1.1 Introduction of Separation Science and Technology

Separation is defined as a methodology by which a mixture is resolved into its components and is achieved by using two methods viz. analytical and preparative. In analytical method, one aims at the isolation of the required component in a high degree of purity for quantitative measurements. Separation step is used to only in situations where the component to be quantitatively measured is subject to interference from the goal, one aims at the measurement step. In the preparative goal, one aims at the separation of the component with the degree of purity required for a specific use of the separated component [1].

In the analysis of air for pollutants, for example, some of the compounds may be present in too low concentration to be analyzed straightaway. In such case, it becomes necessary to raise concentration of those compounds to the level where the required analysis becomes practical. The situation of a different type may arise in certain other analysis. Thus, in the analysis of river water for metals that are present in trace concentrations, erroneous results are obtained because of the interference caused in the analysis by organic compound contained in the sample. In a situation like this interfering substance has to be removed before the analysis can be performed. Also, many analyses now carried out daily in the clinical and forensic laboratories all over the world involve separation as an integral part of the procedure [2].

1.2 Basic principle of separation techniques

The basis of most of the techniques which achieve separation and purifications is that they bring about distribution of component of the starting material between two phases. This partitioning is brought about by taking advantage of difference of component in any of their properties like volatility, solubility, adsorption on a suitable solid material, molecular size etc. In the process of separation, one of the two phases gets considerably enriched in respect of one component, and the other phase in respect of the second
component of starting mixture. The respective distributed components are subsequently recovered from the two phases by using appropriate procedures. In some separation method chemical reaction are required to convert or modify a component of mixture to from which either constitutes a new phase or enable the substance to be distributed to second phase [2].

1.3 Important separation techniques

1.3.1 Crystallization

Crystallization is the simple but old method of purifying solids. Because of the effectiveness of the method, crystallization finds extensive use for the purification of solids. Appreciable difference of solubility of given solid in a suitable solvent at the boiling point and at room temperature is the basis of this purification technique. The amount of impurities present in the solid is of course, much less than that of the principal substance and it is unlikely that they will saturate the solution at room temperature. Therefore, these impurities remain in the mother liquor in the end [2].

1.3.2 Precipitation

Precipitation method is the simplest method used for the separation and extensively in gravimetric analysis. Precipitation is a reaction in which positive ion of one substance combines with negative ion of other substance or with organic precipitant in solution to form sparingly soluble substance. Precipitation can be done either by chemical or by physical method.

1.3.3 Sublimation

Sublimation is the phenomenon by which a solid converts directly to the vapor phase on heating and the change in phase get reversed on cooling. Substance like camphor, naphthalene and anthraquinone having appreciable vapor pressure in the solid state can be freed from less volatile impurities by sublimation.
1.3.4 Solvent extraction

Solvent extraction is a method in which solute distributed in between two phases which are immiscible in each other. This method is extensively used for the separation and purification of metal ions as well as organic compounds. The most interested fundamental research areas now under investigation by solvent extraction chemists and chemical engineers involved in the study of interfacial phenomena, the development of new reagents with higher capacity and greater selectivity, the improvement of pharmaceutical and biological extraction processes, mathematical modeling of extraction processes, and make superior designs for solvent extraction equipment [1, 2].

1.3.5 Ion exchange

As, its name suggest ion exchange chromatography is used for the separation of ionic substances, which range from simple organic and inorganic ion. Separation of inorganic mixtures, especially, metal with similar characteristics, e.g. lanthanides, is among the important application of technique [2]. To the degree that an ion-exchange resins may be considered a solvent extraction reagent immobilized on a solid phase, the both techniques have shared many common research needs and interest [3, 5-6].

1.3.6 Membrane separations

The development of superior membrane separation is an energetic area of research. The majority applications have concerned the processing of aqueous streams. Applications to non aqueous solutions, gaseous systems, and gas-liquid systems are hopeful but comparatively undeveloped. A number of general chemical principles are involved in several solvent extraction, ion-exchange, chromatographic, and membrane processes, and collaboration between workers in these fields will be in the progress of each method, significantly investigated areas, incorporate interfacial and transport phenomena, novel carrier reagents, superior mathematical models, an extended
data base, and the improvement of inorganic and biological membrane materials[3,7].

