UNIVERSITI SAINS MALAYSIA

Second Semester Examination
2010/2011 Academic Session

April/May 2011

KAA 502 – Atomic Spectroscopy
[Spektroskopi Atom]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of **TWELVE** printed pages before you begin the examination.

Instructions:

Answer **FIVE** (5) questions only.

Begin the answer to each question on a new page.

You may answer the questions either in Bahasa Malaysia or in English.

If a candidate answer more than five questions, only the answer to the first five questions in the answer sheet will be graded.

In the event on any discrepancies, the English version shall be used.

1. Lead, magnesium and calcium were simultaneously determined in plant roots by the direct analysis of a slurry using inductively coupled plasma atomic emission spectrometry (SS-ICP-AES). For comparison, microwave digestion was also used to prepare the plant root samples and the digested samples were subsequently analysed by ICP-AES. The analytical figures of merit for the two methods are given below:

Analytical figures of merit

Element	LOD [a]solution (ng mL^{-1})	LOD slurry (ng g^{-1})	RSD, n = 6 [a]solution (%)	RSD, n = 6 slurry (%)
Pb	1.4	2.2	1.6	3.8
Ca	0.9	1.2	1.3	2.7
Mg	0.08	1.3	0.8	2.2

LOD - limit of dectection
RSD – relative standard deviation

[a] closed microwave digestion

(i) Comment on the analytical figures of merit obtained for both SS-ICP-AES and ICP-AES methods for analysing the plant roots.

(ii) What are the advantages of the direct analysis of a slurry by ICP-AES? What problems would be encountered and how could the problems be overcome?

(iii) How would you validate the results obtained by the proposed SS-ICP-AES method?

(20 marks)

2. (a) Indicate whether the following statements are **TRUE** or **FALSE** and briefly explain **WHY**.

(i) The rate of absorption is proportional to the population of the lower-energy state for a transition and the rate of emission is proportional to the population of the higher-energy state for a transition. Since the population of the lower-energy state will always be greater than that of the higher-energy state, absorption measurements result in lower (better) detection limits than do emission measurements.

(ii) Quadrupole mass analyzers operate by accelerating ions to a constant velocity and then separating them based on their kinetic energy differences.

(14 marks)

(b) A spectrophotometer is equipped with a monochromator of focal length, 1 m and a grating density of 3600 grooves mm^{-1}. The grating measures 75 mm x 75 mm. Calculate the first order reciprocal linear dispersion, D^{-1} (Å mm^{-1}) for this monochromator.

(6 marks)

3. (a) What is the function of the electrostatic sector in a double-focussing mass analyzer? Explain briefly.

(5 marks)

(b) You are a supevisor in a laboratory which focuses on the determination of trace and ultra-trace levels of toxic substances in water samples. A graphite furnace atomic absorption spectrometer is usually used for the determination of Pb in water. However, since it was down for repairs, a flame atomic absorption spectrometer was used instead. After establishing that absorbance varied linearly with the Pb concentration, the following absorbance data (for 5 replicate measurements) were obtained for a blank and a sample:

Blank	0.001	Sample	0.003
	0.002		0.002
	0.001		0.004
	0.000		0.002
	0.002		0.003
Average	0.0012	Average	0.0028
Standard deviation	0.0008	Standard deviation	0.0008

The water sample was reported to contain 350 ppb Pb. As the laboratory supervisor, you are responsible for the results to be reported for any analysis. Should the result be reported? Explain your answer.

(10 marks)

(c) ICP-AES is usually used for the determination of the total concentration of an element. How would you use ICP-AES if you were interested in obtaining data on elemental speciation?

(5 marks)

4. (a) Flames are much cooler than ICPs and therefore they 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) How do you propose that simultaneous ICP atomic emission and mass spectrometry be carried out in the same instrument? What would be the benefits of such a combination?

(6 marks)

(c) Potassium is determined by flame emission spectrometry using lithium as an internal standard. The following data were obtained for standard potassium solutions and an unknown sample containing a constant known amount of LiCl as the internal standard.

Concentration of K, ppm	K emission intensity	Li emission intensity
1.0	10.0	10.0
2.0	15.3	7.5
5.0	34.7	6.8
7.5	65.2	8.5
10.0	95.8	10.0
20.0	110.2	5.8
Unknown	45.3	9.1

Calculate the concentration of K in the unknown sample.

(8 marks)

5. (a) In inductively coupled plasma mass spectrometry (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?

(6 marks)

(b) Explain briefly the self absorption phenomenon in flames and its effect on the atomic emission calibration curve. Comment on the occurrence of this phenomenon in plasmas and how it affects the wide dynamic linear range obtained with plasmas.

(4 marks)

(c) The determination of Zn in multivitamin tablets was carried out using atomic absorption spectroscopy. All absorbance values were corrected for the appropriate reagent blank (C_{Zn} = 0.0 ng mL^{-1}). The mean absorbance value for the blank was 0.0000 with a standard deviation of 0.0045 absorbance units. The following absorbance data were obtained:

C_{Zn}, ng mL^{-1}	A
5.0	0.0518
5.0	0.0467
5.0	0.0483
10.0	0.0970
10.0	0.1032
10.0	0.0924
Tablet sample	0.0671
Tablet sample	0.0613
Tablet sample	0.0660

(i) Calculate the detection limit of Zn for the method used.

