Q. P. Code: 22515

TIME: 2.5 HOURS MAX.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.

Q.1 A. Attempt any two of the following:

a) With the help of neat and labeled diagram, explain the working of Michelson’s interferometer in FTIR.

b) Enlist different types of Infrared transducers. Discuss Pyroelectric transducer.

c) Explain: The \( \lambda_{\text{max}} \) of 1, 4 pentadiene is 176 nm and \( \lambda_{\text{max}} \) of 1,3pentadiene is 215nm.

d) What are different types of wavelength selectors used in UV - Visible spectroscopy? Discuss the working of interference filters.

B. Attempt any one of the following:

a) What are the different ways of obtaining ‘Derivative spectra’ in UV and Visible region? What are its applications?

b) A solution containing two absorbing species ‘M’ and ‘N’ was analyzed spectrophotometrically at two wavelengths in a 1.0cm cell. The absorbance of mixture was 0.787 and 0.243 at 740nm and 430nm respectively. Calculate the molar concentration of two species ‘M’ and ‘N’, if the molar absorptivity of the two species at two wavelengths is as follows.

<table>
<thead>
<tr>
<th>Species</th>
<th>Molar absorptivity, ( \varepsilon ) mol(^{-1}) dm(^3) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>740nm</td>
</tr>
<tr>
<td>M</td>
<td>7685</td>
</tr>
<tr>
<td>N</td>
<td>465</td>
</tr>
</tbody>
</table>

Q.2 A. Attempt any two of the following:

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

b) With the help of a neat labeled diagram, explain the principle of mass spectrometer.

c) Explain the absorption and enhancement effects with reference to X-ray fluorescence measurement.

d) With respect to mass Spectroscopy, discuss Time of Flight Mass analyzer.

B. Attempt any one of the following:

a) Compare wavelength dispersive and energy dispersive X-ray fluorescence analysis.

b) Name ion sources used in molecular mass spectrometry. Discuss any one in detail.

Q.3 A. Attempt any two of the following:

a) What are ion selective electrodes? With schematic diagram, describe liquid membrane electrode that is used for determination of divalent ions.

b) What is electrogravimetry? Explain the factors affecting the nature of deposit in electrogravimetry.

c) Give a comparative account of coulometric titration and conventional volumetric titration.

d) Give an account of ‘Ion Selective Field Effect Transistors’.
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B. Attempt any one of the following:
   a) The following cell has been used for the determination of Cadmium in the presence of chloride ions by both electrogravimetry and coulometry:
   \[ \text{Ag(s)} | \text{AgCl(s)}, \text{Cl}^- (0.25 \text{M}), \text{Cd}^{+2} (0.005 \text{M}) | \text{Cd(s)} \]
   Calculate the applied potential that
   i) Must be applied to prevent current from developing in the cell when two electrodes are connected.
   ii) Must be applied to develop an electrolytic current of 1.0 mA, assume that the internal resistance of the cell is 12.0 Ohms.
   Given: \( E^0_{\text{Ag-AgCl/Cl}^-} = 0.222 \text{V} \)
   \( E^0_{\text{Cd/Cd}^{+2}} = -0.403 \text{V} \)
   \[ \frac{2.303 \text{RT}}{F} = 0.0592 \text{ at } 298 \text{K} \]

   b) The following cell was found to have potential of 0.378 V at 298K
   \[ \text{SCE} \parallel \text{Mg}^{+2} (\alpha_{\text{Mg}^{+2}} = 2.5 \times 10^{-3} \text{ M}) | \text{Membrane electrodes for Mg} \]
   When this Mg\(^{+2}\) solution of known concentration was replaced by an unknown concentration of Mg\(^{+2}\) solution the potential was found to be 0.275 V. Calculate the concentration of Mg\(^{+2}\) in the unknown solution as \( \text{pMg} \).

Q.4 A) Attempt any two of the following:
   a) What is pulse polarography? What are its different types? Discuss its advantages over normal polarography.
   b) Discuss the principle and working of Karl fischer method for the determination of moisture in a sample.
   c) Discuss the basic principle of cyclic voltametry with respect to
      i) The triangular waveform of the applied potential.
      ii) The peaks produced in the cycle
   d) Define ‘Half wave potential. Derive an equation showing that half wave potential is normally constant for an electroactive substance. How will you determine the number of electrons involved in a reversible reaction at the working electrode in a polarographic analysis?

   B) Attempt any one of the following:
   a) What are biamperometric titrations? Explain the different types of titration curves obtained in these titrations.
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b) Calculate the concentration of nickel in a sample on the basis of the following information for current measured at -1.1V verses SCE in a polarographic analysis.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Current in μA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) 25.0 cm$^3$ of 0.2 M KCl, diluted to 50.0 cm$^3$ with distilled water</td>
<td>11.5</td>
</tr>
<tr>
<td>(ii) 25.0 cm$^3$ of 0.2 M KCl + 10.0 cm$^3$ of nickel sample solution, diluted to 50.0 cm$^3$ with distilled water</td>
<td>54.5</td>
</tr>
<tr>
<td>(iii) 25.0 cm$^3$ of 0.2 M KCl + 10.0 cm$^3$ of nickel sample solution + 5.0 cm$^3$ of 0.02 M nickel solution, diluted to 50.0 cm$^3$ with distilled water</td>
<td>75.2</td>
</tr>
</tbody>
</table>

Q.5

Attempt any four of the following:

a) Describe the following terms with respect to IR spectroscopy
   (i) Pelleting                    (ii) Mulls
b) With respect to absorption spectroscopy explain the terms,
   (i) Auxochrome                  (ii) Bathochromic shift
c) Give the quantitative applications of X-ray florescence spectroscopy.
d) With reference to mass spectrometry, discuss the purpose and types of inlet system.
e) Describe the enzyme electrodes that can be used to measure blood urea nitrogen.
f) What is Coulometry? Explain its principle.
g) Explain the effect of pH in organic polarography.
h) Distinguish between voltammetry and polarography.