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DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF SWAZILAND

C 304

Instrumental Analysis

May 2005 Final Examination

Time Allowed:

Three (3) Hours

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**Instructions:**

1. This examination has six (6) questions, one (1) graph sheet, and one data sheet. The total number of pages is seven (7) excluding 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. Graph Sheet
2. Data Sheet

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

**Some Useful Physical Constants:**

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$c = 2.998 \times 10^8 \text{ m sec}^{-1}$$

$$N = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$k = 1.381 \times 10^{-23} \text{ JK}^{-1}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

Atomic weights: Fe = 55.85; S = 32.06; O = 16.00; H = 1.008; N = 14.01; C = 12.01

**QUESTION 1 [25]**

- (a) Hemin,  $C_{20}H_{20}N_4Fe$  is a oxygen carrying porphyrin component of the haemoglobin molecule. Being highly conjugated, hemin shows distinct absorption bands in the UV-visible portion of the electromagnetic spectrum.
- List the upper and lower limit of the UV-visible region in wavenumbers ( $cm^{-1}$ ) [1]
  - What type of transition is likely to be taking place when molecules of hemin interact with photons in the subregion mentioned in (i) above? [1]
  - What does the spectroscopic term "bathochromic shift" mean? [1]
- (b) Crystals of hemin were dissolved in concentrated nitric acid and the resultant solution diluted to 100 mL to form a 2 ppm solution. A UV-visible spectrum of the resulting solution as taken, whereby in a 11.7 mm cell, it showed a strong absorption at  $\lambda_{max} = 520$  nm of 0.528 absorbance units.
- Sketch the spectrum of this compound [1]
  - What is the transmittance in % of the sample at  $\lambda_{max}$ ? [2]
  - Calculate the molar absorptivity of this compound at  $\lambda_{max}$  [2]
- (c) The "monochromator" in a spectrometer is a critical component.
- What role does a "monochromator" play in a spectrometer? [1]
  - Describe, using diagrams, the following filters acting as monochromators in a spectrometer:
    - a band pass filter [3]
    - a cut-off filter [3]
- (d)
  - Use equations to explain why the source and sample in a spectrometer are kept in a darkened compartment [4]
  - Use equations to explain why measurements in a spectrometer are taken at the "peak" rather than at the "shoulder" [6]

**QUESTION 2 [25]**

- (a) In the analysis of Fe in natural waters, several reagents are added prior to complexation with 1,10 phenanthroline. Explain the role of the following in this analysis:
- hydroxylamine hydrochloride [1]
  - sodium acetate/acetic acid buffer [1]
  - a blank [1]
- (b) A solution of two isomers, ortho- and para-, are simultaneously determined by uv-visible spectroscopy. At 410 nm, the measured absorbance was 0.353, whereas at 560 nm, the absorbance was 0.251 in a 1.00 cm cell.

Calculate the concentration of the two isomers (molar absorptivities at 410 nm are: 6000 for ortho-, 500 for para-; at 560 nm they are 2152 for ortho-, 5260 for para-) [5]

- (c) Use diagrams to explain how the "Molar Ratio Method" can be used to determine stoichiometry [3]
- (d) Draw the expected Job's plot for a complex  $M_nL_x$  where  $n=x=1$  at low ligand concentration, and  $n=1, x=3$  at high ligand concentration [3]
- (e) Two elements, X and Y, are to be analyzed by flame AA and flame emission. The transition for element X is designated  $^2S_{1/2} \rightarrow ^2P_{3/2}$  and has a wavelength of 852.1 nm. For Y it is  $^1S_0 \rightarrow ^1S_1$  and has a wavelength of 228 nm. What is the ratio of excited to ground state atoms if the flame is operated at 2250 °C for each element? [6]
- (f) Use the ratios obtained in (d) above to decide which element is best analyzed by which method. State a reason for your choice in each case [2]
- (g) Name three elements that are determined by flame photometry in clinical analysis [3]

