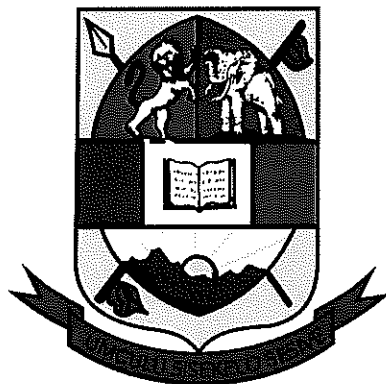


UNIVERSITY OF ESWATINI
DEPARTMENT OF CHEMISTRY



MAIN EXAMINATION 2020/2021

TITLE OF PAPER: THERMAL AND ELECTROANALYTICAL METHODS
COURSE NUMBER: CHE 609
TIME ALLOWED: THREE (3) HOURS
INSTRUCTIONS: ANSWER ANY FOUR (4) QUESTIONS

Special Requirements

None

YOU ARE NOT SUPPOSED TO OPEN THIS PAPER UNTIL PERMISSION TO DO SO HAS BEEN GIVEN BY THE CHIEF INVIGILATOR.

Question 1 [25]

- a) Use diagrams to discuss the principles of thermogravimetry. (7)
- b) Use diagrams to explain how the Differential Thermal Analysis technique works. (6)
- c) Use diagrams to explain how the Differential Scanning Calorimetry technique works. (6)
- d) Explain how the hyphenated technique TG-MS works in the monitoring of the pyrolysis, gasification, and combustion of sewage sludge. (6)

Question 2 [25]

- a) Explain how transfer co-efficients and ionic mobilities are used to select materials for salt bridges in potentiometry (4)
- b) State the Nernst equation used for the potentiometric determination of fluoride ions, and use the Debye-Huckel theory to explain how the activity of fluoride ion is related to its concentration. (8)
- c) i) With the aid of a diagram, use ion exchange theory to explain how a pH glass membrane electrode works. (5)
- ii) Write the Nernst expression for an ideal pH glass electrode, and show that unit calibrations in the readout are in increments of 59mV. (4)
- iii) Explain, using diagrams and equations, how the selectivity coefficient and ion exchange principles enable fabrication of a pNa electrode. (4)

Question 3 [25]

- a) Use the ion exchange theory to explain in detail how the pH glass membrane electrode works. (5)
- b) Use the ion exchange theory to explain in detail the following errors associated with membrane electrodes
- (i) alkaline error (3)
- (ii) acid error (3)
- c) Use the Nernst equation to show how a decade change in $[H^+]$ concentrations leads to a 59mV change in potential when using a pH glass membrane electrode. (5)
- d) The electrical signals involved in redox reactions require magnification through operational amplifiers. For each of the following operational amplifiers, draw the hardware and state its output.
- i) Voltage Follower (3)
- ii) Differential Amplifier (3)
- iii) Integrating Amplifier (3)

Question 4 [25]

- (a) Derive the Ilkovic Equation for polarography from Fick's Law of Diffusion. (8)
- (b) Derive the equation used for determining n , the number of electrons involved in a polarographic reduction of vitamin C, from the rising portion of its polarographic wave. (8)

- (c) Use diagrams to describe the voltage ramps used in fast linear sweep voltammetry. What does the resultant voltammogram look like? (4)
- (d) The data below were obtained when a Ca^{2+} ion-selective electrode was immersed in a series of standard solutions whose ionic strength was constant at 2.0M.

[Ca ²⁺] (M)	E (mV)
3.4×10^{-5}	-74.8
3.6×10^{-4}	-48.4
3.2×10^{-3}	-18.7
3.0×10^{-2}	-10.0
3.5×10^{-1}	+37.7

What is the concentration of Ca^{2+} in the sample if it gave a reading of -22.5mV (5)

Question 5 [25]

- (a) Discuss in detail, the origins of overpotential in voltammetry. (5)
- (b) Use diagrams to describe the voltage ramps used in alternating current voltammetry. What does the resulting voltammogram look like? (5)
- (c) Draw and label the Rotating Disk Electrode (RDE) used in voltammetry. Explain how it works. (5)
- (d) Use the Randles-Sevcik Equation to describe how quantification of electroactive species is carried out using the Rotating Disk Electrode. (5)
- (e) Explain how reaction mechanisms in electroanalytical chemistry are elucidated using the Rotating Ring Disk Electrode (RRDE). (5)

Question 6 [25]

- a) For cyclic voltammetry,
- Draw the potential ramps employed in the technique. (3)
 - Draw the resulting voltammogram. (3)
 - Use equations to explain how cyclic voltammetry is used to determine the reversibility of electrochemical reactions. (7)
- b) Explain how the hyphenated technique TG-FTIR works in the determination of volatiles in water-oil emulsions. (6)
- c) The data below were obtained when a F^- ion-selective electrode was immersed in a series of standard solutions whose ionic strength was constant at 2.0M.

[F ⁻] (M)	E (mV)
2.35×10^{-5}	-74.8
2.62×10^{-4}	-48.4
2.13×10^{-3}	-18.7
1.99×10^{-2}	-10.0
2.48×10^{-1}	+37.7

What is the concentration of F^- in the sample if it gave a reading of -22.5mV (6)