DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SWAZILAND

C304 **INSTRUMENTAL ANALYSIS**

DECEMBER 2006 FINAL EXAMINATION

Time Allowed: **Three (3) Hours**

Instructions:

1. **This examination has six (6) questions and one data sheet. The total number of pages is five (5) 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.**

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QUESTION 1 [25]

a. In the following table:

Region	Wave length (nm)	Frequency (sec^{-1})	Type of Interaction	Energy (J)	Energy(eV)
Gamma ray	10^{-4}		E		C
X-Ray	10		F	B	
Ultraviolet			G		
Visible	750	A	H		
Microwave			I		

i) Calculate A, B, and C [3]

ii) Complete the table by stating E, F, G, H, I [5]

b. Use diagrams to explain what a "double beam" instrument is in IR, and explain its role in this technique [3]

c. i) What is meant by resistance to mass transfer in the mobile phase in GC? [2]

ii) State the HETP equation for resistance to mass transfer in the mobile phase in GC. [2]

d. i) What is meant by resistance to mass transfer in the stationery in GC? [2]

ii) State the HETP equation for resistance to mass transfer in stationery phase in GC. [2]

e. A typical GC instrument has several standard components, each of which is listed below. In each case give a brief description of the component, followed by its function.

i) Filter Cartridge [2]
ii) Soap Bubble Flow meter [2]
iii) Injector [2]

QUESTION 2 [25]

a. i) State Beer's Law and explain all terms appearing in it [2]

ii) Use equations to explain why spectroscopic measurements are taken at the peak of spectral bands rather than at the shoulder [3]

b. i) Describe any one source of emr in uv-visible spectroscopy [3]

ii) Use a diagram to explain how a bandpass filter works [3]

c. Explain using diagrams, why atomic spectra appears as lines, whereas molecular spectra appear as bands [3]

d. Use diagrams to describe the process of "elution" in chromatography. [3]

e. Describe each of the two ways by which elution is performed in Gas Chromatography (GC). [2]

f. Sketch the Van Deempter plot for GC, and indicate the region where mobile phase velocity is optimum for analysis. [3]

g. Use equations to describe the process of "silanization" in GC. [3]

QUESTION 3 [25]

a. Atomic Absorption Spectroscopy (AAS) is one of the most versatile analytical techniques available.

- i) Draw a cross section of an air-acetylene flame and label the main regions that make up the flame. [2]
- ii) What chemical processes occur in each region of the flame? [3]
- iii) Indicate the region where atomization efficiency is at the maximum. [1]

b. One of the problems associated with AA analysis of several elements is the susceptibility to interferences. Not forgetting to quote specific examples in each of the cases below,

- i) Describe ionization interference, and explain how it is eliminated in AA. [2]
- ii) Describe chemical interference, and explain how it is eliminated in AA. [2]
- iii) Describe "matrix effects" and outline one procedure used to combat these effects in AA.[2]

c. What is meant by the "race track" effect in chromatography, and how is it eliminated? [2]

d. Sketch the Van Deempter plot for Liquid Chromatography (LC) and explain how it is different from that of GC. [3]

e.
- i) What is the reason for performing LC in bonded phases? [2]
- ii) Use equations to explain how bonded phases are fabricated. [3]
- iii) Explain the difference between NPBP and RPBP in bonded phase LC. [3]

QUESTION 4 [25]

a. The "monochromator" in a spectrometer is a critical component.

- i) What role does a "monochromator " play in a spectrometer? [1]
- ii) State Snell's Law of refraction, and use it to explain how a prism acts as a monochromator. [3]

b. In spectroscopy, several types of detectors are used. Draw and label a vacuum phototube and explain how it works. [4]

c. The Molar Ratio method for the Cu-bathferon complex shows stoichiometric breaks at 0.25 and at 0.166. What is the ratio of metal to ligand in this complex? [3]

d. One of the applications of GC is the separation of benzene from its mixture with cyclohexane, followed by quantification of the benzene. Toluene is deliberately added to all samples and standards.

