CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

THIRD YEAR EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF EDUCATION SCIENCE

CHEM 351: ANALYTICAL CHEMISTRY I

STREAMS: BED (SCIE) **TIME: 2 HOURS**

DAY/DATE: THURSDAY 04/08/2016 **11.30 AM – 1.30 PM**

INSTRUCTIONS:

Answer Question One and any other Two Questions

Useful Data

$1\text{Å} = 10^{-10}m$

$0℃ = T/K - 273.15$

$1\ cal = 4.184\ J$

$1atm = 101.325\ kpa = 760Torr$

$1l\ atm = 101.325\ J$

$C = 3 \times 10^{8} m/s$

$R = 8.31447 JK^{-1}mol^{-1}$

$= 8.31447 JK^{-1}mol^{-1}$

$1N = 1kg\ ms^{-2}$

$1J = 1\ kg\ m^{2}s^{-2}$

$1\ ev = 1.60218 \times 10^{-19} J$

QUESTION ONE (30 MARKS)

(a) (i) State some of the problems which may arise when using a poorly packed Lcc column. [2 marks]

(ii) Some optimization procedures in LCC originate from the idea of generating the maximum number of plates within the shortest possible time that is, minimizing t_R/N

(I) State the conditions under which this can be achieved. [1 mark]
(II) Because of equipment limitations, state what does the above approach implies in terms of t_R and ΔP. [1 mark]

(iii) The separation of adenosine mono-, di, and triphosphate nucleotides (AMP, ADP and ATP) was accomplished in a little over 3 min using 0.4 M K H_2PO_4 (plus 3% methanol) and a 15 cm by 2-mm column, packed with $10\mu m$ particles of silica to which was bonded a 3-aminopropyl siloxane phase. The mobile phase viscosity was 1.4 cp. Flow rate was 100ml-hr^{-1} at an inlet pressure of 2900 psi. suggest improvements (with reasons) in the operating procedure. [1 ½ marks]

(b) (i) Although no nitrite-selective electrode is available, suggest an indirect method to measure nitrite ion activity. [1 mark]

(ii) A fluoride solid-state electrode has a selectivity coefficient of 0.10 relative to hydroxide ion. At 10^{-2} M fluoride concentration, what hydroxide ion concentration could be tolerated? [1 ½ marks]

(iii) Polarographic curve resemble potentiometric titration curves. When might polarography yield useful data not obtainable by potentiometric methods. [4 marks]

(c) (i) Why is source modulation used in atomic absorption spectroscopy. [4 ½ marks]

(ii) State five advantages of using photographic plates over photomultipliers for detection in emission spectroscopy. [3 marks]

(iii) Why is a grating monochromator preferred to prism monochromator. [4 marks]

(d) Explain briefly the meaning of the following terms as used in analytical chemistry:

(i) Repeatability [½ mark]

(ii) Reproducibility [½ mark]

(iii) Blas [½ mark]

(iv) A sample [½ mark]

(e) (i) State any four responsibilities of the analytical chemist. [2 marks]

(ii) State three ways by which the trueness of results can be demonstrated. [1 ½ marks]

(iii) List any three things which the analytical solving problems in environmental sciences will involve in. [1½ marks]

QUESTION TWO (20 MARKS)

(a) Explain the principles by which qualitative analysis can be performed in gas chromatography with the use of retention times. [2 marks]

(b) Describe the following terms as used in chromatography, stating when and how they are applied

(i) Gradient elution [3 ½ marks]

(ii) Isocratic elution [1 ½ marks]

(iii) Derivatization [8 marks]

(c) In a chromatographic analysis of low-molecular weight acids, butyric acids, isobytyric acids elutes with a retention times of 7.63 min, 5.98 min respectively. The columns void time is 0.31 min

(i) Calculate the capacity factor for both acids. [1 ½ marks]