1.3.7 Chromatography

Nowadays chromatography has a wide popularity amongst all the separation methods due to its simplicity, reliability, accuracy and efficiency. Chromatography is a comparatively simple method of separating a desired compound from its impurities, or of isolating individual component of a mixture. Apart from the high selectivity in separation shown by the technique, one other important advantage of chromatography is that it involves mild experiment conditions as for example; it can be generally carried out at room temperature.

Chromatography now refers to any of diverse group of techniques that effect a separation through a distribution of sample between two immiscible phases. The requirement to distinguish chromatography from other separation technique is that one phase is stationary while the second phase is mobile and percolating through the first phase resulting in selective retention of the components of a mixture by the stationary phase. The stationary phase, which may be solid or liquid or may be consist of mixture of solid and liquid or gaseous, fills the interstices of the stationary phase and is able to flow through the stationary phase [2].

The chromatographic equipment will require advances in the accuracy of models for large-scale operation, as well as novel support materials and equipment design. The improvement of laboratory scale chromatography continues across toward at a remarkable rate [8].

1.3.8 Distillation

Distillation is the most generally used separation technique. The process of converting a liquid into vapor and subsequently collecting it as liquid by condensation of the vapor is known as distillation. This operation is employed to separate a liquid from non-volatile impurities or to separate the various
constituents of mixture of liquid boiling at different temperatures. Amongst the numerous industrial application of distillation, an interesting example is that of purification of metal like zinc, cadmium, mercury and bismuth, which have comparatively low melting point and boiling point and leave behind impurities in the retorts when subjected to distillation [2].

1.3.9 Supercritical fluid extraction

Rapid and efficient separation of non volatile solutes can be carried out using capillary column in conjunction with supercritical fluids. Supercritical fluid constitute mobile phase that have intermediate viscosities and solutes diffusivities between those of liquid and gases. Thus, compared to HPLC, the present technique gives higher mobile phase liner velocities and better separation efficiencies per unit time. Further, fluid compressed to their critical point and above exhibit an extraction effect on chromatographic sample similar to salvation in HPLC. Therefore, supercritical fluid chromatography should provide superior migration of labile and less volatile substance through a capillary column, when compared to GC [2].

The employ of supercritical fluid extraction processes is attracting greater interest for some applications. Because of prospective advantages such as lower energy costs, ease of solvent recovery, faster kinetics, superior process control, and high separation factors. Limitation include the need to operate some processes at high temperature and pressure, which leads to increased capital costs, safety hazards, and increased energy expenditure. Recent applications of supercritical fluid extractions are few, and advance development has been hindered by the lack of theoretical models and thermodynamic and kinetic data in these systems [10].

1.3.10 Photon-enhanced separations

The type of photon-enhanced separations includes some separation process in which light is used as an imperative ingredient of the separation process. Examples incorporate laser isotope separations (LIS) and the employ
of photochemical redox reactions to control oxidation states, and thus separation factors, in solvent extraction systems. LIS techniques have been developed principally for the enrichment of uranium, but their application to the purification of stable and medical isotopes should be explored more widely [11].

1.3.11 Electrophoresis

Electrophoresis involves the movement of a colloidal or dissolved substance relative to a buffer solution as result of an applied field. This leads to migration of particles ions towards electrode depending on effective charge of the particles. The term electrophoresis is used with reference to the physical transport of charged solutes through the paper under the influence of potential gradient. This method is useful for the separation of variety of samples like metal ions, DNA, amino acids, proteins, peptides, nucleic acids, biopolymers and biological macromolecules [13].

1.3.12 Electromagnetic separations

In this account, the term electromagnetic separation refers to mass spectrometry (MS) and its variations. It is accepted that methods such as electrophoresis, electro-dialysis, electrostatic precipitation and the electromagnetic separation of metals from refuse could be incorporated under this title. Conversely, resonance ion mass spectrometry (RIMS), which is one of the most exciting MS techniques currently under wide investigation, can also be classified as a photon-enhanced separation technique. Electromagnetic separation is applied almost wholly on the analytical scale, where it has suit an increasingly multifaceted and useful tool for chemical investigation at the molecular level. Mass spectrometry, particularly when X shared with other separation methods to form the so-called hyphenated techniques (GC/MS, LC/MS etc.), has become the leading technique for separation, identification, and structure determination of the small (microgram) scale. The practical range
of M S has been extended to molecular weights approaching 10,000, important to increased application in the biological sciences [12].