### QUESTION 3 [25]

- (a) The most widely used region in the electromagnetic spectrum for organic functional group identification is the infra-red (IR) region.
  - i) What are the borders of IR in electron volts? [2]
  - ii) Using the  $CO_2$  molecule as an example, describe two (2) common modes of molecular vibrations that give rise to IR radiation [2]
- (b) In dispersive IR, double beam instruments are used, whereby two beams pass through the sampling area before reaching the monochromator and detector.
  - i) Explain why the beam is split into two before reaching the sampling area [2]
  - ii) Explain why the beams pass through the sampling area before reaching the monochromator and not after it [2]
  - iii) Explain why the exact opposite of the arrangement in (ii) above is done in UV-visible instrumentation [2]
- (c) Analytical instruments configured in the Czerny-Turner arrangement of optical components use a "grating" as a monochromator.
  - i) In physical appearance, what does the grating look like? [1]
  - ii) State the Bragg equation for the grating, and explain all the terms that appear in it [3]
  - iii) If the grating is 5 cm wide with 11, 800 lines/mm, calculate its first order resolving power [3]
- (d) Although it is primarily a functional group identification tool, IR spectroscopy may sometimes be successfully used for quantitative analysis of organic compounds. One such case is the quantitative analysis of Thio-Mickler's Ketone (TMK), where the carbonyl functional group of TMK appearing at  $1785\text{ cm}^{-1}$  is used. Supposing a 5.2031-g tablet containing TMK is dissolved in 100 mL, and that this solution, together with TMK standards, yielded the following results:

Sample	I	I <sub>0</sub>	Absorbance
0 ppm standard	A	5638	0.000
2 ppm standard	4351	B	0.103
4 ppm standard	3526	5641	C
Unknown	4025	5636	

- i) Calculate A [1]
- ii) Calculate B [1]
- iii) Calculate C [1]
- iv) Draw the calibration curve of TMK [2]
- v) What was the concentration (in  $\mu\text{g/g}$ ) of TMK in the unknown sample [3]

#### **QUESTION 4 [25]**

- (a) 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.
  - i) Draw and label the hollow cathode lamp [2]
  - ii) Explain how the hollow cathode lamp works [2]
- (b) There are procedures commonly employed by analysts when using a flame atomic absorption spectrophotometer. Explain
  - i) Why in the analysis of Ca in soils, EDTA is added to all solutions [1]
  - ii) Why in the analysis of Sr in foodstuffs, 1000 ppm La is added to all solutions [1]
  - iii) Why in the analysis of Cu in a plant sample, the instrument is operated under "standard additions" mode [1]
- (c) 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? [2]
  - ii) Identify the physical stages involved in a furnace program, and describe the processes that occur during each stage [3]
  - iii) Describe two (2) advantages of graphite furnace AA over flame AA [2]
- (d) In 2001, the Swaziland Water Services Corporation acquired a new atomic spectrometer called the Liberty 110 ICP.
  - i) What does the acronym ICP stand for? [1]
  - ii) Explain how a "doughnut" shaped ICP is formed, and why it is preferred over a "tear-drop" shaped ICP. [3]
  - iii) What are the normal operating values of the ICP in terms of:  
Power in KW----- [1] Temperature in K----- [1]
  - iv) In the ICP, direct reading of several lines at once is possible. With the aid of a diagram, explain how this is possible [3]
  - v) List two (2) advantages of ICP compared to FAAS or GFAAS [2]

**QUESTION 5 [25]**

Gas Chromatographic techniques have many applications in analytical chemistry, especially in the area of pesticide and drug analysis.