(ii) Calculate the concentration of Zn in the tablet sample.

(10 marks)

6. (a) The Cu in an aqueous sample was determined by flame atomic absorption spectroscopy. First, 10.0 mL of the unknown was pipetted into each of 50.0-mL volumetric flasks. Various volumes of a standard solution containing 10.0 ppm Cu were added to the flasks and the solutions were then diluted to volume. The following data were obtained:

Unknown, mL	Standard, mL	Absorbance
10.0	0.0	0.200
10.0	10.0	0.291
10.0	20.0	0.377
10.0	30.0	0.466
10.0	40.0	0.553

Calculate the Cu concentration in the unknown sample.

(8 marks)

(b) Even though inductively coupled plasma mass spectrometry (ICPMS) offers extremely low detection capabalities, the detection limits for a small group of elements are severly compromised by spectral interferences generated by ions derived from the plasma gas, matrix or solvent used to get the sample into solution.

(i) Give an example of a polyatomic spectral interference in ICPMS.

(ii) Describe briefly how such spectral interferences are overcome by using cool plasma conditions, collision-reaction cells and dynamic reaction cells.

(12 marks)

1. Plumbum, magnesium and kalsium dalam akar tumbuhan ditentukan serentak dengan analisis langusng slurri menggunakan spektrometri pemancaran atom plasma berganding secara aruhan (SS-ICP-AES). Sebagai perbandingan, penghadaman mikrogelombang digunakan bagi penyediaan sampel akar tumbuhan dan sampel terhadam seterusnya dianalisis dengan ICP-AES. Perbandingan di antara kedua-dua kaedah diberikan seperti berikut:

Unsur	LOD [a]larutan ($ng\ mL^{-1}$)	LOD slurri ($ng\ g^{-1}$)	RSD, n = 6 [a]larutan (%)	RSD, n = 6 slurri (%)
Pb	1.4	2.2	1.6	3.8
Ca	0.9	1.2	1.3	2.7
Mg	0.08	1.3	0.8	2.2

LOD – had pengesanan
RSD – sisihan piawai relatif

[a] penghadaman mikrogelombang tertutup

(i) Komen tentang perbandingan LOD dan RSD yang diperolehi bagi kaedah SS-ICP-AES and ICP-AES dalam analisis akar tumbuhan.

(ii) Apakah kelebihan analisis langsung slurri dengan ICP-AES? Apakah masalah yang akan dihadapi dan bagaimanakah masalah dapat diatasi?

(iii) Bagaimanakah anda mengesahkan keputusan yang diperolehi dengan kaedah SS-ICP-AES yang dicadangkan?

(20 markah)

2. (a) Nyatakan sama ada pernyataan di bawah adalah **BENAR** atau **SALAH** dan berikan penerangan ringkas.

(i) Kadar penyerapan berkadaran dengan populasi keadaan bertenaga lebih rendah bagi suatu peralihan. Kadar pemancaran berkadaran dengan populasi keadaan bertenaga lebih tinggi bagi suatu peralihan. Oleh sebab populasi keadaan bertenaga lebih rendah selalunya lebih tinggi daripada populasi keadaan tenaga lebih tinggi, ukuran penyerapan menghasilkan had pengesanan yang lebih rendah (lebih baik) daripada had pengesanan bagi ukuran pemancaran.

(**ii**) Penganalisis jisim kutub empat beroperasi dengan memecut ion kepada halaju malar dan memisahkan ion tersebut berdasarkan perbezaan dalam tenaga kinetik ion.

(14 markah)

…9/-

(b) Suatu spektrofotometer mempunyai monokromator dengan panjang fokus 1 m dan ketumpatan parutan 3600 garisan mm^{-1}. Parutan berukuran 75 mm x 75 mm. Kirakan penyerakan linear reciprocal pada tertib pertama, D^{-1} (Å mm^{-1}) bagi monokromator tersebut.

(6 markah)

3. (a) Apakah fungsi sektor elektrostatik bagi penganalisis jisim pemfokusan dubel? Terangkan dengan ringkas.

(5 markah)

(b) Anda adalah seorang penyelia di makmal yang menjalankan penentuan bahan toksik dalam sampel air pada tahap surihan dan ultrasurihan. Biasanya, suatu spektrometer penyerapan atom relau grafit (GFAAS) digunakan bagi penentuan Pb dalam air. Oleh kerana GFAAS rosak, spektrometer penyerapan atom nyala telah digunakan. Setelah mendapatkan penentukuran bagi penyerapan Pb linear dengan kepekatan, data di bawah (bagi 5 sukatan replikat) telah diperolehi bagi larutan blank dan sampel:

Blank	0.001	Sampel	0.003
	0.002		0.002
	0.001		0.004
	0.000		0.002
	0.002		0.003
Purata	0.0012	Purata	0.0028
Sisishan piawai	0.0008	Sisishan piawai	0.0008

Sampel air tersebut dilaporkan mengandungi 350 ppb Pb. Sebagai penyelia makmal, anda bertanggung jawab ke atas keputusan sebarang analisis. Patutkah keputusan tersebut dilaporkan? Jelaskan jawapan anda.