1.3.13 Counter-current distribution

The counter–current distribution method is predominantly used for the separation of complex mixture of organic substances. Separations are achieved under very mild conditions thus the method is ideally suited for handling materials whose stability is sensitive to experimental conditions employed during their separation. No material is wasted, and all material put into a distribution machine can be recovered. It is not successful with compounds of limited solubility with salt or other strongly polar compounds with staturated hydrocarbons.

1.4 Applications

1.4.1 Nuclear fuel reprocessing

Research to concentrate on definite problems in existing Purex plants is required, especially in the area of waste management and disposal. The long-standing research should be focused on the development of fundamentally different separations processes, such as pyrochemical and volatilization methods [3].

1.4.2 Trans-uranium processing

Trans-uranium processing plant (TRU) has been operating for almost twenty years. If there is a requirement for much increased quantities of $^{252}$Cf, completely reduced working costs, or a second high-flux isotope reactor (HFIR) is realized, an extensively improved process for separating and purifying the trans-uranium (TRU) elements from HFIR targets will be require. A novel method based on better aqueous or pyrochemical flow sheets illustrate surety for this application [3].
1.4.3 Analytical separations

Various advanced changes in separation technology come about as a direct result of methods discovered in analytical laboratories, and the progress in generalized models and techniques for the methodical transfer of separation technology from analytical applications to industrial applications could result in the application of dramatically superior methods in different cases. The rising pressure to conclude lower and lower concentrations of chemical species in the environment, food, pharmaceuticals, forensic samples, special materials for the electronics, nuclear, and other industries has led to the improvement of significantly superior analytical techniques. These novel techniques often require the separation and pre-concentration of the species of importance from a multifaceted matrix. The growth of high-resolution techniques to separate and analyze the components of complex biological fluids is a challenging, high-priority area with great assurance for the better detection, diagnosis, and treatment of disease [3].

1.4.4 Ultra purification

Ultrafiltration is a separation process by membranes with pore size in the range of 0.1 to 0.001 micron. In general, ultrafiltration membrane will remove high molecular weight substances, colloidal materials, organic and inorganic polymeric molecules. Low molecular weight organic and ions such as sodium, calcium, magnesium, chloride and sulfate are not easily isolated by ultrafiltration membranes. Because only high-molecular weight species are removed the osmotic pressure difference across the ultrafiltration membrane surface is negligible. The low applied pressures are therefore sufficient to attain high flux rates from ultrafiltration membranes of surface permit time. Flux of membrane is defined as the amount permeates produced per unit area of membrane [14]. The demand of current science, technology, and society for materials, foodstuffs, environments and pharmaceuticals of unique purity will continue and accelerate. The produce and analysis of such materials will, in
turn, continue to be a major driving force for the development of improved separation techniques of all kinds [3].

1.4.5 Toxic wastes separation

The problems presented by the hazardous materials waste that have been, or are being, discharged to the environment are formidable and the solutions to such problems will challenge the limits of separation science and technology on all fronts. While considerable progress has been made by the application of improved separation techniques to environmental safety, the limits of the achievement of these processes also mark the starting point for research and development for improved methods. The methodical improvement and application of all separation technologies are required to reduce the volume of hazardous and radioactive wastes to be treated, to clean up existing waste dumps and to meet the increasingly stringent regulations for handling and disposing of hazardous and radioactive materials. The successful development and application of these technologies will essential an unique degree of co-operation between separation scientists and engineers from all of the disciplines that make up the field, as well as among analytical chemists, toxicologists, environmental chemists and regulatory agencies [3].

1.4.6 Biotechnology

Biotechnology is the use of biological processes, organisms, or systems to manufacture products intended to change the quality of human life. The current biotechnologists were farmers who developed improved species of plants and animals by cross polarization or cross breeding. In recent years, biotechnology has expanded in sophistication, scope and applicability [15].

