UNIVERSITI SAINS MALAYSIA

Second Semester Examination
2007/2008 Academic Session

April/May 2008

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.

…2/-

1. (a) In inductively coupled plasma - mass spectrometry (ICP-MS), 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) What are the advantages of coupling of the flow injection technique with ICP as the detector? What are the problems of this combination?

(4 marks)

2. (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 parts per million or parts per billion range, discuss briefly the major problems encountered in these sample pretreatment steps.

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

(8 marks)

…3/-

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

Solution	Readings		Pb concentration (mg mL^{-1})
	Mg	Pb	
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)

(c) 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.

(6 marks)

…4/-

3. (a) Given below are values of sensitivites for several elements using model X of an inductively coupled plasma – atomic emission spectrometer (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 show the position of the plasma with respect to the monochromator. Explain the differences in sensitivities obtained.

(10 marks)

(b) Flames are much cooler than ICPs 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)

(c) Elemental analysis at parts per billion levels can be performed using ICP-AES or graphite furnace atomic absorption spectrometry (GFAAS). Would either of these techniques be suitable for the daily determination of carcinogenic Cr(VI) in water discharged from a factory? Give a justification for your answer.

(4 marks)

4. (a) In the early 1990s, spectrometers with solid-state detectors such as charge injection devices and charge coupled devices were introduced. These spectrometers used Echelle gratings in their monochromators. Discuss how such instruments promised improvements in accuracy, linear range and sample throughput compared to conventional spectrometers with photomultiplier tubes as detectors.

(10 marks)

…5/-

(b) 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?

(4 marks)

(c) A grating has a groove density of 1500 grooves mm^{-1}. The incident angle with the grating is 20.0^{o}.

(i) Calculate the diffraction angle at which radiation at the wavelengths below will be diffracted from the grating.

500 nm and 600 nm (at first order)

(ii) Calculate the wavelengths in second order that will overlap with the 600 nm in first order.

(iii) Calculate the angular dispersion at 500 nm (first order).

(6 marks)

5. (a) The table below gives the detection limits for several elements obtained with various nebulizers in ICP-AES.

Element*	λ (nm)	Glass concentric (P.N.)	Babington (P.N.)	Ultrasonic nebulizer Al
(I)	308.22	37	36	2.8
Cr (II)	205.55	5.1	5.9	0.42
Cu (I)	324.75	4.8	4.3	0.77
Mn (II)	257.61	1.3	0.99	0.08
Zn (I)	213.86	3.3	2.6	0.37

* I – atomic line. II - ion line
P.N. – pneumatic nebulizer

Explain the significant difference between detection limits obtained for the ultrasonic nebulizer and that for both pneumatic nebulizers in the above table. What is the advantage of the Babington nebulizer?

(6 marks)

…6/-

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

(4 marks)

(c) State whether the following are true or false. Give your reasons.

(i) With a blank measurement of 0.001 ± 0.0005 (average ± standard deviation) and a sample measurement of 0.002 ± 0.0005, it was determined from the calibration curve that Hg was present in drinking water at a level of 500 ppb.

(ii) A common tungsten filament continuum source is ideal for atomic absorption spectrometry.

(10 marks)

6. (a) 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.

(5 marks)

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

(5 marks)

…7/-

(c) 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 GFAAS 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 amount of Pb, the following absorbance data (for 5 replicate measurements) were obtained for a blank and for 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)

…8/-

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

(i) Berapakah resolusi yang diperlukan untuk memisahkan unsur yang diminati daripada unsur gangguan?
(ii) Apakah jenis penganalisis jisim yang dapat meresolusikan gangguan tersebut?
(iii) Bagaimanakah resolusi yang begitu tinggi dapat dihasilkan?

(10 markah)

(b) Cadangkan bagaimana sistem serentak pemancaran atom dan spektrometri jisim plasma berganding secara aruhan (ICP) dapat diwujudkan dalam alatan yang sama. Apakah faedah gabungan ini?

(6 markah)

(c). Apakah kelebihan gandingan teknik suntikan aliran dengan ICP sebagai pengesan? Apa pula masalah gandingan dua teknik ini?

(4 markah)

2. (a) Langkah penting dalam suatu analisis adalah pengolahan sampel termasuk pengekstrakan pelarut. Fungsi utama langkah ini ialah untuk menukar sampel yang diterima kepada suatu keadaan yang mana sampel tersebut boleh dimasukkan ke dalam nyala atau plasma.

(i) Apabila kepekatan logam dalam sampel adalah dalam julat ppm atau ppb, bincangkan dengan ringkas, masalah utama yang dihadapi dalam langkah pengolahan sampel.

(ii) Bagaimana dapat dilakukan analisis langsung sampel pepejal dengan ICP (plasma berganding secara aruhan)? Apakah kelebihan dan kelemahan analisis tersebut?