- i) Explain the role of toluene (explain how it serves this role) in the analysis. [1]
- ii) Explain why a dual column GC is preferred over a single column GC in this separation. [3]
- iii) Describe the solid support Chomosorb P-AW-DMCS employed in the column. [2]

iv) Describe the stationary phase squalene employed in the column. [2]

v) List and discuss three (3) desirable properties of squalene as a stationery phase in GC. [6]

QUESTION 5 [25]

b. The cheapest (affordable) infrared instruments rely on the use of a "Czerny-Turner" arrangement of the optical components.

i) By means of a diagram, explain what is meant by this arrangement. [3]

ii) Explain how this arrangement enables light from the source to be split into individual wavelengths. [3]

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

d. State two (2) reasons why in the *Jasco* instrument the sample is placed before the monochromator, whereas in the *Spectronic 20* instrument the sample is placed after it. [2]

d. i) What is meant by Eddy Diffusion in GC? [2]

ii) State the HETP equation for Eddy Diffusion in a packed bed [2]

e. i) What is meant by Longitudinal Diffusion in GC? [2]

ii)State the HETP equation for Longitudinal Diffusion in a packed bed [2]

f. i) On a single Van Deempter plot, show the difference between He and N_2 when used as carrier gases. [2]

ii) On a single Van Deempter plot, show the differences between 1%, 2% and 3% diethylglyconate succinate stationary phase loading. [3]

QUESTION 6 [25]

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

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

ii) Outline two (2) advantages of graphite furnace AA over flame AA. [2]

b. Perhaps the most sensitive technique in analytical atomic spectrometry in the 1990's is the ICP.

i) In ICP-OES, solutions are normally introduced by the "Venturi Effect". Describe this effect. [3]

ii) Optics in an ICP are mounted in a "Rowland Circle". Draw this optical arrangement, and show how it enhances the multi element capability of ICP. [3]

c. Describe each of the two ways by which elution is performed in LC. [2]

d. i) With the aid of a diagram, explain how a thermal conductivity detector works. [3]

ii) With the aid of a diagram, explain how a flame ionization detector works. [3]

iii) With the aid of a diagram, explain how an electron capture detector works. [3]

e. Use equations to explain the concept of derivatization in the analysis of benzoic acid in GC using an electron capture detector. [3]

1. PERIODIC CHART OF THE ELEMENTS

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18
							1 **H** 1.00794										2 **He** 4.00260
3 **Li** 6.941	4 **Be** 9.01218											5 **B** 10.81	6 **C** 12.011	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.99840	10 **Ne** 20.179
11 **Na** 22.98977	12 **Mg** 24.305											13 **Al** 26.98154	14 **Si** 28.0855	15 **P** 30.97376	16 **S** 32.06	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.0983	20 **Ca** 40.08	21 **Sc** 44.9559	22 **Ti** 47.88	23 **V** 50.9415	24 **Cr** 51.996	25 **Mn** 54.9380	26 **Fe** 55.847	27 **Co** 58.9332	28 **Ni** 58.69	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9059	40 **Zr** 91.22	41 **Nb** 92.9064	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.9055	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.69	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.9045	54 **Xe** 131.29
55 **Cs** 132.9055	56 **Ba** 137.33	57 ★ **La** 138.9055	72 **Hf** 178.49	73 **Ta** 180.9479	74 **W** 183.85	75 **Re** 186.207	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.9665	80 **Hg** 200.59	81 **Tl** 204.383	82 **Pb** 207.2	83 **Bi** 208.9804	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0254	89 ▲ **Ac** 227.0278	104 **Unq** (261)	105 **Unp** (262)	106 **Unh** (263)	107 **Uns** (262)	108 **Uno** (265)	109 **Une** (266)									

A value in brackets denotes the mass number of the longest lived or best known isotope.

