RAJARATA UNIVERSITY OF SRI LANKA

FACULTY OF APPLIED SCIENCES

B.Sc. Third year Semester II Examination – October / November / 2017

CHE 3311 – Advanced Analytical Chemistry II

Answer any six questions.   Time: 3 hours

The use of non-programmable calculator is permitted.

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1) (a) (i)   What is the additive can be used to extract an anion such as perchlorate from an aqueous phase to an organic phase:

        (ii) Which type of compounds in water is most suitable for trapping at low concentrations using solid phase extraction (SPE) with large water volumes if using nonpolar (e.g. C_{18}) stationary phase.

        (iii) Give an advantage of solid phase microextraction (SPME) over most other extraction methods when coupled with GC.

        (iv) List two methods to avoid the emulsion occurs during the liquid liquid extractions.

                                                                        (40 marks)

    (b) Explain the use of drying agent in liquid-liquid extraction. Give the names of any three drying agents and give chemical reactions to explain how they dry.

                                                                        (35 marks)

    (c) Describe two principles used in solvent extraction systems for metal ions. Give examples of each.

                                                                        (25 marks)

2. (i)   Drive an equation to calculate the amount of solute remaining in aqueous solution by multiple batch extractions with equal volumes of organic solvents.

                                                                        (10 marks)

    (ii) The distribution ratio between 1 M HCl and tri-n-butylphosphate for $PdCl_2$ is 2.3. What percent of $PdCl_2$ will be extracted from 25.0 mL of a 7.0×10^{-4} M solution into 10.0 mL tri-n-butylphosphate.

                                                                        (20 marks)

(iii)   Calculate how many extractions must be performed with separate 10.0 mL portions of tri-n-butylphosphate to remove 99% of the $PdCl_2$. Comment your results in (ii) and (iii).

(20 marks)

(b)   (i)   State three reasons for using chromatography.

(18 marks)

(ii)   State the stationary phase in paper chromatography and thin-layer chromatography.

(08 marks)

(iii)   The series of synthetic reactions shown below are in connection with the molecular mechanism of chemical carcinogenesis. Arrange these four compounds in order of their R_f values when analyzed by thin-layer chromatography (TLC) on silica gel-coated plates using CH_2Cl_2 as the developing solvent. Give one reason for your arrangement.
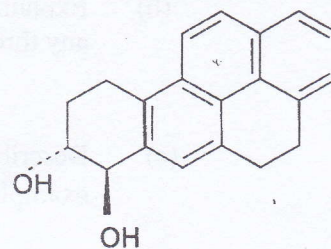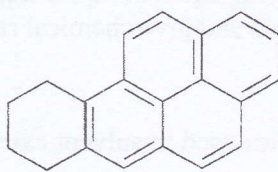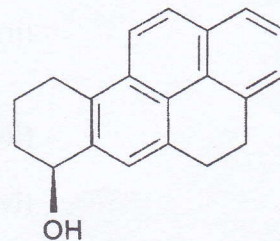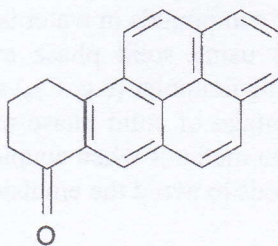
(24 marks)

3)   (a)   Define the following terms used in chromatography.
         (i)   Isothermal Elution.
         (ii)   Gradient Elution.

(16 marks)

(b)   Dicarboxylic acids ($HO_2C(CH_2)_nCO_2H$) cannot be analyzed easily directly by GC. However, by converting them to diesters ($CH_3O_2C(CH_2)_nCO_2CH_3$), good GC separation and detection is possible. What is a major effect of this derivatization that leads to improvement?

