UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2009/2010

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EBS 336/3 – Analytical Chemistry
[Kimia Anilitis]

Duration : 3 hours
[Masa : 3 jam]

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

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

Instruction: Answer **FIVE** questions. If 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.]

1. [a] In an experiment to find the iron content of a sample of steel, 1.40 g of the metal were dissolved by boiling in acid. The iron in the solution was then all converted into the +2 oxidation state and the solution was made up to 100.0 cm^3 using dilute sulfuric acid. 10.0 cm^3 aliquot of this solution were titrated against a 0.02 mol/dm^{-3} solution of potassium permanganate. About 24.2 cm^3 of the potassium permanganate solution were required to reach the end-point of the titration.
The reaction occurring in the titration is:

Dalam satu eksperimen untuk mencari kandungan ferum dalam satu sampel keluli, 1.40 g logam dilarutkan dengan cara pendidihan dalam asid. Kemudian semua ferum dalam larutan ditukarkan kepada keadaan pengoksidaan +2 dan larutan dicairkan kepada isipadu 100.0 cm^3 menggunakan asid sulfurik cair. 10.0 cm^3 alikuot larutan ini dititratkan dengan larutan 0.02 mol/dm^{-3} kalium permanganat. Sebanyak 24.2 cm^3 larutan kalium permanganat diperlukan untuk mencapai takat akhir pentitratan.
Tindakbalas yang berlaku dalam pentitratan adalah:

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

(1.1)

(i) Calculate the mass of iron in the sample of steel.
(Given: At. wt. Fe: 56.0 g/mol)
Kirakan jisim ferum dalam sampel keluli.
(Diberikan: JAR Fe: 56.0 g/mol)

(15 marks/*markah*)

(ii) Calculate the percentage by mass of iron in the steel.
Kirakan peratus jisim ferum dalam keluli.

(15 marks/*markah*)

[b] In acid solution, potassium permanganate reacts with H_2O_2 to form Mn^{2+}

Dalam larutan berasid, kalium permanganat bertindakbalas dengan H_2O_2 membentuk Mn^{2+} :

$$H_2O_2 + MnO_4^- + H^+ \rightarrow Mn^{2+} \quad \textbf{(1.2)}$$

(i) Write a balance equation for equation (1.2).

Tulis satu persamaan seimbang bagi persamaan (1.2).

(20 marks/*markah*)

(ii) Calculate the number of milliliters of 0.1560 M $KMnO_4$ that will react with 28.9 mL of 0.25 M H_2O_2.

Kirakan bilangan milliliter 0.1560 M larutan $KMnO_4$ yang akan bertindakbalas dengan 28.9 mL isipadu 0.25 M larutan H_2O_2.

(20 marks/*markah*)

[c] Briefly explain the Volhard titration of chloride.

Terangkan dengan ringkas pentitratan Volhard bagi klorida.

(30 marks/*markah*)

2. [a] Calculate the percentage of copper by mass in a sample of rock containing 0.50 % by mass of chalcopyrite, assuming this is the only source of copper in the rock.

Kirakan peratus jisim kuprum dalam satu sampel batuan yang mengandungi 0.50 % berat kalkopirit, dengan menganggapkan ia adalah satu-satunya sumber kuprum dalam batuan.

(Given / *Diberikan*: At. wt. : Cu = 63.55; Fe = 55.85; S = 32.07g/mol)

(20 marks/*markah*)

[b] Copper in saltwater near the discharge of a sewage treatment plant is determined by first separating and concentrating it by solvent extraction of its dithiazone chelate at pH 3 into methylene chloride and then evaporating the solvent, ashing the chelate to destroy the organic portion and titrating the copper with EDTA.

Three 1- L portions of the sample are each extracted with 25 mL portions of methylene chloride and the extracts are combined in a 100 mL volumetric flask and diluted to volume. A 50 mL aliquot is evaporated, ashed and titrated.

