UNIVERSITI SAINS MALAYSIA

Second Semester Examination
Academic session 2003/04

February/March 2004

KAA 502 – Atomic Spectroscopy

Time: 3 hours

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

Answer FIVE questions only.

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

1. (a) In atomic absorption spectrometry, why is it preferable for the source line width to be narrower than the absorption profile? How can this be achieved? What are the requirements for resolution in monochromators for atomic emission and for atomic absorption spectrometry?

(8 marks)

(b) 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)

(c) The data which were obtained for the determination of chromium in a wastewater sample from an electroplating company by inductively coupled plasma atomic emission (ICP-AES) is given below. The wastewater sample is diluted 10 times before the determination is carried out.

Flask	Volume of 1 ppm Cr standard (mL)	Volume of sample (mL)	Total volume (mL)	Emission intensity
1	0	5	50	440
2	1	5	50	1540
3	2	5	50	2640
4	4	5	50	4800

Calculate the concentration of chromium in the original wastewater sample.

(8 marks)

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

(10 marks)

(b) If you wished to nebulize sea water with a cross flow/Meinhard nebulizer, what problems would you encounter? Take note that sea water contains 3.5% (w/v) NaCl.

(4 marks)

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(c) A monochromator has a focal length of 0.65 m and an echellette grating with 1800 grooves per mm.

(i) Calculate the reciprocal linear dispersion of the instrument for first order spectra.

(ii) If 2.0 cm of the grating is illuminated, what is the resolving power of the monochromator in the first order?

(iii) At about 500 nm, what is the minimum wavelength difference that could in theory be completely resolved by this instrument?

(6 marks)

3. (a) An important step in analytical work is sample preparation including solvent extraction where the primary function is to convert the sample as received to a state which can be introduced into flames or plasmas.

(i) When the metal concentration in the sample is in the ppm or ppb range, discuss briefly the major problems encountered in these sample pretreatment steps.

(ii) How can direct solids elemental analysis be performed with the ICP (inductively coupled plasma)? What are the advantages and disadvantages of such an analysis?

(8 marks)

(b) Increasing amounts of element X has no effect on the absorbance of a 2 ppm solution of Y at the resonance wavelength, λ_1, for Y. However, at λ_2 for element Y, the absorbance for the same solution increases linearly with increasing amounts of element X. What kind of interference does X have on the determination of Y at λ_2 ? How would you carry out the determination of element Y in a sample containing X?

(6 marks)

(c) The results in a spectrographic determination of lead in an alloy R are shown below. Magnesium was used as an internal standard in the analysis. Calculate the concentration of Pb in the sample R.

Solution	Readings Mg	 Pb	Pb concentration (mg mL^{-1})
1	7.3	17.5	0.151
2	8.7	18.5	0.201
3	7.3	11.0	0.301
4	10.3	12.0	0.402
5	11.6	10.4	0.502
R	8.8	15.5	?

(6 marks)

4. (a) Given below are values of sensitivites for several elements using model X of an ICP-AES which has an Echelle monochromator, with axial and radial optics.

Element	Radial (ppb)	Axial (ppb)
Ag	7	0.6
As	53	3.8
Cd	2	0.2
Cr	7	0.4
Pb	42	1.6
Se	75	3.8

Sketch schematic diagrams of an ICP-AES instrument with radial optics and one with axial optics which shows the position of the plasma with respect to the monochromator. Explain the differences in sensitivities obtained.

(9 marks)

(b) Why are atomic spectroscopic techniques such as AAS (atomic absorption), ICP-AES and FES (flame emission spectrometry) almost never used to analyze Cl and F?

(5 marks)

(c) How is background correction performed in a flame atomic absorption instrument that uses the Smith-Hieftje background correction technique?

(6 marks)

5. (a) Flames are much cooler than ICPs (inductively coupled plasma) and therefore do not provide as high an excitation energy as that available from ICPs. Why then are flame spectrophotometers still used for analysis?

(6 marks)

(b) Label each of the following processes encountered in atomic absorption spectroscopy:

(i) $\mathrm{FeCl_3(solution)} \rightarrow \mathrm{FeCl_3(aerosol)}$
(ii) $\mathrm{FeCl_3(g)} \rightarrow \mathrm{Fe(g)} + \mathrm{3Cl(g)}$
(iii) $\mathrm{FeCl_3(s)} \rightarrow \mathrm{FeCl_3(g)}$
(iv) $\mathrm{Fe(g)} \rightarrow \mathrm{Fe^+(g)} + e^-$

(4 marks)

(c) The concentration of Cu was determined by acidifying a 150.0 mL sample of a caustic solution with 20 mL of concentrated acid, adding 1 mL of 27% w/v H_2O_2 and boiling for 30 min. The resulting solution was diluted to 250.0 mL, filtered and analyzed by flame atomic absorption using matrix matched standards. The results for the analysis are as follows:

Solution	Cu (ppm)	Absorbance
Blank	0.000	0.006
Standard 1	0.200	0.014
Standard 2	0.500	0.034
Standard 3	1.000	0.071
Standard 4	2.000	0.142
Sample	?	0.026

Calculate the concentration of copper in the caustic solution.

(10 marks)

6. (a) In ICPMS, an interfering ion $^{40}Ar^{35}Cl$ appears at mass 74.9312 and the analyte ion ^{75}As has an atomic mass of 74.9216.

(i) What is the resolution required to separate the element of interest from the interference?

(ii) What kind of mass analyzer is capable of resolving such interferences?

(iii) How is such high resolution achieved?

(10 marks)

(b) How do you propose that simultaneous ICP atomic emission and mass spectrometry can be carried out in the same instrument? What would be the benefits of such a combination?

(6 marks)

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

(4 marks)

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