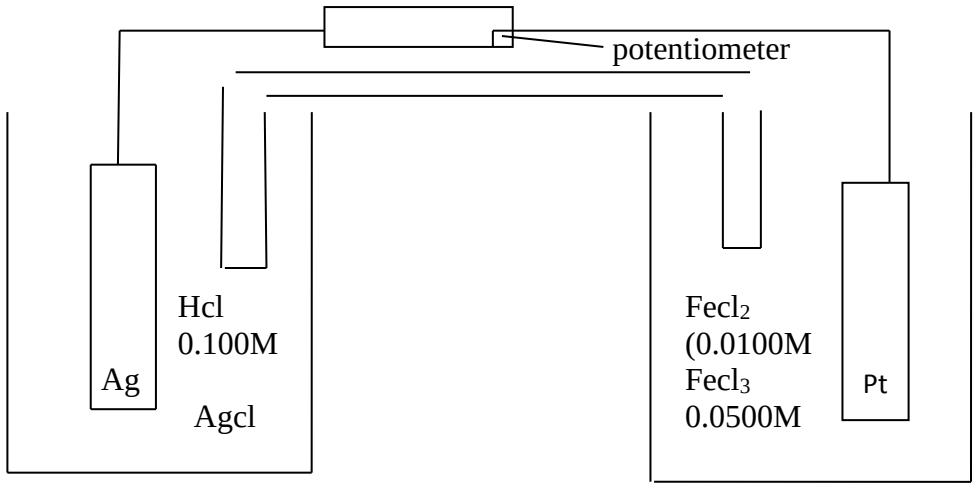
(ii) Calculate the selectivity factor for isobutyric acid and butyric acid. [1 mark]

(d) A 2.031 g sample of dried soil is extracted with 20.0 ml of methylene chloride after filtering to remove the soil. A 1 ml portion of the extract is removed and diluted to 10ml with a cetonitrile. Injecting 5 ml of the diluted extract into an HPLC gives a signal of 0.217 (arbitrar units) for the PAH fluoranthene. When 5 ml of a 20 PPM fluoranthene standard is analyzed using the same conditions a signal of 0.258 is measured. Calculate the concentration of fluoranthene in the soil in PPM. [2 ½ marks]

QUESTION THREE (20 MARKS)

(a) (i) Where are the anodic cathodic, and overall reactions responsible for the potential in the electrochemical cell shown below?

(ii) Write the shorthand notation for electrochemical cell given below



(iii) Calculate the potential (E) of the electrochemical cell shown above. [1 mark]

(iv) Calculate the concentration of Fe^{3+} in an electrochemical cell similar to that shown above, if the concentration of Hcl in the left hand cell is 1.0 M; the concentration of $Fecl_2$ in the right hand cell is 0.051 M and the measured potential is +0.546 V.E^0 at 25℃,V

$Fe^3 + e^- \rightleftharpoons Fe^{2+} = +0.771$

$Agcl(s) + e^- \rightleftharpoons Ag(s) + cl_2 + 0.2223$ [1 mark]

(b) The concentration of ca^{2+} in a water sample was determined by the method of external standards. The ionic strength of the samples and standards was maintained at a nearly constant level by making each solution 0.5 M in KNo_3. The measured cell potentials for the external standards are shown in the following table.

$[Ca^{2+}]$,(M)	1.0×10^{-5}	5.0×10^{-5}	1.0×10^{-4}	5×10^{-4}	1.0×10^{-3}	5.0×10^{-3}	1.0×10^{-2}
E cell (V)	-0.125	-0.103	-0.093	-0.072	-0.065	-0.043	-0.033

(i) Determine the equation for the least square lines. [8 marks]

(ii) Calculate the standard deviation from regression. [1 ½ marks]

(iii) Calculate the standard deviation of the slope [1 mark]

(iv) Determine the standard deviation of the intercept. [1 mark]

(v) Calculate the concentration of Ca^{2+} in a water sample using linear regression if its cell potential is found to be -0.084V. [1 mark]

(vi) Calculate the standard deviation from the results obtained in Q 3b (v) if the cell potential was as the result of three measurement. [1 ½ marks]

QUESTION FOUR (20 MARKS)

(a) Explain the unique and special industrial aspects of the environment for the practice of analytical chemistry. [4 marks]

(b) (i) Outline processes which any excitation source for emission spectroscopy must accomplish. [3 marks]

(ii) Discuss the spectral interference in flame photometry. [10 marks]

(c) Diagrammatically summarize the events occurring when a solution containing a suitable compound of the metal to be investigated by atomic absorption spectrophotometer is aspirated into a flame. [3 marks]
