CHAPTER I

Introduction
1.1 Introduction to Solvent Extraction

The solvent extraction occupies a unique status among the methods of separation because of its rapidity, selectivity and simplicity. The partition of any substance between two immiscible solvent in contact with each other is the basis of liquid-liquid extraction. The process was first utilized in synthetic organic chemistry when it was used for the laboratory scale preparation of certain drugs and dyestuffs. The development of liquid-liquid extraction in inorganic chemistry was marked in nineteenth century. Solvent extraction finds application in two major areas of inorganic chemistry.

(a) Analytical detection and determination of metal ions
(b) Hydrometallurgical processing of ores

In the early stages of its development, solvent extraction was used almost exclusively as an analytical tool. This is still an important area of research but the past 25 years have seen a noticeable increased interest in the development of hydrometallurgical processes based on this technique.

The extraction of uranyl nitrate from aqueous solution by ether was discovered by Pelogot [1] in 1842. Later in 1867 Skay [2] observed the solubility of various thiocynates in ether and suggested the use of liquid extraction to separate the metal ions; cobalt from nickel, gold from platinum. His observation on the extractability of different metallic chlorides in ether did not find application in analytical chemistry until Rothe [3] and Hanroit [4] exploited the important observation that ferric chloride could be extracted by ether from concentrated hydrochloric acid. This method was then applied to iron (III) from many other metal ions [5].

In 1925, dithizone was introduced by Fisher as a precipitant for some metal ions forming stable chelate complexes and later on in 1934, the extraction of metal dithiazonates was reported by some workers [6]. The extraction of metal ions with cupferron [7] and dimethyl glyoxime [8] was also reported in 1930, and that with 1-nitroso-2-napthol [9] or 8-hydroxyquinoline [10] in the early 1949.

The first quantitative aspect of solvent extraction was studied by Berthelot and Jugal Flesh in 1872 [11] who verified experimentally that the ratio of the
concentration of a solute in the two immiscible phases after equilibrium is constant. This was investigated more thoroughly in 1891 by Nernst [12]. The distribution law, “when a material is distributed between two mutually immiscible liquid phases, the concentration ratio in the phases at a given temperature is independent of the total amount”, was applied to the determination of chemical equilibria of various solutes in solutions as early as about 1900 [13-19].

After world war second, chemists were engaged in atomic energy research, encountered the problem of separating and purifying almost all the elements, in amounts ranging from very low traces up to the usual micro levels. Among the solution to these difficult problems were the precipitation method and the ion exchange method. The former was found to be suitable for the treatment of materials in solution at high electrolyte concentrations and the later for the treatment of the ions in dilute solution or for the separation of chemically similar elements such as lanthanides and transplutonium elements. However, the solvent extraction method proved most effective and attractive to separate these metals, because in this method, the separation was almost complete than precipitation method and operation time was very less as compared to ion exchange method. With proper choice of extracting agents, this technique can achieve group separation or selective separation of trace elements with high efficiencies. In analytical applications, solvent extraction may serve the following three purposes:
  i) Preconcentration of trace elements
  ii) Elimination of matrix interference
  iii) Differentiation of chemical species.

This method still remains a standard method of separation and preconcentration, because of its simplicity, speed and applicability to both trace and macro-amounts of metal ions. The liquid-liquid extraction technique has become increasingly popular in comparison with the other extraction methods because of its several major advantages, such as simple to operate, high pre-concentration factor, rapid phase separation and the ability to combine with different detection techniques.
A large number of researches into the subject of inorganic solvent extraction have been published over the past few years describing most aspects of the technique as applied to both the analytical and hydrometallurgical fields. Most of the literature has been comprehensively surveyed in a number of books and reviews. Some of the more general texts which have been written are by Morrison (1950) [20], Irving (1955) [21], Alders (1995) [22], Morrison and Frieser (1957, 1958) [23,24], Martin and Holt (1959) [25], Fomin (1960) [26], Diamond and Tuck (1960) [27], Irving and Williams (1961) [28], Morrison and Frieser (1962) [29], Frolov (1962) [30], Treybal (1963) [31], Marcus (1963) [32], Stary (1964) [33], Schweitzer and Van Willis (1965) [34], Lewis (1965) [35], Fletcher (1966) [36], Marcus and Kertes (1969) [37], Zolvotov (1970) [38], Flett (1970) [39], Khopkar and Chalmers (1970) [40], Hanson (1971) [41], Green (1973) [42], and Ashbrook (1975) [43,44].

The most common extractants used for solvent extraction studies of metal ions are: Alamin336 (tricarpyl amine), Aliquate 336(tricarpyl methyl ammonium chloride), N-n-octyl aniline, n-octyl aniline, Tribenzyl amine, Trioctyl amine, Tri isooctyl amine, derivatives of benzothiazoles, tributyl phosphates, triphenyl phosphine, alkylamides, β-diketones, Schiff bases, derivatives of sulphoxides, crown ethers.

