

UNIVERSITI SAINS MALAYSIA

Second Semester Examination
Academic Session 2002/2003

February/March 2003

KAA 502 -Atomic Spectroscopy

Time: 3 hours

PUSAT PENGAJIAN SAINS KIMIA
UNIVERSITI SAINS MALAYSIA
11800 USM PULAU PINANG

Please make sure this paper consists of SEVEN typed pages before answering the questions.

Answer FIVE questions. Only the first five questions answered by the candidate will be marked.

1. (a) Suggest the most suitable method for the determination of the following analytes. Give reasons for your choice.

- (i) Potassium in blood serum.
- (ii) Selenium in milk.
- (iii) Calcium in tap water.
- (iv) Arsenic in urine.
- (v) Chromium in blood.
- (vi) Antimony in airborne particulates.

(12 marks)

(b) Give a reason why each of the statements below are true.

- (i) Spectral lines in flames often have half widths (full widths at half maximum intensity) on the order of 0.005 to 0.01 nm, whereas natural broadening is predicted to give a line width on the order of 2×10^{-5} nm.
- (ii) A monochromator with a spectral bandpass < 0.1 nm is usually found in atomic emission systems, while in atomic absorption systems the monochromator often has a spectral bandpass in the range of 0.2 to 1.0 nm.

(4 marks)

.../2-

AAS – Atomic Absorption Spectroscopy
ICP – Inductively coupled plasma

AES – Atomic Emission Spectroscopy
MS – Mass Spectrometry

- (c) The flame emission determination of Na in a biological sample is being considered. Discuss the most important factors that will influence the choice of which flame to use. Include the advantages and disadvantages of low and high temperatures for this determination. Suggest a suitable flame to be used from the list in the table given.

Fuel-oxidant	Theoretical stoichiometric temperature (K)
Propane – air	2267
H ₂ – air	2380
C ₂ H ₂ – air	2540
C ₂ H ₂ – N ₂ O	3150
C ₂ H ₂ – O ₂	3342

(4 marks)

2. (a) As the focus of analytical chemistry has changed from macro to trace analysis, the role of the sample preparation chemist has changed with it. In addition to or even instead of sample dissolution, the analyst may have to perform an extraction or preconcentration of the sample. Explain briefly what are the complimentary goals for these procedures. What would be two competing problems that require the analyst's attention?

(8 marks)

- (b) Compare flame atomic absorption spectroscopy to furnace atomic absorption spectroscopy in terms of analysis time, sample volume, operator attention, detection limits and vulnerability to physical/chemical interferences.

(7 marks)

- (c) The following data were obtained for the determination of copper in a contaminated stream by ICP-AES using the 324.754 nm copper line and the method of standard additions.

Vol. of stream water (mL)	Vol. of distilled water (mL)	Vol. of 1 mg L ⁻¹ Cu standard added (mL)	Emission Intensity (cps)
5	5	0	440
5	4	1	1540
5	3	2	2640
5	1	4	4800

Calculate the copper concentration in the original stream water sample.

(5 marks)

.../3-

3. (a) The following blank-corrected readings were obtained for the determination of nickel in steel, using nickel standards dissolved in iron solution (10 g L^{-1}). The determination was performed by atomic absorption spectroscopy using an air-acetylene flame and the 232 nm nickel line.

Nickel concentration (mg L^{-1})	Absorbance
1	0.06
2	0.11
4	0.22
6	0.34
8	0.44
10	0.55
12	0.60

Find the characteristic concentration (i.e. the concentration corresponding to an absorbance of 0.0044) for nickel (in iron solution) using this instrument. If a 1% (w/v) solution of steel gave an absorbance of 0.36, what would be the concentration of nickel in the solution, and in the steel sample as a w/w percentage?

(8 marks)

- (b) Two dimensional detectors incorporating charge-injection devices (CIDs) or charge-coupled devices (CCDs) have been incorporated into commercial instruments. They allow simultaneous measurement of more than 250,000 lines for the CID device and 5000 lines for the segmented CCD instrument. These solid-state detector devices may eliminate photomultiplier-based direct reading ICP emission spectrophotometers altogether. Give reasons to support this statement.

(6 marks)

- (c) Future directions for instrument development might include simultaneous ICP atomic emission and mass spectrometry. How do you propose that this can be accomplished? What would be the potential benefits of such a combination?

(6 marks)

4. (a) The following data were obtained for cadmium at m/z 111 when spraying a standard solution of 0.1 ng mL^{-1} cadmium, using an inductively coupled plasma mass spectrometer with a 60 s scan over the range m/z 5 – 255.

Sample No.	Signal (cps)
1	510
2	430
3	480
4	570
5	550
6	510
7	440
8	490
9	550
10	590
11	590

Calculate the mean count rate and the standard deviation for the series of readings. Calculate the detection limit for cadmium as the concentration which would apparently give a reading equal to three times the standard deviation. Suggest how a lower detection limit might be achieved which would overcome the very noisy signals obtained.

(8 marks)

- (b) Discuss briefly the reasons for the following observations in ICP- MS listed below:
- (i) In the determination of arsenic in an effluent containing large amounts of sodium chloride, the apparent arsenic signal at m/z 75 was reduced when the sample was pretreated by passing it through an anion-exchange column.
 - (ii) The determination of antimony in a lead sample gave a low result when compared with aqueous standards, but improved when the sample was diluted.
 - (iii) Far fewer spectroscopic interferences are observed with a magnetic sector compared to a quadrupole mass analyzer.
 - (iv) The determination of iron in water is greatly improved by the use of cool plasma conditions.

