CHAPTER - I

INTRODUCTION

Analytical Chemistry has always occupied a vital position in the development of chemistry. It deals with the development of methods for the chemical analysis. Analytical chemistry assumes the supporting role of an indispensable tool in advancing the state of knowledge in the field of organic, inorganic and physical chemistry. A thorough background in analytical chemistry is a vital necessity for all who aspire to be chemists, regardless of their field of specialization. The employment of analytical chemistry in modern industry is of inestimable importance. The analytical process involves a logical sequence: defining the problem, obtaining and dissolving the sample, performing the required separations, making the appropriate measurements, and calculating the results. Important considerations for an analytical method include speed, convenience, dynamic range, accuracy, precision, scope, cost of instrumentation, sample preparation required, and so forth.

The purpose of analytical research has been to develop new methods of analysis, or to improve the existing ones. In
most of the analysis, pretreatment of the sample is required in order to remove the interfering substances. Separation technique has been common in practice for pretreatment. The separation methods are based on classical and modern techniques. The modern techniques are comprised of (i) instrumental and (ii) non-instrumental. Although, instrumental techniques find their wide and interesting applications at present but on the other hand non-instrumental methods are also equally important in the field of analysis. Non-instrumental methods involve lower cost than instrumental methods. At present, the various methods being employed in the field of separation science are: ion-exchange / chelation / adsorption chromatography, solvent extraction, electrophoresis, dialysis etc.

'Corpora non agunt nisi fluida siva soluta' – Substance do not react unless in a liquid or dissolved state. – This ancient empirical rule is not universal. One of the noteworthy exceptions is ion-exchange. Ion exchange occurs on a continual basis in many natural phenomenena. It plays a significant part in the formation of caves, the erosion of rocks and land, the corrosion and erosion of highway surfaces, and the corrosion and weakening of metal structures. The biochemistry of the human body and of
plants and many other natural processes depend upon ion exchange.

The first recorded application of ion exchange is found in the Bible. Moses immersed a certain tree in bitter water, which became sweet and potable. Aristotle observed that seawater loses part of its salt content when passed through sand, and it appears that sand filters were used by the greeks to purify seawater and drinking water [1].

In 1833 it was observed that certain clays, on treatment with lime, liberated potassium and sodium ions, and in 1830 it was reported that carbon absorbed silver from silver nitrate solution, and released acidity when placed in contact with a neutral salt, the cation of the salt was absorbed by the carbon (2). Clay was used to decolorize liquid manure and to sorts soluble components.

The English agricultural chemists Thomson and Way have been credited with the recognition of ion exchange [3,4] although Joseph Spence showed in 1845 that soil absorb ammonia. In 1858 base exchange was recognized as a chemical reaction. The inter conversion of leucite (K$_2$O.Al$_2$O$_3$.4SiO$_2$) and analcime (Na$_2$OAl$_2$O$_3$.4SiO$_2$.2H$_2$O) was demonstrated in 1870.
Synthetic ion exchanges, called permutits, were prepared in 1905 and used to soften water [5-9]. The selectivity of the inorganic ion exchangers was studied early in the twentieth century[10-20]. Organic polymers with ion exchange activity were reported first in 1934 [21], the combined use for cation and anion exchange produced water with very low conductivity [22]. Ion exchange resins were prepared first by condensation polymerization and later by addition polymerization [23-32]. Styrene is still the Most important monomer (33). Product uniformity was improved by the introduction of suspension polymerization. Macroporous or macroreticular polymers were discovered in the 1950 [34-46].

Today, ion exchange is firmly established as a unit operation and is extremely variable supplement to other procedures such as filtration, distillation and adsorption. All over the world numerous plants are in operation, accomplishing task that range from the separation of rare earth and from catalysis of organic reaction to decontamination of water in cooling system of nuclear reactors. In the laboratory, ion exchangers are used as an aid in analytical and preparative chemistry. The aims of scientific research with ion exchange membrane extend far into physiological chemistry and biophysics. However the
most important application is still the purification and demineralization of water, a perennial challenge since Moses and Aristotle, and a task which the growth of population and industries has made a more pressing than ever.