(8 markah)

…10/-

(b) Keputusan bagi penentuan spektrograf bagi plumbum dalam suatu aloi R ditunjukkan di dalam jadual yang berikut. Magnesium digunakan sebagai piawai dalaman. Kira kepekatan Pb dalam sampel ini.

Larutan	Bacaan		Kepekatan Pb (mg mL^{-1})
	Mg	Pb	
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 markah)

(c) 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.

(6 markah)

…11/-

3. (a) Nilai kepekaan beberapa unsur daripada model X spektrometer plasma berganding secara aruhan – pemancaran atom (ICP – AES) yang menggunakan monokromator Echelle, bagi optik ‘axial’ dan ‘radial’ adalah seperti di bawah.

Unsur	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

Lakarkan gambarajah skematik bagi alatan ICP-AES dengan optik 'radial' dan juga alatan dengan optik ' axial' yang menunjukkan kedudukan plasma merujuk kepada monokromator. Jelaskan tentang perbezaan kepekaan yang diperolehi.

(10 markah)

(b) 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)

(c) Analisis unsur pada tahap bahagian per sebillion boleh dijalankan ICP-AES atau spektrometri penyerapan atom relau grafit. Adakah salah satu daripada teknik tersebut sesuai bagi penentuan harian Cr(VI) yang karsinogenik dalam air daripada sebuah kilang. Beri penjelasan bagi jawapan anda.

(4 markah)

…12/-

4. (a) Pada awal 1990an, spektrometer yang menggunakan pengesan keadaan pepejal (solid-state) seperti peranti suntikan cas (CID) dan peranti gandingan cas (CCD) telah diperkenalkan. Spektrometer tersebut juga menggunakan parutan Echelle dalam monokromator. Bincangkan

bagaimana alatan tersebut dapat menjanjikan penambahbaikan dalam kejituan, julat linear dan bilangan 'sample throughput' dibandingkan dengan spektrometer konvensional (pengesan tabung pemfotoganda)

(10 markah)

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

(4 markah)

(c) Suatu parutan mempunyai ketumpatan lurah (grooves) 1500 lurah mm^{-1}. Alur tuju bertembung dengan parutan pada sudut 20.0^{o}.

(i) Kiralah sudut pembelauan di mana sinaran pada panjang gelombang di bawah akan terbelau daripada parutan tersebut.

500 nm dan 600 nm (pada tertib pertama)

(ii) Berapakah panjang gelombang pada tertib kedua yang akan bertindih dengan alur 600 nm pada tertib pertama?

(iii) Kiralah penyerakan bersudut pada 500 nm (tertib pertama).

(6 markah)

5. (a) Jadual di bawah memberikan had pengesanan beberapa unsur dengan penggunaan pelbagai jenis penebula dalam ICP-AES.

Unsur*	λ (nm)	Konsentrik kaca (P.P.)	Jenis Babington (P.P.)	Penebula Ultrasonik Al
(I)	308.22	37	36	2.8
Cr (II)	205.55	5.1	5.9	0.42
Cu (I)	324.75	4.8	4.3	0.77
Mn (II)	257.61	1.3	0.99	0.08
Zn (I)	213.86	3.3	2.6	0.37

* I - garisan atom. II - garisan ion
P.P. - penebula pneumatik

Jelaskan perbezaan ketara bagi had pengesanan untuk penebula ultrasonik dibandingkan dengan had pengesanan dua penebula pneumatik yang diberikan dalam jadual. Apakah kelebihan penebula jenis Babington?

(6 markah)

(b) Jelaskan bagaimana modifikasi matriks dalam pengatoman elektroterma menghasilkan penyingkiran matriks yang lebih cekap. Berikan satu contoh tertentu.

(4 markah)

(c) Nyatakan sama ada perkara yang berikut benar atau tidak. Berikan penjelasan anda.

(i) Sukatan blank adalah 0.001 ± 0.0005 (purata ± sisihan piawai) dan sukatan sampel adalah 0.002 ± 0.0005. Daripada keluk penentukuran telah ditentukan bahawa Hg wujud pada tahap 500 ppb dalam air minuman.

(ii) Lampu filamen tungsten biasa adalah sumber unggul bagi spektrometri penyerapan atom.

(10 markah)

…14/-

6. (a) Suatu spektrofotometer mempunyai monokromator yang panjang fokusnya 1 m dan ketumpatan lurah, 3600 lurah mm^{-1}. Kira penyerakan linear reciprokal bagi monokromator tersebut.

(5 markah)

(b) Terangkan fungsi sektor elektrostatik dalam penganalisis jisim pemfokusan dubel.

(5 markah)

(c) Anda adalah seorang supervisor di makmal yang menjalankan penentuan bahan toksik 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	Sisihan piawai	0.0008

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

(10 markah)

-oooOOooo-