DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

C612 **SPECTRO CHEMICAL ANALYSIS**

DECEMBER 2013 FINAL 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 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.**

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) Explain the origins of atmospheric absorptions in infra-red spectroscopy (2)

b) Why are atmospheric absorptions undesirable in IR and how are they eliminated? (2)

c) Infra-red instruments operating in the dispersive mode are widely used for qualitative and semi-quantitative measurements. Explain

(i) Why in dispersive IR the sample is placed before the monochromator and not after it? (2)

(ii) Why dispersive IR instruments suffer from poor resolution. (3)

(iii) Calculate λmax in cm^{-1}, for a Nernst Glower heated to 500K, given its Wein's Displacement constant of 2.9×10^{-3}mK. (2)

(iv) Explain why the Glower heated to 500 K is at the ideal temperature for use as an IR source compared to 10,000K. (2)

d) With regard to IR utilizing a Michaelson interferometer,

(i) Use diagrams to explain how the interferometer works. (4)

(ii) Explain the role of the He-Ne laser used in FT-IR . (2)

(iii) What is meant by the "Jacquinot Advantage" in FT-IR? (2)

(iv) What is meant by the "Connes Advantage" in FT-IR? (2)

(v) What is meant by the "Fellget Advantage" in FT-IR? (2)

QUESTION 2 [25]

a) (i) Of the many applications of UV-visible spectroscopy, the determination of mixtures is of considerable interest. Use equations to explain how is this achieved (3)

(ii) Use equations to explain how polychromatic radiation gives rise to deviations in Beer's Law (6)

b) A typical monochromator using a grating is a rectangular block of glass with 1180 lines etched on every mm of its surface. It is 4.6 cm wide.

(i) State the Bragg's equation for the grating acting as a monochomator, and calculate the primary angle at which radiation of 650 nm is diffracted when it hits the grating. (3)

(ii) Calculate the first order resolving power of this grating, and calculate the resolution at 650 nm. (3)

c) Prisms are widely used in uv-visible spectrometers as monochromators. The base length of a prism is typically 5cm, and the prism material has a dispersion of 2.7×10^{-5}.

(i) State Snell's law for a prism (1)

(ii) Calculate the resolving power of the prism, and the resolution at 5268 A° (3)

(iii) Use diagrams to explain the principle of "Resolution As Limited by the Exit Slit" in spectroscopy (3)

d) There are many applications of uv-visible spectroscopy today. Describe how uv-visible spectroscopy can be used to determine the dissociation constant, Ka, for a weak acid HA. (3)

QUESTION 3 [25]

a) Atomic spectral lines are theoretically infinitely narrow, but in reality they have spectral width due to broadening. Explain how the following phenomena give rise to broadening

(i) Doppler Effect (3)

(ii) Collisional Effect (3)

b) Use equations to explain why:

(i) The optical components of spectrometers are always kept in a darkened compartment. (3)

(ii) uv-visible spectroscopic measurements are always taken at λ_{max} rather than at shoulders of molecular spectra. (4)

c) Photodiode arrays (PDA's) are widely used as dectectors in uv-visible spectroscopy.

(i) Use a diagram to explain how a PDA works. (4)

(ii) What is the major advantage of the PDA over the phototube? (2)

(iii) Given that the signals from a photodiode array detector are in the form of current, which must be converted to voltage for input into a computer for electronic display, draw the operational amplifier that must be used at this stage of signal processing, and state its output. (3)

(iv) After computing the voltage ratio from the reference and sample channels in the PDA, and given that the voltage ratio (transmittance) must be converted to absorbance, draw the operational amplifier that must be used at this stage of signal processing, and state its output. (3)

QUESTION 4 [25]

a) Fourier transform techniques have contributed immensely in spectroscopy. State the Fourier transform integral pair as applied to spectroscopy (2)

b) The following signals are fed into a Michelson interferometer. In each case, draw the output

(i) Two spectral lines of equal intensity (2)

(ii)Two spectral lines of different intensity (2)

(iii) A square wave (2)

(iv) A gaussian peak (2)

c) Matrix effects are problematic in atomic spectroscopy. For each of the following spectroscopic techniques, discuss how matrix effects arise, and state how they can be eliminated in each case.

(i) DC Spark (3)

(ii) Flame Atomic Absorption Spectroscopy (3)

(iii)Electrothermal Vaporization Atomic Absorption Spectroscopy (3)

d) 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, showing the ICP-MS interface. (3)

(ii) Explain how the interface works. (3)

QUESTION 5 [25]

a) The dissolution of samples is a major challenge to spectroscopies that rely on nebulisation as a sample introduction system.

(i)With regards to the classical hot plate method,

- Discuss the mechanism of digestion (2)
- Explain the role of H_2SO_4 in oxidation of samples by HNO_3 (1)
- Explain why the last step in digesting geological samples usually involves HF (1)
- Discuss the precautions that are necessary when digesting with $HClO_4$ (3)

(ii) With regards to the modern methods of analytical dissolution

- Explain why microwave acid digestion is faster than classical methods (1)
- Discuss the mechanism of ultrasonic digestion (3)

b) The DC Arc emission spectroscopic technique is one of the oldest of such techniques, but the mining industry is now seeing its resurgence in metal analysis.