**Elementary Principles**

Ion-exchangers, by common definition are insoluble solid materials which carry exchangeable cations or anions. Carriers of exchangeable cation, *cation exchangers* and carriers of exchangeable anions, *anion exchangers*. Those exchangers which are capable of exchanging both cations and anions are called *amphoteric ion-exchangers*. The ion exchange is a stochiometric process.

A typical cation exchange is

\[ 2Na^+ + CaCl_2 \text{(aq)} \rightarrow Ca^{2+} + 2NaCl \text{(aq)} \]

and a typical anion exchange is

\[ 2XCl^- + Na_2SO_4 \text{(aq)} \rightarrow X_2SO_4 + 2NaCl \text{(aq)} \]

Where \( x \) represents a structural unit of the ion exchanger, solid phases are with bar \( (aq) \) indicates that the electrolytes is in aqueous solution.

Ion exchange is with very few exception a reversible process. Ion exchanger resembles sorption in that, in both cases, a dissolved species is taken by a solid. The characteristic difference between two phenomenon is that
Ion exchange in contrast to sorption is a stochiometric process. Every ion which is removed from the solution is replaced by an equivalent amount of another ionic species of the same sign.

Ion exchangers consist of a frame-work which is held together by chemical bonds or lattice energy. This frame-work carries a positive or negative surplus charge which is compensative by ions of opposite sign, the so called counter-ions. The counter-ions are free to move within the frame-work and thus can be replaced by other ions of the same sign. The frame-work of cation exchange may be regarded as macromolecular or crystalline poly anion, that of an ion exchanger as a poly cation.

The counter-ion content of the ion-exchangers-the so-called ion-exchange capacity.

As a rule, the pores of the ion exchangers are occupied not only by counter-ions but also by solvent and solute which can enter the pores when the ion exchanger is in contact with a solution. Uptake of solvent may result in swelling of the ion exchangers. Uptake of solute is usually called sorption, though it is essentially a distribution of the solute between two liquid phases, namely, the pore liquid and the solution outside.
Ion exchange is a diffusion process. The rate depends on the mobilities of the counter ions. Thus ion exchange kinetics has no resembles to chemical reaction kinetics in the usual sense. However, the simple, well-known rate law of diffusion holds only in exceptional cases. As a rule, electric forces act as the fluxes of ions and cause deviations. The heat evolved in ion-exchange process is usually rather small (of in <2 K cal / mol, unless ion exchange followed by reactions such as neutralisation, etc.).

As a rule, ion exchangers preface one species to other. This shows that the redistribution of counter ions, is not purely statistical. The preference of one species over the others may be due to following causes.

1. The electrostatic interactions between the charged framework and the counter ions depend on the size and in particular, on the valency of the counter ion.

2. In addition to the electrostatic forces, other interactions between the ions and their environment are effective.

3. Large counter ions may be sterically excluded from the narrow pores of the ion exchanger.

All these effects depend on the nature of the counter ion and thus may lead to preferential uptake of a species by
the ion exchanger. The ability of the ion exchanger to distinguish between various *counter ion* species is called selectivity.

**Chelating Ion-Exchangers**

There have been several reviews [47-53] dealing with chelating polymers in separation and pre-concentration methods. C.Kantipuly et al. have published a review paper which is concerned mainly with the application of chelating ion-exchange resins for the separation and concentration of trace metals from rivers, sea, stream and other natural systems.

The analytical application of chelating polymers depends on many factors. Normally a metal ion exists in aqueous solution as a hydrated ion or as a complex species in association with various anions, with little or no tendency to a chelating polymer. To convert a metal ion into an extractable species its charge must be neutralized and some or all of its water of hydration replaced. The nature of the metal species is therefore of fundamental importance in extraction system. Most significant is the nature of the functional group and/or donor atom capable of forming complexes with the metal ions in solution, and it is logical to classify chelating polymers on this basis. Also for simplicity,
it is desirable to classify chelating polymers according to Fig. 1.

