



KENYATTA UNIVERSITY

UNIVERSITY EXAMINATIONS 2010/2011

INSTITUTIONAL BASED PROGRAMME (IBP) – AUGUST SESSION

EXAMINATION FOR THE DEGREE OF MASTER OF SCIENCE

SCH 556: ANALYTICAL ELECTROCHEMICAL METHODS

DATE: TUESDAY 3RD JANUARY 2012

TIME: 9.00 A.M – 12.00 NOON

INSTRUCTIONS:

Answer ALL the questions.

1. (a) State the polarographic wave equation i.e. Heyrovsky – Ilkovic equation for the reduction of a metal ion at the dropping mercury electrode. Define the parameters contained in the equation. [3 marks]
- (b) A student studied the reduction of a certain metal ion M^{n+} at a dropping mercury electrode at 18°C. The data obtained of current as a function of applied potential is given in the table below:

I (μ A)	5	15	25	35	45	50	50
E _{app} (V)	0.465	0.499	0.520	0.341	0.575	0.700	1.00

NB: $I_d = 50 \mu$ A

Determine graphically or otherwise

- (i) the number of electrons (n) involved in the real process and
- (ii) the half – wave potential $E_{1/2}$

[14 marks]

2. (a) What do you understand by the term “selectivity coefficient”. [2 marks]
- (b) Calculate the maximum activity we can tolerate for the interfering bromide ion, if the chloride ion selective electrode is to be used to analyze within a 5% error, solutions whose chloride activity are of the order of $10^{-2} \text{ mol dm}^{-3}$ ($K_{Br,Cl} = 3.00 \times 10^{-2}$) [4 marks]

- (c) What are the options available to an analytical chemist if the activity of the interfering ion exceeds the value allowed? [8 marks]
- (d) In the potentiometric titration of 100 cm^3 of a chloride solution with a $2.00 \times 10^{-3} \text{ mol dm}^{-3}$ solution of silver nitrate, the emf was measured using an Ag^+ ion – reference assembly.

The following results were obtained.

Volume $\text{AgNO}_3 / \text{cm}^3$	emf / mV
2.50	262
3.00	273
3.50	282
4.00	288
4.50	294
5.00	297
5.50	300
6.00	304

Using the Gran's plot method, determine the equivalence point of the titration and the concentration of the chloride solution [4 marks]

3. (a) Distinguish between
- (i) Voltammetry and polarography [2 marks]
 - (ii) a limiting current and a residual current [2 marks]
 - (iii) Differential pulse polarography and linear scan polarography [2 marks]
- (b) Outline a procedure to carry out simultaneous determination of the toxic trace metals Cd, Cu, Pb, and Zn in soils by Differential pulse anodic stripping voltammetry. [6 marks]

- (c) The concentration of Cu^{2+} in sea water may be determined by anodic stripping voltammetry using the method of standard addition. When a 50.0 mL sample is analysed, the peak current is $0.886 \mu\text{A}$. A $5.00\text{-}\mu\text{L}$ spike of 10.0-ppm Cu^{2+} is added, giving a peak current of $2.52 \mu\text{A}$. Calculate the concentration of copper in the sample of sea water in parts per million.
[6 marks]
4. (a) (i) Using a suitable sketch describe a calomel reference electrode?
[2 marks]
- (ii) What are its advantages over the standard hydrogen electrode?
[2 marks]
- (iii) Show that the electrode potential of the calomel electrode depends on its Cl^- (aq) concentration.
[2 marks]
- (iv) List four important features that calomel electrode meets.
[2 marks]
- (v) What are the factors that would affect the effectiveness of calomel electrode?
[2 marks]
- (b) (i) A fluoride ion-selective electrode was used to measure the concentration of F^- in a cup of tea. When immersed in a mixture of 25 cm^3 of tea and 25 cm^3 of ionic strength adjuster (TISAB), the electrode gave a reading of 98 mV. When 2.0 cm^3 of a 100 ppm solution of F^- was added to this mixture, the emf dropped to 73 mV. Calculate the concentration of fluoride ions in the tea.
[2 marks]
- (ii) The components of TISAB are, in concentrations of mole per cubic decimeter ; NaCl, 1.0; CH_3COOH , 0.25; CH_3COONa , 0.75; sodium citrate, 0.001. Identify the purpose or purposes served by these components.
[2 marks]
- (iii) Why should the standards and sample solutions be stored in plastic containers.
[2 marks]
- (iv) The expected slope is -59.16 mV per tenfold change in concentration, what effect will a different slope have on the quantitative analysis of fluoride.
[2 marks]