If the EDTA solution has a $CaCO_3$ titer of 2.69 mg/mL and 2.67 mL is required for titration of the copper, what is the concentration of copper in the seawater in parts per million?

(Given: At. wt.: Cu = 63.54; Ca = 40.08; C = 12.01 and O = 16.0)

Kuprum dalam air garam berhampiran discas loji perawatan kumbahan ditentukan pada mulanya dengan cara pengekstrakkan pelarut di mana ia dipisahkan dan dikonsentratkan dari kelet dithiazon pada pH 3.0 masuk ke dalam metilena klorida dan kemudian penyejatan pelarut diikuti dengan pembakaran kelet untuk memusnahkan bahagian organik dan pentutratan kuprum dengan EDTA.

Tiga-bahagian isipadu 1 L sampel masing-masing diekstrakkan dengan 25 mL bahagian metilena klorida dan ekstrak dicampurkan dalam satu kelalang volumetrik 100 mL dan dicairkan ke isipadu. Satu 50 mL alikuot disejatkan, diabukan dan dititratkan.

Jika larutan EDTA itu mempunyai isipadu titer $CaCO_3$ sebanyak 2.69 mg/mL dan 2.67 mL diperlukan bagi pentitratan kuprum, berapakah kepekatan kuprum dalam air laut dalam bahagian per juta?

(Diberikan: JAR: Cu = 63.54; Ca = 40.08; C = 12.01 and O = 16.0 g/mol)

(50 marks/*markah*)

[c] A buffer solution is prepared by adding 25 mL of 0.05 M sulfuric acid solution to 50 mL of 0.10 M ammonia solution. What is the pH of the buffer?

Satu larutan tampan disediakan dengan menambahkan sebanyak 25 mL 0.05 M larutan asid sulfurik kepada 50 mL 0.10 M larutan ammonia. Apakah pH larutan tampan ini?

Given / *Diberikan*: $K_b = 1.75 \times 10^{-5}$

(30 marks/*markah*)

3. [a] A 0.200 g sample containing copper is analyzed iodometrically. Copper (II) is reduced to Cu (I) by iodide:

Sebanyak 0.200 g sampel yang mengandungi kuprum dianalisakan secara iodometri. Cu (II) diturunkan kepada Cu (I) oleh iodida:

$$2\ Cu^{2+} + 4\ I^- \rightarrow 2\ CuI + I_2$$

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

What is the percent of copper in the sample if 20.0 mL of 0.100 M $Na_2S_2O_3$ is required for the titration of the liberated I_2?

Apakah peratus kuprum dalam sampel jika sebanyak 20.0 mL isipadu 0.100 M $Na_2S_2O_3$ diperlukan dalam pentitratan I_2 yang terbebas itu?

(Given / *Diberikan*: At wt. Cu = 63.5 g/mol)

(35 marks/*markah*)

[b] A hydrogen peroxide solution is analyzed by adding a slight excess of standard $KMnO_4$ solution and back titrating the unreacted $KMnO_4$ with standard Fe^{2+} solution. A 0.587 g sample of the H_2O_2 solution is taken, 25.0 mL of 0.0215 M $KMnO_4$ is added and the back titration requires 5.10 mL of 0.112 M Fe^{2+} solution.
What is the percent of H_2O_2 in the sample?

Satu larutan hidrogen peroksida dianalisiskan dengan menambahkan sedikit berlebihan larutan piawai $KMnO_4$ dan melakukan pentitratan-balik $KMnO_4$ yang tidak bertindakbalas itu dengan larutan piawai Fe^{2+}. Sebanyak 0.587 g sampel dari larutan H_2O_2 itu diambil dan 25.0 mL 0.0215 M larutan $KMnO_4$ ditambahkan dan pentitratan-balik memerlukan sebanyak 5.10 mL 0.112 M larutan Fe^{2+}.
Berapakah peratus H_2O_2 dalam sampel?

