UNIVERSITI SAINS MALAYSIA

First Semester Examination
2014/2015 Academic Session

December 2014 / January 2015

EBS 336/3 – Analytical Chemistry
[Kimia Analitis]

Duration : 3 hours
[Masa : 3 jam]

Please ensure that this examination paper contains FOURTEEN printed pages and TWO pages APPENDIX before you begin the examination.
[Sila pastikan bahawa kertas peperiksaan ini mengandungi EMPAT BELAS muka surat beserta DUA muka surat LAMPIRAN yang bercetak sebelum anda memulakan peperiksaan ini.]

This paper consists of SEVEN questions.
[Kertas soalan ini mengandungi TUJUH soalan.]

Instruction: Answer **FIVE** questions. If a candidate answers more than five questions only the first five questions answered in the answer script would be examined.
*[**Arahan**: Jawab **LIMA** soalan. Jika calon menjawab lebih daripada lima soalan hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.]*

The answers to all questions must start on a new page.
[Mulakan jawapan anda untuk semua soalan pada muka surat yang baru.]

You may answer a question either in Bahasa Malaysia or in English.
[Anda dibenarkan menjawab soalan sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.]

In the event of any discrepancies in the examination questions, the English version shall be used.
[Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah digunapakai.]

...2/-

1. [a] To determine the amount of magnetite, Fe_3O_4, in an impure ore, a 1.5419 g sample is dissolved in concentrated HCl, giving a mixture of Fe^{2+} and Fe^{3+}. After adding HNO_3 to oxidize Fe^{2+} to Fe^{3+} and diluting with water, Fe^{3+} is precipitated as $Fe(OH)_3$ by adding NH_3. Filtering, rinsing, and igniting the precipitate provides 0.8525 g of pure Fe_2O_3. Calculate the % w/w Fe_3O_4 in the sample.

Given: MWt. Fe_2O_3 = 160 g/mol, Fe_3O_4 = 232 g/mol, Fe = 56 g/mol

Untuk menentukan kandungan magnetit, Fe_3O_4, dalam satu bijih yang tak tulen, sebanyak 1.5419 g sampel dilarutkan dalam HCl pekat, memberikan satu campuran Fe^{2+} dan Fe^{3+}. Selepas penambahan HNO_3 untuk mengoksidakan Fe^{2+} ke Fe^{3+} dan pencairan dengan air, Fe^{3+} dimendakkan sebagai $Fe(OH)_3$ dengan penambahan NH_3. Mendakan ini dituras, dibilas dan dibakar untuk menghasilkan sebanyak 0.8525g Fe_2O_3 tulen. Kirakan % w/w Fe_3O_4 dalam sampel.

Diberikan: JMR bagi Fe_2O_3 = 160 g/mol, Fe_3O_4 = 232 g/mol, Fe = 56 g/mol

(40 marks/*markah*)

[b] Calculate the ratio of ammonium chloride to ammonia that is required to make a buffer solution with a pH of 9.00. The K_a for ammonium ion is 5.6×10^{-10}.

The equation for the ionization of ammonium in water:

$NH_4^+ (aq) + H_2O (l) \rightarrow H_3O^+ (aq) + NH_3 (aq)$

Kirakan nisbah ammonium klorida kepada ammonia yang diperlukan untuk menghasilkan satu larutan tampan dengan pH 9.00. Nilai K_a bagi ion ammonium adalah 5.6×10^{-10}.

Persamaan bagi pengionan ammonium dalam air:

$NH_4^+ (aq) + H_2O (l) \rightarrow H_3O^+ (aq) + NH_3 (aq)$

(30 marks/*markah*)

...3/-

[c] Hydrogen peroxide reacts with acidified permanganate solution as shown in the reaction equation below:-

$$5\ H_2O_2 + 2\ MnO_4^- + 6H^+ \rightarrow 2\ Mn^{2+} + 5O_2 + 8\ H_2O$$

A 100mL of hydrogen peroxide solution reacts with 12mL of 0.2M of permanganate solution.

Calculate the concentration of the hydrogen peroxide solution in mol/L.

Hidrogen peroksida bertindakbalas dengan larutan berasid permanganate seperti tindakbalas persamaan di bawah:

$$5\ H_2O_2 + 2\ MnO_4^- + 6H^+ \rightarrow 2\ Mn^{2+} + 5O_2 + 8\ H_2O$$

Sebanyak 100mL larutan hidrogen peroksida bertindak balas dengan 12mL 0.2M larutan permanganate.

