THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme / Stand alone courses in Chemistry
Level 5 – FINAL EXAMINATION – 2016 / 2017

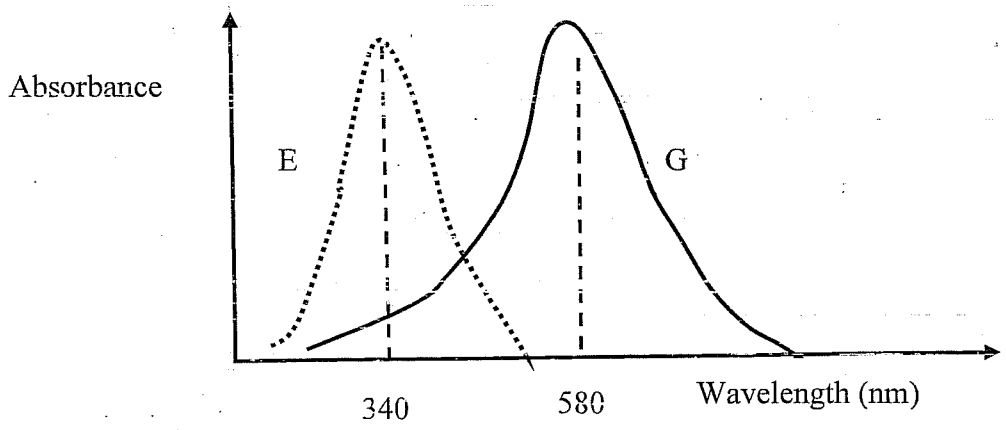
CMU 3128/CME 5128 – Instrumental methods in chemical analysis

Duration: Two hours
Date and time: 7th January, 2018
From 9.30 a.m. to 11.30 a.m.

Instructions to students

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

1.(A) The following figure shows the absorption spectra of the compounds E and G. The absorbance of a solution having only 0.001 M of the compound E was 0.21 0 at λ = 340 nm and When a sample of both E and G was analysed, the absorbance was 0.538 at λ = 340 nm and 0.160 at λ = 580 nm. The molar absorptivity coefficients of the compound G at λ = 340 nm and λ = 580 nm are 750 $Lmol^{-1}cm^{-1}$ and 1100 $Lmol^{-1}cm^{-1}$ respectively. All these measurements were done using a UV/Visible spectrophotometer with a cell having a path length of 1 cm.



(i) Calculate the transmittance of the solution having only 0.001 M of the compound E at λ = 340 nm. (10 marks)

(ii) Calculate the concentrations of E and G in the mixture. (25 marks)

(iii) Write two main differences of UV /Visible spectrophotometer and Emission spectrophotometer. (10 marks)

(iv) Suggest two practical ways of increasing the sensitivity of a flame emission method. (10 marks)

(B) Explain the following in brief.

(i) A solution of 1.0 ppm of sodium gave an emission signal of 115 at λ_{max} of Na. In the same solution, a potassium salt of high purity was dissolved to have 20 ppm of potassium in the solution without changing the concentration of sodium. This mixture gave an emission signal of 125 at λ_{max} of Na when measured under the same conditions. Explain the results. (10 marks)

(ii) When 0.01 M NaOH solution was added to an aqueous solution of phenol the absorbance was increased. (10 marks)

(C) (i) EDTA reacts with both Cu^{2+} and Bi^{3+}. Bi(III)EDTA complex does not absorb light at 745nm but Cu(II)EDTA does. Cu^{2+}, Bi^{3+} and EDTA also do not absorb light at 745nm. Bi(III)EDTA complex is more stable than Cu(II)EDTA complex. Sketch and label the photometric titration curve of a mixture having equal amounts of Cu^{2+} and Bi^{3+}(25.0 mL) with 0.02 M EDTA assuming that there are no errors due to dilution.