- (a) In GC, explain what is meant by
- i) Temperature programming [1]
  - ii) the "race-track" effect [1]
- (b) The power of separation, technically the "resolution" in GC, depends on the plate number, or alternatively the HETP, which has its theoretical origins embodied by the Van Deemter principle. With regards to HETP for a GC packed column,
- i) explain the origin of "Eddy Diffusion"[1]
  - ii) write down the equation that relates HETP to Eddy Diffusion, and explain all terms that appear in it [2]
  - iii) explain the origin of "Longitudinal Diffusion"[1]
  - iv) write down the equation that relates HETP to Longitudinal Diffusion, and explain all terms that appear in it [2]
- (c) Draw the Van Deemter Plot for packed column GC, and identify the point in the plot that is used to determine the optimum velocity of carrier gas [3]
- (d) A GC instrument equipped with a 3-m steel column packed with Chromosorb W-AW on PEGS stationary phase and a Flame Ionization Detector, was used to quantify two alcohols, methanol and ethanol. 2-butanol was used as an internal standard. In the chromatogram, an unretained air peak appeared at 30 sec, while peaks for the two alcohols of interest appeared at 3 and 3.5 min respectively.
- i) What is meant by the prefix "AW" in Chromosorb W-AW? [1]
  - ii) State the order in which the three alcohols will elute out of the analytical column [1]
  - iii) Describe the role of 100%v/v 2-butanol in the analysis [1]
  - iv) Draw and label a diagram of an FID, and explain how it works [4]
  - v) Calculate the capacity factor of ethanol [2]
  - vi) If the column had 320 theoretical plates, what is the width of the methanol peak? [2]
  - vii) Are these two peaks properly resolved? Explain why or why not [3]

**QUESTION 6 [25]**

Liquid Chromatographic techniques have many applications in analytical chemistry, especially in the area of food and drug analysis.

- (a) In LC, explain what is meant by
- i) Solvent programming [1]
  - ii) Isocratic elution [1]

- (b) The power of separation, technically the “resolution” in LC, depends on the plate number, or alternatively the HETP, which has its theoretical origins embodied by the Van Deemter principle. With regards to HETP for an LC packed column,
- i) explain the origins of “Resistance to Mass Transfer in the Stationary Phase” [2]
  - ii) write down the equation that relates HETP to Resistance to Mass Transfer in the Stationary Phase, and explain all terms that appear in it [3]
  - iii) explain the origin of “Resistance to Mass Transfer in the Stagnant Mobile Phase” [2]
  - iv) write down the equation that relates HETP to “Resistance to Mass Transfer in the Stagnant Mobile Phase”, and explain all terms that appear in it [3]
- (c) Draw the Van Deemter Plot for packed column LC, and identify areas in the plot which are different from those of gas chromatography [3]
- (d) HPLC is widely used for Vitamin A analyses. In a typical analysis, after pre-treatment and priming, both sample and standards are injected into an HPLC instrument fitted with a 20-cm 0.5-in. glass column in a reverse-phase bonded phase mode. Eluents are detected by means of a uv detector at 254 nm.
- i) What does the acronym “HPLC” stand for? [1]
  - ii) Describe the process of “priming” in HPLC [1]
  - iii) What is the reason for the use of bonded phases in HPLC? [1]
  - iv) Use chemical equations to describe how bonded phases are synthesized in the laboratory [3]
- (e) In a lot of instances, column materials are “silinized” in chromatography.
- i) What is the role of “silinization” in chromatography [1]
  - ii) Use chemical equations to describe how silinization is achieved in the laboratory [3]

Indicator pH range pKin Acid Base
Thymol blue 1.2-2.8 1.6 red yellow
Methyl yellow 2.9-4.0 3.3 red yellow
Methyl orange 3.1-4.4 4.2 red yellow
Bromocresol green 3.8-5.4 4.7 yellow blue
Methyl red 4.2-6.2 5.0 red yellow
Chlorophenol red 4.8-6.4 6.0 yellow red
Bromothymol blue 6.0-7.6 7.1 yellow blue
Phenol red 6.4-8.0 7.4 yellow red
Cresol purple 7.4-9.0 8.3 yellow purple
Thymol blue 8.0-9.6 8.9 yellow blue
Phenolphthalein 8.0-9.8 9.7 colorless red
Thymolphthalein 9.3-10.5 9.9 colorless blue

