

MODEL ANSWER

B. Sc. (Hon's) (Fifth Semester), 2013, Chemistry (AS-2811)

CBT 501: Analytical Chemistry

Section-A (one mark)

1. (i) (c) Multiple extraction

(ii) (b) Basic

(iii) Ways to express the precisions:

(a) Standard deviation $S = \sqrt{\frac{\sum(xi - \bar{x})^2}{N-1}}$

(b) Standard deviation mean, $S_{\text{mean}} = \frac{S}{\sqrt{N}}$

(c) Relative standard deviation (RSD), %

$$\text{RSD, \%} = \frac{S}{\text{mean}} \times 100\%$$

(iv) (a) 0.54 (2) (b) 0.0144 (3)

(v) Peptization: It is the process where the coagulated form of crystals dispersed in to colloidal state (Free State). This is due to washing of precipitate with pure water.

(vi)

Precipitation	Post precipitation
(a). The process of conversion of an analyte into its insoluble compound by adding suitable precipitating agent is called precipitation.	(a). When precipitate is stand in contact with mother liquor, a second substance will slowly precipitate with precipitating reagent, which is called post precipitation.
(b). e.g. Precipitation of Ba^{2+} as BaSO_4 after mixing with BaCl_2 with HCl	(b). e. g. When calcium oxalate is precipitated in the presence of magnesium and kept for long time in mother liquor, chance of precipitating out as a magnesium oxalate as second precipitate.

(vii)

Normal phase chromatography	Reverse phase chromatography
(a). Stationary phase is polar and mobile phase is non polar in nature.	(a). Stationary phase is non polar and mobile phase is polar in nature.
(b). Stationary phase: Silica Mobile phase: hexane, benzene	(b). Stationary phase: C4, C18 Mobile phase: methanol, acetonitril, water

(viii) Solvents according to their increasing polarity:

n-hexane << Benzene < Toluene < chloroform < butanol, < ethanol < methanol < water

(ix) Lambert's Law: When a beam of monochromatic radiation passes through the homogenous transparent medium, the rate of decrease of intensity of radiation with the thickness of absorbing medium is proportional to the intensity of incident radiation.

$-\frac{dI}{dl} \propto I$ Where I intensity of radiation passed through thickness l, dI small decrease in the intensity of radiation passing through small thickness medium (dl)

(x) Standard Cr (VI) solution (1000 ppm): Dissolve 0.3535 g $K_2Cr_2O_7$ in 100 mL of deionized water (DW).

Sulfuric acid (1:1) solution: 50 mL of conc. H_2SO_4 is added to 50 mL of DW with cooling.

Diphenylcarbazide reagent: 0.2 g reagent in 100 mL of 95% ethyl alcohol.

Potassium permanganate solution (0.002M): Dissolve 0.0316 g solid in 100 mL water.

Sodium Azide (0.5%) : 0.5 g of the substance is dissolved in 100 mL DW.

Section-B (4 marks)

2.

Analytical Chemistry: Chemical characterization of matter both qualitative and quantitative. Analytical Chemistry deals with methods for determining the chemical composition of samples.

Application of Analytical Chemistry:

(i) **Environmental pollution analysis:** Air pollutants like SO_2 , NO, O_3 CO present in air can be monitored and quantitatively determined using analytical instruments.

(ii) **Food and agriculture science:** The micronutrient like Zn, Cu, Ni, Mn, Fe, Mo, Co and Ca present in soil and foods can be analyzed using different analytical techniques.

(iii) **Clinical and medical sciences:** The level of sugar and urea in blood can be analyzed using analytical instruments and MRI technique can be used for scanning the brain for cancer diseases.

(iv) **Material science:** In metallurgy, the composition of the ore contents can be determined using analytical instruments.

(v) **Biology:** The plants pigments can be separated by using chromatographic techniques.

3.

x_i	$x_i - \bar{x}$	$(x_i - \bar{x})^2$
12.50	0.26	0.0676
12.41	0.17	0.0289
12.14	-0.10	0.0100
11.90	-0.34	0.1156
$\bar{x} = 12.24$		$\Sigma(x_i - \bar{x})^2 = 0.222$

$$\text{Std. dev. (s)} = \frac{\sqrt{\Sigma(x_i - \bar{x})^2}}{N-1} = \sqrt{0.222/3} = 0.272 \text{ g}$$

$$\text{Standard deviation} = 0.27 \text{ g}; \quad \text{RSD, \%} = \frac{s}{x} \times 100\%$$

$$= 0.27/12.24 \times 100\% = 2.2\%$$

Relative standard deviation=2.2%

4.