1.1.1 Terms and Conditions in Solvent Extraction

An extractant is a substance primarily responsible for the transfer of a solute (here metal) from one phase to the other. The extractant is dissolved in a suitable diluent and together act as a solvent. The diluent is partially immiscible with other phase which is usually water. The extractant reacts with the solute by solvation, chelation, ion pair formation etc to extract it from the aqueous phase. The distribution equilibrium between two phases is governed by Gibbs phase rule, given by

\[ P + V = C + 2 \]  

Where,

\[ P = \text{is the number of phases,} \]
\[ V = \text{is the variance or degrees of freedom and} \]
\[ C = \text{is the number of components.} \]
In solvent extraction, we have $P=2$ two phases namely aqueous and organic phase, the component is $C=1$, viz. solute, in solvent and water phase and at constant temperature and pressure $V=1$, thus we therefore have

$$2+1=1+2 \quad \text{i.e. } P+V=C+2 \quad (2)$$

According to Nernst distribution law,

If $[X]_1$ is concentration of solute in phase 1 and if $[X]_2$ is the concentration of solute in phase 2 at equilibrium:

$$K_D = \frac{[X]_1}{[X]_2} \quad (3)$$

Where $K_D$ is called as the partition coefficient, this partition or distribution coefficient is independent of the total solute concentration in either of the phases. In the above expression for $K_D$ we have not considered the activity coefficient of the species in the organic as well as in the aqueous phase. We, therefore, use the term distribution ratio ($D$) to account for the total concentration of species in the two phases.

**Distribution Ratio ($D$)**

The distribution of a solute between two immiscible solvents can be described by the distribution ratio “$D$”.

$$D = \frac{[X]_1}{[X]_2} \quad (4)$$

Where $[X]$ represents the stoichiometric or formal concentration of a substance $X$ and the subscripts 1 and 2 refer to the two phases. Since in most cases, two-phase system is of analytical interest, an organic solvent and aqueous are involved, $D$ will be understood to be;

$$D = \frac{[X]_{\text{org}}}{[X]_{\text{aq}}} \quad (5)$$

The subscripts org and aq refer to the organic and aqueous phases respectively. Distribution ratio ‘$D$’ is dimensionless quantity, separation of two solutes by solvent extraction is expressed by the term, separation factor ($\alpha$), which is related to individual distribution ratios,

$$\alpha = \frac{D_A}{D_B} \quad (6)$$
$D_A$ and $D_B$ are the respective distribution ratios of solute $A$ and $B$.

In the simplest extraction case, the distribution ratio is constant in accordance with the classical Nernst distribution law, a solute will distribute itself between two essentially immiscible solvents so that at equilibrium the ratio of the concentrations of the solute in the two phases at a particular temperature will be constant, provided the solute is not involved in chemical interactions in either phases. For such a solute, then $K_D = D$. Now in practical work, instead of using term $K_D$ or $D$ one prefers to use term percentage extraction ($E$).

**Percent Extraction ($E$)**

The more commonly used term for expressing the extraction efficiency by analytical chemist is the percent extraction “E”, which is related to “D” as

$$\%\text{Extraction}(E) = \frac{100D}{D + V_{aq}/V_{org}}$$

Where, $V$ represent solvent volume and the other quantities remain as previously defined. The percent extraction may be seen to vary with the volume ratio of the two phases as well as with $D$.

### 1.1.2 Classification of Extraction Systems

The process of metal extraction is based on the formation of neutral metal chelate. All types of chelating agents find useful applications in metal extraction procedures. Various extraction systems can be classified in several ways. The classical one is based on the nature of the extracted species. The present day classification is based upon the process of extraction. Thus, based upon the process of extraction, extraction systems can be classified into four major classes viz.,

1) Chelate extraction
2) Extraction by solvation
3) Extraction involving ion pair formation
4) Synergic extraction

All the above extractions are based on the fact that neutral or uncharged species are extracted easily in organic solvents. These are described here briefly.
a) Chelate extraction  
In this class, extraction proceeds by the process of formation of chelate or closed ring structure between the chelating agent and the metal ion to be extracted.

  e.g. i) The extraction of Uranium with 8-hydroxyquinoline in chloroform.
        ii) The extraction of Iron with cupferron in carbon tetrachloride.

b) Extraction by solvation  
In this class, the extraction proceeds by the process of solvation of the species which is extracted into organic phase. Oxygenated organic solvents such as alcohols (C-OH), ketones, ethers and esters show some basicity because of the lone pair of electron on the oxygen atom and can therefore directly solvate protons and metal ions and bring about their extraction.

  e.g. i) The extraction of Uranium with tributyl phosphate from nitric acid
       ii) The extraction of Iron (III) with diethyl ether from hydrochloric acid.

c) Extraction involving ion pair formation  
The extraction proceeds with the formation of neutral uncharged species which in turn gets extracted into the organic phase. The best example of this is the extraction of scandium and uranium with trioctyl amine from mineral acids. In this case an ion pair is formed between complex of metal ion with high molecular weight amine and anionic species of mineral acids.

d) Synergic extraction  
In this case, there is enhancement in the extraction on account of use of two extractants.

  e.g. The extraction of Uranium with tributylphosphate (TBP) as well as 2-thionyltrifluoroacetone (TTA).

