



THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 – FINAL EXAMINATION – 2013 / 2014

CMU 3123/CME 5123 – ANALYTICAL CHEMISTRY

Duration: Two hours

Date and time: 26th of June, 2014 from 1.00 p.m. to 3.00 p.m.

Instructions to students

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

1. The effluent of a steel factory collects into a tank for treatment before discharging.

- (i) Suggest a suitable method to obtain a random sample for the analysis assuming that the effluent does not carry any solid particles. (10 marks)
- (ii) What is selectivity of an analysis method? (10 marks)
- (iii) In order to analyze SO_4^{2-} and Cl^- ions in the effluent, the student, Sunil, carried out gravimetric analysis using a silver nitrate solution. The concentrations of Cl^- and SO_4^{2-} found were 0.1 mol dm^{-3} and 0.12 mol dm^{-3} respectively. In the analysis of 100.0 cm^3 of effluent, the first precipitate was obtained after adding 100.0 cm^3 of AgNO_3 . What is the concentration of the AgNO_3 solution added?
(At 25°C solubility product of $\text{AgCl} = 1.1 \times 10^{-10} \text{ mol}^2\text{dm}^{-6}$
solubility product of $\text{Ag}_2\text{SO}_4 = 1.2 \times 10^{-5} \text{ mol}^3\text{dm}^{-9}$) (20 marks)
- (iv) Show mathematical calculations to prove that selective precipitation of the two ions are possible. (15 marks)
- (v) Another student, Gamini, said that the solubility will not be equal to the theoretical value due to "salt effect". Do you agree with this statement? Briefly explain your answer. (15 marks)
- (vi) Sunil was asked to follow the instructions given below when carrying out the analysis. Briefly explain the reason behind each step.
(a) Add very dilute solution of AgNO_3 with stirring.
(b) Once the precipitate is obtained, the solution with the precipitate should be warmed and then allowed to settle at the room temperature. (20 marks)

(vii) Gamini said that sensitivity of gravimetric analysis can be improved by changing the precipitating agent. Comment on his statement. (10 marks)

2. A 25.0 cm³ sample of 0.0100 mol dm⁻³ CaCl₂ solution is mixed with 75.0 cm³ of 0.0075 mol dm⁻³ EDTA and the mixture was buffered at pH=10. (K_{CaY} = 5.0 × 10¹⁰ mol dm⁻³)

(i) pH 10 buffer was made using the weak base (pK_b = 4.8) BOH (0.5 M) and its salt BX. What is the concentration of the BX in this buffer? (25 marks)

(ii) Calculate the concentration of unreacted Ca²⁺ at the equilibrium. (25 marks)

(iii) What are the assumptions you made in the above calculation (ii)? (10 marks)

(iv) It has been found that Al³⁺ is also present in the above solution as an impurity. In order to analyze the concentration of Al³⁺, a back titration with excess EDTA (at pH= 7) against a standard solution Mg²⁺ solution using Eriochrome Black T as the indicator was suggested.

Metal ion	log K _{MY}
Mg ²⁺	8.7
Cd ²⁺	16.1
Al ³⁺	16.3

(a) Write down the following EDTA complexes in the increasing order of stability. Give reasons for your answer. Al-EDTA, Ca-EDTA, Mg- EDTA (15 marks)

(b) Give two possible reasons for direct titration of Al³⁺ with EDTA unsuccessful. (10 marks)

(c) Can you use a standard Cd²⁺ solution instead of Mg²⁺ for the back titration of Al³⁺? Explain your answer in brief. (15 marks)

3. A mineral sample of 5.000g was digested and the final volume was made to 250.0 cm³. In order to find the concentration of Fe³⁺ in the solution, a 25.0 cm³ of this solution was titrated with 0.002 M Z²⁺ solution.

