THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 – FINAL EXAMINATION – 2008 / 2009

### CHU 3129/CHE 5129 – INSTRUMENTAL METHODS IN CHEMICAL ANALYSIS

Duration: Two and half hours

Date and time: 23rd July, 2009 from 1.30 p.m. to 4.00 p.m.

Instructions to students

This question paper consists of **six pages and six questions. Answer any four questions only.**

1. (a)   Comment briefly on the following statements.
    (i)   Very low concentrations of MnO_4^- (permanganate ion) can be determined using UV/visible spectroscopy.
    (ii)   Compounds having only single bonds rarely absorb UV or visible radiation.
    (iii) Fluorescent molecules often absorb UV light and emit visible light.

    (30 marks)

   (b) (i)   What is the necessary property in a molecule to absorb IR radiation?
        (ii)   What is the principle behind Raman Spectroscopy?
        (iii) Give two advantages of Raman Spectroscopy compared to IR spectroscopy.
        (iv)   Describe three main differences in the construction of instruments for IR and UV/ Visible spectroscopy.

    (25 marks)

   (c) The drug tolbutamine (formula weight = 270 g) has an absorptivity of 2.603 cm^{-1}g^{-1}L at 262 nm. One tablet (weight = 1.023 g) was dissolved in water and diluted to 2.0 L. If the solution shows an absorbance of 0.678 at 262 nm in 1.00 cm cell,
        (i)   What is the molar absorptivity of tolbutamine at 262 nm? (Give your answer with correct number of significant figures)
        (ii)   What would have been the transmittance reading?
        (iii) Calculate the percentage of tolbutamine in the tablet.

    (45 marks)

2. (a) What is the principle difference between,
        (i)   Atomic fluorescence spectroscopy and atomic absorption spectroscopy
        (ii)   Atomic fluorescence spectroscopy and atomic emission spectroscopy with respect to atomization.
        (iii) Fluorescence and phosphorescence

    (30 marks)
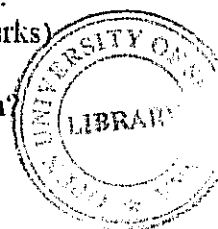
(b) List two advantages of each of the following.
  (i) Photometric titrations over normal (classical) titrations
  (ii) Chemical ionization over electron impact ionization in mass spectroscopy.
  (iii) Inductively coupled plasma (ICP) emission spectroscopy over conventional emission methods

(30 marks)

(c) A plant leaf sample was digested (5.034 g in 10.0 mL) and analyzed for magnesium by atomic absorption spectroscopy using a method of standard additions. Two 1.00 mL portions were diluted to 10.0 mL of water in separate flasks. To one flask, 10.0 μL of 0.0500 M $MgCl_2$ solution was added. The absorbances of the two solutions were recorded as 0.235 and 0.335. What is the percentage of magnesium (Mg = 24.0 g) in the plant leaf?
(Give your answer with correct number of significant figures)

(40 marks)

3. (a) What does these terms describe?
  (i) Retention factor K'
  (ii) Selectivity factor α

(20 marks)

(b) The van Deemter equation for GC column efficiency is,

$$H = A + \frac{B}{u} + Cu$$

  (i) Define all the terms in the equation.
  (ii) Draw and label the van Deemter plot showing the three separate component graphs.
  (iii) Indicate what information you can obtain from the graph.

(30 marks)

(c) Preparative thin layer chromatography basically involves the following steps.

(Step 1) Loading the sample on to TLC plate → (Step 2) Developing the plate → (Step 3) Detection of separated components → (Step 4) Recovery of separated components

  (i) Name three types of adsorbents that can be used in TLC plates.
  (ii) If reverse phase TLC is done, what can you say about the relative polarities of the adsorbent and the mobile phase.
  (iii) Give two methods that can be adopted in step 3 to detect (visualize) the separated components.
  (iv) How do you recover the separated components in pure form in step 4?

