

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SWAZILAND

C512

SPECTROCHEMICAL ANALYSIS

MAY 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 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 sheet.

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

QUESTION 1 [25]

- a) Spectroscopy is an analytical technique based on the interaction between electromagnetic radiation (emr) and atoms/molecules. State where in the emr spectrum radiation of 13.6eV falls, calculate its energy (in joules), frequency (in Hertz), and state what type of transition is taking place to produce the 13.6eV radiation. [4]
- b) For each of the following frequency spectra, draw the input signals and their corresponding interferogram output from a Michelson interferometer:
- Two line frequencies ν_1 and ν_2 of equal intensities [1]
 - Two line frequencies ν_1 and ν_2 of different intensities. [1]
 - A range of frequencies forming a square peak. [1]
 - A range of frequencies forming a Gaussian peak. [1]
- c) i) State Beer's Law as applied to spectroscopy and explain all terms appearing in it. [2]
- ii) What is meant by "stray light" in spectroscopy? Use appropriate equations to explain how stray light causes negative deviations in Beer's Law, and explain how stray light is eliminated in spectroscopy. [3]
- iii) Using appropriate equations, explain why measurements in spectroscopy are best carried out at the "peak" rather than the "shoulder" of molecular spectra. [4]
- d) i) Use equations to describe how uv-visible spectroscopy can be used to simultaneously determine the concentrations of two components in a mixture. [2]
- ii) Describe the "Molar Ratio Method", and explain how it is used to determine stoichiometry. [2]
- iii) Describe the "Jobs Method", and how it is used to determine stoichiometry. [2]
- e) A grating used in IR is 5cm wide with 11,800 lines/cm. Calculate the FWHM of a 400-nm line falling on the grating. [2]

QUESTION 2 [25]

- a) Describe, using diagrams and equations, the following acting as monochromators in a spectrometer:
- The Prism [3]
 - The Grating [3]
- b) The Globar is a useful source of radiation in infrared spectroscopy. However, there is a throughput disadvantage if Globar used in dispersive instruments.
- Describe the Globar as used in IR spectroscopy. [1]
 - Draw a plot of a black body radiator as a source of infrared radiation for spectroscopy in terms of energy density vs wavelength at 6000K, and 10000K. [2]
 - Explain, using the blackbody radiation plot in (ii) above, why dispersive IR instruments are throughput limited. [2]
- c) The most recent advance in IR instrumentation is the development of the FTIR technique.
- What is meant by "FTIR"? [1]
 - Write down the FT integral pair. [2]
 - Draw a block diagram of the FTIR instrument, and label all the components. [3]
 - Explain in detail, what is normally referred to as the "Jacquinot Advantage" in FTIR. [2]
- d) Consider an FTIR instrument, inside of which a mirror is moving at $1.25 \text{ cm}\cdot\text{sec}^{-1}$.
- What would be the frequency (in sec^{-1}) of the interferogram for infra-red radiation of $7.5 \mu\text{m}$. [3]
 - What length of mirror drive is required to produce a resolution sufficient to separate an infra-red doublet at 7.498 and $7.502 \mu\text{m}$. [3]

QUESTION 3 [25]

- a) What is meant by 'classical' methods of analytical dissolution? [1]
- b) In a classical dissolution of soils for the determination of lead, a 500-mg sample is first treated with 15mL nitric acid and 5mL of sulphuric acid at 100°C for 2 hours, followed by addition of 5mL of perchloric acid and heating on a sand bath for 9 hours. A white residue remains after this treatment, which dissolves after addition of HF and fuming to near dryness. In this method of digesting sample, explain the role of:
- Nitric acid. [1]
 - Sulphuric acid. [1]
 - Perchloric acid. [1]
 - Hydrofluoric acid. [1]
- c) Explain why perchloric acid is not added at the beginning of the digestion. [2]
- d) What operational precautions must be taken when using perchloric acid? [2]
- e) Describe the mechanism of dissolution in classical techniques, and explain why this method of digesting samples is time consuming. [2]
- f) Atomic spectroscopy is a powerful tool available to the analyst today.
- Two elements, X and Y are to be analyzed by flame AA and emission. The transition for element X is designed $^2S_{1/2} \longrightarrow ^2P_{2/3}$ and has a wavelength of 855.1 nm. For Y, it is $^1S_0 \longrightarrow ^1S_1$ at 228 nm. What is the ratio of excited to ground state atoms for each element, if the flame is operated at 2250°C? [2]
 - Which of the two elements would be best analyzed by absorption, and why? [2]
- g) Atomic spectroscopic techniques have many applications in agriculture, especially in the area of mine nutrition. Explain, with the aid of suitable diagrams and appropriate equations, the "Doppler Shift" and its effect on atomic spectra. [3]
- h) With respect to Ca, explain chemical interference in flame atomic absorption spectrometry and explain how it is eliminated. [4]