Name of the organic precipitants used for the metal precipitation are: dimethylglyoxime, cupferron, 8-hydroxyquinoline, dithiozone and α -nitroso- β -naphthol.

The use of α -nitroso- β -naphthol in the precipitation of copper, mercury and cobalt:

Nitroso- β -naphthol is recommended as precipitants in the quantitative analysis of several metals. Copper can be estimated in the pH range of 3.96-13.2 while mercury can be precipitated in the range of 1.3-2.1. It is reported that the α -Nitroso- β -naphthol reacted in acidic medium with mercury (II) as nitrate to give an intense red precipitate. The large amount of chloride and also free hydrochloric acid hinder the formation of mercury α -nitroso- β -naphthol complex because these suppress the dissociation of mercury chloride and also lead to the formation of complex $(\text{HgCl}_4)^{2-}$. The mercury complex of α -nitroso- β -naphthol is insoluble in water, dil HNO_3 , dil H_2SO_4 , $\text{C}_2\text{H}_5\text{OH}$, CHCl_3 , CCl_4 . However, it is soluble in dil HCl , isoamyl alcohol. The complex can be dried to constant weight 110 °C

The cobalt can be also precipitate with nitroso- β -naphthol in acidic condition. The cobalt is precipitated by nitroso- β -naphthol and ignited to the oxide or the metal. Besides iron, the

elements that interfere in a precipitation by nitroso- β -naphthol; that may be present in steel are copper, chromium, vanadium, tungsten, molybdenum, tin, and antimony are eliminated. The solution containing cobalt is mixed with 10 mL hydrochloric acid and 6 mL of nitroso- β -naphthol and the precipitate obtained is filtered with Whatman filter paper No. 40. The filtrate is washed with dilute HCl and transferred in to porcelain crucible, and ignite in muffle furnace at 750-900 °C. This will convert Co_3O_4 to CoO and weighed the amount of substance.

5.

Steps of gravimetric precipitation:

i. Precipitation: The process of conversion of an analyte into its insoluble precipitate by adding suitable precipitating agent is called precipitation. The precipitation process must fulfill the following conditions.

- (a) It must have a low solubility otherwise complete precipitation does not take place.
- (b) The precipitate should consist of crystals of large particle size so that it can be filtered easily.
- (c) It must have a stable stoichiometric composition when dried so that its weight can be related to the amount of analyte.

ii. Digestion: The process of allowing the precipitate to stand either at room temperature or at low temperature heating for few hours 12-24 along with mother liquor is called digestion (or aging).

The reasons for digestions: (a) Complete precipitation takes place.

(b) Any contaminate which may be trapped along with the precipitate escapes and pure crystals are results.

(c) Promotes the formation of regular crystals shape and prevents the coprecipitation.

iii. Filtration: It is the process of separation of the precipitate from its mother liquor. It is carried out by means of filtering devices, which includes funnel, filter paper and filtering crucibles.

Sintered-glass crucible, Gooch crucibles and Whatman filter paper are filtering devices available. Whatman No. 42 is used for BaSO_4 (fine crystalline precipitate), No. 41 is used for $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (gelatinous crystals) and No 40. is used for AgCl (medium size crystals).

iv. Washing: The precipitates usually carry impurities on their surface and associated with mother liquor. The surface impurities and mother liquor can be removed by washing the precipitate after filtering.

Ideal characteristics of washing liquid: (a) It should not have the tendency to dissolve the precipitate but have the tendency to dissolve the impurities adhered on the surface of precipitate. (b) It should not have peptizing action upon the precipitate. Peptization means the reverse of coagulation, i.e. the precipitate reverse to colloidal state. Washing with pure water causes the peptization, thus it should be prevented.

v. Drying/Ignition: The main purpose of drying is to remove water present in precipitate.

Condition of drying: (a) Drying should be done at temperature at which electrolyte associated with the precipitate is completely volatilized.