★ Lanthanide series	58 **Ce** 140.12	59 **Pr** 140.9077	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.9254	66 **Dy** 162.50	67 **Ho** 164.9304	68 **Er** 167.26	69 **Tm** 168.9342	70 **Yb** 173.04	71 **Lu** 174.967
▲ Actinide series	90 **Th** 232.0381	91 **Pa** 231.0359	92 **U** 238.0289	93 **Np** 237.0482	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** (260)

2. IONIZATION CONSTANTS (K_A) FOR WEAK ACIDS

Acetic		1.9×10^{-5}
2-Amino-pyridinium Ion		2×10^{-7}
Ammonium Ion		5.6×10^{-10}
Anilinium Ion		2.3×10^{-5}
Arsenic	K_1	5.6×10^{-3}
Benzoic		6.7×10^{-5}
Boric	K_1	5×10^{-10}
Carbonic	K_1	4.3×10^{-7}
	K_2	5.6×10^{-11}
Chloroacetic		1.5×10^{-3}
Chromic	K_2	3.2×10^{-7}
Citric	K_1	8.7×10^{-4}
	K_2	1.8×10^{-5}
	K_3	4×10^{-6}
Dichloroacetic		5×10^{-2}
EDTA	K_1	7×10^{-3}
	K_2	2×10^{-3}
	K_3	7×10^{-7}
	K_4	6×10^{-11}
Formic		2×10^{-4}
α-D(+)-Glucose		5.2×10^{-13}
Glycinium Ion	K_1	4.6×10^{-3}
	K_2	2.5×10^{-10}
Hydrazinium Ion		5.9×10^{-9}
Hydrocyanic		7×10^{-10}
Hydrofluoric		7×10^{-4}
Hydroxyl-ammonium Ion		9.1×10^{-7}
Hypochlorous		3.7×10^{-8}
H_2S	K_1	9×10^{-8}
	K_2	1×10^{-15}
Imidazolium Ion		1.1×10^{-7}
Lactic		1.4×10^{-4}
Methylammonium Ion		2.7×10^{-11}
Monoethanol-ammonium Ion		3×10^{-10}
Nicotinium Ion		9.6×10^{-9}
Oxalic	K_1	6×10^{-2}
	K_2	6×10^{-5}
Phenol		1.3×10^{-10}
Phthalic	K_2	4×10^{-6}
Phosphoric	K_1	7.5×10^{-3}
	K_2	6.2×10^{-8}
	K_3	4.7×10^{-13}
Phosphorous	K_1	1.0×10^{-2}
	K_2	2.6×10^{-7}
Pyridinium Ion		1×10^{-5}
Succinic	K_1	7×10^{-5}
	K_2	2.5×10^{-6}
Sulfuric	K_2	1.2×10^{-2}
Sulfurous	K_1	2×10^{-2}
	K_2	6×10^{-8}
Trimethyl-ammonium Ion		1.6×10^{-10}
Uric		1.3×10^{-4}
Water, K_w, 24°C		1.0×10^{-14}