**POLYMER SORPTION MATERIALS**

- Organic polymers
- Inorganic polymers
  - Co-ordinating chelating resin
    - Co-ordinate covalent bond
  - Non-co-ordinating (simple ion-exchange)
    - \( H^+, Cl^- \)
- Unidentate
- Bidentate and multidentate
  - Hard ligand atom (O)
  - Intermediate ligand atom (N)
  - Soft ligand atom (S)
  - Hard: \( O, C \)
  - Mixture: \( O, S, N \)
  - Soft: \( S, S \)

Rings usually include oxygen, nitrogen and sulphur. Nitrogen can be present in a primary, secondary or tertiary amine, nitro, nitroso, azo, diazo, nitrile, amide and other groups. Oxygen is usually in the form of phenolic, carbonyl, carboxylic, hydroxyl, ether, phosphoryl and some other groups. Sulphur is in the form of thiol, thioether, thiocarbamate, disulphide groups etc.

These groups can be introduced into the polymer by chemical transformation of the matrix or by the synthesis of sorbents from monomeric ligands. The insertion of suitable specific functional groups into the polymeric matrix makes them capable of reacting with metal ions or metal species.
under certain favorable conditions, to form chelate rings. The selective concentration and separation of elements from natural water systems depends both on elemental specification and the chelating properties of the polymer. Examples of chelating groups and their application for selective pre-concentration of inorganic elements were recently reviewed by Myasoedova and Savvin [47] but these authors did not include an important class of commercially available chelating resins. Namely the chelite, duolite and amborane series of resins. However, Schwochau [48] has documented the application of some of these resins for the extraction of metals from sea-water and these form the basis of Table 1.1 and 1.2.

Conventionally, the resin materials can be classified into three main divisions: (a) cation-exchangers, (b) anion-exchangers, and (c) chelating polymeric resins. These can further be subdivided into strong, weak, or intermediate types, depending on the functional group.

The choice of an effective chelating resin and its value in analytical method development is dictated by the physicochemical properties of the resin materials.
**TABLE - 1.1**
Extracting Systems Used For Metal Separation From Natural Water Systems.

<table>
<thead>
<tr>
<th>System and active group</th>
<th>Metal ions</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chelex-100, Dowex A-1</td>
<td>Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Mo, Ag, Cd, In, lanthanides, W, Re; Pb, Bi, Th, U, Al, Sn, Ti</td>
<td>Cation elution with dilute mineral acids, anion elution with 4M ammonia solution</td>
<td>49 - 56, 57- 61</td>
</tr>
<tr>
<td>Retardant II-A8</td>
<td>Li</td>
<td>Concentration factor of 30 in the ethyl alcohol eluent</td>
<td>62</td>
</tr>
<tr>
<td>-CH₂COOH</td>
<td>Ti, Co</td>
<td>Sorption after complexation with SCN⁻ Elution with 2M mineral acids</td>
<td>63, 64</td>
</tr>
<tr>
<td>CH₂N⁺{(CH₃)₃Cl⁻</td>
<td>Ni, Cu, Zn</td>
<td>Nearly quantitative recovery at natural pH of sea-water</td>
<td>65</td>
</tr>
<tr>
<td>Amberlite CG-40U</td>
<td></td>
<td>Separation at natural pH of sea-water; elution with dilute mineral acids</td>
<td>66, 67</td>
</tr>
</tbody>
</table>
Poly(glyoxaltriaminothiophenol)  