1.1.3 Mechanism of Extraction  
Any solvent extraction process proceeds into three stages viz

  i) The formation of uncharged complex;
  ii) The distribution of uncharged complex and
  iii) Interaction in the organic phase
1) The formation of uncharged complex:

The formation of uncharged complex is most important step in the extraction. It is obvious if the complex is charged, it will not be extracted hence it is absolutely essential to have the extracted complex without any charge. Such uncharged complex can be formed by the process of chelation (i.e. neutral chelates), solvation or ion pair formation. Thus, if M is metal ion with valency ‘n’ and if R is the anion of the ligand (HR) then through co-ordination, we have

\[ M^{n+} + nR^- \rightarrow MR_n \]

Now in solvation phenomenon or in extraction involving ion pair formation, the complex formed may be anionic or cationic which in turns gets associated with cation or anion respectively to give uncharged complex which in turn gets extracted into the organic phase as

\[ M^{n+} + bB \rightarrow MB^{n+} \]
\[ MB^{n+} + nX^- \rightarrow (MB^{n+}, nX^-)^0 \text{ cationic complex} \]

Where B= neutral ligand, X=anion, M= metal

\[ M^{n+} + (n + a)X^- \rightarrow MX^{a-(n + a)} \]
\[ MX^{a-(n + a)} + aY^+ \rightarrow (aY^+ MX^{a-(n + a)})^0 \text{ anionic complex} \]

The formation of complex by metal ion depends upon its tendency to fill up vacant atomic orbitals to accomplish stable electronic configuration. Metal chelates represent a type of co-ordination compounds in which a metal ion combines with polyfunctional base capable of occupying two more position in the coordination sphere of the metal ion to form a cyclic compound. The functional group of the chelating agent must be so suited in the molecule that it permits the formation of a stable ring.

In extraction involving ion pair formation, the value of ion pair formation constant is related to dielectric constant (\( \varepsilon \)) and temperature (T) by expression

\[ K = \left[ \frac{4\pi Ne^2}{1000\varepsilon kT} \right] Q (b) \text{ if } b = \frac{e^2}{2\varepsilon kT} \]

Where N= Avogadro’s number, \( e= \) charge,
T= absolute temperature, 
Q (b) = calculable function, k= Boltzmann constant, 
A= empirical parameter dependent upon the distance between charge center of the 
paired ions when in contact. 

Above expression suggest that low value of dielectric constant favors 
expensive association and distribution of the extractable complex depends upon the 
organophilic character of distribuents. Thus, there are two main factors which cause 
the distribuents to favor the organic phase, (a) low affinity of distribuents to aqueous 
phase and (b) high affinity of distribuents to organic phase. The low affinity of 
species for the aqueous phase is because of following factors: 
1) Large size 
2) Zero or small charge 
3) Non polar nature 
4) Absence of electronegative atom at the surface 
5) Low water activity and high ordered water structure 

Salting out agent decreases the availability of water for interaction with 
distribuents. In addition to the parameters of the aqueous phase, ion association 
 extraction systems are especially sensitive to organic phase parameters. These 
variables are dependent on the nature, structure, size and concentration of the 
extractant and the type of diluents used. Each of the factors affects the degree of 
extraction of the metal complex.

2) The distribution of extractable complex:

The species extracted is invariably neutral and is least soluble in aqueous 
phase. Thus, the theory of like dissolves like is mostly applicable. The substitution of 
hydrocarbon group in chelate structure results in an increase in solubility of chelate 
in organic solvents due to structural resemblance.

In the case of extraction by solvation, the solvent itself participates in 
extraction of complex. The basic character of the oxygen atom enables the 
incorporation of the solvent molecule in coordination sphere of the metal ion to form 
solvated complex which molecule in coordination sphere of the oxygen of the metals
ion to form solvated complex which is extractable. Thus, the oxygenated solvents like alcohols, ketones, or neutral organophosphorus compete with water molecule for the acidic metal ion— the competitive strength of water may be reduced by adding salting out agent.

3) Interaction in the organic phase

For covalent metal chelates such problem never arises, however, in extraction by solvation, there is a possibility of polymerization, which results in reducing the activity of the extractable species, but overall equilibrium is shifted in favor of higher distribution ratio.

1.1.4 Methods of Extraction

Three basic methods of liquid-liquid extraction are generally utilized in the analytical laboratory.

1) Batch extraction

Batch extraction, the simplest and most commonly used method, consists of extracting the solute from one immiscible layer by shaking the two layers until equilibrium is attained, after which the layers are allowed to settle before sampling. This is commonly used on the small scale in chemical labs. The most commonly employed apparatus for performing a batch extraction is a separatory funnel. The batch extractions may also be used with advantage when the distribution ratio is large.

