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 thermogravimmetry. (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 a 2.0M.

[Ca2+] (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,

i) Draw the potential ramps employed in the technique. (3)

ii) Draw the resulting voltammogram. (3)

iii) 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)