \times 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\,54 \times 10^{-27}$ kg
Mass of		
electron	m_e	$9.109\,39 \times 10^{-31}$ kg
proton	m_p	$1.672\,62 \times 10^{-27}$ kg
neutron	m_n	$1.674\,93 \times 10^{-27}$ kg
Vacuum permeability†	μ_0	$4\pi \times 10^{-7}$ J s^{2} C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^{2} J^{-1} m^{3}
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}$ J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_0$	$1.112\,65 \times 10^{-10}$ J^{-1} C^{2} m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
Nuclear magneton	μ_N [illegible] $\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
Electron g value	g_e	$2.002\,32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e$	$5.291\,77 \times 10^{-11}$ m
Rydberg constant	$R_\infty = m_e e^4/8h^3c$	$1.097\,37 \times 10^{5}$ cm^{-1}
Fine structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N m^{2} kg^{-2}
Standard acceleration of free fall†	g	$9.806\,65$ m s^{-2}

† Exact (defined) values

Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

PERIODIC TABLE OF ELEMENTS

GROUPS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
PERIODS	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA
1	1.008 H 1																
2	6.941 Li 3	9.012 Be 4										Atomic mass → Symbol → Atomic No. →	10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9
3	22.990 Na 11	24.305 Mg 12						TRANSITION ELEMENTS					26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17
4	39.098 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.942 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.906 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53
6	132.91 Cs 55	137.33 Ba 56	138.91 *La 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85
7	223 Fr 87	226.03 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110							

*Lanthanide Series	140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.93 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	173.04 Yb 70	174.97 Lu 71
**Actinide Series	232.04 Th 90	231.04 Pa 91	238.03 U 92	237.05 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

( ) indicates the mass number of the isotope with the longest half-life.