Kirakan kepekatan larutan hidrogen peroksida dalam mol/L.

(30 marks/*markah*)

2. [a] Calculate the concentrations for each species present in a 0.1000 M aqueous solution of ammonia ($K_b = 1.8 \times 10^{-5}$).

The equation for the reaction of the base with water:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Kirakan kepekatan spesi-spesi yang wujud dalam 0.1000 M larutan akuas ammonia ($K_b = 1.8 \times 10^{-5}$).

Persamaan tindakbalas bes dengan air:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4(aq) + OH(aq)$$

(30 marks/*markah*)

[b] Given the solubility product constant for $AgCl_{(s)}$ is $= 5.0 \times 10^{-13}$, and the remaining step wise formation of $[Ag(S_2O_3)_2]^{3-}$ is as follows:

K_1 $[Ag(S_2O_3)_2]^{3-} = 6.6 \times 10^8$

K_2 $[Ag(S_2O_3)_2]^{3-} = 7.1 \times 10^8$

Write the balanced equation for K_1 and K_2 for the formation of $[Ag(S_2O_3)_2]^{3-}$.

What is the equilibrium constant for the following reaction?

$$AgBr_{(s)} + 2S_2O_3^{2-}{}_{(aq)} = [Ag(S_2O_3)_2]^{3-}{}_{(aq)} + Br^-{}_{(aq)}$$

Diberikan pemalar bagi hasil darab keterlarutan bagi $AgCl_{(s)}$ *is* $= 5.0 \times 10^{-13}$, *dan langkah pembentukan* $[Ag(S_2O_3)_2]^{3-}$ *adalah seperti berikut:*

K_1 $[Ag(S_2O_3)_2]^{3-} = 6.6 \times 10^8$

K_2 $[Ag(S_2O_3)_2]^{3-} = 7.1 \times 10^8$

Tuliskan persamaan seimbang bagi K_1 *and* K_2 *untuk pembentukan* $[Ag(S_2O_3)_2]^{3-}$.

Apakah pemalar keseimbangan bagi tindakbalas berikut:

$$AgBr_{(s)} + 2S_2O_3^{2-}{}_{(aq)} = [Ag(S_2O_3)_2]^{3-}{}_{(aq)} + Br^-{}_{(aq)}$$

(30 marks/*markah*)

[c] Calculate the molar solubility and the mass solubility for $HgCl_2$, given the following solubility reaction and K_{sp} value.

Kirakan keterlarutan molar dan jisim keterlarutan bagi $HgCl_2$, *diberikan tindakbalas keterlarutan dan nilai* K_{sp}

$$HgCl_{2\,(s)} = Hg^{2+} + 2\,Cl^- \qquad K_{sp} = 1.2 \times 10^{-18}$$

(40 marks/*markah*)

3. [a] A single alloy specimen was used to compare the results of two analytical testing laboratories, that use the same standard method of analysis. The standard deviation, *s* and degrees of freedom in pooled data sets are shown below. Use the F-test to determine whether the results from one laboratory works are more precision than the other at the 95% Confidence level. Compare the results separately for Ni and Mn.

Satu spesimen aloi digunakan untuk membandingkan keputusan dua makmal ujikaji yang menggunakan kaedah analisis piawai yang sama. Sisihan piawai, s dan darjah kebebasan dalam set data terkumpul diberikan di bawah ini. Lakukan ujian F untuk menentukan samada keputusan dari satu makmal adalah lebih persis dari satu makmal yang lain pada paras keyakinan 95% . Bandingkan keputusan berasingan bagi Ni dan Mn.

	Laboratory A/*Makmal A*		Laboratory B/*Makmal B*	
Element *Unsur*	***s***	**N**	***s***	**N**
Ni	**0.07**	**13**	**0.04**	**21**
Mn	**0.020**	**5**	**0.035**	**6**

Table 1: Standard deviation, *s* and degree of freedom in pooled data

Jadual 1: Sisihan piawai, s dan darjah kebebasan dalam data terkumpul

(30 marks/*markah*)

[b] Calculate the pH of a buffer that is 0.020 M in NH_3 and 0.030 M in NH_4Cl. What is the pH after adding 1.0 mL of 0.10 M NaOH to 0.10 L of this buffer?

Kirakan pH satu larutan tampan 0.020 M dalam NH_3 dan 0.030 M dalam NH_4Cl. Apakah pH selepas penambahan 1.0 mL 0.10 M NaOH kepada 0.10 L larutan tampan ini?