QUESTION 4 [25]

- a) Describe the "dissolution problem" in analytical chemistry in so far as it relates to productivity in atomic absorption spectrometry. [2]
- b) In 1990, a new method of preparing samples for the determination of total zinc and copper in soil was developed. The method was called "microwave dissolution".
- What frequency (in MHz) is used in analytical microwave digestions? [1]
 - Describe the vessels used in microwave digestions. [2]
 - Describe the mechanism of dissolution in microwave techniques, and explain why this method of digesting samples is faster than classical methods. [2]
 - Describe one operational disadvantage of using this technique for biological materials. [1]
- c) In 1995, two analytical chemists at the University of Alberta in Edmonton, Canada, reported on a new "ultrasonic digestion" method for preparation of biological samples prior to measurement with an AAS instrument.
- What frequency is used in ultrasonic digestion? [1]
 - Describe the process of "cavitation" in ultrasonic dissolution. [2]
 - Describe the mechanism of dissolution in ultrasonic methods and explain why this method is faster than classical methods. [2]

- d) Analytical chemists agree that the technique of atomic absorption came of age with the invention of the hollow cathode lamp by Sir Walsh in 1955. Use diagrams to explain why prior to 1955 AA was not practical, and why the use of hollow cathode lamps overcame the problems of that time in so far as AA work is concerned. [5]
- e) There are several unique techniques employed by the agronomy laboratory at the Simunye Sugar Estate when using the Varian Spectr-AA-10 spectrophotometer. Use diagrams and/or equations to explain:
- Why in the analysis of Sr, 100 ppm La is added to all solutions. [2]
 - Why in the analysis of Cu, the instrument is operated under "standard additions" mode. [2]
- e) Background correction is essential for some elements during flame atomic absorption measurement. Use diagrams to explain how background correction is achievable when employing the "Zeeman Effect". [3]

QUESTION 5 [25]

- a) Nebulization is a very wasteful approach to atomization.
- What does the term "nebulization" mean? [1]
 - Use diagrams to explain how nebulization is carried out in atomic spectroscopy. [2]
 - Use your answer in (a) ii above to explain why nebulization is considered inefficient. [1]
- b) What is the fundamental structural difference between FAAS instruments and GFAAS instruments? [1]
- c) With regards to the Massman atomizer:
- What material is it composed of and why this choice of material? [1]
 - What are the dual roles of the hole on top of it? [1]
 - Explain the role of argon [1]
 - Explain the role of a water jacket associated with it. [1]
- d) For each of the three stages involved in a furnace program;
- Name the stage? [3]
 - State the operational temperature. [3]
 - When is the signal sampled? [1]
- e) What is meant by a "matrix modifier" in GFAAS, give an example of such a material, and explain why used in GFAAS. [3]
- f) Discuss any three (3) advantages of furnace methods. [4]
- g) Discuss any three (3) disadvantages of furnace methods. [4]

QUESTION 6 [25]

- a) The ICP is the most widely used emission system today.
- Give the functional definition of a plasma. [2]
 - How is a plasma formed in "ICP-OES"? [2]
 - Draw the ICP torch and label all its components. [3]
- b) Explain how a tear drop-shaped plasma is formed in ICP-OES, and explain with the aid of a diagram why not analytically useful. [3]

c) With respect to the doughnut-shaped plasma, given an estimate of the following operational parameters.

Temperature [1]

Frequency [1]

Power [1]

d) With the aid of a diagram, explain how the ARL34000 “direct reader” instrument is able to determine up to 30 elements at the same time. [4]

e) “ICP-MS is unrivaled in its capacity for wide linear dynamic ranges in spectroscopy”, explain the meaning and significance of this phrase. [2]

f) Describe the mechanical interface between the plasma and the quadrupole in ICP-MS. [2]

g) What causes “isobaric” interferences in ICP-MS? Using arsenic (AS) as an example, explain how isobaric interferences are eliminated in ICP-MS. [4]

