UNIVERSITY OF SWAZILAND

FACULTY OF SCIENCE

DEPARTMENT OF CHEMISTRY

FINAL EXAMINATION PAPER, MAY 2008

TITLE OF PAPER: INSTRUMENTAL ANALYSIS

COURSE CODE: C 304

TIME ALLOWED: THREE (3) HOURS

INSTRUCTIONS:

1. THIS EXAMINATIONS HAS 6 QUESTIONS AND TWO (2) DATA SHEETS. THE TOTAL NUMBER OF PAGES IS SIX (6) 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 sheets.
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

a. i) Explain the role of a solid support in liquid chromatography. [1]

ii) List and discuss any two (2) desirable properties of a solid support in liquid chromatography. [3]

iii) Describe the nature of the solid support "Chromosorb W-AW". [3]

b. What is meant by a "silanol group" in chromatography? [1]

c. How do silanol groups affect chromatographic separations? [2]

d. Use equations to explain how the effect of silanol groups is eliminated in chromatography. [3]

e. i) Explain the role of stationary phase in LC. [1]

ii) Write down the formula of sqalene used as stationary phase in LC. [1]

iii) Explain why Carbowax 20M would be more efficient for separating a mixture of CH_3OH/CH_3CH_2OH as compared with a mixture of CH_4 and CH_3CH_3. [2]

f. i) What is the reason for performing LC on 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 L.C. [3]

QUESTION 2

a. State the range of the uv-visible portion of the electromagnetic spectrum in nanometers. [2]

b. In the spectrophometric analysis of trace iron using the bipyridine method,

i) Write the full stoichiometric reaction. [3]

ii) State why 1,10-phenanthroline is sometimes referred to as "batho-phenanthroline". [2]

iii) Name the reagent used to convert Fe (III) species to Fe (II) species, and explain why this is necessary. [2]

iv) Explain why sodium acetate and sulphuric acid are added prior to addition of bipyridine. [2]

c. In an experiment to determine the concentration of trace iron in a sample, a 5 ppm Fe solution was prepared by addition of bipyridine and 3M H_2SO_4/10% sodium acetate into a solution of $FeSO_4(NH_4)_2 \cdot 6H_20$. Optical parameters were measured in a Bausch and Lomb Spectronic 20 uv-visible spectrophotometer with the following results:

Wavelength (nm)	480	500	520	540	560	580
Transmittance (%)	51.2	40.9	32.5	41.8	50.3	52.1

i) Plot the spectrum of the iron-bipyridine complex. [3]

ii) On the spectrum, indicate the λmax.
[1]

iii) Calculate the molar absorptivity of the complex if measurements were taken in a 1.11-cm cell. [4]

d. Two isomers, ortho-and para-, are simultaneously determined in a solution by uv-visible spectroscopy. At 410nm, the measured absorbance was 0.353, whereas at 560nm, the absorbance was 0.251 in a 1.00cm cell. Calculate the concentrations of the two isomers (molar absorptivities at 410nm are: 6000 for ortho-, 500 for para-;

QUESTION 3

(a) Explain fully the meaning of the expression "chromatography is a semi-batch, differential migration, phase distribution technique". [3]

(b) Write the equation for Gaussian peaks in chromatography, and explain the analytical significance of its integral. [3]

(c) Describe each of the two ways of performing elution in Gas Chromatography, and explain why one would prefer elution in each case. [2]

(d) Describe each of the two ways of performing elution in Liquid Chromatography, and explain why one would prefer elution in each case. [3]

(e) Use equations to describe "capacity factor" in chromatography, and explain its significance in analytical separations. [3]

(f) Gas chromatography is used to separate cyclohexane and bencene in a mixture. Cyclohexane elutes after 15 sec with a peak width of 1.5 cm, whereas air and benzene elute after 8 sec and 30 sec respectively. The peak width of benzene is 1.2 cm. The chart speed used is 5cm/min, and the column is 2m long.

i) Why is it not possible to separate benzene from cyclohexane by distillation? [2]

ii) Why do the three components elute in the order observed? [2]

iii) What is the capacity factor of benzene? [2]

iv) Calculate the HETP using the cyclohexane peak. [3]

v) Are the two peaks properly resolved? [2]

QUESTION 4

a. i) State the range of the mid IR portion of the electromagnetic spectrum in wave numbers. [2]

ii) Of the two molecules HCI and CI_2, which one is IR-active and which one is not? Give an explanation for each of your answers. [3]

iii) State and explain the differences in sample placement between IR and UV-visible spectroscopy. [3]

b. State Bragg's Law and explain all terms appearing in it. [2]

c. Draw a prism, and use equations to explain how it works as a monochromator. [3]

d. Use equations to explain how stray light leads to deviations in Beer's Law. [3]

e. The following results obtained in an experiment involving the standardization of iron.