3. SOLUBILITY PRODUCT CONSTANTS

AgBr	4×10^{-13}	BaC_2O_4	2×10^{-8}	$KClO_4$	2×10^{-2}
Ag_2CO_3	6×10^{-12}	$BaSO_4$	1×10^{-10}	$MgCO_3$	1×10^{-5}
AgCl	1×10^{-10}	$CaCO_3$	5×10^{-9}	MgC_2O_4	9×10^{-5}
Ag_2CrO_4	2×10^{-12}	CaF_2	4×10^{-11}	$MgNH_4PO_4$	2×10^{-13}
$Ag[Ag(CN)_2]$	4×10^{-12}	CaC_2O_4	2×10^{-9}	$Mg(OH)_2$	1×10^{-11}
AgI	1×10^{-16}	CdS	1×10^{-28}	MnS	1×10^{-15}
Ag_3PO_4	1×10^{-19}	$Cu(OH)_2$	2×10^{-20}	$PbCrO_4$	2×10^{-14}
Ag_2S	1×10^{-50}	CuS	1×10^{-36}	PbS	1×10^{-28}
AgCNS	1×10^{-12}	$Fe(OH)_3$	1×10^{-36}	$PbSO_4$	2×10^{-8}
$Al(OH)_3$	2×10^{-32}	Hg_2Br_2	3×10^{-23}	$SrCrO_4$	4×10^{-5}
$BaCO_3$	5×10^{-9}	Hg_2Cl_2	6×10^{-19}	$Zn(OH)_2$	3.6×10^{-16}
$BaCrO_4$	1×10^{-10}	HgS	1×10^{-52}	ZnS	1×10^{-24}

4. NET STABILIT
CONSTANTS

$Ag(CN)_2^-$	5 × 1
$Ag(NH_3)_2^+$	1.6 × 1
$Ag(S_2O_3)_2^{-3}$	4.7 × 1
$Al(OH)_4^-$	1.0 × 1
$Ca(EDTA)^=$	1.0 × 1
$Cd(CN)_4^=$	8.3 × 1
$Cd(NH_3)_4^{++}$	5.5 × 1
$Co(NH_3)_6^{+3}$	2 × 1
$Cr(OH)_4^-$	4 × 1
$Cu(CN)_4^{-3}$	1 × 1
$Cu(NH_3)_4^{++}$	1.2 × 1
$Fe(CN)_6^{-3}$	4.0 × 1
$Fe(CN)_6^{-4}$	2.5 × 1
$Fe(SCN)^{++}$	1.0 × 1
$HgCl_4^=$	1.3 × 1
$Hg(CN)_4^=$	8.3 × 1
$Hg(SCN)_4^=$	5.0 × 1
$HgI_4^=$	6.3 × 1
$Mg(EDTA)^=$	1.3 × 1
$Ni(NH_3)_4^{++}$	4.7 × 1
$Pb(OH)_3^-$	7.9 × 1
$Zn(CN)_4^=$	4.2 × 1
$Zn(NH_3)_4^{++}$	7.8 × 1
$Zn(OH)_4^=$	6.3 × 1

5. FIRST IONIZATION ENERGIES, e.v.

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1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A
5.4	9.3											8.3	11	15	14	17
5.1	7.6											6.0	8.1	11	10	13
4.3	6.1	6.6	6.8	6.7	6.8	7.4	7.9	7.9	7.6	7.7	9.4	6.0	8.1	10	9.8	12
4.2	5.7	6.6	7.0	6.8	7.2		7.5	7.7	8.3	7.6	9.0	5.8	7.3	8.6	9.0	10
3.9	5.2	5.0 6.9	5.5	6	8.0	7.9	8.7	9.2	9.0	9.2	10	6.1	7.4	8		

6. ELECTRONEGATIVITIES, Pauling

2.1

1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A
1.0	1.5											2.0	2.5	3.0	3.5	4.0
0.9	1.2											1.5	1.8	2.1	2.5	3.0
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.6	1.8	2.0	2.4	2.8
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5
0.7	0.9	1.1	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2

7. ATOMIC RADII picometers

37

1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A
155	112											98	91	92	73	71
190	160											143	132	128	127	99
235	197	162	147	134	130	135	126	125	124	128	138	141	137	139	140	114
248	215	178	160	146	139	135	134	134	137	144	154	166	162	159	160	133
267	222	187	167	149	141	137	135	136	139	146	157	171	175	170	176	

