UNIVERSITI SAINS MALAYSIA

Second Semester Examination
2008/2009 Academic Session

April/May 2009

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.

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1. (a) Multielemental atomic absorption spectrometry with integrated background measurement and correction possibilities are now possible with the availability of high intensity continuum radiation sources such as Xenon arcs and W-X-lamps and of high resolution Echelle spectrometers using charge coupled devices (CCD). Discuss on how multielemental atomic absorption spectrometry has been made possible.

(14 marks)

(b) A monochromator has a focal length of 0.78 m and an echellette grating with 2500 grooves per millimeter.

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

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

(iii) At about 430 nm, what is the minimum wavelength difference that could in theory be completely resolved by this instrument?

(6 marks)

2. (a) An important step in analytical work is sample preparation which may include 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 inductively coupled plasma (ICP)? What are the advantages and disadvantages of such an analysis?

(10 marks)

(b) What are the differences between glow discharge optical emission spectrometry and ICP emission spectrometry in terms of basic principles of the techniques and instrumentation involved?

(10 marks)

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 either axial or 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? Justify 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)

(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) 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)

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 differences between the detection limits obtained for the various nebulizers in the above table.

(10 marks)

(b) 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) The concentration of Cu was determined by acidifying a 150.0 mL aliquot of a sample 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 sample solution.

(10 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 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)

1. (a) Teknik spektrometri penyerapan atom multiunsur dengan sukatan dan pembetulan latar belakang berintegrasi boleh dikendalikan dengan wujudnya sumber sinaran kontinuum berkeamatan tinggi seperti arka Xenon dan lampu W-X dan juga spektrometer Echelle resolusi tinggi yang menggunakan peranti gandingan cas. Bincangkan bagaimana spektrometri penyerapan atom multiunsur boleh dikendalikan dengan keadaan tersebut.

(14 markah)

(b) Suatu monokromator dengan panjang fokus, 0.78 m dibekalkan dengan parutan echellette yang mempunyai 2500 garisan per milimeter.

(i) Kira penyerakan linear reciprokal alatan tersebut bagi spektrum tertib pertama.

(ii) Jika 2.0 cm daripada parutan disinari, berapakah kuasa resolusi monokromator tersebut pada tertib pertama?

(iii) Pada lebih kurang 430 nm, berapakah perbezaan panjang gelombang minimum yang dapat diresolusikan oleh alatan tersebut secara teori?

(6 markah)

2. (a) Langkah penting dalam suatu analisis adalah pengolahan sample yang mungkin melibatkan 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?

(10 markah)

(b) Apakah perbezaan di antara spektrometri pemancaran optik glow discas dan spektrometri pemancaran ICP dari segi prinsip asas bagi teknik dan peralatan yang digunakan?

(10 markah)

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 menggunakan ICP-AES atau spektrometri penyerapan atom relau grafit. Adakah salah satu daripada teknik tersebut sesuai bagi penentuan harian Cr(VI) yang karsinogenik dalam air buangan daripada sebuah kilang. Beri penjelasan bagi jawapan anda?

(4 markah)

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

(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 di antara had pengesanan bagi pelbagai penebula yang diberikan dalam jadual.

(10 markah)

(b) 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) Sumber kontinuum filamen tungsten biasa adalah sumber unggul bagi spektrometri penyerapan atom.

(10 markah)

6. (a) Kepekatan Cu ditentukan dengan mengasidkan alikuot 150.0 mL suatu larutan sampel dengan 20 mL asid pekat, menambah 1 mL 27% (w/v) H_2O_2, dan mendidihkan larutan selama 30 minit. Larutan yang dihasilkan dicairkan kepada 250.0 mL, dituras dan dianalisis dengan penyerapan atom nyala. Matriks larutan piawai dipadankan dengan matriks sampel. Keputusan bagi analisis tersebut adalah seperti berikut:

Larutan	Cu (ppm)	Keserapan
Blank	0.000	0.006
Piawai 1	0.200	0.014
Piawai 2	0.500	0.034
Piawai 3	1.000	0.071
Piawai 4	2.000	0.142
Sampel	?	0.026

Kira kepekatan kuprum dalam larutan sampel tersebut.

(10 markah)

(b) Anda adalah seorang penyelia di makmal yang menjalankan penentuan bahan toksik pada tahap surih dan ultrasurih. 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 penyelia makmal, anda bertanggung jawab ke atas keputusan sebarang analisis. Patutkah keputusan tersebut dilaporkan? Jelaskan jawapan anda.

(10 markah)

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