2) Continuous extraction

The second type, continuous extraction, makes use of a continuous flow of immiscible solvent through the solution or a continuous countercurrent flow of both phases. Continuous extractions are particularly applicable when the distribution ratio is relatively small. Continuous extraction devices operate on the same general principle, which consists of distilling the extracting solvent from a boiler flask and condensing it and passing it continuously through the solution being extracted. The extracting liquid separates out and flows back into the receiving flask, where it is again evaporated and recycled while the extracted solute remains in the receiving
flask. When the solvent cannot easily be distilled, a continuous supply of fresh solvent may be added from a reservoir.

3) Countercurrent extractions

Extraction by continuous countercurrent distribution is the third general type and is used primarily for fractionation purposes. The separation through continuous countercurrent method is achieved by virtue of the density difference between the fluids in contact. In vertical columns, the denser phase enters at the top and flows downwards while the less dense phase enters at the bottom and flows upwards.

The choice of method to be employed will depend primarily upon the value of the distribution ratio of the solute of interest, as well as on the separation factors of the interfering materials.

1.1.5 Factors Influencing the Extraction Efficiency

Primary requirement of solvent extraction for separation/removal purposes is a high distribution ratio of the solute of interest between the two liquid phases. Though, continuous and countercurrent distribution techniques may be used for the cases where low distribution ratios are present, it is generally desirable to attain as high a value as possible for the development of simple analytical procedures. It is useful to employ a number of different techniques for enhancing the distribution ratio. These depend on the nature of the species being extracted and extraction system. The attainment of selectivity in an extraction procedure is also very important. Some of the factors, which affect the distribution of solute of interest, are given below.

1. Choice of solvent

Use of a suitable solvent for effective separation is very important. Metal chelates and many organic molecules, being essentially covalent compounds do not impose many restrictions on the solvent and the general rules of solubility are of great use. In ion association systems and particularly in oxonium type ions, the role of solvents is very important. This is due to involvement of solvent in the formation of extractable species.
In addition to the consideration of the distribution of the solute in a particular solvent system, the ease of recovery of the solute from the solvent is important for subsequent analytical processing. Thus, the boiling point of the solvent or the ease of stripping by chemical reagents is considered in the selection of a solvent where the choice exists. Similarly, the degree of miscibility of the two phases, the relative specific gravities, viscosity and tendency to form emulsions should be considered. With regard to safety, the toxicity and flammability of the organic solvents must be considered. Sometimes it is possible to achieve the desired characteristics of a solvent by employing a mixed-solvent system.

2. Acidity of an aqueous phase

The extractability of metal complexes is greatly influenced by the acidity of an aqueous phase, so it is necessary to assure optimum concentration of H\(^+\) ions for maximum extraction. In the case of chelate extraction, the chelating reagent concentration is maintained constant; the distribution of the metal in a given system is a function of pH. For this reason, curves of extractability versus pH at constant reagent concentration are of great analytical significance.

3. Salting-out agents

A technique that has resulted in marked enhancement of extraction of metals is the use of salting-out agents. The addition of high concentrations of inorganic salts to the aqueous phase greatly increases the distribution ratio of many metal complexes to the organic phase. This salting-out effect may be explained in part by the pronounced effect of the added salt on the activity of the distributing species, the common ion effect, as well as the strong ability of these ions to bind water around them, thereby depleting the aqueous phase of water molecules for use as a solvent. High concentrations of inorganic salts are usually required to produce the desired effect, the aqueous phase often being saturated with the added salt. It is essential that the added salt is not extracted to an appreciable extent with the desired species in order to maintain the optimum effect and to permit direct use of the organic extract without further separation. Sometimes the aqueous phase after extraction may be of interest so that the presence of large amounts of added cations prevent...
further use of this phase in the subsequent analytical steps unless the added salt can be easily removed or destroyed, like ammonium salts.

In addition to enhancement of the extraction of the metal of interest using salting-out agents, it is also possible to increase the extraction of impurities in the system. Thus, it is necessary to choose an agent that produces a favorable separation factor between the element of interest and the impurities. However, it must be remembered that anomalies sometimes result from specific interaction effects. Aluminum or calcium salts are strong salting-out agents, whereas ammonium salts are much weaker but analytically more convenient.

4. Stripping

Stripping is the removal of the extracted solute from the organic phase for further processing or analysis. It is the reverse of extraction. The usual procedure is to shake the organic layer with a volume of water alone or water containing an appropriate concentration of acid, an oxidizing or reducing agent or a masking agent. The metal ion is then back extracted in the stripping aqueous phase. The conditions employed depend upon the metal ion and the particular extraction system and are such that they promote the reversal of extraction. Pure water or water adjusted to an appropriate pH/molarity of acid are the more popular and convenient stripping agents. Washing the organic layer with an oxidizing or reducing agent changes the metal ion to be stripped in an oxidation state in which it is not extracted under the specific conditions.