(20 marks)

(d) Gel electrophoresis is a good separation technique. But it is not a chromatographic technique. Explain why?

(15 marks)

(e) Explian what is meant by super - critical fluid chromatography.

(15 marks)

4. (a) Briefly explain the following statements regarding HPLC.
   (i) Helium gas is passed through the mobile phase before they enter the mixing chamber.
   (ii) Amperometric detectors cannot be used with normal phase HPLC.

(20 marks)

(b) A student faced the following problems when HPLC is carried out on a sample using isocratic elution.

   A. First few compounds eluted fast and the resolution was poor.
   B. Compounds eluted later took a long time to elute and gave broad bands.

   (i) What is meant by isocratic elution?
   (ii) Suggest solutions for the above two problems.
   (iii) If problem B is observed in GC what would your solution be?

(40 marks)

(c) What are the two types of columns used in GC? Compare the similarities and differences between them.

(20 marks)

(d) Briefly describe the structural features of resins (polymers of styrene and divinylbenzene) which are used as ion exchangers.

(20 marks)

5. (a) List three different types membranes used in constructing membrane electrodes.

(12 marks)

(b) Describe an advantage and a disadvantage of potentiometric titrations.

(20 marks)

(c) (i) Imagine that you are given a solution of a particular (known) ionic species. List the three major experimental steps, performance of which allows you to determine the concentration of the ionic species in the solution using an indicator electrode whose potential obeys a Nernst like equation.

   (ii) The potential of an X^{2-} (aq) ion selective electrode obeys the equation

   $E = \text{constant} - 0.0592 \log\left[X^{2-} (aq) \right]$. The measured potential of the

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electrode when it was inserted in a solution of $X^{2-}(aq)$ where the concentration of it is $1.00\,mmol\,dm^{-3}$ was $-0.230\,V$. A solution, A, of $X^{2-}(aq)$ gave a potential value of $-0.300\,V$. Calculate the concentration of $X^{2-}(aq)$ in A.

(30 marks)

(d) The standard reduction potentials for the reactions $A^{4+}(aq) + e^- \rightarrow A^{3+}(aq)$ and $B^{4+}(aq) + e^- \rightarrow B^{3+}(aq)$ at $25^0 C$, are $-0.799\,V$ an $1.229\,V$ respectively.

(i) Giving reasons, determine the overall spontaneous cell reaction (under standard conditions) and the standard cell potential of a cell constructed by establishing the electrical contact between the solution phases of $Pt(s)\big| A^{4+}(aq), A^{3+}(aq)$ and $Pt(s)\big| B^{4+}(aq), B^{3+}(aq)$ electrodes using a salt bridge at $25^0 C$.

(ii) The spontaneous reaction in part (i) above can be used in determining the appropriate ionic species of A using a standard solution of the appropriate ionic species of B. Giving reasons sketch the variation of the electrode potential of the indicator electrode (platinum wire immersed in titration mixture) in such a titration when a standard solution of the ionic species of B is used as the titrant.

(38 marks)

6. (a) Briefly explain what is meant by the following terms.
   (i) Overpotential
   (ii) Ohmic drop
   (iii) Electrode polarisation

(30 marks)

(b) Sketch the experimental set-up used in constant potential Coulometry and label all the components in it.

(20 marks)

(c) Phenol is easily brominated according to the chemical equation $C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$. This reaction allows the phenol content of samples to be determined via a Coulometric titration using Br_2 generated electrochemically from Br^- according to the reaction $2Br^- \rightarrow Br_2 + 2e^-$. A 200 ml sample of polluted water was acidified and 5 g of KBr (excess) was added. Coulometric titration of the sample required 362 seconds at 28.6 mA to reach the end point. Calculate the phenol content of water sample, in $mg\,dm^{-3}$, The molecular weight of phenol is $94.1\,g\,mol^{-1}$. $\left[F = 96,500\,C\,mol^{-1} \right]$

(50 marks)

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