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.F. t50 t90 t95 t9
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 2.65 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°
Na+ + e ⇌ Na -2.713
Mg2+ + 2e ⇌ Mg -2.37
Al3+ + 3e ⇌ Al -1.66
Zn2+ + 2e ⇌ Zn -0.763
Fe2+ + 2e ⇌ Fe -0.44
Cd2+ + 2e ⇌ Cd -0.403
Cr3+ + e ⇌ Cr2+ -0.38
Ti2+ + e ⇌ Ti -0.336
V3+ + e ⇌ V2+ -0.255
Sn2+ + 2e ⇌ Sn -0.14
Pb2+ + 2e ⇌ Pb -0.126
2H+ + 2e ⇌ H2 0.000
S4O62- + 2e ⇌ 2S2O42- 0.09
TiO2 + 2H+ + e ⇌ Ti3+ + H2O 0.10
S + 2H+ + 2e ⇌ H2S 0.14
Sn4+ + 2e ⇌ Sn2+ 0.14
Cu2+ + e ⇌ Cu+ 0.17
SO42- + 4H+ + 2e ⇌ H2O + H2SO3 0.17
AgCl + e ⇌ Cl- + Ag 0.222
Saturated calomel (0.244)
Hg2Cl2 + 2e ⇌ 2Cl- + 2Hg 0.268
Bi3+ + 3e ⇌ Bi 0.293
UO22+ + 4H+ + 2e ⇌ U4+ + 2H2O 0.33
VO2+ + 2H+ + e ⇌ V3+ + H2O 0.34
Cu+ + 2e ⇌ Cu 0.34
Fe(CN)63- + e ⇌ Fe(CN)64- 0.355
Cu+ + e ⇌ Cu 0.52
I3- + 2e ⇌ 3I- 0.545
H3AsO4 + 2H+ + 2e ⇌ H3AsO3 + H2O 0.56
I2 + 2e ⇌ 2I- 0.621
2HgCl2 + 2e ⇌ Hg2Cl2 + 2Cl- 0.63
O2 + 2H+ + 2e ⇌ H2O2 0.69
Quinone + 2H+ + 2e ⇌ Hydroquinone 0.70
Fe3+ + e ⇌ Fe2+ 0.771
Hg22+ + 2e ⇌ 2Hg 0.792
Ag+ + e ⇌ Ag 0.799
Hg2+ + 2e ⇌ Hg 0.851
2Hg2+ + 2e ⇌ Hg22+ 0.907
NO3- + 3H+ + 2e ⇌ HNO2 + H2O 0.94
HNO2 + H+ + e ⇌ NO + H2O 0.98
VO2+ + 2H+ + e ⇌ VO2+ + H2O 0.999
Br2 + 2e ⇌ 2Br- 1.08
2IO3- + 12H+ + 10e ⇌ 6H2O + I2 1.19
O2 + 4H+ + 4e ⇌ 2H2O 1.229
MnO2 + 4H+ + 2e ⇌ Mn2+ + 2H2O 1.23
Cr2O72- + 14H+ + 6e ⇌ 7H2O + 2Cr3+ 1.33
Cl2 + 2e ⇌ 2Cl- 1.358
2BrO3- + 12H+ + 10e ⇌ 6H2O + Br2 1.50
MnO4- + 8H+ + 5e ⇌ 4H2O + Mn2+ 1.51
Ce4+ + e ⇌ Ce3+ 1.61

13. MEAN ACTIVITY COEFFICIENTS
M KCl Na2SO4 ZnSO4
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
H2 218 H+ 0.0 H2O -242
O2 249 Na+ -240 H2O1 -286
C2 717 Ag+ 106 CO2 -111
N2 473 NH4+ -133 CO2g -394
F2 79 OH- -230 NH3g -46
Cl2 122 F- -333 NO2 90
Br2 112 Cl- -167 NO2g 33
I2 107 Br- -122 N2O4g 9
S8 279 I- -55 SO2g -297
P4 315 S= 33 SO3g -396
Na2 107 SO4= -909 H2Sg -21
K2 88 CO3= -677 NaF -574
Na2g 609 HFg -271 NaCl -411
K2g 514 HClg -92 KF -567
F2g -255 HBr -36 KCl -437
Cl2g -233 HI 26 AgCl -127
CH4g -75 HCN 135 AgBr -100
C2H2g 227 PH3g 5 PCl3g -287
C2H4g 52 C6H6l 49 PCl5g -375
C2H6g -85 CH3OHl -238
C3H8g -105 C2H5OHg -235
nC4H10g -127 C2H5OHl -278
nC8H18g -209 COCl2g -219
CCl4l -135 CH3Clg -81