Hydrous aluminum oxide  

Polystyrene-bound 1,3-diketone  

Ethylenediaminetriacetic acid on porous glass  

p-Dimethylaminobenzylidenerhodanine on silica gel  

Au  

Li  

UO$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Fe$^{3+}$  

Cu, Zn, Pb  

Pd, Ag, Au  

Separation at natural pH of seawater; elution with dilute mineral acids  

Elution with boiling water; maximal concentration factor in the eluate  

Sea-water buffered at pH 5.6; elution with 1M HCl  

Quantitative retention from acidified sea-water; elution with 0.1M HCl containing thiourea
<table>
<thead>
<tr>
<th>Material</th>
<th>Elements Absorbed</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitin</td>
<td>Co, Sb, Au, Hg</td>
<td>Sorption at pH 7</td>
</tr>
<tr>
<td>Chitosan</td>
<td>Co, Zn, Cu, Mo, Pd, Sb, Cs, Ir, Au, Hg, U</td>
<td>Sorption at pH 7</td>
</tr>
<tr>
<td>Amidoxime</td>
<td>Na, Mg, Ca, V, Fe, Cu, Sr, Ba, Au, U</td>
<td>Sorption at natural pH of seawater; elution with dilute mineral acids; uranium capacity &gt; 3600 ppm</td>
</tr>
<tr>
<td>Dithiocarbamate cellulose derivative</td>
<td>Cu, Cd, Hg, Pb, U</td>
<td>Sea and tap water</td>
</tr>
<tr>
<td>Poly(malic anhydride)</td>
<td>Pb</td>
<td>Tap water</td>
</tr>
<tr>
<td><strong>Flotation Systems:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron(III) hydroxide + sodium dodecylsulphate</td>
<td>V, Mo, U</td>
<td>More than 80% recovery at the appropriate pH</td>
</tr>
<tr>
<td>Complexing Agents /Organic Solvents:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>--</td>
<td>-------------------</td>
</tr>
<tr>
<td>Iron(III) hydroxide + dodecylamine</td>
<td>Cu, Zn</td>
<td>More than 90% recovery at pH 7.6 81, 82</td>
</tr>
<tr>
<td>Lead sulphide + stearylamine</td>
<td>Ag</td>
<td>Almost quantitative separation at pH2 83</td>
</tr>
<tr>
<td>2- Mercaptobenzothiazole co-precipitate</td>
<td>Ag</td>
<td>More than 95% recovery at pH 84</td>
</tr>
<tr>
<td>without surfactant</td>
<td></td>
<td>Quantitative separation at pH 1 85</td>
</tr>
<tr>
<td>Cadmium sulphide+ octadecyltrimethylammonium chloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complexing Agents /Organic Solvents:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium pyrrolidine dithiocarbamate /methyl isobutyl ketone, chloroform or Freon TF</td>
<td>V, Cr, Mn, Fe, Co, Ni Cu, Zn, Cd,Pb</td>
<td>Extraction at pH 3-5 86-90</td>
</tr>
<tr>
<td>4-Benzoyl-3-methyl-1-phenyl-5-pyrazolone/isoamyl alcohol or methyl isobutyl ketone</td>
<td>Cu, Mo</td>
<td>Extraction of Cu at pH 7, Mo 91-92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>extraction at pH 1-3</td>
</tr>
</tbody>
</table>
TABLE - 1.2
Uranium Loading Of Selected Inorganic, Organic, And Biological Sorbents In Natural Sea-Water

