NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
BACHELOR OF SCIENCE HONOURS DEGREE
END OF SECOND SEMESTER EXAMINATIONS – AUGUST 2009
ANALYTICAL CHEMISTRY II – SCH 2106
TIME: 3 HOURS

INSTRUCTIONS TO CANDIDATES

1. Answer ***FOUR*** questions, ***TWO*** from Section A and ***TWO*** from Section B. Each question carries 25 marks. Illustrate your answer, where appropriate, with large clearly labelled diagrams.

SECTION A

1. (a) Explain the difference between electric charge, electric current and electric potential. (6 marks)

(b) Define the following terms:

(i) Junction potential. (2 marks)
(ii) Salt bridge. (2 marks)

(c) (i) How much work is required to move 2.36 mmol of electrons through a potential difference of 1.05V? (3 marks)

(iii) State the relationship between free energy and electric potential. (2 marks)

(d) From the overall formation constant of $Ni(glycine)^{2+}_2$ plus the value of E^o for the Ni^{2+} I Ni(s) couple,

$Ni^{2+} + 2glycine \leftrightarrow Ni(glycine)^{2+}_2$ $\quad K \equiv \beta_2 = 1.2 \times 10^{11}$

$Ni^{2+} + 2e^- \leftrightarrow Ni(s)$ $\quad E^- = -0.236$ V

Deduce the value for E^o from the following reactions:

(i) $Ni^{2+} + 2$ glycine $\leftrightarrow Ni(glycine)^{2+}_2$ (5 marks)

(ii) $Ni(glycine)^{2+}_2 + 2e^- \leftrightarrow Ni(s) + 2glycine$ (5 marks)

2. (a) The most widely employed ion-selective electrode for measuring pH is the

glass electrode.

(i) State five (5) limitations of a glass electrode on pH measurement. (5 marks)

(ii) State four (4) advantages of ion selective electrodes. (4 marks)

(b) Define the following terms as applied in electrogravimetry:

(i) Overpontential (2 marks)
(ii) Concentration polarization (2 marks)
(iii) Ohmic potential (2 marks)

(c) A perchlorate ion-selective immersed in 50.0 mL of unknown perchlorate solution gave a potential of 358.7 mV versus S.C.E. When 1.00 mL of 0.050 M $NaClO_4$ was added, the potential changed to 346.1 mV. Assuming that the electrode has a Nernstian response ($\beta = 1.00$), find the concentration of ClO^-_4 in the unknown. (10 marks)

3. (a) A solution containing 0.402 49 g of $CoCl_2$. *x* H_2O was exhaustively electrolysed to deposit 0.099 37 g of metallic cobalt on a platinum cathode.

$$Co^{2+} + 2e^- \rightarrow Co(s)$$

Calculate the number of moles of water per mole of cobalt in the reagent. (8 marks)

(b) Giving examples, if possible, explain the role of mediators in coulometric analysis. (5 marks)

(c) Draw a fully labelled diagram of a liquid based ion selective electrode and explain how it works. (12 marks)

SECTION B

4. (a) Distinguish between the following terms used in spectrophotometry:

(i) Chromophore and auxochrome. (2 marks)
(ii) Natural band width and spectral band width. (2 marks)
(iii) Bathochromic shift and hypsochromic shift. (2 marks)
(iv) Extinction and transmittance. (2 marks)
(v) Resolution and dispersion. (2 marks)

(b) Describe how light energy is changed into electrical energy in a photomultiplier tube. (7 marks)

(c) A sample contains two metallic ions, CO^{2+} and Cr^{3+} whose absorption spectra overlap. Explain how you could determine the concentration of both species using absorption spectrophotometry. (λ_{max} is 510 nm and 575 nm for CO^{2+} and Cr^{3+} respectively). (8 marks)

5. (a) Draw a diagram illustrating the main parts of an atomic absorption spectrophotometer. (5 marks)

(b) Write notes on the functions of the following:

(i) Nebulizer. (2 marks)
(ii) Premix chamber. (2 marks)
(iii) Flame. (3 marks)
(iv) Hollow cathode lamp. (2 marks)

(c) (i) Describe how you would digest a sample by dry ashing. (Volumes and weights not required). (6 marks)

(ii) State the positive and negative attributes of the method. (5 marks)

6. (a) A solution containing a complex formed between Bi(III) and thiourea has a molar absorptivity of $9.32 \times 10^3 Lcm^{-1}mol^{-1}$ at 470 nm.

(i) What is the absorbance of a $6.24 \times 10^{-5}M$ solution of the complex in a 5 mm cell? (2 marks)

(ii) What is the molar concentration of the complex when measured in a 5 cm cell? (2 marks)

(iii) What is the percentage transmittance in the solution described in (i)? (2 marks)

(b) Write short notes on the Czenny-Turner configuration as a model of a grating monochromator. (8 marks)

(c) The following is data relating to a spectrophotometric titration of a solution of phycoerythrobilin dimethylester in chloroform titrated against zinc acetate in methanol.

Absorbance	**Volumes of Zinc (µl)**
0.100	20
0.200	30
0.300	40
0.400	50
0.500	60
0.600	80
0.605	90
0.610	100
0.613	110
0.612	120
0.613	130

(i) Determine the end-point of the titration. (4 marks)

(ii) Highlight the advantages of spectrophotometric end-point determinations over visual end-point detections. (5 marks)

(d) Distinguish between end-point and equivalence point. (2 marks)

End of question Paper!!!