

**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SWAZILAND**

C512

SPECTRO ANALYTICAL METHODS

DECEMBER 2008 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.**

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), its frequency (in Hertz), and state what type of transition is taking place to produce 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. Using appropriate equations, explain why measurements in spectroscopy are best carried out at the "peak" rather than at the "shoulders" of molecular spectra. [4]
- d. Use diagrams to explain how a photodiode array (PDA) works as a detector in uv-visible spectroscopy. [5]
- e. 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]
- f. A grating used in IR is 5cm wide with 11,800 lines/cm. Calculate the FWHM of a 400-nm line falling on this grating. [2]

QUESTION 2 [25]

- a. The Globar is a useful source of radiation in infrared spectroscopy. However, there is a throughput disadvantage if a Globar used in dispersive instruments.
- Describe the Globar as used in IR spectroscopy. [1]
 - Draw a plot of a blackbody radiator as a source of infrared radiation for spectroscopy in terms of energy density vs wavelength at 6000K, and at 10000K. [2]
 - Explain, using the blackbody radiation plot in (ii) above, why dispersive IR instruments are throughput-limited. [2]
- b. Use a diagram to explain how a "thermistor" detects infra-red radiation. [2]
- c. Use a diagram to explain how a "bolometer" detects infra-red radiation. [4]
- d. 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]
- e. 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 of 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 a 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 the 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 grounded state atoms for each element, if the flame is operated at 2250°C? [5]
 - 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 mineral nutrition. Explain, with the aid of suitable diagrams and appropriate equations, the “Doppler Shift” and its effects 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 novel “ultrasonic digestion” method for preparation of biological samples prior to measurement with an ICP instrument.
- What frequency is used in ultrasonic digestions? [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, 1000 ppm La is added to all solutions prior to measurement. [2]
 - Why in the analysis of Cu, the instrument is operated under "standard additions" mode. [2]
- f. 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. [3]
 - Use your answer in (a) ii above to explain why nebulization is considered inefficient. [2]
- b. What is the fundamental structural difference between FAAS instruments and GFAAS instrument? [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 is sampled? [1]
- e. What is meant by a "matrix modifier" in GFAAS, give an example of such a material, and explain why it is used in GFAAS. [3]
- f. Discuss any three (3) advantages of furnace methods. [3]
- g. Discuss any three (3) disadvantages of furnace methods. [3]

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. i). Explain how a flame causes chemical interferences in atomic absorption spectroscopy. [3]

- ii). Explain why an inductively coupled plasma has fewer chemical interferences as compared to a flame in atomic spectroscopy [2]
 - iii). Explain why electrothermal methods of atomization are considered more efficient than flame or plasma methods in atomic spectroscopy. [2]
- c. With the aid of a diagram, explain how the ARL34000 "direct reader" instrument is able to determine up to 35 elements at the same time. [4]
- d. "ICP-MS is unrivaled in its capacity for wide linear dynamic ranges in spectroscopy", explain the meaning and significance of this phrase. [2]
- e. Describe the mechanical interface between the plasma and the quadrupole in ICP-MS. [2]
- f. What causes "isobaric" interferences in ICP-MS? Using arsenic (AS) as an example, explain how isobaric interferences are eliminated in ICP-MS. [4]

Values of Student's *t*

Degrees of freedom	Confidence level (%)				
	50	80	90	95	99
1	1.000	3.078	6.314	12.706	63.657
2	0.816	1.886	2.920	4.303	9.925
3	0.765	1.638	2.353	3.182	5.841
4	0.741	1.533	2.132	2.776	4.604
5	0.727	1.476	2.015	2.571	4.032
6	0.718	1.440	1.943	2.447	3.707
7	0.711	1.415	1.895	2.365	3.500
8	0.706	1.397	1.860	2.306	3.355
9	0.703	1.383	1.833	2.262	3.250
10	0.700	1.372	1.812	2.228	3.169
15	0.691	1.341	1.753	2.131	2.947
20	0.687	1.325	1.725	2.086	2.845
∞	0.674	1.282	1.645	1.960	2.576

Note: In calculating confidence intervals, σ may be substituted for s in Equation 4-6 if you have a great deal of experience with a particular method and have therefore determined its "true" population standard deviation. If σ is used instead of s , the value of t to use in Equation 4-6 comes from the bottom row of Table 4-2.

Values of *t* for ν Degrees of Freedom for Various Confidence Levels*

ν	Confidence Level, 90%	95%	99%	99.5%
1	6.314	12.706	63.657	127.32
2	2.920	4.303	9.925	14.089
3	2.353	3.182	5.841	7.453
4	2.132	2.776	4.604	5.598
5	2.015	2.571	4.032	4.773
6	1.943	2.447	3.707	4.317
7	1.895	2.365	3.500	4.029
8	1.860	2.306	3.355	3.832
9	1.833	2.262	3.250	3.690
10	1.812	2.228	3.169	3.581
15	1.753	2.131	2.947	3.232
20	1.725	2.086	2.845	3.183
25	1.708	2.060	2.787	3.078
∞	1.645	1.960	2.576	2.807

* $\nu = N - 1 =$ degrees of freedom.

Values of F at the 95% Confidence Level

v_2	$v_1 = 2$	3	4	5	6	7	8	9	10	15	20	30
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.70	8.66	8.62
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.86	5.80	5.75
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.62	4.56	4.50
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	3.94	3.87	3.81
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.51	3.44	3.38
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.22	3.15	3.08
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.01	2.94	2.86
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.85	2.77	2.70
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.40	2.33	2.25
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.20	2.12	2.04
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.01	1.93	1.84

Rejection Quotient, Q , at Different Confidence Limits^a

No. of Observations	Confidence level		
	Q_{90}	Q_{95}	Q_{99}
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568
15	0.338	0.384	0.475
20	0.300	0.342	0.425
25	0.277	0.317	0.393
30	0.260	0.298	0.372

^aAdapted from D. B. Rorabacher, *Anal. Chem.*, 63 (1991) 139.