DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

C304 **ANALYTICAL CHEMISTRY I I**

JULY 2013 SUPPLEMENTARY EXAMINATION

Time Allowed: Three (3) Hours

Instructions:

1. This examination has six (6) questions and one (1) data sheet. The total number of pages is four (4), including this page.
2. Answer any four (4) questions fully; diagrams should be clear, large and properly labeled. Marks will be deducted for improper units and lack of procedural steps in calculations.
3. Each question is worth 25 marks.

Special Requirements

1. Data sheet.
2. Graph paper.

YOU ARE NOT SUPPOSED TO OPEN THIS PAPER UNTIL PERMISSION TO DO SO HAS BEEN GIVEN BY THE CHIEF INVIGILATOR.

QUESTION 1 [25]

a) For a spectroscopic band occurring at 589 nm,

(i) convert to energy in joules [1]
(ii) state in which region of the electromagnetic spectrum the band falls [1]
(iii) state the kind of transition expected in this region [1]

b) Explain the difference in sample placement between IR and uv-visible spectroscopy [4]

c) In regards to the Czerny-Turner arrangement of optical components in a spectrometer:

(i) Explain by means of a diagram, what is meant by this arrangement. [3]
(ii) Explain how this arrangement enables light from the source to be split into individual wavelengths. [3]

d) A typical GC instrument has several standard components and accessories, each of which is listed below. Give a brief, but informative description of its functions.

(i) Nitrogen Gas Cylinder [2]
(ii) Filter Cartridge [2]
(iii) Soap Bubble Flow Meter [3]
(iv) Syringe [2]
(v) Oven [3]

QUESTION 2 [25]

a) The mobile phase is a critical component in chromatography.

i) Explain the role of the mobile phase in gas chromatography. [1]

ii) List and discuss any two (2) desirable properties of a mobile phase in gas chromatography. [2]

iii) Explain how silanol groups are deactivated in chromatography [3]

b) State Beer's Law as applied to spectroscopy, and explain all terms appearing in it. [2]

c) i) What is meant by "stray light" in spectroscopy? [1]

ii) Use equations to explain why stray light leads to negative deviations from Beer's Law [3]

iii) How is stray light eliminated in spectroscopy? [1]

d) Draw a schematic diagram of a Ge(Li) detector, connect it to an electrical circuit, and show how the voltage measured is directly related to intensity of uv-visible radiation in a spectrometer. [4]

e) Draw and label a vacuum phototube and explain how it works. [3]

f) Draw and label the "PMT", explain how it works, and explain its advantage over other detectors used in uv-visible spectrometers. [5]

Question 3 [25]

a) Analytical chemists agree that the technique of atomic absorption came of age with the invention of the hollow cat lamp by Sir Walsh in 1955.

(i) Draw and label the hollow cathode lamp [2]
(ii) Explain how the hollow cathode lamp works [2]

b) There are several unique techniques employed by the agronomy laboratory at the Simunye Sugar Estate when usin Varian Spectr-AA-10 spectrophotometer. Explain:

(i) Why in the analysis of Sr, 100 ppm La is added to all solutions [2]
(ii) Why in the analysis of Cu, the instrument is operated under "standard additions" mode [2]

c) A major breakthrough in atomic absorption spectrophotometry since the invention of the hollow cathode lamp graphite furnace AA.

(i) What is the major structural difference between flame AA and graphite furnace AA? Use diagrams to support answer [3]

(ii) Identify the physical stages involved in a furnace program and describe the processes that occur during stage. At what stage is the signal sampled, and why? [5]

(iii) Outline three (3) advantages of graphite furnace AA over flame AA [3]

d) In 2001, the Swaziland Water Services Corporation acquired a new atomic spectrometer called Liberty 110 ICP.

(i) What does ICP stand for? [1]
(ii) With the aid of a diagram briefly describe the ICP torch, how the ICP is initiated, and how it is maintainec stabilized. [3]
(iii) Discuss two major advantages of ICP over flame or graphite furnace atomic absorption. [2]

Question 4 [25]

a) The cheapest (affordable) uv-visible instruments rely on the use of filters as monochromators.

(i) By means of a diagram, explain what is meant by a cut-in filter. [3]
(ii) By means of a diagram, explain what is meant by a band-reject filter. [3]

b) In the *Jasco* instrument used by researchers at the University of Swaziland for functional group identificatic molluscicidal compounds in traditional herbs, a bolometer is used for detection. With the aid of a diagram, explain this component works. [4]

c) Physically, how does a grating look like, and use equations to explain how it works as a monochromator? [5]

d) With the aid of a diagram, briefly but informatively explain the function of one of the following detectors

i) Electron Capture Detector for GC[5]

ii) uv-visble flow through detector for LC [5]

Question 5 [25]

a) For the molecule CH_2O, formaldehyde, its UV and UV-visible spectra are attributed to "outer electron" transitions molecular orbitals. In regard to this,

i). Draw the molecular energy level diagram showing these orbitals [2]

ii). Show how a $\sigma \longrightarrow \sigma^*$ transition takes place when the molecule absorbs radiation. [1]

iii). Show how an $n \longrightarrow \pi^*$ transition takes place when the molecule absorbs radiation. [1]

iv). Of the transitions in ii and iii above, λ_{max} is observed at 350 nm and 780 nm. Assign these wavelengths each of the two transitions. [2]

v). Use diagrams to explain how the $\sigma \longrightarrow \sigma^*$ transition would result in an absorption band rather tha single line. [3]

b) i). In liquid chromatography, two solvent reservoirs are usually used. Explain the reason for this. [2]

ii). In gas chromatography, dual columns are often used simultaneously. Explain the reason for this. [2]

c) One of the applications of GC is the separation of benzene from its mixture with cyclohexane, followed by quantificat of the benzene.

(i) In GC, what is meant by lateral diffusion? [3]
(ii) State the equation that relates resistance to mass transfer in the mobile phase to linear velocity [3]
(iii) In GC, what is meant by resistance to mass transfer in the stationery phase? [3]
(iv) State the equation that relates resistance to mass flow in the stationery phase to linear velocity [3]

Question 6 [25]

a) Of the many applications of UV-visible spectroscopy, the determination of mixtures is of considerable interest. U equations to explain how is this achieved [4]

b) The Nernst Glower is a useful source of radiation in infrared spectroscopy.
i) Describe the Nernst Glower as used in IR spectroscopy. [1]
ii) Which of the molecules oxygen and hydrogen chloride is IR active and why? [2]
iii) Why is it not possible to carry out quantitative analyses on dispersive IR? [2]

c) Nebulization is a very wasteful approach to atomization.

i) What does the term "nebulization" mean? [1]
ii) Use diagrams to explain how nebulization is carried out in atomic spectroscopy. [3]
iii) Use your answer in (a) ii above to explain why nebulization is considered inefficient. [2]

d) Bandbroadening is important for peak resolution in HPLC.

i) Use a drawing to explain the importance of linear velocity on HETP [3]
ii) On this drawing, indicate the optimum linear velocity [2]
iii) Use diagrams to explain the phenomenon of "race track effect", how it affects bandbroadening, and how i eliminated. [5]

PERIODIC TABLE OF ELEMENTS

GROUPS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1.008 H 1																	4.003 He 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	20.180 Ne 10
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	39.948 Ar 18
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	83.80 Kr 36
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	131.29 Xe 54
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	(222) Rn 86
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.

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	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
Electron g value	g	$2.002\,32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11}$ 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}