UNIVERSITI SAINS MALAYSIA

Second Semester Examination
2011/2012 Academic Session

June 2012

KAA 502 – Atomic Spectroscopy
[Spektroskopi Atom]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of **12** 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 answers 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 samples by the direct analysis of plant slurries using inductively coupled plasma atomic emission spectrometry (S-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 S-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 S-ICP-AES method?

(20 marks)

2. (a) An electrochemical system has been developed to convert Cr(VI) in solution to Cr(III). Discuss briefly how you would study the efficiency for the conversion of Cr(VI) to Cr(III) by this system using atomic absorption spectrometry for the determination of chromium as well as the determination of Cr(VI) using the diphenylcarbazide spectrophotometric method.

(8 marks)

(b) Many applications require a highly sensitive, spatially resolved determination of elements and/or their isotopes in solid samples. The traditional approach of acid digestion of the solid samples before analysis suffers from contamination during digestion and dilution and limits sample throughput. Describe briefly the principles and instrumentation of laser ablation inductively coupled plasma mass spectrometry (ICPMS) and how this technique can overcome such problems.

(12 marks)

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

(5 marks)

(b) 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)

(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) 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)

(b) Sketch a schematic diagram for a single beam and a double beam spectrometer used in flame atomic absorption spectrometry. What are the advantages and disadvantages of the double beam spectrometer?

(8 marks)

5. Lead was determined in a flour sample by graphite furnace atomic absorption spectrometry (GFAAS). After undergoing enzymatic hydrolysis pretreatment, the flour sample was analysed using a calibration technique based on aqueous standards. The results obtained were compared to analyses done with the method of standard additions. Table 1 gives the linear regression equations and R^2 for the two methods of calibration used.

Table 1. Calibrations against aqueous standards and by method of standard additions for enzyme pretreated samples

Element	Method	Calibration	Linearity
Pb	Aqueous standards	y= 0.0037x - 0.0064	R^2 = 0.9993
	Method of standard additions	y= 0.0036x + 0.0021	R^2 = 0.9992

Concentration Pb, 10 – 100 ng mL^{-1}

(i) What is the method of standard additions used for?

(ii) Why is a matrix modifier, $NH_4H_2PO_4$ necessary for the analysis using GFAAS?

(iii) Comment on the results obtained for the direct analysis of the flour sample using both calibration techniques.

(iv) How would you validate the results obtained by the proposed direct determination of Pb in the flour sample by enzymatic hydrolysis pretreatment followed by GFAAS analysis?

(20 marks)

6. (a) The Au in solutions containing high concentrations of diverse ions can be determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). First, 20.0 mL of the unknown was pipetted into each of 100.0-mL volumetric flasks. Various volumes of a standard solution containing 10.0 ppm Au in 20% H_2SO_4 were added to the flasks and the solutions were then diluted to volume. The following data were obtained:

Unknown, mL	Added Au, mg L^{-1}	Emission intensity, counts
25.0	0.0	12,568
25.0	2.5	19,324
25.0	5.0	26,622
25.0	10.0	40,021

Calculate the Au concentration in the unknown sample.

(8 marks)

(b)

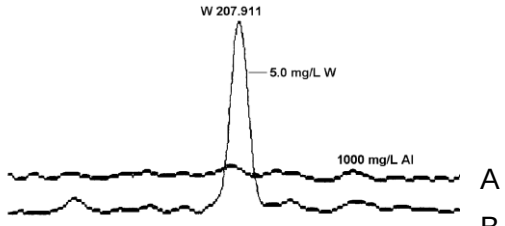

Fig. 1

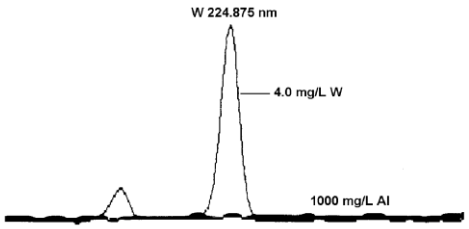

Fig. 2

Figure 1 shows a scan (A) obtained by introducing an aqueous solution containing 1000 mg L^{-1} of aluminum into an inductively coupled plasma-atomic emission spectrometer and scanning across a 0.25 nm spectral range centered on the analyte wavelength of tungsten at 207.911 nm. Scan B was obtained by introducing an aqueous solution of 5.0 mg L^{-1} of tungsten and scanning across the same spectral region using the same analytical conditions.

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Figure 2 shows a scan of a solution containing 1000 mg L^{-1} of aluminium and another scan of a solution of 4.0 mg L^{-1} tungsten which are centered on another emission line of tungsten, 224.875 nm.

Based on the information obtained from Figures 1 and 2, discuss briefly two ways how to overcome the spectral interference caused by a continuum radiation emitted by a high concentration of aluminium in the wavelength range centered at 207.911 nm.

(12 marks)

TERJEMAHAN

Sila pastikan bahawa kertas peperiksaan ini mengandungi 12 muka surat yang bercetak sebelum anda memulakan peperiksaan ini.

Jawab LIMA soalan sahaja.

Jika calon menjawab lebih daripada lima soalan hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

1. Plumbum, magnesium and kalsium dalam akar tumbuhan ditentukan serentak dengan analisis langusng slurri menggunakan spektrometri pemancaran atom plasma berganding secara aruhan (S-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 S-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 S-ICP-AES yang dicadangkan?

(20 markah)

2. (a) Suatu sistem elektrokimia telah dibangunkan untuk menurunkan Cr(VI) dalam larutan kepada Cr(III). Bincangkan dengan ringkas bagaimana anda akan mengkaji keberkesanan penurunan Cr(VI) kepada Cr(III) oleh sistem tersebut menggunakan spektrometri penyerapan atom bagi penentuan kromium dan juga penenentuan Cr(VI) menggunakan kaedah spektrofotometri difenilkarbazida.

