DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

C612 **SPECTRO CHEMICAL ANALYSIS**

DECEMBER 2015 **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. 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. The ICP is the most widely used emission system today.

i) Draw the ICP torch and label all its components. [4]

ii) State the Saha Equation, and explain how it is used to estimate temperature inside an inductively coupled plasma. [3]

c. Explain why an inductively coupled plasma has fewer chemical interferences as compared to a flame in atomic spectroscopy [2]

d. "ICP is unrivaled in its capacity for wide linear dynamic ranges in spectroscopy", explain the meaning and significance of this phrase. [3]

QUESTION 2 [25]

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

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

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

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

(iv) Explain why dispersive IR instruments suffer from poor resolution. [2]

b. Atomic spectroscopic techniques have many applications in agriculture, especially in the area of mineral nutrition. Explain, with the aid of suitable diagrams and appropriate equations:

i) the "Doppler Shift" and its effect on atomic spectra. [3]

ii) "Natural line broadening" and its effect on atomic spectra. [3]

c. Describe the path of a Ca atom (starting as off Ca Cl_2 solution) as soon as it enters the spray chamber in an AA instrument, up until it emits in flame emission spectrometry. [4]

e. Atomic spectroscopy is a powerful tool available to the analyst today.

i) Two elements, X and Y are to be analyzed by flame AA and emission. The transition for X is designated $^2S_{1/2} \longrightarrow {}^2P_{3/2}$ and has a wavelength of 852.1 nm. For Y, it is $^1S_0 \longrightarrow {}^1S_1$ at 228 nm. What is the ratio of excited to state atoms for each element, if the flame is operated at 2250 ^{0}C [5]

ii) Which of the two elements would be best analyzed by absorption, and why? [2]

QUESTION 3 [25]

a. The noise associated with signals generated by analytical instruments is a limiting factor in detection limits. With regards to noise

   i) Define "detection limit' of an instrument. [2]

   ii) Explain why for metals in general, the detection limits improve when moving from flame atomic absorption spectroscopy to graphite furnace atomic absorption spectroscopy, to inductively coupled plasma optical emission. [3]

b. i) Explain how the silt width affects resolution in dispersive infra-red spectroscopy. [1]

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

c. i) Gratings are one of the widely used monochromators in analytical instrumentation today. Given a grating that is 4.6 cm wide with 1000 lines/mm, calculate the first order resolving power of the grating, and the resolution at 750 nm. [3]

   ii) Prisms are one of the widely used monochromators in analytical instrumentation today. Given a prism length of 5 cm and a dispersion of 2708 cm^{-1}, calculate the resolving power of the prism, and the resolution at 5268 angstroms. [4]

d. Use the photon counting experiment to demonstrate the nature of a PMT signal. [3]

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

f. Describe the principle of Attenuated Total Reflectance (ATR) and how it forms the basis of sensitive IR sampling technique. [3]

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 a classical dissolution of soils for the determination of lead, a 500-mg sample is first treated with 15 mL nitric acid and 5 mL of sulphuric acid at 100 ^{0}C for 2 hours, followed by addition of 5 mL 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 a sample, explain the role of:

   i) Nitric acid. [1]

   ii) Sulphuric acid. [1]

   iii) Perchloric acid. [1]

   iv) 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. 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".

i) What frequency (in MHz) is used in analytical microwave digestions? [1]

ii) Describe the vessels used in microwave digestions. [2]

iii) Describe the mechanism of dissolution in microwave techniques, and explain why this method of digesting samples is faster than classical methods. [2]

iv) Describe one operational disadvantage of using this technique for biological materials. [1]

g. In 1995, two analytical chemists at the University of Alberta in Edmonton, Canada, reported on a novel "ultrasonic digestion" method for preparation of biological samples prior to measurement with an ICP instrument.

i) What frequency is used in ultrasonic digestions? [1]

ii) Describe the process of "cavitation" in ultrasonic dissolution. [2]

iii) Describe the mechanism of dissolution in ultrasonic methods, and explain why this method is faster than classical methods. [4]

QUESTION 5 [25]

a. 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]

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? [3]

QUESTION 6 [25]

a. Use a drawing to explain how the Michaelson interferometer works in FTIR spectrometry [3]

b. State the Fourier Transform intergral pair that describes the output of a Michaelson interferometer [2]

c. Describe the following with regards to FTIR

i) The Jacquinot Advantage [2]
ii) The Multiplex Advantage [2]
iii) The Connes Advantage [2]

d. Consider an FTIR instrument, inside of which a mirror is moving at 1.25 $cm.sec^{-1}$.

i) What would be the frequency (in sec^{-1}) of the interferogram of infra-red radiation of 7.5 μm. [3]

ii) What length of mirror drive is required to produce a resolution sufficient to separate an infra-red doublet at 7.498 and 7.502 μm. [3]

e. For each of the following frequency spectra, draw the input signals and their corresponding interferogram output from a Michelson interferometer:

i) Two line frequencies v_1 and v_2 of equal intensities [2]

ii) Two line frequencies v_1 and v_2 of different intensities [2]

iii) A range of frequencies forming a square peak. [2]

iv) A range of frequencies forming a Gaussian peak. [2]