(15 marks)

(ii) How do you practically avoid the error caused by dilution in the above titration? (10 marks)

2.(A) The element X can be in the form of X^{2+} and X^{3+}. X^{3+} is more stable than X^{2+}. X is a toxic element and the permissible level of X in drinking water is 15.5 ppm. They form the complexes XY and XZ with Y^{2-} and Z^{3-} respectively. Qualities of the complexes are given below. (Assume that Y and Z exists as Y^{2-} and Z^{3-} only.)

property	XZ	XY
1. Complexes with	X^{3+}	X^{2+}
2. λ_{max} (nm)	510	595
3.Molar absorptivity coefficient ($Lmol^{-1}cm^{-1}$)	11,000	22,000
4. Stability	low	high
5. Stoichiometry	varies	stoichiometric
6. Control of pH	not required	required
7.Minimum detection limit	5 ppm	10 pm

(i) Some well water samples (expected level of X in well water is around 14 ppm) were given to check the suitability of water for drinking. What could have been the complex selected to determine the total amount of X in well water? Justify your answer. (25 marks)

(ii) What are the disadvantages of the complex selected? (10 marks)

(iii) State one more information that could have helped to decide on the complex. (05 marks)

(B) (i) What is the principle behind IR spectroscopy in structure determination?

(10 marks)

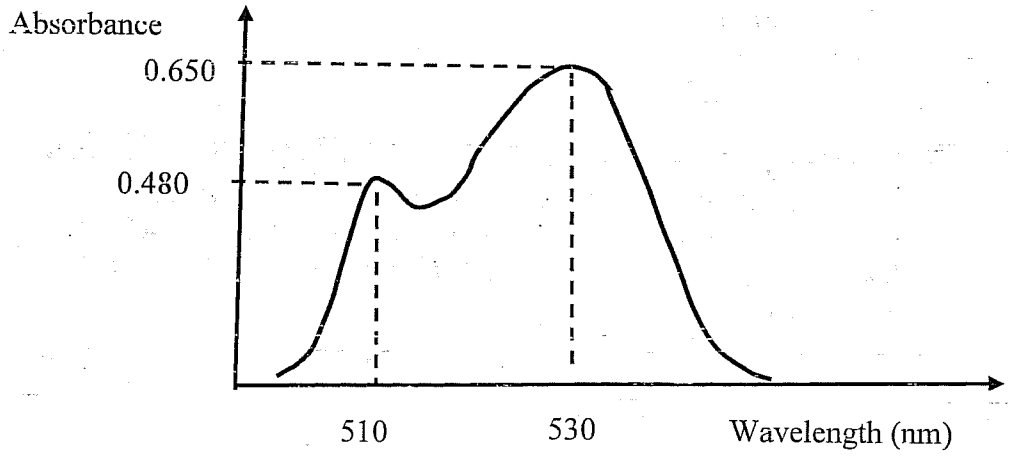
(ii) Sketch and label a schematic diagram of an IR spectrum. (10 marks)

(iii) State two differences of IR spectrophotometer with that of Mass Spectrophotometer. (10 marks)

(iv) Briefly explain how the mass spectrum of Electron impact Mass Spectroscopy (EIMS) is resulted.

(15 marks)

(C) The following figure shows the absorption spectrum of a dye. The molar absorptivity coefficient of the dye at $\lambda = 530$ nm is 1000 $Lmol^{-1}cm^{-1}$. Calculate the molar absorptivity coefficient of the dye at $\lambda = 510$ nm. (15 marks)



3. (A) What is the principle behind quantitative neutron activation analysis?

(16 marks)

(B) State three factors of the sample which affect the activity generated by Neutron activation analysis?

(12 marks)

(C) A sample subjected to neutron activation analysis was decayed emitting gamma rays.

(i) Suggest a suitable detector to measure the activity of gamma rays giving reasons for your selection over the other detectors. (16 marks)

(ii) State possible errors in measuring radioactivity and suggest ways to overcome them. (16 marks)

(D) Comment briefly on the following statement.

"Isotope dilution method cannot be used to analyse any compound that cannot be fully separated."

(20 marks)

(E) A rock contains ${}^{212}_{84}D$ radioactive atoms which undergoes the following decaying reaction (half-life is 3000 years).

$${}^{212}_{84}D \rightarrow {}^{200}_{80}Q + 3{}^{4}_{2}He + 2{}^{0}_{-1}e$$

A sample of the rock was analysed and 40 µg of ${}^{212}_{84}D$ and 120 µg of ${}^{200}_{80}Q$ was detected. What was the age of the rock at the time analysis was carried out?

(20 marks)

4. (A) Define the following terms.

(i) Retention factor K'

(ii) Selectivity factor α (20 marks)

(B) Efficiency of a packed column can be explained in terms of the Van Deemter equation.