dye	pH range	pKin	Acid	Base
diator				
ci blue	1.2-2.8	1.6	red	yellow
yl yellow	2.9-4.0	3.3	red	yellow
thyl orange	3.1-4.4	4.2	red	yellow
omocresol green	3.8-5.4	4.7	yellow	blue
thyl red	4.2-6.2	5.0	red	yellow
lorophenol red	4.8-6.4	6.0	yellow	red
omothymol blue	6.0-7.6	7.1	yellow	blue
enol red	6.4-8.0	7.4	yellow	red
esol purple	7.4-9.0	8.3	yellow	purple
ymol blue	8.0-9.6	8.9	yellow	blue
enolphthalein	8.0-9.8	9.7	colorless	red
ymolphthalein	9.3-10.5	9.9	colorless	blue

n	Q ₃₀	n	Q ₅₀	n	Q ₉₀
3	0.94	6	0.56	9	0.44
4	0.76	7	0.51	10	0.41
5	0.64	8	0.47		

15. Bond Enthalpies						
kJ mol ⁻¹ at 25°C (i.e. Bond Energies)						
Single	O	N	C	S	F	Cl
H	463	391	413	368	563	432
C	358	305	346	272	489	328
N	222	163	MISC.		275	192
S-S	251	H-H	436	C=C	615	
S-F	327	N=N	946	C≡C	812	
S-Cl	271	N=O	607	C=O	749	

D.P.	t ₅₀	t ₉₀	t ₉₅	t ₉₉
1	1.0	6.3	13	64
2	0.82	2.9	4.3	9
3	0.76	2.35	3.2	5
4	0.74	2.13	2.8	4
5	0.73	2.02	2.57	4
6	0.72	1.94	2.45	3
7	0.71	1.90	2.36	3
8	0.71	1.86	2.31	3
9	0.70	1.83	2.26	3
10	0.70	1.81	2.23	3
20	0.69	1.72	2.09	2
30	0.68	1.70	2.04	2
∞	0.67	1.64	1.96	2

12. ELECTRODE POTENTIALS, E°

Li ⁺ + e ⇌ Li	-2.713
Mg ²⁺ + 2e ⇌ Mg	-2.37
Al ³⁺ + 3e ⇌ Al	-1.66
Zn ²⁺ + 2e ⇌ Zn	-0.763
Fe ²⁺ + 2e ⇌ Fe	-0.44
Cd ²⁺ + 2e ⇌ Cd	-0.403
Cr ³⁺ + e ⇌ Cr ²⁺	-0.38
Tl ⁺ + e ⇌ Tl	-0.336
V ³⁺ + e ⇌ V ²⁺	-0.255
Sb ³⁺ + 2e ⇌ Sb	-0.14
Pb ²⁺ + 2e ⇌ Pb	-0.126
H ₂ + 2e ⇌ 2H ⁻	0.000
O ₂ + 2e ⇌ 2O ²⁻	0.09
Ti ³⁺ + 2H ⁺ + e ⇌ Ti ²⁺ + H ₂ O	0.10
2H ⁺ + 2e ⇌ H ₂	0.14
Sn ⁴⁺ + 2e ⇌ Sn ²⁺	0.14
Cu ²⁺ + e ⇌ Cu ⁺	0.17
O ₄ ²⁻ + 4H ⁺ + 2e ⇌ H ₂ O + H ₂ SO ₃	0.17
AgCl + e ⇌ Cl ⁻ + Ag	0.222
Saturated calomel	(0.244)
Hg ₂ Cl ₂ + 2e ⇌ 2Cl ⁻ + 2Hg	0.268
Bi ³⁺ + 3e ⇌ Bi	0.293
UO ₂ ²⁺ + 4H ⁺ + 2e ⇌ U ⁴⁺ + 2H ₂ O	0.33
VO ²⁺ + 2H ⁺ + e ⇌ V ³⁺ + H ₂ O	0.34
Cu ²⁺ + 2e ⇌ Cu	0.34
Fe(CN) ₆ ³⁻ + e ⇌ Fe(CN) ₆ ⁴⁻	0.355
Cu ⁺ + e ⇌ Cu	0.52
3I ⁻ + 2e ⇌ 3I ²⁻	0.545
AsO ₄ ³⁻ + 2H ⁺ + 2e ⇌ AsO ₃ ³⁻ + H ₂ O	0.56
I ₂ + 2e ⇌ 2I ⁻	0.621
HgCl ₂ + 2e ⇌ Hg ₂ Cl ₂ + 2Cl ⁻	0.63
O ₂ + 2H ⁺ + 2e ⇌ H ₂ O ₂	0.69
Quinone + 2H ⁺ + 2e ⇌ Hydroquinone	0.70
Fe ³⁺ + e ⇌ Fe ²⁺	0.771
Hg ₂ ²⁺ + 2e ⇌ 2Hg	0.792
Ag ⁺ + e ⇌ Ag	0.799
Hg ²⁺ + 2e ⇌ Hg	0.851
2Hg ²⁺ + 2e ⇌ Hg ₂ ²⁺	0.907
NO ₃ ⁻ + 3H ⁺ + 2e ⇌ HNO ₂ + H ₂ O	0.94
HNO ₂ + H ⁺ + e ⇌ NO + H ₂ O	0.98
VO ₂ ⁺ + 2H ⁺ + e ⇌ VO ²⁺ + H ₂ O	0.999
Br ₂ + 2e ⇌ 2Br ⁻	1.08
2IO ₃ ⁻ + 12H ⁺ + 10e ⇌ 6H ₂ O + I ₂	1.19
O ₂ + 4H ⁺ + 4e ⇌ 2H ₂ O	1.229
MnO ₂ + 4H ⁺ + 2e ⇌ Mn ²⁺ + 2H ₂ O	1.23
Cr ₂ O ₇ ²⁻ + 14H ⁺ + 6e ⇌ 7H ₂ O + 2Cr ³⁺	1.33
Cl ₂ + 2e ⇌ 2Cl ⁻	1.358
2BrO ₃ ⁻ + 12H ⁺ + 10e ⇌ 6H ₂ O + Br ₂	1.50
MnO ₄ ⁻ + 8H ⁺ + 5e ⇌ 4H ₂ O + Mn ²⁺	1.51
Ce ⁴⁺ + e ⇌ Ce ³⁺	1.61