(Given / *Diberikan*: At. wt.: Fe = 55.85; H = 1.0; O = 16.0 and Mn = 54.9 g/mol)

(35 marks/*markah*)

[c] In the nuclear industry, detailed records are kept of the plutonium received, transported or used. Each shipment of plutonium pellets received is carefully analyzed to check that the purity and hence the total quantity is as the supplier claims. A particular shipment is analyzed with the following results: 99.93, 99.87, 99.91 and 99.86%. The listed purity as received from the supplier is 99.95%. Is the shipment acceptable?

Dalam industri nuklear, rekod terperinci bagi plutonium yang diterima, dipindahkan atau digunakan disimpan. Setiap bekalan pelet plutonium dianalisakan dengan teliti untuk mengesahkan bahawa ketulenan dan seterusnya kuantiti totalnya adalah seperti yang dinyatakan oleh pembekal. Suatu bekalan dianalisiskan dengan keputusan berikut: 99.93, 99.87, 99.91 dan 99.86%. Ketulenan seperti yang diterima dari pembekal adalah 99.95%. Adakah bekalan ini boleh diterima?

(30 marks/*markah*)

4. [a] Calculate the pH at 25.0, 50.0 mL and 60.0 ml addition of titrant in the titration of 50.0 mL of 0.100 M acetic acid with 0.100 M NaOH.

Kirakan pH selepas penambahan 25.0, 50.0 mL dan 60.0 ml isipadu titrant dalam pentitratan 50.0 mL 0.100 M asid asetik dengan 0.100 M NaOH.

Given / *Diberikan*: K_a (CH_3COOH) = 1.75 x 10^{-5}.

(30 marks/*markah*)

[b] Calcium in powdered milk is determined by ashing a 1.50 g sample and then titrating the calcium with EDTA solution, 12.1 mL being required. The EDTA was standardized by titrating 10.0 mL of a zinc solution prepared by dissolving 0.632 g zinc metal in acid and diluting to 1 L (10.8 mL EDTA required for titration). What is the concentration of calcium in the powdered milk in parts per million?

Kalsium dalam susu tepung ditentukan dengan melakukan "ashing" ke atas 1.50 g sampel dan mentitratkan kalsium dengan larutan EDTA. Pentitratan ini memerlukan 12.1 mL isipadu titer. Pempiawaian EDTA dilakukan dengan mentitratkan 10.0 mL satu larutan zink yang disediakan dari pelarutan 0.632 g logam zink dalam asid dan pencairan ke 1 L (10.8 mL EDTA diperlukan dalam pentitratan pempiawaian). Apakah kepekatan kalsium dalam susu tepung dalam bahagian per seribu?

(At.wt. Zn = 65.4 , Ca = 40.1)

(40 marks/*markah*)

[c] Replicate samples of a silver alloy are analyzed and determined to contain 95.67, 95.61, 95.71 and 95.60 % Ag. Calculate:

(i) the standard deviation.

(ii) the standard deviation of the mean.

(iii) the relative standard deviation of the mean (in percent) of the individual results.

Sampel replikat satu aloi perak dianalisiskan dan ditentukan mengandungi 95.67, 95.61 dan 95.60% Ag. Kirakan:

(i) sisihan piawai.

(ii) sisihan piawai bagi purata.

(ii) sisihan piawai relatif bagi purata (dalam peratus) keputusan individu.

(30 marks/*markah*)

5. [a] You have received three shipments of uranium ore of equal weight. Analysis of the three ores indicated contents of 3.978 $\pm$ 0.004%, 2.536 $\pm$ 0.003%, and 3.680 $\pm$ 0.003% respectively. What is the average uranium content of the ores and what are the absolute and relative uncertainties?