The continued progress in biotechnology depends heavily on progress in separation science, while developments in biotechnology have led to vital developments in separation science. The separation of homogeneous, functionally specific populations of cells is one of the chief obstacles to progress in biotechnology. The separation and purification of the desired
components from fermentation broths in an efficient, economic way are major challenges to separation science. On the other hand, the development of improved separation agents based on biological enzyme-substrate models, the development of improved membranes based on the structure of biological membranes, and the utilize of genetically engineered microbes to degrade hazardous material in the environment are outstanding examples of the application of biotechnology to separation science[3].

1.4.7 Acid precipitation

The improvement of better methods for separating toxic and hazardous materials from the solid, gaseous and liquid wastes generated by the burning of fossil fuels will involve an integrated, systems approach to treatment across the complete fuel utilization cycle. Processes for the treatment of natural gas come into view to be adequate, but improvement methods for treating oil will probably be desired as regulations become more strictly [3].

1.5 Introduction solvent extraction

Solvent extraction is most prominent method in separation science and hydrometallurgy, because it is most simple, fast, selective and sensitive separation method [16-17]. Solvent extraction is carried out using only simple separating funnel and do not require any sophisticated instrument. The operation of equilibrium is possible in minimum time even by shaking. It is applying for isolation and purification of compounds, either inorganic material or organic substances trace and macro level concentrations [18]. The technique had not only fascinated chemists, no matter whether they are analytical, inorganic, physical but also chemical engineers and technologists. Several plot plant scale process, for the recovery of copper, zinc and iron are operation in Europe.

The solvent is liquid state and substance is generally organic, it is practically immiscible with other liquid (i.e. aqueous phase) which has potentially able to resolving substance or metal species at certain level. An
extractant is a substance with solvent properties used in solution in suitable diluents. The solute species chemically react with extractant by solvation, chelation, ion-pairing, ion exchange to separation from second phase. The physical properties of extractant better with solvent as compare to only extractant itself. Therefore, extractant and diluents both combine to act as a solvent [19].

The properties of the organic solvent is immiscible a dissolved solute species electrically neutral. Such properties are useful by separation and purification of solutes either by extraction into the organic phase. (e.g., the majority organic compounds) are called as lipophilic (liking fat) or hydrophobic (disliking water), even as the species that prefer water (e.g., electrolytes) are called as hydrophilic (liking water), or lipophobic (disliking fat). Since of this, a hydrophilic inorganic solute must be delivered hydrophobic and lipophilic in order to enter the organic phase [20].

Since last four decades the solvent extraction methods have made great strides. It has published so many monographs [21-25]. Dealing with various aspects of solvent extraction, some of them put emphasis on the theory of chelates extraction [22-25], while others have dwelt on rigorous treatment of extraction equilibriums [24-25] or on the mechanism of extraction. Few of them have ramification with aspects of solvent extraction [21-22]. The chemical engineering aspects pertaining to design and development have been covered by worthwhile monographs [27-29]. The handbook [30] of solvent extraction is an excellent source of information on all aspects of the extraction.

The modern chemistry of supramolecules in solvent extraction is very well covered in recent research monographs [30] by the author. An account of various separation methods [32-36] like chromatography, reversed osmosis, electrophoresis, and dialysis are available in the monographs [16,37-43]. They indicate how an excellent instrumental method of analysis can be used if supplemented by an efficient separation technique.
1.5.1 Basic Principals of solvent extraction

The solvent extraction methods are based on the four basic principals

a) Gibb’s phase rule
b) Distribution ratio (D)
c) Partition coefficient (P)
d) Percentage of extraction

a) Gibb’s phase rule

For all phase distribution the classical Gibb’s phase rule is

\[ P + V = C + 2 \]  \hspace{1cm} (1)

Where,
P = number of phases
C = number of components
V = degrees of freedom.

In solvent extraction we have two phase aqueous and organic phases. Component is \( c = 1 \) solute in solvent and water phases. At constant pressure and temperature the value of \( V = 1 \) i.e. \( P + V = C + 2, \hspace{0.5cm} 2 + 1 = 1 + 2 \) [15].

b) Distribution ratio (D)

The general principle for the distribution of a molecular species, the distribution law, was presented by Berthelot [44] and systematized thermodynamically by Nernst [45]. The distribution law stated that a solute will be distribute between two essentially immiscible solvent in such a manner that, at equilibrium, the ratio of the concentration of the solute in the two phase at a particular temperature will be a constant provided the solute has same molecular weight in each phase.

