

- N.B. :**
- (1) All questions are compulsory.
  - (2) Figures to the right indicate full marks.
  - (3) Use of non-programmable calculator is allowed.
  - (4) Atomic weight: H=1, C=12, N=14, O=16, Na=23, Al=27, S=32, Cl=35.5, K=39, Ca=40, Ag=108, Ba=137, Pb=207, Mg=24.3, F=19, Ni=58.7, Cr=52, Zn=65.4

1. (a) Attempt Any Two of the following:

- (i) With respect to quantitative performance criteria of an analytical instrument, discuss the terms, 'Calibration sensitivity' and 'Analytical sensitivity'. What are the advantages of analytical sensitivity? 4
- (ii) What is quality audit? How is it carried out? 4
- (iii) Define 'Figures of Merit' for analytical methods? Enlist the figures of merit for precision of analytical methods. 4
- (iv) What do you mean by 'Quality Management System'? Discuss quality assurance and quality control with respect to quality management system. 4

(b) Attempt Any One of the following:

- (i) What are the responsibilities of quality manager in maintaining and improving the quality system of laboratory? 4
- (ii) The selectivity coefficient for an ion selective electrode for  $K^+$  with respect to  $Na^+$  is reported to be 0.045. Calculate the relative error in the determination of  $K^+$  in a solution that has a  $K^+$  concentration  $2.4 \times 10^{-3}M$ , if the  $Na^+$  concentration is
  - (1)  $1.4 \times 10^{-2}M$
  - (2)  $1.4 \times 10^{-3}M$
  - (3)  $1.4 \times 10^{-4}M$Assume that instrumental signal for blank  $S_{bl}$  was approximately zero.

2. (a) Attempt Any Two of the following:

- (i) (1) Calculate the pH of  $1.0 \times 10^{-2} M$  solution of ammonium hydroxide. 2  
( $k_b$  for  $NH_4OH = 1.78 \times 10^{-5}$ )  
(2) How many milligrams per litre of  $CuSO_4 \cdot 5H_2O$  are present in 0.15 molar solution? 2
- (ii) 0.2 mole of ammonia dissolved in a sufficient quantity of water to make  $0.5 dm^3$  solution. The solution was found to have  $[OH^-] = 1.28 \times 10^{-4} M$ . Calculate ionization constant of ammonia. 4
- (iii)  $20 cm^3$  of  $0.2 M$  silver nitrate solution is mixed with  $50 cm^3$  of  $0.05 M K_2CrO_4$  solution. Calculate the concentration of  $K^+$ ,  $Ag^+$ ,  $NO_3^-$  and  $CrO_4^{2-}$  at equilibrium. 4  
[Given  $K_{sp}$  of  $Ag_2CrO_4 = 1.12 \times 10^{-12}$ ]
- (iv) Chloroform reacts with chlorine, to form  $CCl_4$  and hydrogen chloride. In an experiment 25-gm of chloroform and 15 gm of chlorine were allowed to react. Which is the limiting reagent? What is the maximum yield of  $CCl_4$  in moles and in grams? 4



(b) Attempt Any One of the following:

- (i) (1) How many Hydrogen atoms are present in 3.0 moles of methanol? (Avogadro's number  $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$ ) 2  
 (2) 25.0 cm<sup>3</sup> of saline sample was found to contain 0.3 mg of NaCl. Calculate the concentration of NaCl and Na<sup>+</sup> ion in ppm. 2
- (ii) Given 12% (w/v) solution of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (specific gravity 1.02 g/cm<sup>3</sup>). What is normality of the solution? How many cm<sup>3</sup> of 3.0 M KOH would be neutralized by 20 cm<sup>3</sup> of same oxalic acid? 4

3. (a) Attempt Any Two of the following:

- (i) Derive mathematical expression to relate distribution ratio (D) to pH of aqueous solution in solvent extraction involving chelation. 4  
 (ii) With the help of neat labeled diagram describe the construction and working of double beam densitometer used in HPTLC. 4  
 (iii) How does the stability of chelate depends on 4  
 (1) Ring size of chelate (2) Resonance and steric effect  
 (iv) Explain with suitable examples Synergistic extraction. 4

(b) Attempt Any One of the following:

- (i) 75 cm<sup>3</sup> of 0.025 M aqueous solution of a substance was extracted with ether. For each extraction 10 cm<sup>3</sup> of ether was used. (Distribution ratio in favour of organic solvent is 15) Calculate: 4  
 (1) Concentration of substance remaining in aqueous phase after two extractions  
 (2) The percentage extractions after three extractions.  
 (ii) Describe the technique of solid phase extraction. What are its advantages over solvent extraction? 4

4. (a) Attempt Any Two of the following:

- (i) Give an account of mobile phase reservoirs and solvent treatment systems used in HPLC. 4  
 (ii) With the help of suitable diagram describe construction and working of electron capture detector. 4  
 (iii) Why high pressure pumps are necessary in HPLC? What are the functions of guard column in HPLC? 4  
 (iv) Describe the types of open tubular columns used in gas chromatography? Why is temperature programming used in gas chromatography? 4

(b) Attempt Any One of the following:

- (i) How normal phase chromatography and reverse phase chromatography influence the separation of compounds? Explain with suitable example. 4  
 (ii) Substances A and B have retention times 13.30 minutes and 15.71 minutes respectively on a 30 cm long column. An unretained species passes through in 2.20 minutes. The peak widths at the base for A and B were 1.34 minutes and 1.54 minutes respectively. Calculate the selectivity factor and resolution for A and B. 4

[TURN OVER]



5. Attempt Any Four of the following:

- (a) Define data domain. Differentiate between analog domain and time domain.
- (b) Discuss the role of quality manager in analytical laboratory.
- (c) Calculate the solubility of  $\text{BaSO}_4$  in  $0.02 \text{ M Na}_2\text{SO}_4$ . The solubility product of  $\text{BaSO}_4$  is  $1.1 \times 10^{-10}$ .
- (d) A solution is prepared by dissolving  $1596 \text{ mg of CuSO}_4 \cdot 5\text{H}_2\text{O}$  in  $750 \text{ cm}^3$  of distilled water. Calculate molar concentration and w/v percentage of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .
- (e) Explain the principle of ion exchange chromatography.
- (f) Discuss in brief 1) sample preparation 2) sample application in HPTLC.
- (g) On the basis of van Deemter equation, explain the effect of eddy diffusion on band broadening.
- (h) What is the difference in the role of mobile phase in liquid chromatography and gas chromatography?