Anda telah menerima tiga bekalan kapal yang mengandungi bijih uranium dengan berat yang sama. Analisis ketiga-tiga bekalan bijih menunjukkan kandungan 3.978 $\pm$ 0.004%, 2.536 $\pm$ 0.003%, dan 3.680 $\pm$ 0.003% masing-masing. Apakah purata kandungan uranium dalam bijih dan apakah ketidakpastian mutlak dan relatif?

(30 marks/*markah*)

[b] Sodium hydroxide and Na_2CO_3 will titrate together to phenolphthalein end point ($OH^- \rightarrow H_2O$; $CO_3^{2-} \rightarrow HCO_3^-$).

A mixture of NaOH and Na_2CO_3 is titrated with 0.25 M HCl, requiring 26.2 mL for the phenolphtahalein end point and an additional 15.2 mL to reach the modified methyl orange end point. How many milligrams NaOH and Na_2CO_3 are in the mixtures?

Natrium hidroksida dan Na_2CO_3 boleh dititratkan bersama untuk mencapai takat akhir fenolfthalein ($OH^- \rightarrow H_2O$; $CO_3^{2-} \rightarrow HCO_3^-$).

Satu campuran NaOH dan Na_2CO_3 yang dititratkan dengan 0.25 M HCl, memerlukan sebanyak 26.2 mL untuk mencapai takat akhir fenolfthalein dan sebanyak 15.2 mL isipadu tambahan untuk mencapai perubahan takat akhir metil jingga. Berapakah miligram NaOH dan Na_2CO_3 yang wujud dalam campuran?

(20 marks/*markah*)

[c] The copper present in waste water near the discharge of a sewage treatment plant is determined by first separating and concentrating it by solvent extraction of its dithiozone chelate at pH 3 into methylene chloride and then evaporating the solvent, ashing the chelate to destroy the organic portion and titrating the copper with EDTA. Three 1-L portions of the sample are each extracted with 25 -mL portions of methylene chloride and the extracts are combined in a 100-mL volumetric flask and diluted to volume. A 50-mL aliquot is evaporated, ashed and titrated. If the EDTA solution has a $CaCO_3$ titer of 2.69 mg/mL and 2.67 mL is required for titration of the copper, what is the concentration of copper in the waste water in parts per million?

Kehadiran kuprum dalam air sisa berhampiran dengan loji perawatan kumbahan ditentukan pada mulanya dengan cara pemisahan dan pengkonsentratan melalui pengekstrakan pelarut dengan mengekstrak masuk ke dalam metilena klorida menggunakan pengkelet dithiozon pada pH 3. Ini diikuti dengan proses penyejatan pelarut, pengabuan (ashing) bahan pengkelet untuk menyingkirkan bahagian organik dan mentitratkan kuprum dengan EDTA. Setiapnya tiga 1-L bahagian sampel diekstrakkan dengan 25-mL bahagian metilena klorida dan ekstrak ini dicampurkan dalam satu kelalang volumetrik 100-mL dan dicairkan ke isipadu. Satu 50-mL alikuot disejatkan, diabukan dan dititratkan. Jika larutan EDTA memberikan titer $CaCO_3$ sebanyak 2.69 mg/mL and 2.67 mL diperlukan untuk pentitratan kuprum, apakah kepekatan kuprum dalam air sisa dalam bahagian per juta (ppm)?

(Given / *Diberikan*: Formula wt. $CaCO_3$ = 100.1 g/mol, At. Wt. Cu = 63.5 g/mol)

(50 marks/*markah*)

6. [a] Distinguish between Iodimetry and iodometry.State briefly, the method for the determination of end-point for a redox titration.

Bezakan di antara iodimetri dan iodometri. Nyatakan dengan ringkas, kaedah penentuan takat akhir bagi suatu pentitratan redoks.

