UNIVERSITI SAINS MALAYSIA

Second Semester Examination
Academic Session 2004/2005

March 2005

KAA 502 – Atomic Spectroscopy

Time: 3 hours

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

Answer FIVE questions only. This paper contains SIX questions.

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

1. (a) How would you carry out the determination of calcium in a yogurt sample using flame atomic absorption spectrometry? Please include the sample preparation method and calibration technique used. Outline all steps taken to ensure that all chemical and physical interferences are overcome. How do you validate your results?

(10 marks)

(b) How is background correction based on the Zeeman effect performed in a graphite furnace atomic absorption spectrometer?

(6 marks)

(c) The maximum burning velocity for an air/acetylene flame is 160 cm s^{-1} whereas that for a nitrous oxide/acetylene flame is 285 cm s^{-1}. How does this influence the kind of slot burners used for both flames?

(4 marks)

2. (a) Explain how matrix modification may lead to more efficient matrix removal in electrothermal atomization. Give an example.

(4 marks)

(b) Why is an echelle monochromator most suitable to be used with an array detector?

(5 marks)

(c) The determination of trace elements in seawater is carried out using a graphite furnace atomic absorption spectrometer. Calibration is achieved by the method of standard additions. The trace metals are first separated from their complex in high salt matrix by coprecipitating them with Fe^{3+}. A 5.00 mL of 2000 ppm Fe^{3+} solution was added to a 1.00 L sample of sea water to precipitate the $Fe(OH)_3$ after the pH is adjusted to 9. The precipitate is isolated, rinsed and dissolved in 2 mL concentrated HNO_3 and diluted to volume in a 50 mL volumetric flask. To analyze for Mn^{2+}, a 1.00 mL sample of this solution was diluted to 100 mL in a volumetric flask. The following samples were injected into a graphite furnace and analyzed.

Solution	Absorbance
2.5 μL sample + 2.5 μL 0 ppb Mn^{2+} standard	0.223
2.5 μL sample + 2.5 μL 2.5 ppb Mn^{2+} standard	0.294
2.5 μL sample + 2.5 μL 5.0 ppb Mn^{2+} standard	0.361

Report the concentration of Mn^{2+} in the sample of seawater in ppb.

(11 marks)

3. (a) The requirements for a monochromator in flame emission and atomic absorption are rather different. Assume that your laboratory is considering the purchase of a monochomator. Your choice is a variable slit width system (lowest spectral bandwidth = 0.5 Å) with high resolution but is expensive and another system with fixed slit widths (spectral bandwidth = 10 Å), medium resolution and is less expensive. Which system will you choose for your laboratory if you are only involved with atomic absorption measurements? Give reasons for your choice (with respect to functions of the monochromator for both techniques and the role of the monochromator in overcoming interferences).

(10 marks)

(b) Suggest the most suitable method for the following determinations. Please give justifications for your answer.

(i) Calcium in blood serum.

(ii) Selenium in milk.

(iii) Calcium in tap water.

(iv) Chromium in blood.

(v) Antimony in air particulates.

(10 marks)

4. (a) Give a scientific reason for the following statements:

(i) Ionization interferences are usually not as severe in the inductively coupled plasma (ICP) as in flames.

(ii) Potassium salts (such as KCl) are frequently added when one wants to measure elemental sodium by flame photometer.

(10 marks)

(b) Potassium concentration in a blood serum is to be analyzed using the method of standard addition by flame emission spectrometry. Two extractions of 0.5 mL of serum were taken to create two identical solutions and then both were diluted further with distilled water to a final volume of 5 mL. A 10 µL of 0.2 M KCl is introduced to one of these. The values obtained from the apparatus were 32.1 and 58.6 arbitrary units. What is the potassium concentration (M) of the serum?

(10 marks)

5. (a) (i) What advantages does an ICP source offer over an electrical discharges source? Do electrical discharge sources have any advantages over ICP sources? Explain.

(ii) Flame atomic absorption spectrometry has achieved very wide use as a routine method for the determination of trace metals in solution. However, for alkali metals flame photometry has remained popular. Why is this?

(iii) What is the purpose of an internal standard in ICP-MS?

(10 marks)

(b) The chromium in a series of steel samples was determined by ICP-AES. The spectrometer was calibrated with a series of standards containing 0, 2.0, 4.0, 6.0 and 8.0 µg $K_2Cr_2O_7$ per mL. The instrument readings for these solutions were 3.1, 21.5, 40.9, 57.1 and 77.3 respectively, in arbitrary units. The following data were obtained for replicate 1.00 g samples of cement dissolved in HCl and diluted to 100.0 mL after neutralization. Calculate the percentage of Cr_2O_3 in each sample. What is the reproducibility for each determination?

	Emission readings		
	Blank	Sample A	Sample B
Replicate 1	5.1	28.6	40.7
Replicate 2	4.8	28.2	41.2
Replicate 3	4.9	28.9	40.2

(10 marks)

6. (a) Explain clearly why atomic emission methods with an ICP source are better suited for multielement analysis than flame atomic absorption methods.

(5 marks)

(b) What are the main ionization and excitation mechanisms that occur in the ICP?

(5 marks)

(c) How does an ion sampling interface system used for ICP-MS compare with those used for ICP-AES?

(5 marks)

(d) Give your opinions why has ICP-MS become an important and widely used analytical method.

(5 marks)

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