(30 marks/*markah*)

[c] A 750.0 mg sample of iron ore was dissolved in acid and treated to oxidize all of the iron to ferric iron. After destroying any remaining oxidizing agent, excess KI was added. The liberated I_2 requires 28.50 mL of 0.075 M $Na_2S_2O_3$ for titration.

What is the % of Fe in the sample?

Given: At. wt. of Fe = 55.85 g/mol

The reaction equations:

$$2\,Fe^{3+} + 2\,I^- \rightarrow 2\,Fe^{2+} + I_2$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-}$$

Satu 750.0 mg sampel bijih besi dilarutkan dalam asid dan dirawat untuk mengoksidakan semua ferum kepada ion ferrik. Selepas menyingkirkan semua agen pengoksidaan yang tinggal, KI yang berlebihan ditambahkan. I_2 yang terbebas memerlukan 28.50 mL 0.075 M $Na_2S_2O_3$ bagi pentitratan.

Apakah % Fe dalam sampel?

Diberikan: JAR Fe = 55.85 g/mol

Persamaan tindak balas:

$$2\,Fe^{3} + 2\,I^- \rightarrow 2\,Fe^{2} + I_2$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2\,I + S_4O_6^{2-}$$

(40 marks/*markah*)

4. [a] What is meant by water hardness?
State the differences between soft water and hard water.
State the causes of temporary and permanent hardness in water and how to remove them.

Apakah yang dimaksudkan dengan keliatan air?
Nyatakan perbezaan di antara air lembut dan air liat?
Nyatakan punca keliatan sementara dan keliatan kekal dalam air dan bagaimanakah cara untuk menyingkirkannya.

(30 marks/*markah*)

[b] Describe briefly the application of EDTA titration techniques in the determination of the hardness of water.

Terangkan secara ringkas aplikasi teknik pentitratan EDTA dalam penentuan keliatan air.

(30 marks/*markah*)

[c] A 25.0 mL aliquot of a solution containing Hg^{2+} in dilute nitric acid was treated with 10.0 mL of 0.04882 M EDTA and the pH was adjusted to 10.0 with an ammonium buffer. Two drops of a freshly prepared EBT indicator solution were added and the excess EDTA back titrated with 0.01137 M Mg^{2+}, requiring 24.66 mL to reach the end point.
What is the molarity of Hg^{2+} in the sample?
Note: Both Hg^{2+} and Mg^{2+} form 1:1 complexes with EDTA

Sebanyak 25.0 mL alikuot satu larutan mengandungi Hg^{2+} dalam asid nitrik cair dirawat dengan 10.0 mL 0.04882 M EDTA dan pH diubahsuai kepada 10.0 menggunakan larutan tampan ammonium. Dua titis larutan zat penunjuk EBT yang baru disediakan ditambahkan dan EDTA berlebihan dititratkan dengan 0.01137 M Mg^{2+}, memerlukan sebanyak 24.66 mL untuk mencapai takat akhir.
Apakah kemolaran Hg^{2+} dalam sampel?
Catatan: Kedua-dua Hg^{2+} dan Mg^{2+} membentuk kompleks 1:1 dengan EDTA

(40 marks/*markah*)

5. [a] For the following reaction at 25 °C:

$$5\ Fe^{2+}_{(aq)} + MnO_4^-{}_{(aq)} + 8\ H^+_{(aq)} = 5\ Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)} + 4H_2O\ (l)$$

Given the standard state reduction potentials for the half equations are:

$E°_{Fe^{3+}/Fe^{2+}} = 0.771$ V and $E°\ MnO_4^- / Mn^{2+} = 1.51$ V

Calculate the:

(i) standard potential

(ii) equilibrium constant

(iii) potential under these conditions:

Given : $[Fe^{2+}] = 0.50$ M, $[Fe^{3+}] = 0.10$ M, $[MnO_4^-] = 0.025$ M, $[Mn^{2+}] = 0.015$ M and a pH of 7.00.

