DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

C612/CHE 607 **SPECTRO CHEMICAL ANALYSIS**

DECEMBER 2017 **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 four (4), 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) 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) 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) Discuss any three (3) advantages of AC Spark over DC Arc emission spectroscopy in the determination of Al in steels. (3)

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

(i) Use a diagram to show why it is possible for the ICP to measure up to 35 elements simultaneously. (4)

(ii) How does the "order of magnitude" of the ICP compare with that of the atomic absorption techniques, and what are the implications of this? (2)

d) (i) Use diagrams to explain how a helium neon (He-Ne) laser works (4)

(i) Describe the main characteristics that make the He-Ne laser desirable as a source of electromagnetic radiation in UV-Visible spectroscopy. (2)

QUESTION 2 [25]

a) Fourier transform techniques have contributed immensely to 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)

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) Describe the principle of cold vapour atomic absorption spectroscopy, and explain why it is preferred over flame AAS (4)

e) Describe the mechanism of analytical dissolution using ultrasound, and explain why this method of digesting samples is faster than classical hot plate methods. (4)

QUESTION 3 [25]

a) There are certain operational difficulties associated with coupling a quadrupole mass spectrometer to an inductively coupled plasma spectrometer.

(i) Draw a schematic diagram of an ICP-MS instrument that uses a quadrupole unit, showing the ICP-MS interface. (4)

(ii) Explain how the interface works. (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 2.7×10^{-5}.

(i) State Snell's law for a prism (2)

(ii) Calculate the resolving power of the prism, and the resolution at 5268 A° (4)

(iii) Use diagrams to explain the principle of "Resolution As Limited by the Exit Slit" in spectroscopy (4)

c) Photodiode arrays (PDA's) are widely used as dectectors in uv-visible spectroscopy. Use a diagram to explain how a PDA works. (4)

d) Describe the principle of Attenuated Total Reflectance (ATR) and how it forms the basis of sensitive IR sampling technique. (4)

QUESTION 4 [25]

a) The DC Arc emission spectroscopic technique is one of the oldest atomic emission 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)

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

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

(iii) 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)

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)

b) Use diagrams to explain why it was not possible to measure metals by atomic absorption spectroscopy before the advent of the hollow cathode lamp. (5)

QUESTION 5 [25]

a) Define "detection limit" in analytical measurements. (4)

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

(i) Use the Planck-Einstein equation to explain why dispersive IR instruments suffer from poor resolution. (4)

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

(iii) Explain why the Glower heated to 500 K is at the ideal temperature for use as an IR source compared to 10,000K. (3)

c) Describe the mechanism of microwave acid digestion when preparing samples for flame atomic absorption spectroscopy, and explain why this digestion method is preferred over the more traditional hot plate method. (5)

d) Use equations to describe chemical equilibration processes occurring in a flame when a $CaCl_2$ solution is aspirated to in an atomic absorption spectrophotometer (6)

QUESTION 6 [25]

a) Use a diagram to illustrate Rayleigh's criterion for resolution of peaks in spectroscopy. (2)

b) Use the photon counting experiment to demonstrate the nature of a PMT signal. (4)

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) What is meant by the "Connes Advantage" in FT-IR? (3)

(v) What is meant by the "Fellget Advantage" in FT-IR? (3)

d) (i) Give a brief description of the ICP as a source of emission signals. (2)

(ii) State the SAHA equation and explain how temperature measurements in a non-chemical flame of the ICP is carried out using it. (2)