Concentration µg/mL	1.16	3.48	4.65
Absorbance	0.125	0.372	0.502

An unknown solid, weighing 0.5062g, was digested to a volume of 50mL, from which an aliquot of 10mL was pipeted into a 100mL volumetric flask prior to addition of reagents and dilution to volume. Absorbance readings obtained for the sample are on average 0.337.

i) Plot the calibration curve. [3]

ii) Calculate the concentration of iron in the sample in parts-per-million. [7]

QUESTION 5

a. Write brief notes on the following used in gas chromatography:

i) Carrier gas. [2]
ii) Purifier catridge [2]
iii) Soap bubble. [2]

a. Use diagrams to explain the following as relates to "race track" effect

i) its cause [1]
ii) its effect on peak width [2]
iii) how it is eliminated in GC [2]

c. Use diagrams to describe the "Flame Ionization Detector", and list any three compounds that cannot be detected by this method. [4]

d. i) Use a diagram to explain the concept of "laminar flow" in chromatography. [2]

ii) Use a diagram to explain the phenomenon of "longitudinal diffusion" in chromatography. [2]

iii) State the HETP equation for longitudinal diffusion in an open tube, and explain how it is different from a packed tube. [2]

iv) Explain the effect of linear velocity of mobile phase on band broading due to longitudinal diffusion. [2]

v) How and why does longitudinal diffusion effect hand broading in liquid chromatography? [2]

QUESTION 6

a. i) Describe the role of each of the reagents used in the analytical dissolution of sugar-cane soils by open vessel digestion in the determination of trace zinc. [3]

ii) Draw the cross-flow nebulizer and explain how it works. [3]

b. Discuss the path followed by $ZnCl_2$ as it is aspirated from solution up until it reaches the flame in atomic absorption spectroscopy. [3]

c. Draw the hollow cathode lamp, explain how it works, and explain why it was not possible to perform atomic spectroscopic measurements prior to its invention in 1955? [4]

d. For each of the following interferences in flame atomic absorption spectroscopy, describe the interference and explain how it is eliminated.

i) ionization [2]
ii) chemical [3]

e. "Nebulization in atomic spectroscopy is inefficient". Explain the meaning of this statement. [2]

f. Describe the three stages involved in a furnace program in graphite furnace AAS, and explain why or why not the signal is sampled at each stage. [3]

g. List and describe two (2) advantages of graphite furnace atomic absorption spectroscopy over flame methods. [2]

1. PERIODIC CHART OF THE ELEMENTS

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	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)

4. NET STABILITY CONSTANTS

$Ag(CN)_2^-$	5 × 10
$Ag(NH_3)_2^+$	1.6 × 10
$Ag(S_2O_3)_2^{-3}$	4.7 × 10
$Al(OH)_4^-$	1.0 × 10
$Ca(EDTA)^=$	1.0 × 10
$Cd(CN)_4^=$	8.3 × 10
$Cd(NH_3)_4^{++}$	5.5 × 10
$Co(NH_3)_6^{+3}$	2 × 10
$Cr(OH)_4^-$	4 × 10
$Cu(CN)_4^{-3}$	1 × 10
$Cu(NH_3)_4^{++}$	1.2 × 10
$Fe(CN)_6^{-3}$	4.0 × 10
$Fe(CN)_6^{-4}$	2.5 × 10
$Fe(SCN)^{++}$	1.0 × 10
$HgCl_4^=$	1.3 × 10
$Hg(CN)_4^=$	8.3 × 10
$Hg(SCN)_4^=$	5.0 × 10
$HgI_4^=$	6.3 × 10
$Mg(EDTA)^=$	1.3 × 10
$Ni(NH_3)_4^{++}$	4.7 × 10
$Pb(OH)_3^-$	7.9 × 10
$Zn(CN)_4^=$	4.2 × 10
$Zn(NH_3)_4^{++}$	7.8 × 10
$Zn(OH)_4^=$	6.3 × 10

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^{-6}
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}

5. FIRST IONIZATION ENERGIES, e.v.

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A
								14 (H)								
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

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A
								2.1 (H)								
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

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A
								37 (H)								
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	136	134	134	137	144	154	166	162	159	160	133
267	222	187	157	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 da
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

$(RT)_{298.15K}$=2.4789 kJ/mol

$(RT/F)_{298.15K}$=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=Le	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	$\mu_B = eh/2m_e$	9.274 02x10^{-24} JT^{-1}
Nuclear magneton	$\mu_N = eh/2m_p$	5.05079x10^{-27} JT^{-1}
Gravitational constant	G or g	6.67259x10^{-11} Nm^{2}kg^{-2}
Bohr radius	a_o	5.291 77x10^{-11} m