13. MEAN ACTIVITY COEFFICIENTS

M	KCl	Na ₂ SO ₄	ZnSO ₄
0.001	0.965	0.89	0.70
0.01	0.901	0.72	0.39
0.1	0.769	0.45	0.15

16. HEATS OF FORMATION

ΔH° in kJ mol⁻¹ at 25°C
All ions in H₂O solution except as noted
All Elements = 0

H ₂	218	H ⁺	0.0	H ₂ O _g	-242
O ₂	249	Na ⁺	-240	H ₂ O _l	-286
C _g	717	Ag ⁺	106	CO _g	-111
N _g	473	NH ₄ ⁺	-133	CO _{2g}	-394
F _g	79	OH ⁻	-230	NH _{3g}	-46
Cl _g	122	F ⁻	-333	NO _g	90
Br _g	112	Cl ⁻	-167	NO _{2g}	33
I _g	107	Br ⁻	-122	N ₂ O _{4g}	9
S _g	279	I ⁻	-55	SO _{2g}	-297
P _g	315	S=	33	SO _{3g}	-396
Na _g	107	SO ₄ ⁼	-909	H ₂ S _g	-21
K _g	88	CO ₃ ⁼	-677	NaF _g	-574
Na _g	609	HF _g	-271	NaCl _g	-411
K _g	514	HCl _g	-92	KF _g	-567
F _g	-255	HBr _g	-36	KCl _g	-437
Cl _g	-233	HI _g	26	AgCl _g	-127
CH _{4g}	-75	HCN _g	135	AgBr _g	-100
C ₂ H _{2g}	227	PH _{3g}	5	PCl _{3g}	-287
C ₂ H _{4g}	52	C ₆ H _{6g}	49	PCl _{5g}	-375
C ₂ H _{6g}	-85	CH ₃ OH _l	-238		
C ₃ H _{8g}	-105	C ₂ H ₅ OH _g	-235		
nC ₄ H _{10g}	-127	C ₂ H ₅ OH _l	-278		
nC ₈ H _{18g}	-209	COCl _{2g}	-219		
CCl _{4l}	-135	CH ₃ Cl _g	-81		

17. ABS. ENTROPY S°

J mol⁻¹ K⁻¹ at 25°C

H ₂	131	P _{4wh}	164	SF _{6g}	292
N ₂	192	HF _g	174	NO _g	211
O ₂	205	HCl _g	187	NO _{2g}	240
Cl ₂	223	H ₂ O _g	189	N ₂ O _{4g}	304
F ₂	203	CO _g	198	NH _{3g}	192
Cgra	5.7	CO _{2g}	214	PCl _{3g}	312
S _g	254	SO _{2g}	248	PCl _{5g}	365
CH _{4g}	186	SO _{3g}	256	BF _{3g}	254
C ₂ H _{6g}	229	CH ₃ OH _l	127		
C ₃ H _{8g}	270	C ₂ H ₅ OH _g	283		
C ₂ H _{2g}	201	C ₂ H ₅ OH _l	161		
C ₂ H _{4g}	219	(CH ₃) ₂ O _g	266		
C ₆ H _{6g}	269	CH ₃ COOH _g	282		