(b) Drying is usually done by keeping the sintered-glass crucible containing the precipitate in air oven at 110-120 °C for 1-2 hours.

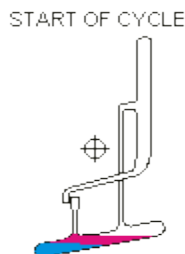
Purpose of ignition: (a) To convert the precipitate in to some other stable form of definite composition.

((b) To remove strongly adsorbed or occluded water from precipitate.

vi. Weighing: After drying or ignition the precipitate in the sintered crucible/porcelain crucible is weighed in analytical balance to constant weight. Before, it should be cooled in desiccator to prevent the absorption of water.

6.

Countercurrent extraction is a method multiple liquid-liquid extractions that permits the separation of substances with different distribution coefficients. It is a clever design known as Craig apparatus is used for this purpose by Lyman C. Craig, 1943. Craig apparatus consists of a series of glass tubes (r: 0, 1, 2....) that are designed and arranged such that the lighter liquid phase is transferred from one tube to the next.



* The lower (heavier) phase of the two-phase solvent system (e.g. water, blue layer in the picture) is the "stationary phase", whereas the upper (lighter) phase (e.g. hexane, red layer in the picture) is the "mobile phase". In the beginning, tube #0 contains the mixture of substances to be

separated in the heavier solvent and all the other tubes contain equal volumes of the same solvent. The lighter solvent is added to tube #0, extraction (equilibration) takes place and the phases are allowed to separate. The upper phase of tube #0 is then transferred to tube #1 and fresh solvent is added to tube #0, and the phases are equilibrated again. The upper layers of tubes #0 and #1 are simultaneously transferred to tubes #1 and #2 respectively. This cycle is repeated to carry on the process through the other tubes of the apparatus.

* It is interesting to examine the distribution of a substance A in each tube after a given number of equilibration/transfer cycles. Supposing that the volumes of each solvent are equal (V), and let W represent the weight of A in the sample, p and q represent the fraction of A with distribution ratio of D in the upper (organic solvent, o) and lower (water, w) phase, then it is

$$D = \frac{(C_A)_o}{(C_A)_w} = \frac{p W/V}{q W/V} = \frac{p}{q}$$

Since $p+q = 1$, we have

$$p = \frac{D}{D+1}$$

$$q = \frac{1}{D+1}$$

* The total fraction of solute in tube r after n transfers is given by (remember that $0!=1$).

$$f_{nr} = \frac{n!}{r!(n-r)!} p^r q^{n-r}$$

By combining with the previous expressions of p and q we finally obtain

$$f_{nr} = \frac{n!}{r!(n-r)!} \cdot \frac{D^r}{(D+1)^n}$$

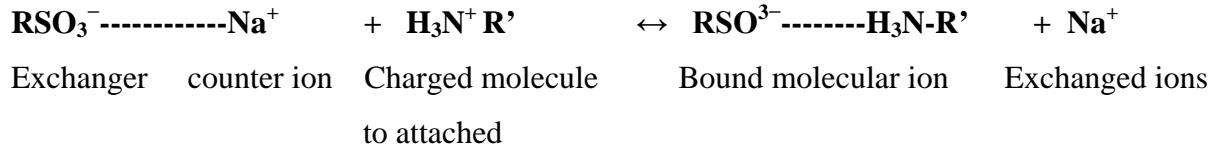
7.

Ion Exchange Chromatography: Chromatography in which a reversible reaction takes place and where a mobile ions of solid called ion exchange are exchange for different ions of similar charge present in the solution.

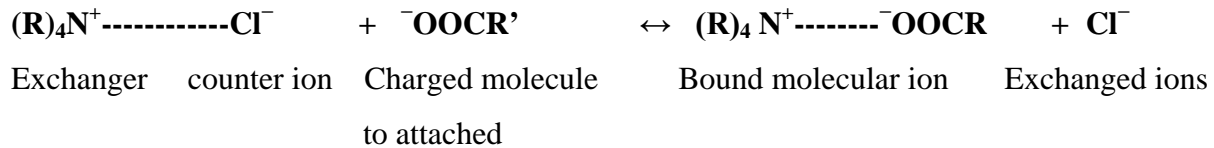
Principle of ion exchange chromatography: The principle is based on the attraction between oppositely charged particles. The stationary phase is an ion exchange resin to which cationic or anionic groups are covalently bonded. Ion exchange chromatography is similar to partition chromatography in that it has a coated solid as the stationary phase. The coating is referred to as

a resin, and has ions (either cations or anions, depending on the resin) covalently bonded to it and ions of the opposite charge are electrostatically bound to the surface.