(20 marks)

(c)   Use the following gas chromatogram of a mixture of dioxane and cyclohexane eluted on a non-polar column to answer the following:

1,4-dioxane   Cyclohexane
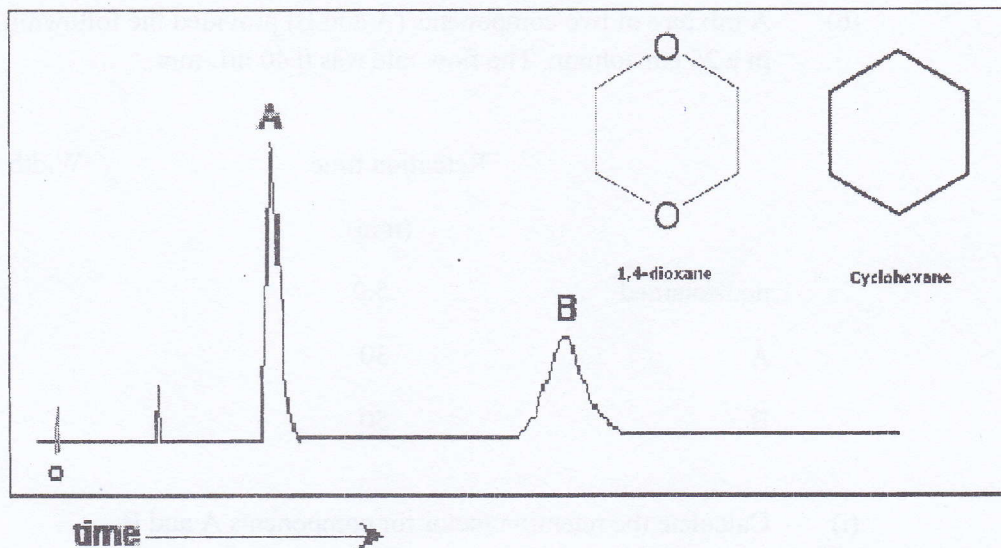
    (i)   What is the identity of the substance labelled peak A? Explain the answer.
    (ii)   The area measured for peak A is 2 cm^2 and the area measured for peak B is 3 cm^2. Assuming that the detector response is the same for both substances, calculate the mol% of A in the mixture.

(30 marks)

(d)   (i)   State two ways to decrease H,(height equivalent to theoretical plate) of the column:

(16 marks)

(ii) Briefly discuss the use of temperature programming in gas chromatography separations.

(18 marks)

(4) (a) (i) Sketch a typical van Deemter plot and what useful information can be found from the plot?

(ii) Describe different type of contribution to the band broadening by the constants in the van Deemter equation.

(iii) Why is the van Deemter B term in GC much greater than in HPLC?

(30 marks)

(b) A mixture of two components (A and B) provided the following data obtained in a 25 cm column. The flow rate was 0.40 mL/min.

	Retention time (min)	Width of Peak Base (min)
non-retained	5.0	-
A	30	18
B	50	22

(i) Calculate the retention factor for components A and B.

(10 marks)

(ii) Determine the resolution between two peaks.

(10 marks)

(iii) What column length required to achieve a resolution 1.75? Comment your answer.

(30 marks)

(c) Why is a thermal conductivity detector a much more universal GC detector than a flame ionization detector?

(20 marks)

5. (a) (i) A solution with a concentration of 0.14 M is measured to have an absorbance of 0.43. Another solution of the same chemical is measured under the same conditions and has an absorbance of 0.37. What is its concentration?

(15 marks)

(ii) The absorptivity of a particular chemical is 1.5/M·cm. What is the concentration of a solution made from this chemical if a 2.0 cm sample has an absorbance of 1.20?