18. ΔG° FORMATION

kJ mol⁻¹ at 25°C

H ₂	203	HF _g	-273	H ₂ O _g	-229
F ₂	62	HCl _g	-95	H ₂ O _l	-237
Cl ₂	106	HBr _g	-54	SO _{2g}	-300
O ₂	232	HI _g	1.7	SO _{3g}	-371
NO _g	87	NH _{3g}	-16	PCl _{3g}	-268
NO _{2g}	51	CO _g	-137	PCl _{5g}	-305
N ₂ O _{4g}	98	CO _{2g}	-394	CH _{4g}	-51
C ₂ H _{4g}	68	C ₂ H _{2g}	209	C ₂ H _{6g}	-33
C ₆ H _{6l}	125	CH ₃ OH _l	-162		
CCl _{4l}	-65	C ₂ H ₅ OH _l	-175		
BF _{3g}	-1120	CHCl _{3g}	-70		
SF _{6g}	-1105	CH ₃ COOH _g	-374		

20. CONC. ACIDS AND BASES

	M.W.	Density	Wt. %	Mol. lit
Acetic	60.05	1.05	99.5	1
H ₂ SO ₄	98.07	1.83	94	1
HF	20.01	1.14	45	2
HCl	36.46	1.19	38	1
HBr	80.91	1.52	48	
HNO ₃	63.01	1.41	69	1
HClO ₄	100.46	1.67	70	1
H ₃ PO ₄	98.00	1.69	85	1
NaOH	40.00	1.53	50	1
NH ₃	17.03	0.90	28	

21. DENSITIES (g cm⁻³)

Water at	Air (70 cm)	Mol. lit	
0°C	0.9168	Glass	2.7
10°	0.9997	Na ₂ CO ₃	2.5
20°	0.9982	NaCl	2.2
22°	0.9978	BaSO ₄	4.5
24°	0.9973	AgCl	5.6
26°	0.9968	Aluminum	2.7
28°	0.9963	Iron	7.9
30°	0.9956	Brass	8.4
90°	0.9653	Mercury	13.6
100°C	0.0006	Platinum	21.4

22. MOBILITIES (m²V⁻¹s⁻¹ × 10⁴)

Li ⁺	39	H ₃ O ⁺	350	1/2 Ba ²⁺
Na ⁺	50	NH ₄ ⁺	73	1/3 La ³⁺
K ⁺	74	Ag ⁺	62	1/2 SO ₄ ²⁻
Cl ⁻	76	OH ⁻	198	1/2 PO ₄ ³⁻
Br ⁻	78	I ⁻	77	NO ₃ ⁻

23. WATER V.P. (torr)

0°C	4.6	25°
15°	12.8	30°
20°	17.5	50°

24. MISCELLANEOUS

Std. dev. = $\sqrt{\frac{\sum(X_i - \bar{X})^2}{(n-1)}}$
 Conf. limits = $\bar{X} \pm t_s \cdot \sqrt{n}$
 $E = E^\circ - (0.0592/n) \log([Red]/[Ox])$
 $\log I, I, = abc = A = \log 1/T$
 $\log N_r = \log N_0 = 0.301T/T_1$
 $x = (-b \pm \sqrt{b^2 - 4ac})/2a$
 $n\lambda = 2d \sin \theta$
 $2.303 \log_{10} a = \log_e a$
 $h = 6.626 \times 10^{-34} \text{ J s}$
 $e = 1.602 \times 10^{-19} \text{ C}$
 $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
 $F = 96487 \text{ C}$
 $g = 9.807 \text{ m s}^{-2}$
 $c = 2.998 \times 10^8 \text{ m s}^{-1}$
 $1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg}$
 $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$
 $= 0.08206 \text{ litre atm mol}^{-1} \text{ K}^{-1}$
 $= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
 $= 8.314 \text{ kPa dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$
 $0^\circ \text{C} = 273.15 \text{ K}$
 $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$
 $1 \text{ cal} = 4.1840 \text{ J}$