(2½ Hours)   [Total Marks : 60

N.B. : (1) **All questions are compulsory.**
      (2) **Figures to the right indicate full marks.**
      (3) Use of **logarithmic table/non-programmable** calculator is **allowed.**

1. (a) Attempt any **two** of the following :—

      (i) Describe different monochromators used in uv-visible spectroscopy.   4

      (ii) Explain the principle and use of pyroelectric detector used in IR   4
spectroscopy.

      (iii) What are the different ways of obtaining 'Derivative spectra' in uv-visible   4
region ? Explain any one in detail.

      (iv) In what way does Fourier transform spectroscopy differ from conventional   4
IR spectroscopy ? What are the advantages of Fourier transform
instruments ?

(b) Attempt any **one** of the following :—

      (i) With suitable examples, explain 'bathochromic shift' and 'hypsochromic   4
shift' in uv-sisible spectroscopy.

      (ii) Molar absorptivities of coloured complexes of metal 'X' and 'Y' are as   4
follows :—

Complex	Molar absorptivity $\varepsilon(dm^3 \ mol^{-1} cm^{-1})$	
	At 365 nm	At 700 nm
X	3250	525·5
Y	2780	22·4

Calculate the molar concentration of 'X' and 'Y' in the solution of mixture of
their complexes which gave the absorbance reading of 0·875 and 0·135 in a
cell of thickness 1·0 cm, at λ_{max} values of 365 nm 700nm respectively.

2. (a) Attempt any **two** of the following :—

      (i) Name the different methods which have been developed to compensate   4
matrix effects in X-ray fluorescence analysis. Describe any one method.

      (ii) With reference to mass spectrometry, discuss the purpose and types   4
of inlet system.

      (iii) With the help of a labeled schematic diagram, describe lithium drifted   4
silicon detector used in X-ray spectroscopy.

      (iv) With a suitable labeled diagram, describe the construction and working   4
of ion trap mass analyzer.

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(b) Attempt any **one** of the following :—

    (i)   Name ion sources used in molecular mass spectrometry. Discuss any   **4**
one in detail.

    (ii) Disuss wavelength dispersive instruments used in X-ray fluorescence   **4**
spectroscopy.

3. (a) Attempt any **two** of the following :— .

    (i)   Discuss the classification of ion selective electrodes, with suitable   **4**
examples. In what respect do these electrodes differ from ion specific
electrodes.

    (ii) What are the applications of coulometric titrations ?   **4**

    (iii) Describe the enzyme electrode that can be used to measure blood urea   **4**
nitrogen.

    (iv) What is controlled potential electrogravimetry ? Explain the factors   **4**
affecting the nature of deposit in electrogravimetry.

(b) Attempt any **one** of the following :—

    (i)   A constant current of 780 mA is used to deposit copper at cathode and   **4**
oxygen at anode of an electrolytic cell. Calculate the number of grams
of each product formed in 12 minutes and 15 seconds assuming no
other redox reactions.

       Given :   1 Faraday = 96,500 coulombs

             At. wts :   Cu = 63.5 and O = 16.

    (ii) The following cell —   **4**

       SCE $\|$ 50.0 cm^3 of Pb^{+2} solution of unknown concentration $\|$ Pb(s)
develops a potential of −0.4706 V. To the same solution, when 6.0 cm^3
of standard 0.02 M lead soultion is added, the potential shifted to
−0.4490 V. Calculate the molar concentration of lead in the solution.

4. (a) Attempt any **two** of the following :—

    (i)   What is organic polarography ? Explain the effect of pH in organic   **4**
polarography.

    (ii) What is pulse polarography ? In what way is differential pulse   **4**
polarography superior to conventional polarography ? Give any two
applications of this technique.

    (iii) Explain the basic principles of cyclic voltammetry with respect to —   **4**

       (1) the triangular wave form of the applied potential and

       (2) the peaks produced in the cycle.

    (iv) Explain the voltage excitation program that is followed in anodic stripping   **4**
voltammetry for determining cadmium and copper in an aqueous solution
of these ions. Why are stripping methods more sensitive than other
voltammetric methods ?

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(b)   Attempt any one of the following :—

   (i)   A certain metal undergoes reduction at DME by accepting 3 electrons.   **4.**
         The average diffusion current of $5 \cdot 0 \times 10^{-3}$ M solution of the metal is
         21·5 µA. The value of capillary characteristics is found to be 3·15.
         Calculate the diffusion coefficient of the metal.

   (ii) Determine the concentration of Cd^{2+} in the sample solution on the basis   **4**
         of following information for current measured at −1·1V versus SCE in
         polaragraphic analysis.

Volume of 0·1 M K_2SO_4 in cm^3	Volume of distilled water in cm^3	Volume of Cd^{2+} sample solution cm^3	Volume of Cd^{2+} Std. Solution $(2 \cdot 5 \times 10^{-3}M)$ in cm^3	Total Volume of the mixture in cm^3	Diffusion current in in µA
25	25	—	—	50	18·4
25	15	10	—	50	42·1
25	10	10	05	50	62·5

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5.   Attempt any **four** of the following :—

   (a)   Describe the Glober source with respect to IR spectroscopy.
   (b)   With respect to uv absorption spectroscopy, explain the terms, 'chromophore' and 'auxochrome'.
   (c)   Discuss the applications of energy dispersive X-ray fluorescence method.
   (d)   Explain basic principle of mass spectrometry.
   (e)   List out differences between amperostatic coulometry and potentiostatic coulometry.
   (f)   Explain how ion selective field effect transistors are useful in determination of pH.
   (g)   Why biamperometric titration method is also called 'dead stop end point' ?
   (h)   What is Karl Fischer reagent ? Give any four advantages of Karl Fischer method.

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