DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

C612 SPECTRO CHEMICAL ANALYSIS

DECEMBER 2010 FINAL EXAMINATION

Time Allowed: Three (3) Hours

Instructions:

1. This examination has six (6) questions. nThe 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.

Useful Physical Constants

1. $k_{HCl} = 400\ Nm^{-1}$ $N = 6.02 \times 10^{23}$ $H = 1.008$ $Cl = 35.45$
2. $h = 6.626 \times 10^{-34}\ Js^{-1}$ $C = 2.998 \times 10^{8}\ cm\ sec^{-1}$ $1\ eV = 1.602 \times 10^{-19}\ J$

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

QUESTION 1 [25]

a) The Globar is one of the most widely used sources in infra red spectroscopy.

(i) Give a brief description of the Globar. (1)

(ii) Calculate λ_{max} in cm^{-1}, for the Globar heated to 500K, given its Wein's Displacement constant of 2.9 x 10^{-3}mK.(2)

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

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

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

(ii) How does quantum mechanics explain the appearance of a fundamental vibration band of HCl at approximately 1800 cm^{-1}.(3)

(iii) Explain why dispersive IR instruments suffer from poor resolution. (3)

c) 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? (3)

(iv) How does quantum mechanics explain the hyperfine appearance of the H-Cl fundamental vibration band, i.e., the equally-spaced lines making up this band being separated by 10 cm^{-1}? (3)

QUESTION 2 [25]

a. 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 300 mm is diffracted when it hits the grating. (3)

(ii) Calculate the first order resolving power of this grating, and calculate the resolution at 750 mm.(3)

b. 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 x 10^{-5}.

(i) State Snells law for a prism. (1)

(ii) Calculate the resolution power of the prism, and the resolution at 5268 Å. (3)

(iii) Use diagrams to explain the principle of "Resolution As Limited by the Exit Slit" (2)

c. Draw the circular type Photo Multiplier Tube (PMT) and explain how it works. (3)

d. Use the photon counting experiment to demonstrate the nature of a PMT signal. (3)

e. There are many applications of uv-visible spectroscopy today.

(i) Describe how uv-visible spectroscopy can be used to determine the dissociation constant, Ka, for a weak acid HA. (3)

(ii) Describe the "Jobs Method of Continuous Variation", and explain how it was used to arrive at the conclusion that the stoichiometry of the palladium-Thio Mickler's Ketone complex is 1:1 at low ligand concentrations, and 1:4 at high ligand concentrations. (4)

QUESTION 3 [25]

a. (i) Use the molecular orbital diagram of CH_2O, formaldehyde, to explain the origin of the n $\longrightarrow$ π^* transition, and explain why it appears as a spectroscopic band. (4)

(ii) State the difference between "bathochromic" and "hypsochromic" shift in uv-visible spectroscopy.(2)

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. In the table below,

Spectral Region	Energy (J)	Type of Transition	Wavelength (nm)	Frequency (sec^{-1})	Wavenumber (cm^{-1})	Energy (eV)
gamma rays				10^{20}		A
x-ray		B				120
uv-visible			700			
infra-red		D			4,000	
micro-wave			G	10^{8}	F	

(i) Use a diagram to describe the transition labelled "B". (3)

(ii) Calculate "A" in MeV. (3)
(iii) Use a diagram to describe the transition labelled "D". (3)
(iv) Calculate "G" (3)
(v) Calculate "F" (1)

b. 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) ICP-OES (3)

(ii) DC Spark (3)

(iii) Flame Atomic Absorption Spectroscopy (3)

(iv) Electrothermal Vaporization Atomic Absorption Spectroscopy (3)

QUESTION 5 [25]

a. (i) Use the hydrogen Grotrian diagram and Bohr-Rydberg equation to explain the atomic lines of hydrogen spectra.(3)

(ii) Explain why ultrasonic digestion of a biological sample is faster than a conventional digestion.(3)

(iii) Use diagrams and equations to show why atomic absorption measurements are most sensitive when carried out using the resonance line of an atom. (3)

(iv) Starting with the sample before aspiration, trace the path of Ca in a solution in flame atomic absorption spectroscopy, up until the final number of absorbing atoms per unit volume in a flame. (4)

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. (3)

(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 (3) desirable characteristics of an internal standard, and how are analytes quantified using it? (3)

QUESTION 6 [25]

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

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

(ii) What are the six (6) events that take place in the analytical gap of an AC Spark spectrometer (6)

(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 three (3) advantages of using a photographic plate as a detector in AC Spark emission over a photomultiplier tube. (3)

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) 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)