Bagi tindakbalas berikutnya pada 25 °C:

$$5\ Fe^{2+}_{(aq)} + MnO_4^-{}_{(aq)} + 8\ H^+_{(aq)} = 5\ Fe^{3}_{(aq)} + Mn^{2}_{(aq)} + 4H_2O\ (l)$$

Diberikan keupayaan penurunan pada keadaan piawai bagi tindak balas setengah seperti berikut:

$E°_{Fe^{3+}/Fe^{2+}} = 0.771$ V dan $E°\ MnO_4^- / Mn^{2+} = 1.51$ V

Kirakan:

(i) *keupayaan piawai*

(ii) *pemalar keseimbangan*

(iii) *keupayaan di bawah keadaan berikut:*

Diberikan : $[Fe^{2}] = 0.50$ M, $[Fe^{3}] = 0.10$ M, $[MnO_4] = 0.025$ M, $[Mn^{2}] = 0.015$ M *dan pH adalah 7.00.*

(45 marks/*markah*)

[b] Iron(II) sulphate can be oxidised using acidified potassium permanganate solution. Calculate the mass of iron(II) sulphate which will completely react with 200 mL of 0.25 M of acidified permanganate solution.

The redox reaction equation:

$2\ MnO_4^- + 5\ Fe^{2+} + 16H^+ \rightarrow 2\ Mn^{2+} + 5\ Fe^{3+} + 8\ H_2O$

Given: At.wt of Fe = 56 g/mol, S = 32 g/mol and O = 16 g/mol

Ferum(II) sulfat boleh dioksidakan menggunakan larutan berasid kalium permanganate. Kirakan jisim ferum(II) sulfat yang akan bertindakbalas lengkap dengan 200 mL 0.25 M larutan berasid kalium permanganate.

Persamaan tindak balas redoks:

$2\ MnO_4^- + 5\ Fe^{2+} + 16H \rightarrow 2\ Mn^{2+} + 5\ Fe^{3+} + 8\ H_2O$

Diberikan: JAR bagi Fe = 56 g/mol, S = 32 g/mol dan O = 16 g/mol

(30 marks/*markah*)

[c] A sodium thiosulfate solution is standardized by weighing and dissolving 250.0 mg of pure copper metal. The copper solution is treated with excess KI and the liberated iodine requires 44.90mL of the thiosulfate titrant to reach the end-point.

What is the molarity of the sodium thiosulfate?
Given: AWt of Cu = 63.54 g/mol

The reaction equations:

$$2Cu^{2+} + 4I^{-} \rightarrow 2CuI\,(s) + I_2$$
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^{-} + S_4O_6^{2-}$$

Satu larutan thiosulfat dipiawaikan dengan menimbang dan melarutkan sebanyak 250.0 mg logam kuprum tulen. Larutan kuprum dirawat dengan KI berlebihan dan iodine yang terbebas memerlukan sebanyak 44.90 mL titran tiosulfate untuk mencapai takat akhir.

Apakah kemolaran natrium thiosulfat?
Diberikan: JAR bagi Cu = 63.54g/mol

Persamaan tindakbalas:

$$2Cu^{2+} + 4I^{-} \rightarrow 2CuI\,(s) + I_2$$
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^{-} + S_4O_6^{2-}$$

(25 marks/*markah*)

6. [a] Describe the principle of flame emission spectrometry, plasma emission spectrometry and atomic absorption spectrophotometry. Sketch the basic component of an Inductive Couple Plasma (ICP) spectrometer.

Huraikan prinsip spektroskopi penyerakan nyalaan, spektroskopi penyerakan plasma dan spektofotometri serapan atom. Lakarkan komponen asas alatan spektrometer serakan plasma.

(30 marks/*markah*)

[b] What do you understand about detection limits, instrument detection limits (IDL) and method detection limits (MDL), and briefly discuss how this detection limits have effect on the precision of ICP and AAS measurement.

Apa yang anda faham tentang had pengesanan, had pengesanan alatan dan had pengesanan kaedah dan bincang dengan ringkas bagaimana had-had pengesanan ini memberi kesan kepada kejituan pengukuran ICP dan AAS.

(25 marks/*markah*)

[c] The standard addition method involves adding known amount of standard to one or more aliquots, compensating for a sample constituent that enhances or depresses the analyte signal. Data given below were obtained from Mn leached liquor by using standard addition method. The concentration of Mn standard is 12.3 ppm. All solutions are diluted to final volume of 50 ml. Plot the graph of the instrument signal obtained against the added volume of standard. Find the intercept and calculate the Mn concentration in ppm unit.

