THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 – FINAL EXAMINATION – 2015 / 2016

CMU 3128/CME 5128/CHU 3129 – Instrumental methods in chemical analysis

Duration: Two hours
Date and time: 10th January, 2017
From 9.30 a.m. to 11.30 a.m.

Instructions to students

This question paper consists of six pages and six questions. Answer any four questions only.

1. In the analysis of Mn in a steel sample (5.2350 g), the sample was oxidized to $KMnO_4$ and the solution was diluted to 100.0 mL using distilled water. A 10.0 mL of this solution was warmed and subjected to photometric titration with 0.01 M Fe^{2+} solution prepared in sulfuric acid and the absorbance was measured at 520 nm at which $KMnO_4$ shows absorption.

   (i) Draw and label the photometric titration curve for the above titration. (10 marks)

   (ii) State three advantages of the photometric titration compared to classical redox titration. (06 marks)

   (iii) What is the reason for showing a high absorbance value by $KMnO_4$? (10 marks)

   (iv) Give possible reason/s for measuring absorbance only at 520 nm. (12 marks)

   (v) If the end point resulted by the above titration was 20.00 mL, calculate the percentage of Mn in the steel sample. (Mn = 54.93 g) (25 marks)

   (vi) Another 10.0 mL of the above $KMnO_4$ solution was subjected to Atomic Emission Spectroscopy and the percentage of Mn in the steel sample found by the emission results was higher than that was found by photometric titration. Give possible reasons. (15 marks)

   (vii) State two differences in the spectrophotometers used in the above two analytical methods. (12 marks)

   (viii) Comment on the following statement.
   "IR spectra are band spectra and not line spectra." (10 marks)

2. The Ca^{2+} amount in a waste water sample (10.0 mL) of a coir industry was analysed using Fluorescence spectroscopy. In this analysis, a series of Ca^{2+} solutions in the range of 1- 4 μg *per* 25 mL was used as standards. To each standard solution, 5.0 mL of 0.40 M KOH and 1.0 mL of calcene solution was added before diluting to 25.0 mL with distilled water. Fluorescence of each sample was measured at 540 nm with excitation at 330 nm. The sample which may have calcium in different forms in addition to Ca^{2+} was also treated in the same manner.

(i) What may be the reason for adding calcene solution? (08 marks)

(ii) Explain in brief how the fluorescence light is resulted. (10 marks)

(iii) Why do you have to limit the concentration of the standard series to the above stated range? (10 marks)

(iv) Explain what is meant by the sentence underlined. (10 marks)

(v) The standard solution having 2 μg of Ca^{2+} *per* 25 mL gave a reading of 15.0 and the reading of the sample was 12.0. Calculate the weight of Ca^{2+} in the waste water sample. The stoichiometry between Ca^{2+} and calcine for the reaction between each other is 1:1. (20 marks)

(vi) When the same waste water sample was analysed using Atomic Absorption Spectroscopy, the concentration of calcium resulted was more. Give possible reason/reasons. (15 marks)

(vii) State two differences in the spectrophotometers used in the above two analytical methods. (12 marks)

(viii) Briefly explain how the mass spectrum of Electron impact Mass Spectroscopy (EIMS) is resulted. (15 marks)

3. (i) (a) The following cell reactions are said to be not feasible. Explain.

$$I_{2(g)} + M^{2+}{}_{(aq)} \text{ ---------> } 2I^-{}_{(aq)} + M_{(l)}$$

$$2I^-{}_{(aq)} + M^{2+}{}_{(aq)} \text{ ------> } I_{2(g)} + M_{(l)}$$

$[M^{2+}{}_{(aq)} / M_{(l)}\ E^o = -1.06\ V\ ;\ I_{2\,(g)} / I^-{}_{(aq)}\ E^o = 0.54\ V]$

(b) Write down the correct cell reaction corresponding to the above Half reactions and hence, determine the standard cell potential. (18 marks)

(ii) Write down the half - cell reaction corresponding to the calomel electrode (08 marks)

(iii) The following half - cell equations represent the changes taking place at the cathode and anode, respectively.

$M^{2+}(aq) + 2e \text{ -------> } M(s)$
$H_2O \text{ ----> } H^+_{(aq)} + O_{2(g)} + 4\,e$

(a) Derive the overall balanced cell reaction.

(b) In an experiment involving electrolysis to determine the concentration of a cation X^{3+} it was found that 2.50 g of X(s) (Rel. atomic mass = 100) was deposited on the cathode. Assuming that all the X^{3+} have been reduced and that a volume of 100.00 ml of this solution was used for electrolysis,

(α) calculate the quantity of electricity that was passed through this solution (Faraday's Constant = 96,500 C mol^{-1}).

(β) determine the initial concentration of X^{3+}.

(36 marks)

(iv) (a) Outline the **principle** involving Coulometry and Electro-gravimetry, two quantitative electro-analytical techniques (experimental details NOT necessary)

(b) A coulometric titration (constant current) was carried out to determine the amount of dissolved phenol in a certain water sample. The basis of this determination was the stoichiometric and fast reaction between phenol and electrochemically generated bromine to give tribromophenol.