17. ABS. ENTROPY S°
J mol-1 K-1 at 25°C
H2 131 P4wh 164 SF6 292
N2 192 HF 174 NO 211
O2 205 HCl 187 NO2 240
Cl2 223 H2O 189 N2O4 304
F2 203 CO 198 NH3 192
Cgra 5.7 CO2 214 PCl3 312
Sgr 254 SO2 248 PCl5 365
CH4 186 SO3 256 BF3 254
C2H6 229 CH3OH 127
C3H8 270 C2H5OH 283
C2H2 201 C2H5OH 161
C2H4 219 (CH3)2O 266
C6H6 269 CH3COOH 282

18. ΔG° FORMATION
kJ mol-1 at 25°C
H2 203 HF -273 H2O -229
F2 62 HCl -95 H2O1 -237
Cl2 106 HBr -54 SO2 -300
O2 232 HI 1.7 SO3 -371
NO 87 NH3 -16 PCl3 -268
NO2 51 CO -137 PCl5 -305
N2O4 98 CO2 -394 CH4 -51
C2H4 68 C2H2 209 C2H6 -33
C6H6 125 CH3OH -162
CCl4 -65 C2H5OH -175
BF3 -1120 CHCl3 -70
SF6 -1105 CH3COOH -374

20. CONC. ACIDS AND BAS
M.W. Density Wt. % Mol. ity
Acetic 60.05 1.05 99.5 1
H2SO4 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 1
HNO3 63.01 1.41 69 1
HClO4 100.46 1.67 70 1
H3PO4 98.00 1.69 85 1
NaOH 40.00 1.53 50 1
NH3 17.03 0.90 28 1

21. DENSITIES (g cm-3)
Water at Air (70 cm) 0.00
0°C 0.9168 Glass 2.7
10°C 0.9997 Na2CO3 2.5
20°C 0.9982 NaCl 2.2
22°C 0.9978 BaSO4 4.5
24°C 0.9973 AgCl 5.6
26°C 0.9968 Aluminum 2.7
28°C 0.9963 Iron 7.9
30°C 0.9956 Brass 8.4
90°C 0.9653 Mercury 13.6
100°C 0.0006 Platinum 21.4

22. MOBILITIES (m2 V-1 s-1 x 10-4)
Li+ 39 H3O+ 350 1/2 Ba2+
Na+ 50 NH4+ 73 1/2 La3+
K+ 74 Ag+ 62 1/2 SO4=
Cl- 76 OH- 198 1/2 PO4=
Br- 78 I- 77 NO3=

23. WATER V.P. (torr)
0°C 4.6 25°C
15°C 12.8 30°C
20°C 17.5 50°C

24. MISCELLANEOUS
Std. dev. = √Σ(Xi - X̄)² / (n-1)
Conf. limits = X̄ ± ts / √n
E = E° - (0.0592/n) log (Red)/(Ox)
log I1 I2 = abc = A = log 1/T
log Nr = log Nu = 0.301T/T1
x = (-b ± √(b² - 4ac)) / 2a
nλ = 2d sin θ
2.303 log10 a = loge a
h = 6.626 x 10-34 J s
e = 1.602 x 10-19 C
NA = 6.022 x 1023 mol-1
F = 96487 C
g = 9.807 m s-2
c = 2.998 x 108 m s-1
1 amu = 1.661 x 10-27 kg
R = 1.987 cal mol-1 K-1
= 0.08206 litre atm mol-1 K-1
= 8.314 J mol-1 K-1
= 8.314 kPa dm3 mol-1 K-1
0°C = 273.15 K
1 eV = 1.602 x 10-19 J
1 cal = 4.1840 J

