Foreward

A revolutionary development in Chemistry took place with the separation of chlorophyl-a and chlorophyl-b and pigments from extracts of plant leaves by Tswett in 1906 by a process named chromatography which he defined as 'a method in which the components of a mixture are separated on an adsorbent column in a flowing system'. However, the importance of this great discovery remained unnoticed for nearly 30 years till the same process was used in the separation of pigments in egg yolk. The 1940's saw the development of new techniques like partition-paper and gas-chromatography and wide application of them along with Tswett's column chromatography in fields of research and routine work in chemistry, biology and medicine.

This demanded a fresh definition of chromatography by IUPAC which read as 'a method used primarily for the separation of the components of a sample, in which the components are distributed between two phases, one of which is stationary while the other moves. The stationary phase may be a solid or a liquid supported on a solid or a gel. The stationary phase may be packed in a column, spread on a layer or distributed as a film etc; in these definitions 'chromatographic bed' is used as a general term to denote any of the different forms in which the stationary phase may be used. The mobile
phase may be gaseous or liquid. Ion-exchange chromatography was used first by Taylor and Urey (1938) through the separation of some alkali metals using inorganic ion-exchangers. Samuelson in 1939 developed the first synthetic organic ion exchangers though the original patents of such synthetic exchangers were due to Adams and Holnes (1935).

Though these ion-exchangers were first used in softening of water soon its importance was perceived during the second world war. The 'Manhattan Project' a closely guarded research work on the development of the nuclear bomb in the USA had a wing developing the separation of fission products, the 'rare earths' and also the discovery of new elements like promethium and some of the transuranium elements. It will not be too much optimistic to say, now, that whichever pair of elements (excepting the inert gases) are given, they can be separated by ion-exchange process. Such ion-exchangers contain acidic groups (e.g., −SO₃H, −COOH etc.) for separation of cations or basic groups (e.g., quarternary and tertiary amines) for separation of anions.

The next stage saw the introduction of some functional groups containing chelating properties into the synthetic resins and the resulting resin being called chelating resin. Skogseid (1947) developed the first of this group of resins by reacting picryl chloride with nitrated and reduced poly-styrene.
Ion-exchange resins (cation- or anion-exchangers) are capable of sorbing all ions of the same type (cations or anions) depending on the particular group attached to the resin, the strength of sorption depending on the hydrated size of the ion and its charge. But chelating resins are more selective as they can absorb one or few of the ion more firmly depending on the nature of the chelating group or groups. Thus, they have become very popular when one particular ion has to be removed from a mixture or concentrated from a very dilute solution as they require less chemical and less time than required by other ion-exchangers.

Once the importance was noted the development of new chelating resins advanced in rapid pace since the 1960's through the introduction of common organic chelating groups used in analytical chemistry. The list of examples include groups like dipicrylamine, dimethylglyoxime, hydroxamic acids, iminodiacetic acid, 8-hydroxyquinoline, thiourea, picolinic acid, benzoylacetonilide etc. The resin bases used also varied widely. The resulting chelating resins have found wide industrial and environmental uses such as recovery of potassium from sea water, treatment of effluents from alkali or battery industry for removal of mercury etc.

Quinaldinic acid is a well established analytical reagent for a number of metal ions in their gravimetric determination. These metals are zinc(II), cadmium(II), mercury(II),
copper(II), iron(II), cobalt(II), nickel(II), manganese(II), lead(II), silver(I) etc. The present investigation is on the introduction of the quinaldinic acid group into a resin matrix keeping the functional group in its, study the adsorption pattern of different metal ions on it and develop some methods for the separation and concentration of the more important metals from low grade ores, water and other natural or commercial samples. However, it was expected that the behavior of quinaldinic acid group might not remain the same due to two reasons:

(1) The acid dissociation of the functional group in quinaldinic acid might not be the same in the free acid and the acid bound to the resin matrix and (2) the free reagent forms inner metal complexes with metal ions while the chance of combining more than one group to a metal ion is remote in the resin.

This dissertation describes the synthesis of a styrene-divinyl benzene based ion-exchanger containing the essential chelating groups of quinaldinic acid, studies on the characteristics of the new resin and its applications.

Chapter 1 of this dissertation is an introductory one containing a brief resume of the development of chromatography with special reference to chelating ion-exchangers and a review of the work reported so far on the latter. The aim of the present investigations has been focused in the Second Chapter of the introductory part. The rest of the dissertation is devoted to the report on the experimental work done.
Chapter 3 describes the method adopted for the synthesis of quinaldinic acid containing resin in the form of the acid amide as the functional group. The new resin has been characterised by determining its water regain value, stability towards acids, alkali, heat and γ-radiation and i.r. spectra.

Chapter 4 describes general method of determination of sorption capacity as a function of pH of Na(I), K(I), Ag(I), Ca(II), Mg(II), Be(II), Zn(II), Cd(II), Hg(II), Cu(II), Ni(II), Pb(II), Co(II), Mn(II), Fe(II), Fe(III), Ce(III), Au(III), Ti(IV), Th(IV), Sn(IV) and U(VI). The sorption capacities of the resin for gold(III), silver(I) and mercury(II) were high and for uranium(VI), lead(II) and copper(II) were also appreciable. Hence it was concluded that the resin could be used successfully for the concentration of Au(III), Ag(I), Hg(II), U(VI), Pb(II) and Cu(II) and separation from other metal ions.

Chapter 5 of this dissertation describes the studies on mercury(II). Mercury(II) was separated from synthetic mixtures containing one or more of the following metal ions: Na(I), K(I), Ca(II), Mg(II), Zn(II), Cd(II), Pb(II), Cu(II), Ni(II) and Fe(III). This resin have been applied for the concentration and separation of mercury(II) from laboratory waste water and industrial waste water.
Chapter 6 describes investigations on uranium(VI). Uranium(VI) was separated from Na(I), K(I), Be(II), Ca(II), Mg(II), Zn(II), Cd(II), Cu(II), Pb(II), Ni(II), Bi(III), Fe(III), Ce(III), Th(IV) and Ti(IV). Uranium was separated and determined successfully in uraninite ore.

Chapter 7 describes studies on silver(I) and gold(III). Gold(III) was separated from Na(I), K(I), Ag(I), Ca(II), Mg(II), Cu(II), Zn(II), Cd(II), Ni(II), Pb(II) and Fe(III). Silver(I) was separated from Na(I), K(I), Ca(II), Mg(II), Cu(II), Zn(II), Cd(II), Ni(II) and Fe(III). Gold was concentrated and separated from mud samples and street dust near workshops of goldsmiths and silver from rock samples. Separation of gold from silver was affected by controlling the pH.

Chapter 8 describes studies on lead(II) and copper(II). Lead(II) was separated from Na(I), K(I), Ca(II), Mg(II), Zn(II), Mn(II), Cu(II), Ni(II), Cd(II), Fe(III), Bi(III), Ce(III), Th(IV), Sn(IV) and U(VI). Copper(II) was separated from Na(I), K(I), Ca(II), Mg(II), Zn(II), Cd(II), Ni(II) and Fe(III). Lead(II) was also separated from mud and rock samples.
Chapter 9 describes summary of the results obtained from experiments on investigations of mercury(II), uranium(VI), gold(III), silver(I), lead(II) and copper(II) by the resin and also the inference which could be drawn.

The closing pages of the dissertation have been devoted to the analysis of the results from which it could be concluded that the new resin synthesised and the methods developed can be adopted in analytical separations and preconcentration. Even it can be stretched to the point that with suitable modifications, the procedures could be applied to industries dealing with low concentrated metals and for treatment of industrials effluents.