A water sample (50.0 ml) was acidified and an excess of KBr was added. Coulometric titration was then carried out at a constant current of 20 mA. The end point was reached in 8.0 minutes. With the aid of the relevant chemical equations, calculate the concentration of phenol in the water sample.

(38 marks)

4. (i) van Deemter equation describes the efficiency of a chromatographic column.

(a) Write down the van Deemter equation and define all the terms in it.

(b) Draw the van Deemter plot, H vs. u including all component graphs and label them.

(c) Describe how eddy diffusion term contributes to zone broadening.

(30 marks)

(ii) A three component mixture was separated in a 20 m capillary column and following data were obtained.

Compound	t_r/min.	W/min.
X	8.01	0.15
Y	8.23	0.15
Z	8.40	0.16

(a) Calculate the average number of theoretical plates for the column.

(b) What is the average height of a theoretical plate?

(c) Explain why each compound X, Y and Z has different number of theoretical plates.

(d) How does the number of theoretical plates relate to the Efficiency of the column?

(40 marks)

(iii) In gas chromatography (GC), stationary phase is inside a tubular column.

(a) Name and compare the two types of columns used in GC.

(b) Compare the stationary phases and process of separation in gas solid chromatography (GSC) and gas liquid chromatography (GLC).

(c) List down three properties you expect for a stationary phase of GLC to have. (30 marks)

5. (i) Define the following terms in relation to chromatography.

(a) Dead time

(b) Gradient elution

(c) R_f value

(30 marks)

(ii) Giving reasons explain the following in brief.

(a) In gel electrophoresis, no mobile phase is involved.

(b) Larger molecules are eluted first in gel permeation chromatography.

(c) Polar solvents have to be used in reverse phase thin layer chromatography.

(30 marks)

(iii) Thermal conductivity detector (TCD) is one of the most common detectors coupled to gas chromatographs.

(a) Explain how TCD works.

(b) Compare the advantages and the disadvantages of TCD over flame ionization detector (FID)?

(25 marks)

(iv) Explain the principle behind ion exchange chromatography.

(15 marks)

6. Answer either Part I or Part II

Part I

(i) A cyanide ion-selective electrode obeys the equation $E = C - \frac{RT}{F} \ln[CN^-]$

where C is a constant and E is the electrode potential. A 1.5×10^{-2} mol dm^{-3} CN^- solution gave a value of - 0.300 V for the electrode potential measured under standard conditions (T = 25 °C). Calculate the expected value of the potential, measured under the same conditions when the concentration of CN^- is 1.5 mmol dm^{-3}
[R = 8.314 J mol^{-1} K^{-1}, T is the temperature in Kelvin, F = 96500 C]

(24 marks)

(ii) Concentration polarization is a type of polarization which is useful in electro analytical methods; it occurs when the ***transfer*** of reacting species from the bulk solution to the electrode surface becomes limiting.

(a) **Name and outline** the three factors that contribute to the ***transfer*** mentioned above

(b) **Name** the three other types of polarizations other than concentration polarization as a result of which an electrode of an electrolytic cell can become polarized. (30 marks)

(iii) A dropping mercury electrode (DME) is a micro electrode used in a polarography.

(a) Name the two advantages of using a dropping mercury electrode (DME) in polarographic analysis

(b) Sketch a clearly labeled, typical polarogram.

(c) What is meant by "half-wave potential'

(28 marks)

(iv) Write down the balanced equation with respect to the reduction of the following compounds that take place at a DME, when subjected to a polarographic analysis under mild acidic conditions.

(a) benzaldehyde

(b) ethyl bromide

(c) Propyl cyanide (18 marks)

Part II

Isotope dilution method was followed to find the concentration of Al in a rock sample. In this method, to a 6.040 g of the rock sample 0.302 g of Al^{28} ($t_{½}$ = 2.2 min.) having a specific activity of 40.0 counts min^{-1} mg^{-1} was added. After mixing, 0.100 g of Al was separated and purified gave an activity of 400 counts min^{-1} by the Gas flow counter.

(i) Why may be the reason for using Isotope dilution method for the above analysis?

(10 marks)

(ii) What is the principle behind Isotope dilution analysis?

(15 marks)

(iii) State two assumptions that you have to make when taking measurements in Isotope dilution analysis. (14 marks)

(iv) State one advantage of using the Gas flow counter instead of Geiger Muller counter. (06 marks)

(v) Calculate the

(vi) percentage of Al in the rock sample. (15 marks)

(vii) Another sample of the same rock was taken to analyse $^{35}_{17}Cl$ quantitatively using neutron activation analysis. The neutron source used was ^{238}Cf.

(a) What is the principle behind quantitative neutron activation analysis?

(15 marks)

(b) Write an equation showing the neutron capture by $^{35}_{17}Cl$.

(07 marks)

(c) In this method, after irradiation by the neutrons, the sample is kept for "cooling down" for some time. Why? (10 marks)

(d) State two differences in "fast" and "thermal" neutrons. (08 marks)