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Functional group</th>
<th>Uranium loading</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inorganic:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrous aluminum oxide</td>
<td><img src="#" alt="OH" /></td>
<td>61µg/ g Al</td>
<td>93</td>
</tr>
<tr>
<td>Hydrous iron(III) oxide</td>
<td><img src="#" alt="Fe" /></td>
<td>60µg/ g Al</td>
<td>93</td>
</tr>
<tr>
<td>Silica gel</td>
<td><img src="#" alt="Si" /></td>
<td>27µg/ g Sorbent</td>
<td>94</td>
</tr>
<tr>
<td>Compound</td>
<td>Formula</td>
<td>Concentration</td>
<td></td>
</tr>
<tr>
<td>-----------------------------------------</td>
<td>---------</td>
<td>------------------------</td>
<td></td>
</tr>
<tr>
<td>Hydrous lanthanum oxide</td>
<td>-La(OH)</td>
<td>38µg/ g La</td>
<td></td>
</tr>
<tr>
<td>Hydrous titanium oxide</td>
<td>-Ti(OH)</td>
<td>550µg/ g Ti</td>
<td></td>
</tr>
<tr>
<td>Hydrous titanium oxide (freshly precipitated)</td>
<td></td>
<td>1150µg/ g Ti</td>
<td></td>
</tr>
<tr>
<td>Basic zinc carbonate</td>
<td></td>
<td>540 µg/ g Zn</td>
<td></td>
</tr>
<tr>
<td>Hydrous tin oxide</td>
<td>-Sn(OH)</td>
<td>17µg/ g Sn</td>
<td></td>
</tr>
<tr>
<td>Hydrous zirconium oxide</td>
<td>-Zr(OH)</td>
<td>13 µg/ g Zr</td>
<td></td>
</tr>
</tbody>
</table>
### Organic:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Concentration(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene-methylene phosphonic acid</td>
<td>-CH$_2$PO(OH)$_2$</td>
<td>24 μg/g sorbent 93</td>
</tr>
<tr>
<td>Resorcinolarsonic acid/ formaldehyde copolymer</td>
<td>-AsO(OH)$_2$</td>
<td>1112 μg/g sorbent 93</td>
</tr>
<tr>
<td>Duotite ES 467</td>
<td>-CH$_2$ -NH-CH$_2$ -</td>
<td>45 μg/g sorbent 97</td>
</tr>
<tr>
<td>Duolite ES 346 Poly(acrylamidoxime)</td>
<td>PO$_3$Na$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3600 μg/g sorbent 74,76</td>
</tr>
<tr>
<td>Oxamidoxime-terephthalic acid chloride condensation polymer (fibres)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>240 μg/g sorbent 98</td>
</tr>
<tr>
<td>Poly (glyoxaltriaminophenol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>45 μg/g sorbent 94</td>
</tr>
<tr>
<td>Material</td>
<td>Bioremoval (µg/g sorbent)</td>
<td></td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>---------------------------</td>
<td></td>
</tr>
<tr>
<td>Hyphan on cellulose</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Macrocyclic hexacarboxylic acid on polystyrene</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Macrocyclomide resin 508</td>
<td>930</td>
<td></td>
</tr>
<tr>
<td>Biological:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halimeda opuntia (green alga)</td>
<td>1.85</td>
<td></td>
</tr>
<tr>
<td>Laurencia papillosa (red alga)</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>Dictyota diricata (brown alga)</td>
<td>2.14</td>
<td></td>
</tr>
<tr>
<td>Oscillatoria spec (blue-green alga)</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>Phytoplankton (North Pacific Ocean)</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>Zooplankton (North Pacific Ocean)</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>Chitosan phosphate</td>
<td>2.60</td>
<td></td>
</tr>
</tbody>
</table>
Some Novel Chelating Ion Exchange Resins

Iminodiacetic Acid Resin

Among the earliest chelating resins to be studied were analogues of EDTA, viz. Dowex A-1, Chelex-100 and Chelex-20. The uses of Chelex resins have been well documented, [106,107] and these resins continue to be useful in a wide variety of systems. Some of the metals extracted from seawater and other systems with Chelex-100 and Dowex A-1 are listed in Table 1.

Immobilized Polyhydroxyanthraquinones

Nine polyhydroxyanthraquinones and two polyhydroxyanthraquinones have been screened to determine which have the greatest ability to accumulate uranium, [108].
The immobilized 1,2-dihydroxyanthraquinone had the most favorable features, such as high selectivity, rapid sorption rate, and applicability in both column and batch methods.