Distribution ratio can be defined as it is the ratio of concentration of metal in the organic phase to the concentration of metal in metal in the aqueous phase [15].

For a given metal M, present as various species \( M_1, M_2 \ldots \) \( M_i \), and partitioned between an organic and aqueous phase, the extraction can be defined in the following terms and the distribution ratio (D) can be written
as,

\[ D = \frac{\text{Total concentration of metal in the organic phase}}{\text{Total concentration of metal in the aqueous phase}} \]

\[ D = \frac{[M]_{\text{org.}}}{[M]_{\text{aq.}}} \]

c) Partition coefficient (P)

The partition coefficient is independent of the total quantity of partitioned solute in the two phases, it is a true constant. For a single species over the range for which the activity coefficients in the two phases are identical, then the Nernst partition isotherm is validation. In other words under indistinguishable conditions where the solute exists in the same form in both phases, the phase are entirely immiscible, there is no interactions between solute and solvent and association or dissociation reactions do not occur, the terms extraction coefficient and partition coefficient becomes equivalent [16].

d) Percentage of extraction (%E)

The quantitatively percentage of extraction is practical importance in the reported extraction. It is used for the percentage extraction (%E). The percentage extraction is related to distribution ratio (D) by an expression

\[ %E = \frac{100D}{D + (V_w/V_o)} \]  

\[ D = \frac{(V_w/V_o) \times %E}{100 - %E} \]

Where,

\[ V_w = \text{Volume of aqueous phase} \]
\[ V_o = \text{Volume of organic phase} \]
\[ % E = \text{Percentage extraction} \]

When the volume of organic and aqueous phases is equal, then the relation
between percentage extraction and distribution ratio can be written as

\[ D = \frac{\% E}{100 - \% E} \quad \ldots \ldots \text{(4)} \]

If the extraction is near to 100 % then the distribution ratio nearby infinity [16].

1.6 Classification of solvent extraction systems

Extractions are classified on the basis of nature extractant species and process of extraction.

I] Nature of extracted species

II] Process of extraction

I] Nature of extracted species

(a) Chelate extraction

(b) Ion association

II] Process of extraction

(a) Extraction by chelation or Chelate formation

(b) Extraction by ion pair formation

(c) Extraction by solvation

(d) Synergistic extraction

Now a day’s extraction based on the process of extraction is widely used and it is explained as follows.

1.6.1 Extraction by chelation or chelate formation

Chelating ligand may play an important role in extraction of metal. The substance which brings about chelation is called as chelating agent. 

\[
\text{Metal ion} + \text{chelating agent} \xrightarrow{\text{Metal chelate}}
\]

eg. The chelates are classified according to the type of basic group present. If both the basic groups are uncharged it results into a positively charged metal chelate. However, if the reagent has one anionic group, a neutral chelate is formed while multiple negative charges on chelating agent results
in negative charged chelates. The neutral chelates are easily extracted in organic solvent [18].

1.6.2 Extraction by Ion pair formation

The extraction will proceed with formation of a neutral uncharged species, which is extracted into organic phase. Most of the high molecular weight amines or so called liquid ion exchanger comes under this group. The mechanism of extraction by ion pair formation can be described as follows.

\[ R_3N_{\text{org}} + H^+_{\text{aq}} + A^-_{\text{aq}} \rightleftharpoons R_3NH^+A^-_{\text{org}} \text{ (Extraction)} \]

\[ R_3NH^+A^-_{\text{org}} + B^+_{\text{aq}} \rightleftharpoons R_3NH^+A^-_{\text{org}} + A^-_{\text{aq}} \]

Best separations are possible with good diluents. The control of temperature and activity is most important in accomplishing quantitative separations. In ion pair, extraction the metal may be incorporated with by co-ordination in either the cation or anion of the extractable ion pair [18].

