

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.

4) At. Wts: 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

Q.1 a) Attempt any two of the following: -

i) What are 'Figures of Merit' for analytical methods? Enlist the figures of merit for precision of analytical methods. 4

ii) Discuss the role of Quality Manager in analytical laboratory. 4

iii) What is data domain? Discuss the classification of data domain in brief. 4

iv) What do you understand 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) With respect to an analytical laboratory, discuss different standards and their main features. 4

ii) A least square analysis of calibration data for the determination of cadmium based upon its flame emission spectrum yielded the equation

$S = 1.15 C_{Cd} + 0.422$, where C_{Cd} is the concentration of cadmium in parts per million and S is a measure of relative intensity of the cadmium emission line. The following replicate data were then obtained;

Conc. of Cd in ppm.	No. of replications	Mean value of S	Standard deviation
10.0	10	12.12	0.14
1.00	10	1.12	0.014
0.000	25	0.029	0.008

Calculate :-

(i) the calibration sensitivity

(ii) the analytical sensitivity at 1 and 10 ppm of Cd

(iii) the detection limit.

- Q.2 a) Attempt any two of the following:-**
- i) (1) If the solubility product of CuS is 6×10^{-16} . Calculate the solubility of CuS in mol/dm^3 . 2
- (2) Calculate the amount of succinic acid (M.F.: $\text{C}_4\text{H}_6\text{O}_4$) required to prepare 250cm^3 of 0.15M solution in water. 2
- ii) Calculate the molarity of 95.8% by weight of sulphuric acid solution that has a specific gravity of 1.91. 4
- iii) What mass of AgNO_3 is needed to convert 2.55 grams of Na_2CO_3 to Ag_2CO_3 ? What mass of Ag_2CO_3 will be formed? 4
- iv) Calculate the pH of a buffer solution obtained by mixing 0.2M NH_3 and 0.3M NH_4Cl . Find the pH change that takes place when 100cm^3 of 0.1M HCl is added to 500cm^3 of above buffer. (Dissociation constant for ammonia, $K_b = 1.75 \times 10^{-5}$) 4
- b) Attempt any one of the following:-**
- i) A 0.45g sample of AR grade Na_2CO_3 required 35.4cm^3 of H_2SO_4 solution for neutralization. Calculate the molarity of H_2SO_4 solution. 4
- ii) Hg^{+2} ions reacts with Cl^{-1} ions in two steps. 4
- $$\text{Hg}^{+2} + \text{Cl}^{-1} \rightleftharpoons \text{HgCl}^{+1}, \quad K_1 = 5.5 \times 10^6$$
- $$\text{HgCl}^{+1} + \text{Cl}^{-1} \rightleftharpoons \text{HgCl}_2, \quad K_2 = 3.0 \times 10^6$$
- Calculate the concentration of Hg^{+2} at the equivalence point in the titration of 2.0mmol of Hg^{+2} with Cl^{-1} ions. The final volume of solution is 100cm^3 .
- Q.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) Explain with suitable examples the classification of various solvent extraction systems. 4
- iii) Describe the technique of counter current extraction. 4
- iv) What are the advantages and limitations of liquid-liquid extraction? 4
- b) Attempt any one of the following:-**
- i) With the help of neat labeled diagram describe the construction and working of fluorimetric detector used in HPTLC. 4
- ii) 100cm^3 of an aqueous solution containing 90mg of solute, when extracted once with 20cm^3 of ether, 68mg of solute was 4

transferred to ether. Calculate percentage extraction after two extractions if same volume of ether is used for each extraction.

- Q.4.** a) Attempt any two of the following: –
- i) With the help of neat labeled diagram, describe construction and working of rotary sampling valve used in HPLC. 4
 - ii) Describe construction and working of differential refractive index detector used in HPLC. 4
 - iii) What are the characteristics of ideal carrier gas used in gas chromatography? Give an account of different carrier gases used in gas chromatography. 4
 - iv) Why is temperature programming used in gas chromatography? 4
- b) Attempt any one of the following: –
- i) What are the factors that are to be considered for the selection of liquid stationary phase in GLC? 4
 - ii) Using a 30 cm column the retention times for two components A and B were 12.5 minutes and 14.1 minutes respectively. The corresponding peak widths at the base were 1.15 minutes and 1.75 minutes respectively. The unretained species passes through in 1.20 minutes. Calculate 1) the number of plates in each peak 2) the plate height for the column and 3) the resolution. 4
- Q.5.** — Attempt any four of the following: – 12
- a) Define 'Sensor' with respect to analytical device. Discuss quartz crystal microbalance in detail.
 - b) Define the term 'Quality Audit'. Discuss the different types of audit.
 - c) A 10.0 cm³ of saline sample was found to contain 0.09 mg of NaCl. Calculate the concentration of NaCl salt and Na⁺ ion in ppm.
 - d) Calculate the pH of 2.0 x 10⁻³ M solution of acetic acid. K_a for acetic acid is 1.75 X 10⁻⁵.
 - e) Explain the principle of electrochromatography.
 - f) What are the advantages of HPTLC over TLC?
 - g) On the basis of van Deemter equation, explain the effect of mass transfer between the phases on band broadening.
 - h) How the dissolved gases in mobile phase are removed in HPLC?