

- 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) What are the different sources of continuous infrared radiation ? Describe the Nernst Glower. 4
 - (ii) Explain with suitable examples, the importance of charge transfer absorption in photometric methods. 4
 - (iii) With the help of schematic diagram of FTIR spectrometer, describe the components involved in it. 4
 - (iv) With the help of labeled diagram, describe the components and working of prism monochromator. 4
- (b) Attempt any one of the following :-
- (i) The observed λ_{max} value of 1, 4-pentadiene is 185 nm, whereas that of 1, 3-pentadiene is 205 nm. Explain. 4
 - (ii) A simultaneous determination of Vanadium (V) and Titanium (IV) is based upon absorption by their respective peroxy complexes in acidic medium. The absorbance of the mixture of titanium and vanadium peroxy complexes was found to be 0.540 and 0.275 at 245 nm and 460 nm respectively. Calculate the molar concentration of titanium and vanadium in the mixture by using following data :- 4

| Peroxo Complex | Molar absorptivity ($\epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) | |
|----------------|---|-----------|
| | at 245 nm | at 460 nm |
| Titanium | 2846 | 450 |
| Vanadium | 285 | 1745 |

The path length of cell used for analysis is 1.00 cm.

2. (a) Attempt any two of the following :-
- (i) Discuss crystal monochromator with respect to X-ray diffraction spectroscopy. 4
 - (ii) Describe the chemical ionisation source used in mass spectrometry. 4
 - (iii) Describe the following techniques with respect to compensation of matrix effect in X-ray spectroscopy. 4
 - (1) External standard Calibration.
 - (2) Use of internal standard.
 - (iv) With the help of suitable diagram, describe the construction and working of Quadrupole mass analyzer. 4

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- (b) Attempt any one of the following :-
- (i) Give the quantitative applications of X-ray fluorescence method. 4
 - (ii) Explain the use of mass spectrometer as a detector in chromatography. 4
3. (a) Attempt any two of the following :-
- (i) With the help of schematic diagram, describe a gas sensing probe used for determination of dissolved CO₂ in a sample solution. 4
 - (ii) What are the advantages of coulometric titrations over volumetric titrations ? 4
 - (iii) Describe the liquid membrane electrode with a suitable example. 4
 - (iv) Explain controlled cathode potential electrogravimetry with suitable diagram. 4
- (b) Attempt any one of the following :-
- (i) Calculate the time required to deposit 0.250 gm of Co(II) as 4
 - (1) Elemental cobalt on surface of cathode,
 - (2) CO₃O₄ on an anode,
 on passing a constant current of 0.852 A through the solution. Assume 100% current efficiency for both gases.
 Given : 1 Faraday = 96,500 Coulombs
 At. wts : Co = 58.9 Molar mass of CO₃O₄ = 240.7.
 - (ii) The following cell - 4

$$\text{SCE} \parallel \text{MA}_2 (a_{\text{M}^{2+}} = 9.1 \times 10^{-5}) \mid \text{Membrane electrode for M}^{2+}$$
 gave a potential of 0.415 V. When the solution of known M²⁺ activity was replaced with an unknown solution, the potential was found to be 0.475 V. What is the p^M of this unknown solution ?
4. (a) Attempt any two of the following :-
- (i) Define : Half wave potential E_{1/2}. 4
 Explain : The shift in E_{1/2} of a metal ion after complexation is directly proportional to the concentration of a ligand.
 - (ii) Describe differential pulse polarography with respect to the excitational signals used in analog as well as digital instrument and the resulting 4
 What is the advantage of this technique ?

(b) Attempt any one of the following :-

(i) Calculate the concentration of bivalent metal ion in the sample solution which gave a diffusion current of $78.0 \mu\text{A}$. 4

Given : (1) Diffusion coefficient, $D = 6.8 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$.

(2) Rate of flow of mercury, $m = 6 \text{ mg s}^{-1}$

(3) Drop time, $t = 5 \text{ s}$.

(ii) Calculate the concentration of lead ion in the sample solution on the basis of the following information for current measured at -1.1 V versus SCE in a polarographic analysis. 4

| | Solution | Current in μA |
|----|--|--------------------------|
| 1. | 25.0 cm ³ of 0.1M Na ₂ SO ₄ solution, diluted to 50.0 cm ³ with distilled water. | 15.8 |
| 2. | 25.0 cm ³ of 0.1M Na ₂ SO ₄ solution + 10.0 cm ³ of lead sample solution, diluted to 50.0 cm ³ with distilled water. | 53.4 |
| 3. | 25.0 cm ³ of 0.1M Na ₂ SO ₄ solution + 10.0 cm ³ of lead sample solution + 5.0 cm ³ of 0.003 M standard lead sample solution, diluted to 50.0 cm ³ with distilled water. | 79.2 |

5. Attempt any four of the following :-

- (a) Describe the use of Bolometer in IR spectroscopy.
- (b) Discuss the components of laser source in spectroscopic studies..
- (c) With respect to X-ray absorption spectroscopy, discuss
- (1) absorption edges
 - (2) Mass absorption coefficient.
- (d) What are the advantages of gaseous and desorption sources used in mass spectrometry ?
- (e) What is Coulometry ? Discuss its principle.
- (f) Explain the significance of selectivity coefficient (k) in Ion selective electrodes.
- (g) Describe the principle of Karl Fisher titration.
- (h) State the Randles-Sevick equation for peak current used in cyclic voltammetry and give the significance of each term involved in it. How is the peak potential (E_p) for a reversible process related to half wave potential ($E_{1/2}$) ?