(8 markah)

(b) Terdapat banyak aplikasi yang memerlukan penentuan unsur dan/atau isotop unsur tersebut yang sangat peka dan diresolusikan dari segi ruang bagi sampel pepejal. Pendekatan tradisional iaitu penghadaman asid bagi sampel pepejal mempunyai masalah pencemaran semasa penghadaman dan pencairan dan 'throughput' sampel yang terhad. Terangkan secara ringkas prinsip dan peralatan teknik laser ablation ICPMS dan bagaimana teknik ini dapat mengatasi masalah tersebut.

(12 markah)

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

(5 markah)

(b) 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)

(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) 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)

(b) Lakarkan gambarajah skematik bagi spektrometer alur tunggal dan dua alur yang digunakan dalam spektrometri penyerapan atom nyala. Apakah kelebihan dan kekurangan spektrometer alur dua dibandingkan dengan spektrometer alur tunggal?

(8 markah)

5. Plumbum ditentukan dalam sampel tepung menggunakan spektrometri penyerapan atom relau grafit (GFAAS). Setelah diolah dengan hidrolisis berenzim, sampel tepung dianalisis menggunakan teknik penentukuran berdasarkan larutan piawai akueus. Keputusan yang diperolehi dibandingkan dengan keputusan analisis menggunakan kaedah penambahan piawai. Jadual 1 menunjukkan persamaan regresi linear dan R^2 bagi kaedah penentukuran yang digunakan.

Jadual 1. Penentukuran menggunakan larutan piawai akueus dan kaedah penambahan piawai bagi sampel terolah oleh enzim.

Unsur	Kaedah	Penentukuran	Kelinearan
Pb	Piawai akueus	y= 0.0037x - 0.0064	R^2 = 0.9993
	Kaedah penambahan piawai	y= 0.0036x + 0.0021	R^2 = 0.9992

Kepekatan Pb, 10 – 100 ng mL^{-1}

(i) Untuk apakah digunakan kaedah penambahan piawai?

(ii) Kenapakah perlu digunakan penukar matriks, $NH_4H_2PO_4$ bagi analisis dengan GFAAS?

(iii) Komen tentang keputusan yang diperolehi bagi analisis terus sampel tepung menggunakan kedua-dua teknik penentukuran.

(iv) Bagaimanakah anda mengesahkan keputusan yang diperolehi dengan kaedah penentuan terus Pb dalam sampel tepung menggunakan pengolahan hidrolisis enzim diikuti dengan analisis GFAAS yang dicadangkan?

(20 markah)

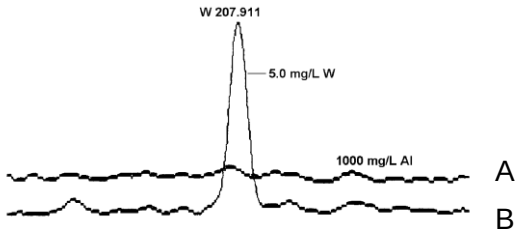
6. (a) Kandungan Au dalam larutan yang mengandungi pelbagai ion pada kepekatan yang tinggi boleh ditentukan menggunakan spektrometri pemancaran atom-plasma berganding secara aruhan (ICP-AES). Pertama sekali, 20.0 mL larutan anu dipipet ke dalam setiap kelalang volumetri 100.0 mL. Pelbagai isipadu larutan piawai 10.0 ppm Au dalam 20% H_2SO_4 ditambah kepada setiap kelalang dan larutan dicairkan ke tanda. Data yang berikut diperolehi:

Larutan anu, mL	Au yang ditambah, mg L^{-1}	Keamatan pemancaran, kiraan
25.0	0.0	12,568
25.0	2.5	19,324
25.0	5.0	26,622
25.0	10.0	40,021

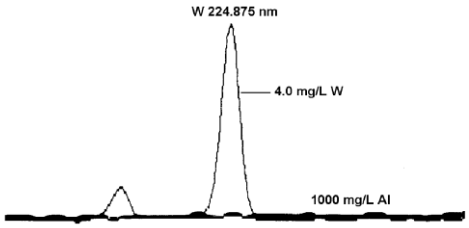
Kirakan kepekatan Au dalam larutan anu.

(8 markah)

(b)



Rajah 1



Rajah 2

Rajah 1 menunjukkan imbasan (A) yang diperolehi apabila larutan akueus 1000 mg L^{-1} aluminum dimasukkan ke dalam ICP-AES dan imbasan dilakukan melalui julat spektrum 0.25 nm berpusat pada panjang gelombang tungsten pada 207.911 nm. Imbasan B diperolehi apabila 5.0 mg L^{-1} of tungsten dimasukkan dan imbasan dilakukan melalui kawasan spekrum yang sama pada keadaan analisis yang sama.

Rajah 2 menunjukkan imbasan bagi larutan yang mengandungi 1000 mg L^{-1} aluminium dan imbasan bagi larutan 4.0 mg L^{-1} tungsten yang berpusat pada garisan pemancaran yang lain bagi tungsten iaitu 224.875 nm.

Berdasakan maklumat yang diperolehi daripada Rajah 1 dan 2, bincangkan secara ringkas dua cara bagaimana mengatasi gangguan spektrum yang disebabkan oleh sinaran kontinuum yang dipancarkan oleh aluminium berkepekatan tinggi dalam julat panjang gelombang berpusat pada 207.911 nm.

(12 markah)

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