(10 markah)

(c) Biasanya teknik ICP-AES digunakan bagi penentuan kepekatan total suatu unsur. Bagaimana pula jika anda berminat untuk memperolehi data tentang penspesiesan unsur tersebut?

(5 markah)

4. (a) Nyala adalah lebih sejuk daripada ICP dan tidak dapat membekalkan tenaga pengujaan setinggi ICP. Oleh itu, kenapakah spektrofotometer nyala masih digunakan untuk menjalankan analisis?

(6 markah)

(b) Cadangkan bagaimana pemancaran atom dan spektrometri jisim ICP dapatkan dijalankan serentak dalam alatan yang sama. Apakah kelebihan gabungan tersebut?

(6 markah)

(c) Kalium ditentukan dengan spektrometri pemancaran nyala dengan menggunakan litium sebagai piawai dalaman. Data beikut diperolehi bagi larutan piawai kalium dan larutan sampel anu yang semuanya mengandungi amaun LiCl sama banyak sebagai piawai dalaman.

Kepekatan K, ppm	Keamatan pemancaran K	Keamatan pemancaran Li
1.0	10.0	10.0
2.0	15.3	7.5
5.0	34.7	6.8
7.5	65.2	8.5
10.0	95.8	10.0
20.0	110.2	5.8
Sampel anu	45.3	9.1

Kirakan kepekatan K dalam larutan anu.

(8 markah)

5. (a) Dalam spektrometri jisim plasma berganding secara aruhan (ICP-MS), suatu ion gangguan $^{40}Ar^{35}Cl$ mempunyai jisim 74.9312 dan ion analit ^{75}As mempunyai jisim atom 74.9216.

(i) Apakah resolusi yang diperlukan untuk memisahkan unsur yang diminati daripada ion gangguan?

(ii) Apakah jenis penganalisis jisim yang berupaya untuk mengatasi gangguan tersebut?

(iii) Bagaimanakah terhasilnya resolusi yang tinggi?

(6 markah)

(b) Jelaskan fenomenon penswaserapan dalam nyala dan kesannya ke atas keluk penentukuran pemancaran atom. Komen tentang fenomenon ini dalam plasma dan hubungannya dengan julat dinamik linear besar yang diperolehi dengan plasma.

(4 markah)

(b) Penentuan Zn dalam pil multivitamin dijalankan menggunakan spektroskopi penyerapan atom. Semua nilai keserapan telah dibetulkan dengan reagen blank yang sesuai (C_{Zn} = 0.0 ng mL^{-1}). Nilai purata keserapan bagi larutan blank adalah 0.0000 dengan sisihan piawai 0.0045 unit keserapan. Data keserapan berikut diperolehi:

C_{Zn}, ng mL^{-1}	A
5.0	0.0518
5.0	0.0467
5.0	0.0483
10.0	0.0970
10.0	0.1032
10.0	0.0924
Sampel pil	0.0671
Sampel pil	0.0613
Sampel pil	0.0660

(i) Kirakan had pengesanan bagi zink dengan kaedah yang digunakan.

(ii) Kirakan kepekatan zink dalam sampel pil.

(10 markah)

6. (a) Kandungan kuprum dalam suatu sampel akueus ditentukan dengan spektrometri penyerapan atom. Sebanyak 10.0 mL larutan anu telah dipipet ke dalam setiap kelalang volumetri 50.0 mL. Pelbagai isipadu larutan piawai 10.0 ppm Cu ditambah kepada setiap kelalang dan larutan dicairkan ke tanda. Data berikut telah diperolehi:

Larutan anu, mL	Larutan piawai, mL	Keserapan
10.0	0.0	0.200
10.0	10.0	0.291
10.0	20.0	0.377
10.0	30.0	0.466
10.0	40.0	0.553

Kirakan kepekatan kuprum dalam larutan anu.

(8 markah)

(b) Walaupun spektrometri jisim plasma berganding secara aruhan (ICPMS) menawarkan keupayaan pengesanan yang sangat rendah, pengesanan sekumpulan kecil unsur menghadapi masalah dengan gangguan spektrum ion yang dihasilkan daripada gas plasma, matriks atau pelarut yang digunakan untuk melarutkan sampel.

(i) Berikan satu contoh gangguan spektrum poliatom dalam ICPMS.

(ii) Terangkan dengan ringkas bagaimana gangguan spektrum tersebut dapat diatasi dengan keadaan plasma sejuk, penggunaan sel hentaman-tindak balas dan juga sel tindak balas dinamik.

(12 markah)

oooOOooo