1.6.3 Extraction by solvation

The solute molecules are associated with the solvent molecules this is known as solvation. In extraction by solvation solvent molecules are directly involved in formation of the ion association complex. The value of ion pair formation constant (K) is related to dielectric constant and temperature.

\[ D = \frac{4\Pi Ne^2Q(b)}{1000\epsilon K_T} \quad \text{............... (5)} \]

\[ b = \frac{e^2}{a\epsilon K_T} \quad \text{............... (6)} \]

Where,

\[ N = \text{Avogadro’s number} \quad K_T = \text{Boltzmann’s constant} \]
Q (b) = Calculable function  \( a = \) empirical parameter
\( \varepsilon = \) dielectric constant

In case of solvent extraction, the solvent itself participates in extraction of complex. E.g. Extraction of Fe\(^{3+}\) from 5.5 M HCl by diethyl ester

\[
\text{FeCl}_3 + \text{HCl} \rightarrow \text{H} + \text{FeCl}_4^- \rightarrow \text{H}_3\text{O}^+\text{FeCl}_4^-
\]

In case of extraction by solvation the extracted species is solvated with a definite number of solvent molecules and provided that the solvent must be inert [18].

### 1.6.4 Synergistic extraction

This process of extraction involves two extractants i.e. chelating ligand and solvating solvent. Following conditions is necessary for extractions in synergistic extraction.

I. The chelating ligand HX should neutralize the metal charge by chelation.

II. The solvent should co-ordinates less strongly than chelating ligand.

III. The solvent should displace any residual co-ordinate water from the neutral metal complex, rendering it less hydrophilic.

IV. The maximum co-ordination number of the metal and geometry of the ligand should be favorable.

E.g. Extraction of uranyl ion by tributyl phosphate (TBP) and thinly trifluoroacetate (HTTA).

\[
\text{UO}_2^{2+} + 2\text{HTTA} \rightarrow \text{UO}_2(\text{TTA})_2 + 2\text{H}^+
\]

\[
\text{UO}_2(\text{TTA})_2 + \text{TBP} \rightarrow [\text{UO}_2(\text{TTA})_2 \text{TBP}] \text{ (Adduct)}
\]

Due to adduct formation the extraction efficiency of uranyl ion by HTTA in the presence of TBP increases this is called as synergism [15].
1.7 Method of extraction

This is generally accomplished by selective transferring the material from one phase in which it is dissolved or dispersed in another liquid phase, although it is sometimes possible to selectively extract interfering element and leave the material of interest in the original phase. In liquid–liquid extraction is commonly using three methods of extraction. This method is namely batch extraction, continuous extraction, discontinuous counter current distribution, extraction, respectively [17].

1.7.1 Batch extraction

In this batch extraction method solute volume is touched with solvent volume until equilibrium is attained, then formation of two layers easily separation done. This is useful for any analytical separations purpose.

This is a simple extraction procedure possible and it is also the beginning or investigative operation employ in the study of unknown systems. Then it is designed to yield the quantitative distribution information which will give out as a guide in the final choice of the extraction method. The batch extraction is significance role, if the distribution ratio is large, in such cases a few extraction will effect quantitative separation achieve [17].

1.7.2 Continuous extraction

In this method, make use of a continuous immiscible solvent through the solution or continuous countercurrent flow of both phases. In continuous extraction the used up solvent isstriped and recycled by distillation, or fresh solvent is added continuously from a reservoir. This is the method a predominantly applicable at distribution ratio is comparatively small; therefore a large number of batch extraction would normally be necessary to effect quantitative separation achieve [17].
1.7.3 **Countercurrent distribution extraction**

This is the method used for fractional purposes. It is the third general type extraction and involves the employ of series of separating funnel or more sophisticated touching the vessel to achieve a lot of individual extraction speedily in series. It is used to great benefit for separating materials for isolation or purification purpose, so it is also used wide in engineering problem [17].

1.8 **Techniques in extraction**

1) Choice of solvent
2) Stripping reagent
3) Back stripping
4) Treatment of emulsions
5) Variation of oxidation state
6) Use of masking agents
7) Use of salting out agents

**1) Choice of solvent**

The solvent is significant role in solvent extraction method. The extracting solvent is to use organic diluents. The selective solvent has been particularly extractive ability. The ionic substances are less insoluble in organic solvents than water. The neutral substances are less soluble in water than solvents. The solubility of solute in a particular solvent, the simple recover of the solute from solvent intrinsic for subsequent analytical processing. The solvent has a low boiling point with the ease of stripping by a chemical reagent go into the solvent. The according to green approach solvent is necessary less toxicity, inflammability of organic solvent. The different organic compound like kerosene, xylene, and other hydrocarbon are used as to dilute the extractant [17].