(12 marks)

.../5-

5. (a) The following table lists the detection limits of various elements for several types of nebulizers used in ICP – AES.

Element*	λ (nm)	Concentric glass (P.N.)	Babington (P.N.)	Ultrasonic Nebulizer
Mo (I)	386.41	103	78	7.2
Ni (I)	341.48	50	36	3.7
Cu (I)	324.75	4.8	4.3	0.77
Ca (II)	315.89	11	16	1.5
Zn (I)	213.86	3.3	2.6	0.37

* I – atom lines. II – ion lines

P.N. – pneumatic nebulizer

Explain briefly the significant difference between detection limits obtained with the ultrasonic nebulizer to that obtained with the two pneumatic nebulizers given in the table above. What is the advantage of the Babington nebulizer?

(6 marks)

- (b) Analytes introduced into inductively coupled plasma torches spend about 2 ms at temperatures between 4000 – 8000 °C and this temperature cross section of the torch is relatively uniform. How do these characteristics influence the performance of an ICP torch for atomic emission spectroscopy?

(4 marks)

- (c) The following data was collected in the lab from an experiment.

Concentration (mg L ⁻¹)	Signal from internal standard	Signal from analyte
0	1.356	0.041
1	1.539	0.908
2	0.881	1.013
5	1.906	5.394
Unknown #1	1.383	1.978
Unknown #1	1.102	1.638
Unknown #1	1.356	1.863

Determine the concentration of the unknown.

(5 marks)

- (d) Figure 1 shows the effect of increasing amounts of phosphate on the absorbance of 20 mg L^{-1} calcium in the absence of lanthanum, La, and in the presence of lanthanum at a final concentration of 0.1 % or 1 %.

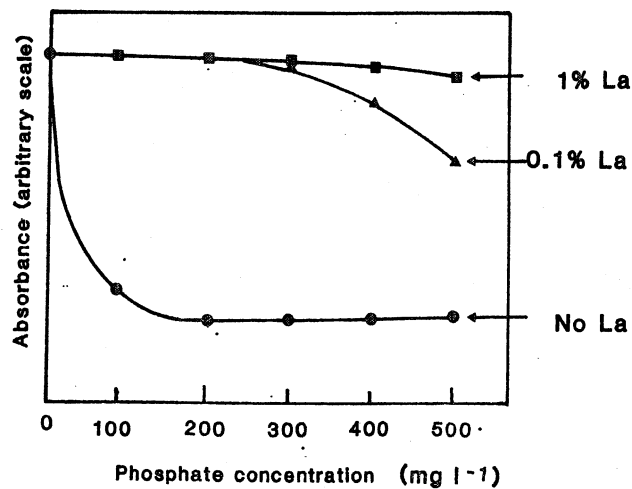


Figure 1

Explain the curves obtained in Figure 1. How would the presence of trace amounts of analyte impurity in the lanthanum solution affect the determination of the analyte?

(5 marks)

6. (a) Discuss the reasons for the following:
- (i) Compared with flame atomizers, electrothermal atomizers generally result in enhanced sensitivity for atomic absorption spectroscopy.
 - (ii) Metals dissolved in organic solvents can show either enhanced or reduced sensitivity compared with those in aqueous solutions in atomic spectroscopy.
- (6 marks)
- (b) Why is an echelle monochromator ideal for use with an array detector?
- (5 marks)
- (c) What are the advantages of isotope dilution analysis compared to external calibration?
- (4 marks)

- (d) Figure 2 shows the effect of increasing amounts of europium on the apparent absorbance of 1 mg L^{-1} copper at the main copper resonance lines.

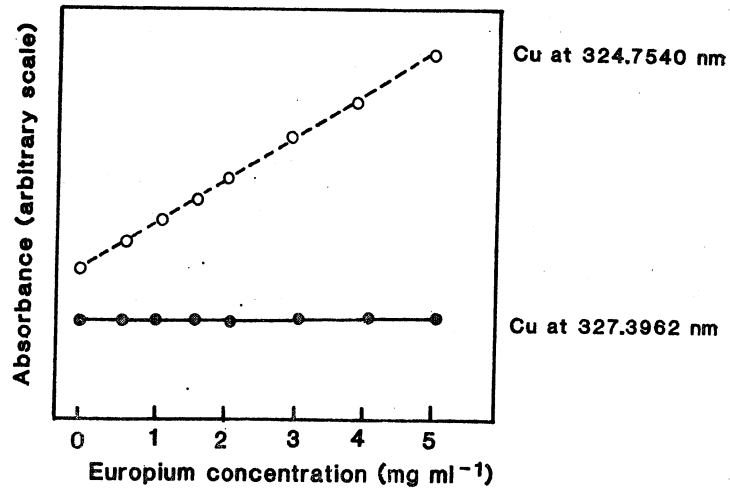


Figure 2

What kind of interference does europium present for the determination of copper? Which line of copper should be used in the determination of copper in a sample containing europium? Give your reasons.

(5 marks)

oooOooo