5. Masking

In the extraction procedures for metal pairs that are difficult to separate; masking or sequestering agents are introduced to improve the separation factor. The masking agent forms water-soluble complexes with the metals in competition with the extracting agent.

Masking agents form sufficiently strong complexes with interfering metals to prevent their reactions with the extraction agents, either altogether or at least until the pH is much higher than the value needed for quantitative extraction of the metal of interest. Very often the metal of interest also forms a complex with masking agent, with the result that a somewhat higher pH range is needed for the extraction. The
application of masking agents, which include cyanide, tartarate, citrate, fluoride, and EDTA, is restricted largely to metal chelate extraction systems, since in the highly acidic solutions encountered in many inorganic extraction systems most masking agents, being weak bases, do not function effectively. EDTA, which has been proved as most useful masking agent, forms anionic complexes with a number of metal ions.

6. Backwashing

An auxiliary technique used with batch extractions to effect quantitative separations of elements is backwashing. The combined organic phases from several extractions of the original aqueous phase contain practically all the desired elements and possibly some of the impurities that have been extracted to a much smaller extent. This combined organic phase when shaken with one or more small portions of a fresh aqueous phase containing the optimum reagent /salting agent concentration, acidity, etc., will result in a redistribution of the impurities in favour of the aqueous phase since their distribution ratios are low. Under optimum conditions, most of the elements of interest will remain in the organic layer, since their distribution ratio are high. This technique is analogous in many respects to the re-precipitation step in a gravimetric precipitation procedure. With the proper conditions, most of the impurities can be removed by this backwashing operation, with negligible loss of the main component, thereby attaining a selective separation.

7. Oxidation state

A useful method of increasing the selectivity of metal extractions involves modification of the oxidation states of the interfering ions present in solution, in order to prevent the formation of their extractable metal complexes. For example, the extraction of iron from chloride solutions can be prevented by reduction to iron-II, which is not extractable. Similarly, antimony-V may be reduced to the tetravalent state to suppress its extraction. Conversely, it is important in the preparation of a solution for extraction to adjust the proper valence state of metal ion required for the formation of the complex in order to ensure complete extraction of that element. Selectivity can also be achieved by variation of the oxidation state of the co-extracted interfering ions during the stripping operation.
8. Synergic Extraction

Synergism is defined as the combined action of two complexing reagents, which is greater than the sum of the actions of the individual reagents used alone. An example of the synergic extraction of Ce (III) with picrolonic acid and benzo-15-crown-5.

1.2 Introduction to Spectrophotometry

Analysts have developed large number of instrumental techniques and which are extremely sensitive and can yield results rapidly to a high degree of accuracy. Among these instrumental analytical techniques, spectrophotometric technique occupies a unique position, because of its simplicity, sensitivity, accuracy and rapidity. Spectrophotometry is the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength [45]. Spectrophotometric method is the most important for determining metals in alloys, minerals and complexes, owing to its selectivity. In comparison with atomic emission spectroscopy, atomic absorption spectroscopy and similar techniques, offers the advantage of having calibration graphs that are linear over a wider range. A very extensive range of concentration of substances ($10^{-2}$-$10^{-8}$ M) may be covered.

The basis of spectrophotometric methods is the simple relationship between the absorption of radiation by a solution and the concentration of colored species in the solution (Lambert’s-Beer’s law). A molecule or an ion exhibits absorption in the visible or ultra-violet region when the radiation causes an electronic transition in molecules containing one or more chromophoric groups. The color of a molecule may be intensified by substituents called auxochromatic groups, which displace the absorption maxima towards longer wavelength (bathochromic shift). The color determining factors in many molecules is the introduction of conjugated double bonds by means of electron donor or electron acceptor groups [46].

1.2.1 Calibration Curve

The spectrophotometric technique requires the construction of a calibration curve for the constituents being determined. For the purpose, suitable quantities of the constituents are taken and treated in exactly the same way as the sample solution
for development of the color, followed by the measurement of the absorption at the optimum wavelength. The absorbance is then plotted against concentration of the constituents. A straight line is obtained if Beer’s law is followed. This calibration curve may then be used in future determinations of the constituents under the same conditions. The calibration curve needs frequent checking at intervals.

1.2.2 Sensitivity of Spectrophotometric Methods

The sensitivity is often described in terms of the molar absorptivity ($\varepsilon$, Lmol$^{-1}$cm$^{-1}$) of the metal ligand complex. The awareness of the sensitivity is very important in spectrophotometric determination of trace metals. The numerical expression [50-52] is the molar absorptivity (max) of the colored species.

$$\text{Molar absorptivity (}\varepsilon\text{)} = \frac{A}{cl}$$

Sensitivity depends on the monochromaticity of the radiation. With monochromatic light of very narrow bandwidth corresponding to the wavelength of $\lambda_{\text{max}}$, the maximum value of molar absorptivity is obtained.

Savvin [53] suggested a relation between sensitivity and molar absorptivity. He suggested the following criteria for describing the sensitivity.