Kaedah penambahan piawai melibatkan penambahan larutan piawai yang diketahui isipadunya ke dalam satu atau lebih larutan ***aliquot****, bagi menggantikan konstituen sampel yang telah meninggikan atau merendahkan signal analit. Data di bawah diperolehi daripada penentuan Mn dalam satu larutan pelarutlesapan dengan menggunakan kaedah penambahan piawai. Kepekatan paiwai Mn ialah 12.3 ppm. Kesemua larutan telah dicairkan kepada isipadu akhir sebanyak 50ml.*

Plot satu graf signal alatan yang diperolehi melawan isipadu piawai tambahan. Cari garisan pintasan dan kirakan kepekatan Mn dalam unit ppm.

Sample volume (ml) *Isipadu sampel (ml)*	**Standard volume (ml)** *Isipadu piawai (ml)*	**Instrument signal** *Signal alatan*
10.0	0	0.215
10.0	5	0.424
10.0	10	0.695
10.0	15	0.932
10.0	20	1.243
10.0	25	1.450

(45 marks/*markah*)

7. [a] Sir William Henry Bragg and William Henry Bragg were awarded the Nobel Prize of Physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS and diamond by the means of X-ray. They introduced Braggs Law, which was used to explain the interference pattern of X-rays scattered by crystals.

Sir William Henry Bragg dan William Henry Bragg telah dianugerahkan Hadiah Nobel untuk Fizik pada tahun 1915 bagi kerja mereka menentukan struktur kristal bermula dengan NaCl, ZnS dan intan menggunakan sinar-X. Mereka memperkenalkan Hukum Bragg, yang telah digunakan untuk menerangkan interferens corak sinar-X yang diserakkan oleh kristal-kristal.

(i) Write the complete equation for Bragg's Law.

Tuliskan persamaan yang lengkap untuk Hukum Bragg.

(10 marks/*markah*)

(ii) Derive mathematically Braggs's Law.

Terbitkan secara matematik Hukum Bragg.

(20 marks/*markah*)

(iii) Explain the FOUR main applications of XRD.

Terangkan EMPAT aplikasi utama bagi XRD.

(10 marks/*markah*)

[b] Both XRD and XRF utilizes X-ray applications for analysis.

(i) Distinguish how XRD differ from XRF in terms of analysis results.

Kedua-dua XRD dan XRF menggunakan aplikasi-aplikasi sinar-X sebagai analisis.

(i) Kenalpastikan bagaimana XRD berbeza dari XRF dari segi analisis keputusan

(10 marks/*markah*)

(ii) Tabulate FOUR advantages and FOUR disadvantages of XRF analysis.

Jadualkan EMPAT kelebihan dan EMPAT kekurangan analisis XRF.

(20 marks/*markah*)

(iii) Explain the principles of XRF. Clarify as well the Auger electron emission phenomena and its effect on the XRF yield.

Terangkan prinsip-prinsip XRF. Jelaskan juga fenomena pemancaran elektron Auger dan kesannya pada hasil XRF.

(30 marks/*markah*)

APPENDIX / *LAMPIRAN*

Table A: Values of t for ν ,Degrees of freedom for various confidence level

Jadual A: Nilai-nilai t bagi darjah kebebasan, ν pada pelbagai paras keyakinan

	Confidence Level *(Paras Keyakinan)*			
ν	**90 %**	**95 %**	**99 %**	**99.5 %**
1	6.314	12.706	63.657	127.32
2	2.920	4.303	9.925	14.089
3	2.353	3.182	5.841	7.453
4	2.132	2.776	4.604	5.598
5	2.015	2.571	4.032	4.773
6	1.943	2.447	3.707	4.317
7	1.895	2.365	3.500	4.029
8	1.860	2.306	3.355	3.832
9	1.833	2.262	3.250	3.690
10	1.812	2.228	3.169	3.581
15	1.753	2.131	2.947	3.252
20	1.725	2.086	2.845	3.153
25	1.708	2.060	2.787	3.078
∞	1.645	1.960	2.576	2.807

* ν = N -1 = degrees of freedom

APPENDIX / *LAMPIRAN*

Table B: Values of F at the 95% Confidence Level

Jadual B: Nilai-nilai bagi F pada paras keyakinan 95%

	$\nu_1 = 2$	3	4	5	6	7	8	9	10	15	20	30
$\nu_2 = 2$	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.70	8.66	8.62
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.86	5.80	5.75
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.62	4.56	4.50
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	3.94	3.87	3.81
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.51	3.44	3.38
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.22	3.15	3.08
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.01	2.94	2.86
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.85	2.77	2.70
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.40	2.33	2.25
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.20	2.12	2.04
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.01	1.93	1.84

*Adapted from D.B. Rorabacher. Anal. Chem., 63 (1991) 139.