(20 marks/*markah*)

[b] Copper in an ore sample is at a concentration of about 3 % (wt/wt). How many samples should be analyzed to obtain a percent relative standard deviation of 5% in the analytical result at 95% confidence level, if the sampling precision is 0.15 % (wt/wt)?
Please refer to **Table** in the Appendix

Satu sampel bijih kuprum mengandungi sebanyak 3% (berat/berat). Berapa bilangan sampel yang perlu dianalisiskan untuk memperolehi peratus sisihan piawai relatif sebanyak 5% (rsd) dalam keputusan analisis pada paras keyakinan 95%, jika kepersisan pensampelan adalah 0.15% (berat/berat)?
Sila rujuk kepada ***Jadual*** *dalam Lampiran.*

(20 marks/*markah*)

[c] A calibration curve for the colorimetric determination of phosphorous in a waste sample is prepared by reacting standard solution of phosphate with molybdenum (VI) and reducing the phosphomolybdic acid complex to produce the characteristic blue color. The measured absorbance A is plotted against the concentration of phosphorous. From the following data, determine the linear least-squares line and calculate the phosphorus concentration in the waste sample. Use a graph paper to accurately draw the straight lines.

Given that:

Satu lengkuk kalibrasi bagi penentuan fosforus dalam satu sampel sisa disediakan dengan melakukan tindakbalas satu larutan piawai fosfat dengan molibdenum (VI) dan penurunan kompleks asid fosfomolibdik tersebut untuk menghasilkan warna biru ciri. Absorban A yang diukur diplotkan melawan kepekatan fosforus. Dari data berikut, tentukan garisan "linear least squares" dan kirakan kepekatan fosforus dalam sampel sisa tersebut. Gunakan kertas graf untuk melukis dengan jitu garisan lurus tersebut.

Diberikan:

$$m = \frac{\Sigma (x_i y_i) - [(\Sigma x_i \Sigma y_i) / n]}{\Sigma x_i^2 - [(\Sigma x_i)^2 / n]} \qquad (6.1)$$

$$b = y - m x \qquad (6.2)$$

Table 6.1: Data for Absorbance measured at varying concentration of P

Jadual 6.1: Data Absorban yang diukur pada pelbagai kepekatan P

P (ppm)	A (abs)
1.00	0.205
2.00	0.410
3.00	0.615
4.00	0.820
Waste sample / *Sampel sisa*	0.625

(60 marks/*markah*)

…14/-

7. [a] Draw a schematic diagram of an atomic absorption instrument. Describe briefly the principles of an atomic absorption spectrophotometry.

Lukiskan satu gambarajah skema satu peralatan penyerapan atom. Huraikan secara ringkas prinsip satu spektrofotometri penyerapan atom.

(25 marks/*markah*)

[b] The sources of interference in absorption and emission measurements can be classified into spectral, chemical and physical interferences.
Discuss briefly all **four** examples of these type of interferences.
Why is a high concentration of a potassium salt is sometimes added to standards and samples in flame absorption or emission methods?

Sumber gangguan dalam pengukuran penyerapan dan pemancaran boleh dikelaskan kepada gangguan spektral, kimia dan fizik.
*Bincangkan secara ringkas **empat** contoh gangguan-gangguan tersebut.*
Mengapakah kepekatan yang tinggi larutan garam kalium kadang-kadang ditambahkan kepada larutan piawai dan larutan sampel dalam kaedah penyerapan atau pemancaran nyalaan?

(50 marks/*markah*)

[c] With the aid of diagrams, compare the operations of a single-beam spectrophotometer and a double-beam spectrophotometer.

Dengan bantuan gambarajah-gambarajah, bandingkan antara operasi satu spektrofotometer bim tunggal dan spektrofotometer bim dubel.

(25 marks/*markah*)

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APPENDIX / *LAMPIRAN*

Table A: Values of t for ע ,Degrees of freedom for various Confidence level
Jadual A: Nilai-nilai t bagi darjah kebebasan, ע pada pelbagai paras keyakinan

	Confidence Level			
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

[a] $\nu = N - 1$ = degrees of freedom.