- Low sensitivity, $\varepsilon < 2 \times 10^4$, Lit. mol$^{-1}$ cm$^{-1}$
- Moderate sensitivity $\varepsilon = 2 - 6 \times 10^4$, Lit. mol$^{-1}$cm$^{-1}$
- High sensitivity $\varepsilon > 6 \times 10^4$, Lit. mol$^{-1}$cm$^{-1}$

It is generally stated [54] that the molar absorptivity will not exceed approximately beyond $10^5$. Other ways of specifying sensitivity are as specific absorptivity [55] or the Sandell’s sensitivity [56]; both methods give the sensitivity in terms of mass of analyte per unit volume of solution. Such an approach is perhaps more convenient than using molar absorptivities as a basis of comparison. The Sandell’s sensitivity is the concentration of the analyte (in $\mu$gmL$^{-1}$) which will give an absorbance of 0.001 in a cell of path length 1 cm and is expressed as $\mu$g cm$^{-2}$. Organic reagents with high molecular weights furnish maximum sensitivity if used as chromogenic agents.
1.3 Aim and objectives of the proposed work

Under the name of PMs (Precious Metals) or noble metals are grouped the six elements of the platinum group of metals, PGMs: ruthenium, rhodium, platinum, palladium, osmium and iridium together with gold and silver [57]. Platinum group metals and gold play an important role in the world economy due to their great inertness in the normal aqueous systems found in everyday life. This property leads to their labelling as “noble metals” and worldwide application in jewellery almost from the beginning of time. Together with an increase in the development of their chemical behavior, an increasing application as catalysts occurred during earlier years for the synthesis of both inorganic and organic chemicals. More recently, their role as catalysts greatly increased in the form of auto catalytic syntheses.

Because of their resistance to corrosion and oxidation, high melting points, electrical conductivity, catalytic activity and biological inertness, these elements have wide applications in chemical, electrical, electronic, glass, medicine and automotive industries [58].

Recently, the emphasis on the removal of platinum group metal ions has led to a considerable growth in the development of new methods in analytical chemistry for extraction, separation, and determination of various metal ions.

The direct determination of the trace metals in solid or a powder sample solution in complicated matrix by spectroscopic methods is often difficult due to their extremely low concentrations and matrix interferences. Therefore, a separation/pre-concentration step is required. Typically, the reason for performing a separation and/or preconcentration step is to bring the concentration of the trace element to a detectable level and/or separate it from interfering substances in the sample matrix. Several preconcentration procedures are available for this purpose, however, most of these are time consuming and costly, but, liquid-liquid extraction method still remains a standard method of separation and preconcentration, because of its simplicity, speed and applicability to both trace and macro-amounts of metal ions. The liquid-liquid extraction (LLE) technique has become increasingly popular in comparison with the other extraction methods because of its several major
advantages, such as (i) simple to operate; (ii) high pre-concentration factor; (iii) rapid phase separation.

Thus far, a large number of extractants have been commercially used in the field of hydrometallurgy. The most important factor in the solvent extraction of metals is high selectivity of the extractant for the recovery of a specified metal. Precious metals are always in association with base metals such as copper, nickel, iron and so on. Furthermore, the separation of individual precious metal is difficult because of the similarity of their chemical properties and chemical species in the chloride media; therefore it is necessary to develop a more effective recovery process for their separation and purification.

Many factors need to be considered in the design of an extractant. For example, apart from both high lipophilicity and chemical stability, extractants should give rise to rapid complexation and decomplexation rates and ideally show selectivity for the metals of interest. Suitable solubility characteristics for use in the chosen two phase system are also necessary. However the most important factor in the solvent extraction of metals is the selectivity of the extractants towards the specified metal ion to be recovered. In order to develop or design highly selective reagents for precious metals, we should take into account the HSAB principle. The term “HSAB principle” which was suggested by R.G. Pearson refers to the rule that “hard acids” prefers to associate with “hard bases”, and “soft acids” prefers to associate with “soft bases” [59-61]. Since the sulphur atom has a high affinity for so-called “soft metals” such as gold, palladium, and ruthenium, a sulphur containing reagent is expected to have a highly selective for these metals. Pearson’s theory has been found to be more selective than cations and anion exchangers. Therefore, the extraction of these metals has become easily possible with enhanced efficiency in comparison to the non sulphur extractants [62-66].

There are several general features which are essential for an extractant, if it has achieved the selective extraction of several metals. These are as follows:

1) To be selective for the required metal.

2) The ability to extract the metal at the desired acidity or pH.
3) Ease of formation of complex with metal of interest and high solubility of metal organic species in the organic phase.

4) Ease of recovery of the metal from the organic phase.

5) It must be stable throughout the principle stages of solvent extraction.

6) It is to be prepared in laboratory in large scale.

7) To have acceptable rates of extraction and stripping.

8) Regeneration of extractant for recycling in economical large scale processes.

9) There is no emulsion formation.