(i) Write down the Van Deemter equation and define all the terms in it.

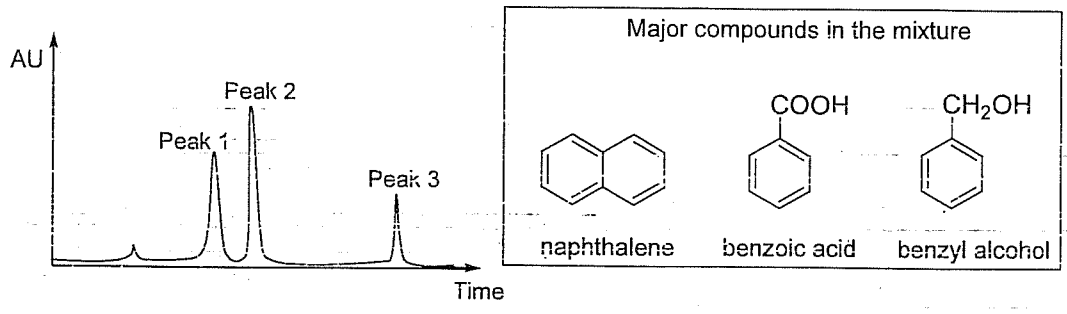
(ii) Draw the Van Deemter plot showing all separate component graphs and label them.

(iii) Which factor is independent of flow rate? Explain why.

(iv) Describe how longitudinal diffusion term contributes to zone broadening.

(40 marks)

(C) Given below is a chromatogram obtained for a sample containing three major compounds on isocratic elution with a non-polar solvent using a silica gel column.



(i) What is isocratic elution?

(ii) Assign each compound to the correct peak giving reasons.

(iii) Draw the chromatogram you expect to obtain if the mixture is run using a reverse phase column with a polar solvent. Indicate the compound responsible for each peak.

(40 marks)

5. (A) Describe the following terms in relation to chromatography.

(i) Dead time

(ii) R_f value (20 marks)

(B) Account for the following statements.

(i) A GC with a flame ionization detector (FID) cannot be coupled to a mass spectrometer.

(ii) Gel electrophoresis cannot be considered as a chromatographic method. (30 marks)

(C) Tabulate the similarities and differences between paper chromatography (PC), high performance liquid chromatography (HPLC) and thin layer chromatography (TLC) under the following parts.

(i) Stationary phase

(ii) Mobile phase

(iii) Separation mechanism (30 marks)

(D) Out of capillary columns and packed columns which one is more efficient? Give reasons for your answer. (20 marks)

6. (A) $M|M^{2+} \parallel Cl^-$ (saturated) $|Hg_2Cl_2, Hg|Pt$

(i) Write down the half-cell reactions for the anode and cathode and hence, the overall spontaneous cell reaction.

(ii) Calculate the standard cell potential for this cell assuming that standard conditions exist for this cell.

$E^\circ_{M|M^{2+}} = -1.10\,mV$ $E^\circ_{Hg_2Cl_2|Hg} = 0.268\ V$

(20 marks)

(B) Technique of electro-gravimetry, involves the deposition of the substance of interest whose concentration is to be determined.

(i) Write down the important properties of the deposit in order for the above technique to be effective.

(ii) Name three (3) factors that affect the properties of such a deposit

(20 marks)

(C) A student carried out the following experiment involving electrolysis to relate the mass deposited on the cathode to that of the known / expected amount from a standard solution of $CuSO_4$ (0.5 M). It was found that 3.10 g of Cu(s) was deposited on the cathode from a 100.0 ml of the standard solution. Assuming that all the copper ions have been reduced (Faraday's Constant = 96,500 C mol^{-1}) [Cu : 63.5; S = 32: O = 16]

(i) Calculate the quantity of electricity passed to complete the above deposition.

(ii) Calculate the expected amount of Cu and hence the yield.

(28 marks)

(D) (i) Define Concentration polarization, a transfer process that is useful in electro analytical methods.

(ii) **Name and outline** the three factors that contribute to the ***transfer*** mentioned above.

(iii) Name the two advantages of using a dropping mercury electrode (DME) in polarographic analysis.

(iv) What is the purpose for adding a supporting electrolyte such as KCl in a polarographic analysis?

(32 marks)