(i) Discuss the principles of DC Arc emission spectroscopy using a circuit diagram to illustrate. (4)

(ii) What are the three (3) main advantages of DC Arc emission spectroscopy over the more recent flame atomic absorption spectroscopy? (3)

(iii) Discuss the problem of fractional volatization in the DC Arc method, and explain how it is overcome. (3)

(iv) Fully quantitative DC Arc emission measurements are achieved by means of an internal standard, an old but useful concept for this purpose (Gerlach, *ZAnorg Allem. Chem.*, 142, 383, (1925)). What are the three desirable characteristics of an internal standard, and how are analytes quantified using it?(4)

QUESTION 6 [25]

a) The AC Spark electrothermal method is widely used in the steel industry.

(ii) Discuss the principles of AC Spark emission spectroscopy using a circuit diagram to illustrate. (4)

(iii) Discuss any three (3) advantages of AC Spark over DC Arc emission spectroscopy in the determination of Al in steels. (3)

b) Discuss any two (2) advantages of using a photographic plate as a detector in AC Spark emission over a photomultiplier tube. (2)

c) The inductively Coupled Plasma (ICP) optical emission is now the widely preferred atomic spectroscopic technique.

(i) Give a brief description of the ICP as a source of emission signals. (3)

(ii) Use a diagram to show why it is possible for the ICP to measure up to 35 elements simultaneously. (3)

(iii) State the SAHA equation and explain how temperature measurements in a non-chemical flame of the ICP is carried out using it. (3)

(iv) How does the "order of magnitude" of the ICP compare with that of the atomic absorption techniques, and what are the implications of this? (3)

d) Discuss each of the following interferences in ICP-MS

i) Isobaric interferences (2)

ii) Polyatomic interferences (2)

CHEMISTRY DATA SHEET

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.

	58	59	60	61	62	63	64	65	66	67	68	69	70	71
★ Lanthanide series	Ce 140.12	Pr 140.9077	Nd 144.24	Pm (145)	Sm 150.36	Eu 151.96	Gd 157.25	Tb 158.9254	Dy 162.50	Ho 164.9304	Er 167.26	Tm 168.9342	Yb 173.04	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^{20}
$Ag(NH_3)_2^+$	1.6×10^7
$Ag(S_2O_3)_2^{-3}$	4.7×10^{13}
$Al(OH)_4^-$	1.0×10^{33}
Ca(EDTA)=	1.0×10^{11}
$Cd(CN)_4$=	8.3×10^{17}
$Cd(NH_3)_4^{++}$	5.5×10^6
$Co(NH_3)_6^{+3}$	2×10^{35}
$Cr(OH)_4^-$	4×10^{28}
$Cu(CN)_4^{-3}$	1×10^{28}
$Cu(NH_3)_4^{++}$	1.2×10^{11}
$Fe(CN)_6^{-3}$	4.0×10^{43}
$Fe(CN)_6^{-4}$	2.5×10^{35}
$Fe(SCN)^{++}$	1.0×10^3
$HgCl_4$=	1.3×10^{15}
$Hg(CN)_4$=	8.3×10^{38}
$Hg(SCN)_4$=	5.0×10^{20}
HgI_4=	6.3×10^{29}
Mg(EDTA)=	1.3×10^9
$Ni(NH_3)_4^{++}$	4.7×10^7
$Pb(OH)_3^-$	7.9×10^{13}
$Zn(CN)_4$=	4.2×10^{16}
$Zn(NH_3)_4^{++}$	7.8×10^8
$Zn(OH)_4$=	6.3×10^{14}

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}

5. FIRST IONIZATION ENERGIES, e.v.

1A	2A											3A	4A	5A	6A	7A	25
5.4	9.3											8.3	11	15	14	17	22
5.1	7.6	3B	4B	5B	6B	7B		8B		1B	2B	6.0	8.1	11	10	13	16
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	14
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	12
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			11

6. ELECTRONEGATIVITIES, Pauling

1A	2A											3A	4A	5A	6A	7A	
1.0	1.5											2.0	2.5	3.0	3.5	4.0	
0.9	1.2	3B	4B	5B	6B	7B		8B		1B	2B	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	1.8	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											3A	4A	5A	6A	7A	32
155	112											98	91	92	73	71	69
190	160	3B	4B	5B	6B	7B		8B		1B	2B	143	132	128	127	99	97
235	197	162	147	134	130	135	126	125	124	128	138	141	137	139	140	114	110
248	215	178	160	146	139	136	134	134	137	144	154	166	162	159	160	133	130
267	222	187	167	149	141	137	135	136	139	146	157	171	175	170	176		145

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 ENERGIES

(All negative) kJ/mol

	F	Cl	Br	I
Li	1030	840	781	718
Na	914	770	728	681
K	812	701	671	632
Rb	780	682	654	617
Cs	744	630	613	585

10. HALF LIVES

H^3	12.3 years	K^{40}	1.28×10^9y	I^{131}	8.1 days
F^{20}	11.4 secs	Ca^{45}	165 days	Cs^{137}	30 years
C^{14}	5730 years	Fe^{59}	45 days	Au^{198}	2.69 days
Na^{24}	15.0 hours	Co^{60}	5.26 y	Ra^{226}	1620 yrs.
P^{32}	14.3 days	Br^{82}	35.5 hours	U^{235}	7.1×10^8y
S^{35}	88 days	Sr^{90}	28 years	U^{238}	4.51×10^9y
Cl^{36}	3.1×10^5y	I^{129}	1.7×10^7y	Pu^{230}	24,400 y

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