Due to greater selectively of sulphur containing extractants towards the noble metals, a number of sulphur containing extractants have been reported in the literature [67-88], but variety of sulphur containing reagents was still limited. Therefore, we have preferred the sulphur containing ligands for the extraction of platinum group metals. Hence, it is planned to synthesise water repellent sulphur containing extractants which are selective towards the noble metals.

The nature of synthesized extractants is Schiff base. Schiff bases are attractive as analytical reagents because they enable simple and inexpensive determinations of various organic and inorganic substances. In general, there are two principal ways of their analytical applications: first, determination of organic compounds bearing an amino or an active carbonyl group by the formation of coloured (chromophore-containing), fluorescent or insoluble Schiff bases, and secondly, the determination of various metal ions, using complex formation reactions [89]. The analytical methods based on complex formation are used more frequently.

Owing to the relatively simple preparation procedures of Schiff bases, it is possible to obtain ligands of different design and characteristics by selecting appropriate reactants. So far, heteroaromatic Schiff bases have seldom been applied for analytical purposes and show promising properties [90-92].

Due to greater selectively of sulphur containing extractants towards the noble metals and as no substantial work done on the extraction of these metals, it is planned to syntheses water repellent sulphur containing extractants for the effective separation and quantification of noble metals from various alloy, synthetic mixtures, real samples and pharmaceutical samples (Ayurvedic samples).
The present study is focused on the recovery of precious metals with sulphur containing extractants through solvent extraction technique. This subject is of great importance due to the high value and scarcity of precious metals, consequently the need of developing and consolidating the new and effective extractants is necessary.

The summary of different extractants, containing N/S/O/P used for liquid-liquid extractions of many metals from different aqueous solutions is tabulated in Table 1.4.
1.4 Summary of the extractant systems used for solvent extraction