Chelating resins with a nitrosoresorcinol group

A macroreticular polystyrene-based chelating resin with nitrosoresorcinol as functional group was synthesized by Sugii and Ogawa, [109].

\[
\text{\begin{tikzpicture}
\draw (0,0) circle (0.5cm);
\draw (0,0) -- (1,1);
\draw (0,0) -- (1,-1);
\draw (0,0) -- (-1,1);
\draw (0,0) -- (-1,-1);
\draw (0,0) -- (0,2);
\draw (0,0) -- (0,-2);
\draw (0,0) -- (2,0);
\draw (0,0) -- (-2,0);
\draw (0,0) -- (0,0);
\draw (0,0) -- (0,0);
\end{tikzpicture}}
\]

The resin shows selectivity for \( \text{Cu}^{2+}, \text{Fe}^{3+} \) and \( \text{Co}^{2+} \). The sorption behaviour of \( \text{Co}^{2+} \) was examined in detail, with the intention of using the resin analytically. \( \text{Fe}^{3+} \) and \( \text{Co}^{2+} \) were separated on a column by stepwise elution with oxalic acid and hydrochloric acid respectively.

Chelating resin containing an oxime group

Sugii et al. [110] synthesized a macroreticular polystyrene-based chelating resin with oxime and diethylamino functional groups. The resin was stable in acid and alkaline solutions.
The resin had higher selectivity for Cu$^{2+}$ than for other metal ions tested and the time required for 50% uptake of copper from 0.03M copper nitrate was 15 min. The highest capacity for Cu$^{2+}$ was 2.0 m mole g$^{-1}$ at pH 6.0. In a column operation, copper was quantitatively recovered by elution with 1M hydrochloric acid and the resin could be reused. The presence of neutral salts such as sodium chloride or sodium nitrate (0.5M) did not affect the sorption of Cu$^{2+}$.

*Poly (Iminoethylene) Dithiocarbamate Co-Polymer*

This was prepared by substitution of Cs$_2$ at the primary and secondary amino groups of poly(iminoethylene), [111].
The binding of the transition metal ions \( \text{VO}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Co}^{2+}, \text{Co}^{3+}, \text{Ni}^{2+} \) and \( \text{Cu}^{2+} \) was investigated by uptake studies and physical measurements. The metal ions may be bounded by both the dithiocarbamate and amino groups of the co-polymer. Factors such as the binding sites and stereochemistry of the co-polymer, which determine the relative uptake of the metal ions, were discussed. Binding to nitrogen (in addition to binding to sulphur) increased in the order \( \text{Fe}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} \) and accounted for the metal ion uptake by the co-polymer increasing in the same order.

**Bifunctional Ion-Exchange / Co-Ordination Resins**

Alexandratos et al. [112] have synthesized bifunctional resins that complex metal ions by both ion-exchange and co-ordination.

The trivalent ions of the group IIIA elements Al, Ga, In and Tl form anionic complexes with chloride and bromide which increase markedly in stability with increase in atomic weight of the metal. The best current ion-exchange procedure using a single column for the sequential separation of all four elements, is based on this fact. It is a cation-exchange procedure which employs the sequence 0.1 M hydrochloric acid in 50% aqueous acetone, 0.5 M hydrochrolic acid in 50% aqueous acetone, 2.0 M hydrochloric acid in 70:30 v/v acetone-water mixture and
3.0M aqueous hydrochloric acid for the elution of Ti, In, Ga and Al, respectively. The separation are quite sharp and recoveries quantitative for 1-100 mg amounts of all four elements.

Ion-exchange chromatography assumed a new role in chemical analysis with the introduction of the two-column technique by Small et al. [114]. The first of the two columns, which are in series, performs the separation, while the second, the suppressor column, removes the ionic contribution from the eluting medium, enabling and conductivity detector, placed after the second column, to act as a sensitive universal detector for the ions in the original sample. A single-column version which operates without a suppressor and uses conductivity detection was introduce by Fritz et al. [115].

Such techniques have undergone modifications, the most important of which are probably the replacement of the suppressor column by a self-regenerating membrane system based on hollow fibers and of indirect photometric detection [116] in the single column technique. Chromatographs with background suppression and conductivity detectors have been developed commercially by the Dionex corporation, Sunnyvale, California.
It has been found that macro reticular resins prepared from various cross-linked organic polymers, available commercially (Amberlite XAD-resins, Rohm and Haas, Philadelphia), have the ability to retain long-chain quaternary ammonium salt, presumably with the hydrocarbon component of the molecule incorporated with in the resin pores and the ionic group exposed at the surface [117,118]. This provides a very simple and convenient means of producing a low-capacity anion exchanger.

