SUMMARY

The present work describes the studies on inorganic ion exchangers and determination of organic compounds spectrophotometrically. The subject matter of this dissertation is organized into 7 chapters. The first chapter deals with the introduction; the second, third and fourth chapters deal with two new inorganic ion exchangers. Chapter V deals with the applications of an inorganic ion exchanger in organic analysis. Sixth and seventh chapters are devoted to the determination of amines and nitro compounds spectrophotometrically.

A new inorganic ion exchanger, ferric arsenate has been prepared by mixing decimolar solutions of ferric nitrate and sodium arsenate (or arsenic acid) in different ratios. A sample of ferric arsenate was also prepared by homogeneous precipitation method by changing arsenite to arsenate using hydrogen peroxide. The product formed by homogeneous precipitation method is most stable. The ion exchange capacity for alkali metal ions and alkaline earth metal ions has been determined by column operation and varies from 0.30 to 0.80 meq/gm of the exchanger. The ion exchange capacity so obtained depends upon hydrated radii of the exchanging cation and there is a linear relationship between capacity and hydrated radii of the ions of the same group.

The chemical composition of the various samples of ferric arsenate has been determined and the results are compared with those obtained by electrometric titrations. The effect of drying temperature
on ion exchange capacity has also been studied. pH-titration curves with and without added salts have been discussed.

Distribution coefficients of 26 metal ions in nitric acid ($10^{-3}$M) and phenol (0.1M) solutions are determined. On the basis of a large difference in Kd values some important separations are tried. As a result the separation of $\text{Ba}^{2+}$ from $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{Sr}^{2+}$, $\text{Pb}^{2+}$ and $\text{Al}^{3+}$ from $\text{Ga}^{3+}$ have been achieved quantitatively within the experimental error range.

Another new inorganic ion exchanger aluminium antimonate is synthesized by mixing aluminium nitrate and antimony pentachloride in different ratios at the required pH. A sample is prepared by refluxing for comparison. The ion exchange capacities for the direct and reverse process of exchange are determined on the column of aluminium antimonate. The ion exchange capacity of the material depends upon the pH at the time of preparation.

The pH titration curves with and without added salts are plotted for different alkalies and combined with their respective chloride salts. Aluminium antimonate in $\text{H}^+$ form works as a monofunctional weak acid.

Chemical composition of the material gives an apparent mole ratio of $\text{Al}:\text{Sb}$ as 4:1. This exchanger is most stable of all the antimonates studied so far as ion exchanger. A comparison of stability is given. Hydrolysis of aluminium antimonate is also studied and the results of various samples are compared.
A study of distribution coefficients in 9 solvent systems is made and on the basis of differential selectivity important separations were tried, separations of Th\(^{4+}\)–UO\(^{2+}\), Ni\(^{2+}\)–Cu\(^{2+}\)–Ag\(^{+}\), Mg\(^{2+}\)–Ca\(^{2+}\), Mg\(^{2+}\)–Sr\(^{2+}\) and Mo\(^{6+}\)–Ti\(^{4+}\)–W\(^{6+}\) have been achieved. The separation limits are given.

The reproducibility of aluminium antimonate has been checked by its replicate preparation in five different batches under the similar conditions. The physical properties, ion exchange capacity, chemical composition and distribution coefficients of common metal ions are compared. These results indicate the reproducible synthesis of aluminium antimonate under these conditions. Some important separations of Mg–Ba, Zr–Ti, Hg–Cd–Zn and Ti–V are achieved quantitatively. Infra red spectra is discussed and a tentative structure is given.

Ion exchange chromatography has been applied for the separation and determination of amines. Amines are first converted to amine ions (hydrochlorides). Their aqueous solutions are chromatographed on papers impregnated with stannic molybdate, an inorganic ion exchanger. On the basis of difference in \(R_F\) values the separations are tried on the columns of stannic molybdate. Various important separations are listed. The theoretical behaviour of movement of amine hydrochlorides on these papers is discussed with the help of plots of pH versus \(R_M\) (where \(R_M = \log \left(\frac{1}{R_F} - 1\right)\)). These plots show a linear relationship between \(R_M\) and pH. The elution order from the column is in accordance with the \(R_F\) values on papers impregnated with stannic molybdate.
A sensitive method for the spectrophotometric determination of aliphatic as well as aromatic primary, secondary and tertiary amines is described. The determination is based on the formation of greenish violet colour by the reaction of amino compound with acetyl chloride and ferric ion. The method is applicable for 50 μg - 10 mg of amino compound. The reaction is performed at 65°C and at pH 1.8 and the absorbance is recorded at 550 nm.

The effect of various variables viz., temperature, concentration of ferric nitrate, amount of acetyl chloride and pH is studied. The results of calibration curves for aniline, diphenylamine, pyridine, diethylaniline, phenylenediamine, p-toluidine, methylamine, ethylamine, isopropylamine, amylamine, 1,3 diaminopropane, morpholine and piperidine are given. Studies of precision and interferences are made. Mechanism of the reaction is given with experimental evidences.

Aromatic nitro compounds (nitrobenzene, p-nitro aniline, m-nitrobenzaldehyde, p-nitro toluene and p-nitrophenol) can be determined using zinc in the presence of ammonium chloride as a reducing agent. The aryl hydroxyl amine which is formed reacts with acetyl chloride and iron(III) to produce a violet coloured complex $\lambda_{\text{max}}$ is 550 nm. The determination is applicable for the range of 50 μg to 10 mg for nitrobenzene, p-nitro aniline, m-nitrobenzaldehyde, p-nitro toluene and p-nitro phenol. The effect of pH and time on the formation of complex has been studied.