<table>
<thead>
<tr>
<th>Extractants</th>
<th>Metal ion</th>
<th>Diluent</th>
<th>Medium</th>
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<tr>
<td>Benzothiazoyl sulfoxide</td>
<td>Pd(II)</td>
<td>Benzene</td>
<td>HCl [93]</td>
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<td>Triphenyl phosphene oxide</td>
<td>Fe(III)</td>
<td>Acetone</td>
<td>Thiocyanate [94]</td>
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<td>Triphenyl phosphene oxide</td>
<td>Cu(II)</td>
<td>Chloroform</td>
<td>Aqueous Solution [95]</td>
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<td>Glyoxime</td>
<td>Pd(II)</td>
<td>Chloroform</td>
<td>HNO₃ [96]</td>
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<td>Triphenyl phosphene</td>
<td>PGMs</td>
<td>Chloroform</td>
<td>HCl [97]</td>
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<td>1,12-Di-2-Thienyl-2,5,8,11-tetradecane</td>
<td>Pd(II)</td>
<td>Chloroform</td>
<td>Aqua regia [98]</td>
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<td>N,N-Dialkyl-N-benzoyl-thioureas</td>
<td>Pd(II),Au(III)</td>
<td>Chloroform</td>
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<td>Benzo-15-crown-5</td>
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<td>HCl [100]</td>
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<td>2,4-dihydroxyacetophenone</td>
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<td>HCl [101]</td>
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<td>2,4,6-trihydrazinopyrimidine</td>
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<td>Benzene</td>
<td>Acetate Buffer [102]</td>
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<td>p-tert-butylcalix[4]arene</td>
<td>Hg(II)</td>
<td>Chloroform</td>
<td>HCl [103]</td>
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<td>N,N-dimethyl-2,7-dihexyl-3,6-diazoctanic acid diethyl ester</td>
<td>Ag(I)</td>
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<td>Calyx[4]arene</td>
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<td>Sodium malonate pH-10 [107]</td>
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<td>W</td>
<td>Dichloromethane</td>
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<td>Triphenyl phosphene sulphide</td>
<td>Hg(II)</td>
<td>Toluene</td>
<td>pH 5-6 [110]</td>
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<td>Os,Ru(III)</td>
<td>Benzene</td>
<td>HCl [111]</td>
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<td>Tri-n-octyl amine</td>
<td>Te</td>
<td>Xylene</td>
<td>NaI,HClO₄ [112]</td>
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<td>Mixed mineral acids [113]</td>
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<td>Np,Ta,Zr</td>
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<td>Xylene</td>
<td>mineral acids [115]</td>
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<td>Tri-n-octyl amine</td>
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<td>Benzene</td>
<td>HCl or HBr H₂SO₄ [116]</td>
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<td>Orthophosphoric acid [117]</td>
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<td>Mo,W,Cu(II),Ni(II),Co,Mn</td>
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<td>HCl [118]</td>
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<tr>
<td>Alamine336</td>
<td>Zn(II)</td>
<td>Xylene</td>
<td>HCl,HBr [119]</td>
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<td>Alquat336</td>
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<td>Xylene</td>
<td>Chloride [120]</td>
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<td>Alamine336, Alquat336, Amberlite LA-1, Primene JMT</td>
<td>Zn,Cd,Hg,In and Tl</td>
<td>Benzene</td>
<td>NH₄SCN [121]</td>
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<td>Alquat336</td>
<td>Am,Eu</td>
<td>Cychohexane</td>
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<td>U,Np</td>
<td>Xylene</td>
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<td>Al(III)</td>
<td>Chloroform</td>
<td>Tartaric acid Oxalic acid [126]</td>
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<tr>
<td>Aliquot 336</td>
<td>Mn, Ni(II),Co, Cu(II)</td>
<td>Benzene</td>
<td>SCN⁻ [127]</td>
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<td>Aliuat 336</td>
<td>Cd(II)</td>
<td>Benzene</td>
<td>SCN⁻ [128]</td>
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<td>HCl [129]</td>
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<td>-</td>
<td>mineral acids</td>
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<td>CCl₄ HCl ,HBr [135]</td>
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<td>-</td>
<td>Malonate [138]</td>
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<td>Zn(II), Cd(II)</td>
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<td>Mineral acid, Citric acid [139]</td>
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<td>Th(IV)</td>
<td>Benzene</td>
<td>Succinate [140]</td>
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<td>Aliquot 336</td>
<td>Y, Nd</td>
<td>Benzene</td>
<td>Succinate [141]</td>
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<td>Xylene</td>
<td>Malonic acid [143]</td>
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<td>Toluene</td>
<td>H₂SO₄ [144]</td>
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<td>Solvent</td>
<td>Additive</td>
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<td>Chloroform</td>
<td>Tartaric acid, Citric acid [145]</td>
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<td>Nb, Ta</td>
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<td>Tri-n-octyl amine, Tri-iso-octylamine</td>
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<td>Amberlite Al-2</td>
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<td>1,2-Dichloroethane</td>
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<td>N-n-octylaniline</td>
<td>Zn(II), In(III)</td>
<td>Benzene</td>
<td>HCl [154]</td>
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<td>Benzene</td>
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<td>Chloroform</td>
<td>HCl, HBr, HI [156]</td>
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<td>Benzene</td>
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<td>Aliquot336</td>
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<td>Long chain primary amine N octanol</td>
<td>Ir(IV)</td>
<td>Di chloro-ethane</td>
<td>HCl [163]</td>
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<td>Alamine336,Alquat336</td>
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<td>Isodecanol benzene</td>
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<td>Alquat336 or Tri-n-octyl amine hydrochloride</td>
<td>Pd(II)</td>
<td>Chloroform</td>
<td>PH 3-6 [165]</td>
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<td>Benzene</td>
<td>HCl [166]</td>
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<td>Trioctylamine</td>
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<td>Kerosene</td>
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<td>Tetrabutyl 1,3 Xylenedi phospate</td>
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<td>1,2 DCE</td>
<td>HCl [168]</td>
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<tr>
<td>Alamaine 304</td>
<td>Au(III), Pt(IV)</td>
<td>Xylene</td>
<td>HCl [169]</td>
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<td>Crown ether 12-crown-4</td>
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<td>Chloroform</td>
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<td>Cyanex 923</td>
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<td>Sulphate media [171]</td>
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<td>1,3 bis (2-acetoxyethyl thio butyl-3-thiobutylpropyl)-6-methyl uracyl</td>
<td>Au(III)</td>
<td>Chloroform</td>
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<td>p-[4-(3,5-dimethylisoxazolyl) azo phenyl azo] calyx(4)arene</td>
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<td>Ca(II)</td>
<td>Chloroform</td>
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<td>2-hydroxy-5-methyl acetophenone iso nicotinoyl hydrazone</td>
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<td>Chloroform</td>
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<td>1-benzoyl-3-[6-(3-benzoyl-</td>
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<td>1,2 DCE</td>
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<td>Solvent</td>
<td>Additive</td>
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<td>(thioureido)-hexyl thiourea</td>
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<td>MIBK</td>
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<td>Pd(II)</td>
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<td>5-chloro-2-hydroxythio-benzahydrazide</td>
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<td>5-amino-1,2,4 thia diazole derivatives</td>
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<td>1,2 DCE</td>
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<td>Bi(III)</td>
<td>Xylene</td>
<td>H2SO4 [181]</td>
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<td>Chloroform</td>
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<td>Chloroform</td>
<td>HCl &amp; HBr [183]</td>
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<td>2-Octylamino pyridine</td>
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<td>Chloroform</td>
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<td>1-(2,4-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol</td>
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<td>1,2 DCE</td>
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<td>Alamine 336</td>
<td>Ni(II)</td>
<td>Xylene</td>
<td>HCl [186]</td>
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<td>Cyanex 301</td>
<td>Co(II), Ni(II)</td>
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<td>Tris(2 ethylhexyl)amine(TEHA)</td>
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<td>Xylene</td>
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<td>1, 10 Phenanthroline</td>
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<td>Pd(II)</td>
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<td>HCl [190]</td>
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