Polymeric reagents and reagents immobilized on polymeric support are extensively used in organic synthesis because of the advantages they offer in easy workup, mild experimental conditions, high turnover and also the possibility of carrying out chemoselective and site-specific reactions. Several reviews on the subject are available [119-122].

Chelating sorbents obtained by immobilization of organic reagents on solid supports have recently gained growing importance in pre-concentration and separation of elements, [123,124]. They provide high efficiency and simplicity of procedure and may be combined with a variety of highly sensitive methods of determination.
The attention paid to removal of trace metals from industrial effluents and the degree of sophistication of separation methods have both increased enormously in recent years. Use of chelating resin for removal and separation of metal ions is of wide interest owing to its simplicity, elegance and range of variations.

The strong chelating power of hydroxamic acid ligands has been utilized in the manufacture of chelating resins containing these acids as functional groups. Poly(hydroxamic acid) resins have been synthesized from the polymethacrylate, [125] Amberlite IRC-50 [126] Amberlite XAD-4 and styrene-divinylbenzene copolymer, [127,128] and acrylonitrile-divinylbenzene copolymer, [129-132].

The need for more highly specific, metal recovery processes in both hydrometallurgical and environmental applications has led to an increasing interest in selective ion exchange. In particular, the search for ‘ion-specific’ resins which, under proper operating conditions, are selective for only one ionic species [133-136] has intensified. Important properties of such ions exchangers should include high capacity, high selectivity and fast kinetics. Most of the commercial resins, [133] when tested in waste-water treatment show a high capacity, but a very poor selectivity towards different metal ions. In some cases the kinetics are
slow, due to hydrophobic character of the polymer backbone.

Quinaldinic acid is a well established analytic reagent, predominately used for the gravimetric determination of several cation [137]. A new chelating resin containing quinaldinic acid amide as the functional group incorporated into the macro-reticular styrene divinyl benzene copolymer beads was synthesized.

Ion exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotic purification, and separation of radioisotopes, and finds large scale applications in water treatment and pollution control, [138,139]. Various commercial exchangers have a polymeric base (styrene, acrylic acid, phenol-formaldehyde, etc.) with cationic or anionic units as the site of exchange.

Synthetic resins derived from hydroxyl and amino aromatic compounds have attracted the attention of many researchers because of their versatile use as ion exchangers [140,141], photographic binders, thermal stabilizers, etc. [142-146].

Ion-exchange liquid chromatography has been widely used in the separation and purification of proteins. This method can be conducted in an aqueous buffer system,
which prevents denaturation and/or inactivation of their biological functions. Presently, many ion exchangers with outstanding properties suitable for protein separation are commercially available [147-149] 4-Vinyl pyridinium polymer (4VP) column in high-performance liquid chromatography (HPLC) is useful in separating human/bovine serum albumin component such as mercaptalbumin and non mercaptalbumin [150,151]. It is postulated that these protein interact with only the functional group on the outer surface of the resin, because the pore sizes of the resin are to be small to be penetrated by proteins. The retention of proteins on 4VP is substantially based on an approach comparable to that of the nonporous type or pellicular supports[152-154].

The macroporous chelating resin [155-166] (RNH_DVB) containing amidoxime groups, prepared from acrylonitrile (AN) Divinyl benzene (DVB) copolymer beads, posses an effective physical pore structure for recovery of uranium in nature seawater.