8. IONIC RADII pm

Li^+	60	Sr^{+2}	113	S^{-2}	184
Na^+	95	Ba^{+2}	135	Se^{-2}	198
K^+	133	B^{+3}	20	Te^{-2}	221
Rb^+	148	Al^{+3}	50	F^-	136
Be^{+2}	31	N^{+3}	171	Cl^-	181
Mg^{+2}	65	P^{+3}	212	Br^-	195
Ca^{+2}	99	O^{-2}	140	I^-	216

9. LATTICE ENERGIE

(All negative) kJ/m

	F	Cl	Br
Li	1030	840	781
Na	914	770	728
K	812	701	671
Rb	780	682	654
Cs	744	630	613

10. HALF LIVES

H^3	12.3 years	K^{40}	1.28×10^9y	I^{131}	8.1 day
F^{20}	11.4 secs	Ca^{45}	165 days	Cs^{137}	30 yea
C^{14}	5730 years	Fe^{59}	45 days	Au^{198}	2.69 da
Na^{24}	15.0 hours	Co^{60}	5.26 y	Ra^{226}	1620 y
P^{32}	14.3 days	Br^{82}	35.5 hours	U^{235}	7.1×10
S^{35}	88 days	Sr^{90}	28 years	U^{238}	4.51×10
Cl^{36}	3.1×10^5y	I^{129}	1.7×10^7y	Pu^{230}	24,400

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Useful Relations

$(RT)_{298\cdot15K}$=2.4789 kJ/mol

$(RT/F)_{298\cdot15K}$=0.025 693 V

T/K:	100.15	298.15	500.15	1000.15
T/Cm^{-1}:	69.61	207.22	347.62	695.13

1mmHg=133.222 N m^{-2}

hc/k=1.438 78x10^{-2} m K

1atm	1 cal	1 eV	1cm^{-1}
1.01325x10^{5} Nm^{-2}	4.184 J	1.602 189x10^{-19} J	0.124x10^{-3} eV
760torr		96.485 kJ/mol 8065.5 cm^{-1}	1.9864x10^{-23}J

SI-units:

1 cal (thermochemical) = 4.184 J

dipole moment: 1 Debye = 3.335 64x10^{-30} C m

force: 1N=1J m^{-1} = 1kgms^{-2}=10^{5} dyne pressure: 1Pa=1Nm^{-2} =1Jm^{-3}

power: 1W = 1J s^{-1} potential: 1V =1 J C^{-1}

magnetic flux: 1T=1Vsm^{-2}=1JCsm^{-2} current: 1A=1Cs^{-1}

Prefixes:

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

General Data		
speed of light	c	2.997 925x10^{8} m^{-1}
charge of proton	*e*	1.602 19x10^{-19} C
Faraday constant	F=L*e*	9.648 46x10^{4} C mol^{-1}
Boltzmann constant	k	1.380 66x10^{-23} J K^{-1}
Gas constant	R=Lk	8.314 41 J K^{-1} mol^{-1}
		8.205 75x10^{-2} dm^{3} atm K^{-1} mol^{-1}
Planck constant	h	6.626 18x10^{-34} Js
	$\hbar = \frac{h}{2\pi}$	1.054 59x10^{34} Js
Avogadro constant	L or N_{av}	6.022 14x10^{23} mol^{-1}
Atomis mass unit	u=10^{-3} kg/(Lmol)	1.660 54x10^{-27} kg
Electron mass	m_e	9.109 39x10^{-31} kg
Proton mass	m_p	1.672 62x10^{-27} kg
Neutron mass	m_n	1.674 93x10^{-27} kg
Vacuum permittivity	$\varepsilon_o = \mu_o^{-1}c^{-2}$	8.854 188x10^{-12} J^{-1} C^{2} m^{-1}
Vacuum permeability	μ_o	4πx10^{-7} Js^{2}C^{-2} m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	9.274 02x10^{-24} JT^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.05079x10^{-27} JT^{-1}
Gravitational constant	G or g	6.67259x10^{-11} Nm^{2}kg^{-2}
Bohr radius	a_0	5.291 77x10^{-11} m