(15 marks)

(b) The analyst used two sets of standard solutions and blanks to determine the calibration curves for the two solutions. The absorbances were plotted on the same axes. The graph is shown below.
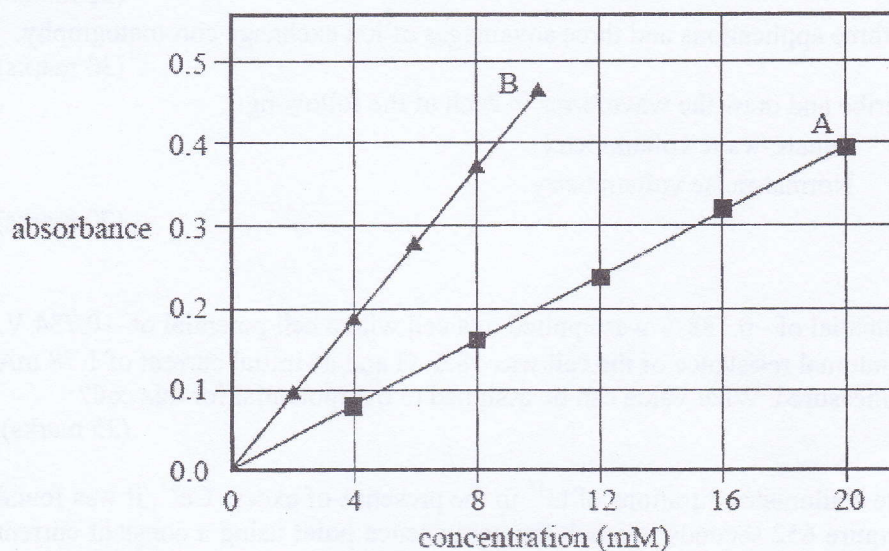
(i) The analyst found that, when it was measured at the appropriate wavelength, solution A had an absorbance of 0.2. If solution A was cobalt (II) nitrate, $Co(NO_3)_2$, determine its concentration in mg L^{-1}.
(molar mass of $Co(NO_3)_2$ = 182.9 g mol^{-1})

(10 marks)

(ii) In another mixture, the pink compound in solution A and the green compound in solution B, each have a concentration of approximately 1.5×10^{-2} M. Could the analyst reliably use both of the calibration curves to determine the concentrations for solution A and solution B by UV-visible spectroscopy? Justify your answer.

(15 marks)

(c) Explain the mechanism of a hollow cathode lamp (HCL) used in atomic absorption spectrophotometry (AAS).

(25 marks)

(d) Draw a block diagram of atomic emission spectroscopy (AES) and give one advantage and one disadvantage of this method.

(20 marks)

6). (a) Give one example in each of the natural, anionic and synthetic ion exchange resins. Discuss the physical properties of the ion exchange resins.

(30 marks)

(b) State four requirements for the substance to select as an ion exchange resin.

(20 marks)

(c) List three applications and three advantages of ion exchange chromatography.

(30 marks)

(d) Describe and draw the waveforms in each of the following:
(i) Square-wave voltammetry.
(ii) Normal-pulse voltammetry.

(20 marks)

7). (a) A potential of - 0.788 V was applied to a cell with a cell potential of – 0.734 V. The internal resistance of the cell was 18.0 Ω and an initial current of 1.78 mA was measured. What value can be assigned to overpotential for this cell?

(25 marks)

(b) In the coulometric titrations of U^{4+} in the presence of excess Ce^{3+}, it was found to require 652 seconds to reach the equivalence point using a constant current of 100.0 mA. How many moles of U^{4+} were present in the solution?

(25 marks)

(c) For a polarography experiment, the bulk solution concentration of an oxidized species is 2.7 mM, its diffusion coefficient is 1.8×10^2 cm^2/s, the area of the electrode is 0.050 cm^2, and the scan rate is 25 mV/s. The mass flow rate of the mercury is 1.2 mL/min and the drop life is 10 seconds. Take n = 1 and the density of Hg as 13.534 g/cm^3.

(i) Calculate the drop area.
(ii) Calculate the current at the end of drop life.
(iii) Calculate the average current over drop life.

(30 marks)

(d) Briefly describe three-electrode setup used in voltammetry. give two advantages of three electrode system over two electrode system.

(20 marks)

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