Cation ion exchangers possess negatively charged groups and these attract positively charged molecules. These exchangers are also called as acidic ion exchange materials.



Anionic ion exchangers have positively charged groups which will attract negatively charged molecules.



Applications of ion exchange chromatography

(i) Separation of metal ions and anions

Ion exchange chromatography can be used for the separation of metal ion and there will be different sorption behavior of different metal ions on Dowex-1 (strong anion exchanger) in the complete range of acidity of hydrochloric acid.

(ii) Removal of radicals: In the estimation of Ca²⁺ or Ba²⁺ ions by the oxalate or sulphate method, phosphate ion is found to interfere. Therefore, its removal becomes necessary which is achieved by passing a solution of Ca²⁺ or Ba²⁺ ions having phosphate ions through a sulphonic acid cation exchanger.

(iii) Softening of hard water: The present of water is due the present of Ca²⁺ or Mg²⁺ ions. These ions may be removed by passing hard water through cation exchangers charged with Na⁺ when the following exchange reaction takes place



The Ca²⁺ or Mg²⁺ ions are retained in the column where as the Na⁺ ions pass into solution.

(iv) Separation of Organics: Ion exchange is equally effective for the separation of organic molecules like amino acids, sugars, nucleic acid and peptides.

8.

Spectrophotometric determination of Iron

Principle: Ferric iron, Fe(III) reacts with excess of ammonium thiocyanate forming a blood-red complex ion $[\text{Fe}(\text{SCN})_6]^{3-}$ in acidic solution. This colored complex can then be estimated by visual colorimetry or spectrophotometry. When the water sample contains both ferrous Fe(II) and Fe(III), only the ferric iron is estimated when thiocyanate is used as the reagent. The ferrous iron present in water sample can be oxidized to ferric iron by KMnO_4 and then total iron estimated.

Reagents preparation:

Standard ferric solution (1000 ppm): Dissolve 0.8608 g $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 10\text{H}_2\text{O}$ in 25 mL warm 1:1 H_2SO_4 . Cool and make up this solution to 100 mL. This will be standard ferric solution of 1000 ppm (mg/L)

100 ppm Fe (III) solution: 5 mL of 1000 ppm Fe(III) iron solution is taken in 50 mL of volumetric flask and make up to 50 mL of DW.

Ammonium thiocyanate solution (5.0 M): Dissolve 38 g NH_4CNS in water and make up to the 100 mL DW.

Potassium permanganate solution (0.002M): Dissolve 0.0316 g KMnO_4 solid in 100 mL water.

Hydrochloric acid solution (5.0 M): Dilute 40 mL of conc. HCl to 100 mL of deionized water (DW).

Procedure: Take aliquots of 0.2, 0.4, 0.8, 1.5, 2.0 of 100 ppm Fe (III) solution into six separately 50-mL volumetric flasks. Add to each flask 1 mL of HCl (2.0 M), 5 mL NH_4CNS (5.0 M) and make up to 50 mL of DW and after shake the flask. This will give five calibration Fe (III) standard solutions (0.4, 0.8, 1.6, 3.0 and 4.0 ppm). Measure the absorbance of each solution at 480 nm. Draw linear calibration curve by plotting the absorbance values against iron concentration.

Determination of total iron in water sample:

Take 20 mL of water sample in to 50 mL of volumetric flask, and add 5 mL dilute sulfuric acid and one drop of KMnO_4 solution to it. If the color is discharged, add one more drop of KMnO_4 solution. Add 5 mL NH_4CNS (5.0 M) solution and make up to 100 mL of DW and after shake the flask. Measure the absorbance of solution and find out the Fe(III) concentration from the graph. The concentration of ferrous iron Fe(II) can be obtained by subtracting Fe^{3+} from the total iron.