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.674\text{V} \quad E_{\text{Z}^{3+}/\text{Z}^{2+}}^0 = 0.15\text{V}$$

- (i) Comment on the E⁰ value of the half reaction of a suitable redox indicator for this titration.
(10 marks)
- (ii) Find the potential at the equivalence point.
(10 marks)
- (iii) Sketch and explain the titration curve.
(25 marks)
- (iv) If OH⁻ ions and also Cl⁻ ions were in the solution, comment on how these ions would have affected the formal potential of the half cell reaction of Fe³⁺/Fe²⁺.
(20 marks)
- (v) If another metal ion M²⁺ is present in the solution, will it be possible to titrate Fe³⁺ selectively following the same above procedure?
 $E_{\text{M}^{2+}/\text{M}^+}^0 = 0.400\text{V}$ (20 marks)
- (vi) Suggest a suitable method to find the concentration of Fe³⁺ in the presence of M²⁺ and briefly state why it is possible with the method suggesting.
(15 marks)
4. (i) HX is a strong acid and YOH is a weak base. Sketch and explain the expected conductometric titration curve of a titration between 25.0 cm³ of 0.01 mol dm⁻³ HX and 0.01 mol dm⁻³ YOH.
The molar conductivities increase in the order of Y⁺ < X⁻ < OH⁻ < H⁺
(25 marks)
- (ii) When you carry out conductometric titrations the resultant graph is non linear. Why? Suggest two ways to avoid this error when you do the titration practically.
(15 marks)
- (iii) State one disadvantage and one advantage of potentiometric titrations when compared to classical redox titrations.
(10 marks)

- (iv) Thermogravimetric analysis of 0.500 g of a hygroscopic sample of calcium hydroxide showed the following losses in weight.

Temperature range ($^{\circ}\text{C}$)	Weight loss (g)
100 – 120	0.012
900-950	0.036

- (a) Briefly explain how the weight losses had taken place. (10 marks)
- (b) Assuming that there is no weight loss with further heating, calculate the weight the sample taken for analysis. (Ca=40, H=1, O=16) (14 marks)
- (c) State whether the following changes are exothermic or endothermic and show the changes in Differential Thermal Analysis (DTA) curves.
Loss of moisture
Solidification (16 marks)
- (d) A thermometric titration is being carried out between A^{2+} (25.0 cm^3) and B^{2+} . The reaction between A^{2+} and B^{2+} are exothermic. Draw the thermometric titration curve for the titration. (10 marks)

5. (i) Explain the following in brief.

- (a) Hollow cathode lamp provides a better radiation source for Atomic Absorption Spectroscopy than tungsten lamp.
- (b) Organic compounds having OH^- , NH_2 as substituent shows a better sensitivity in UV/Visible spectroscopy.
- (c) In Atomic Absorption Spectroscopy, in the cases where spectral interference can take place, may use an absorption wavelength different to the resonance wavelength. (45 marks)

- (ii) What is meant by “noise” in a signal of an instrument used for analytical measurements? (10 marks)

(iii) State five differences of Atomic Absorption Spectrophotometry and UV/Visible Spectrophotometry.

(20 marks)

(iv) A 25.0 cm³ sample of a natural fertilizer was diluted to 250.0 cm³ and was analysed for Mg²⁺ using Atomic Absorption spectroscopy.

(a) The absorbance obtained with a 2.0 cm optical path length was 0.444. The molar absorptivity coefficient was $2.22 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. What is the concentration of Mg²⁺ in the fertilizer?

(15 marks)

(b) For the same sample when standard addition method was applied, the concentration of Mg²⁺ obtained was different to the above result. What may be the reason for getting a different result?

(10 marks)

6. (i) A solute has a distribution coefficient (K_D) of 5.00 between water and chloroform. A 50.00 cm³ sample of 0.050 mol dm⁻³ aqueous solution of the solute is extracted with 15.00 cm³ of chloroform.

(a) Calculate the extraction efficiency of the sample.

(b) What is the volume of chloroform needed to extract 99.9% of the solute?

(c) Derive an expression to calculate the solute concentration in the organic phase after ' n ' number of extractions.

(d) Calculate the minimum number of extractions with 50.00 cm³ portions of chloroform needed to extract 99.9% of the solute.

(60 marks)

(ii) Thin layer chromatography and paper chromatography are two types of planar chromatography. Compare these two types of chromatography under the following.

(a) Mobile phase

(b) Stationary phase

(c) Sorption process

(12 marks)

(iii) Electrophoresis is a non chromatographic separational method.

(a) Briefly describe the principle behind the separation process in electrophoresis.

(b) What is the role played by the buffer here?

(c) Explain how gel electrophoresis contributes in size exclusion mechanism.

(28 marks)