Much research is being directed toward the preparation of polymeric chains, which are propogated because of the formation of metallic chelates. During the last four decades, interest in the chemistry of coordination compound has increased substantially because of the
compound biological interest. Most of the workers in the field of polymeric chelates were primarily interested in the synthesis of chelating [157]. Pennington and Williams [158] used the batch equilibrium method to determine selectivity and capacity of chelating polymers with solution of metal ions containing a buffer of high capacity. Pennington and Williams [159] prepared a chelating ion exchange resin by condensing resacetophenone with formaldehyde in the presence of NaOH as a catalyst, Sykora and Dubsky [160] have prepared a selective ion exchange resin by reacting a condensation product of resacetophenone and anthronilic acid with formaldehyde. Parmar et al. [161] have syntherized resacetophenone formaldehyde resin in an acidic medium and have studies their chelate ion exchange properties.

Increasing interest in the cation exchange resins and chelating resins for separations, Preconcentration and recovery of trace metals led us to under take the present investigations.

A new chelating resins based on a phenol - formaldehyde copolymer containing diethylenetriaminepentacetic acid (DTPA) as a functional species has been synthesis. Capacity and sorption kinetics have been studied. The complexation ability (distribution coefficients)
of the sorbents towards 19 metal ions has been studied the resins has successfully been applied for the selective separation and recovery of some metal ions.

A new chelating sorbent containing diethyldithiocarbamate (DEDTC) as a functional group immobilized on resorcinol - formaldehyde co polymer has been prepared and characterized. Distribution coefficient of 17 metal ions were determined in different pH system. The Preconcentration and recovery experiments for Ag⁺, Zr⁴⁺, and Hf⁴⁺, have been demonstrated.

A chelating resin containing 8 - Hydroxyquinoline was synthesized and characterized. On the basis of distribution studies carried out in different pH systems, some quantitative separations of metal ions of analytical interest have been reported.

Distribution coefficients of 13 metal ions were determine on Amberlite IRP-69 (NH₄⁺) in ammonium iodide systems of varying concentration. Distribution coefficients on Amberlite IRP – 69 (H⁺) were also studied for 18 metal ions in HCl- acetone media. Some quantitative separations of metal ions of analytical interest have been reported.
REFERENCES


6. Ger. Pat. 197,111 (1906), R. Gans; U. S. Pat. 914, 405 (1909); U. S. Pat. 943, 535 (1909); U. S. Pat. 1,131,503 (1915).


22. Br. Pat. 450, 308 (1936), B.A. Adams and E.L. Holmes;
   Br. Pat. 450, 309 (1936); Br. Pat. 474, 361 (1937);
   Fr. Pat. 796, 796 (1936); Fr. Pat. 796, 797 (1936);
   2, 191, 853 (1940), U.S. Pat. 2, 191, 853.
   (1940) (to I.G. farbenindustrie).
25. H. Wassengger, R. Griessbach and W. Sutterlin U.S. Pat
   2, 228, 159 (1940) (to I.G. farbenindustrie).
26. H. Wassengger Ger. Pat. 733, 679 (1943) (to I.G.
   farbenindustrie).
27. G.B. Hewstad and W.C. Bauman U.S. Pat. 2, 448, 029
   (1948) (Dow chemical Co.).
   2, 223, 930 (1940) (to I.G. farbenindustrie).
29. H.C. Cheetham and R.J. Myers U.S. Pat. 2,341,907 (1944), (to The Resinous Products and Chemical Co.).

30. J.R. Little, U.S. Pat. 2,259,169 (1941), (to United States Rubber Co.).

31. U.S. Pat. 2,366,007 (1944), G.F. D'Alelio (to General Electric Co.).

32. U.S. Pat. 2,340,110 (1944), G.F. D'Alelio (to General Electric Co.).


121. G. V. Myasoedova and S.B. Savvin, khela
toobrazuyuchie sorbenty, nauka, Moscow, 1984.
123. W. Kerm and R.C Schultz, Angew. Chem. Int. Ed
(1965) 919.
418.
(1976) 369.
317.
131. P. M. Vanbarkel, W. I. Driessen, G. J. Anthony, A.
(1984) 59, M. J. Hundson Ion Exchange Science and


160. V. Sykera and F. Dubsky, CA (1964) 61.