**2) Stripping reagent**

The strippant is a chemical reagent; it has potential to removal of the
extracted solute substance from the organic phase. The extracting solvent is non-volatile and then solute to strip from the organic solvent by chemical means, generally procedure being to shake the solvent with a volume of water contains acid or another reagent employs that condition solute extractable complex is destroyed. The quantitatively back extractions of metal ion in stripping aqueous phase [17].

3) **Batch extraction**

An addition technique assists in batch extractions as result quantitatively recovery of element or solute is that of back washing. When was using combine organic phase for various extraction that time original aqueous phase contain impurities remaining organics phase small extent, which is depending relative distribution ratio. This is combined organic phase shake with one or more small portion of a fresh aqueous phase containing the optimum reagent concentration, salting out agent. The bulk of the impurities, back-extracted to the fresh aqueous phase because their least distribution ratios. This technique is correspondent in many respect to re-precipitation removed impurities can be isolated by back washing operation [17].

4) **Treatment of emulsions**

By mixing immiscible liquids, after that shaking up may result may be possible one liquid is dispersed in a continuously of the other. From the point of outlook of liquid–liquid extraction, the stability of the dispersion is its most significant property because, it is essential to separate the phase for further steps in the analytical procedure. For an emulsion to break or separate into its phase, both sedimentation and coalescence of the droplets of the dispersed phase necessity occur [17].

5) **Variation of oxidation state**

A helpful method to increase the selectivity of an extraction, it involves change of the oxidation states of the ions present in the solution in order to
avoid the formation of a metal complex essential for extraction. Thus the extraction of iron from chloride solution can be prohibited by reduction of iron (II), which does not extract [17].

6) Use of masking agents

The masking agent itself acts as metal-complexing agent, which serve to avoid particular metals from taking part in their usual reactions and therefore remove their inference without the requirement of a real separation. Because the masked metal must remain in solution, the complex surely must be water soluble. For this reason, we find that masking agent give rise to charged complex. The masking agents are used to avoid definite metal from forming extractable complexes in solvent extraction. Therefore, greatly increases the selectivity of the extraction methods in which masking agents are used for EDTA, cyanide, tartrate etc [17].

7) Use of salting out agents

This technique employs then given impressive result, as well as the enhancement of extraction of metal. Particularly in the oxonium type of extraction, it is slating–out agents. The addition of inorganic salts to the aqueous increase the distribution ratio of metal complexes may be in favor of the extracting phase.

The magnitude of improvement of extraction by addition of a salt depends on the both the charge and ionic size of the added cation for a given anion. When performing a batch extraction strong salting-out agent should be used to minimize the extraction impurities [17].

1.9 Theory of spectrophotometry

The basis of the spectrophotometric method is the simple relationship between the absorption of radiation by a solution and the concentration of coloured species in the solution. In order to determine a species
spectrometrically it is usually converted into a coloured complex.

Spectrometric methods are remarkable for their versatility, sensitivity and precision. Almost all the element except noble gases can be determined directly. A very extensive range of concentration from macro quantities (1-50%) to trace ($10^{-8}$-$10^{-6}$%) may be covered. Spectrophotometric methods are among the most precise instrumental a methods of analysis.

Visible light represents a very small part of the electromagnetic spectrum and generally considered to extend from 380-780 nm. A solution appears coloured when it transmits or absorption only part of radiation in visible spectrum. The optical characteristic of the substance is its absorption spectrum. There is a close relation between the colour of a substance and it electronic structure [46].

Theory of spectrophotometry which is helpful in the quantitative analysis of samples is very well explained [29]. When monochromatic light is incident upon a homogeneous medium, then the intensity of the incident light is expressed by $I_0$, that of the absorbed light by $I_a$, that of the transmitted light by $I_t$, and that of the reflected light by $I_r$, then

$$I_0 = I_a + I_t + I_r \quad \text{............... (7)}$$

For air-glass interfaces consequent upon the use of glass cells, it may be stated that about 4% of the incident light is reflected. Therefore measurements are always made with respect to reference solution in a similar cell (cuvette). $I_r$ is usually regarded as constant and neglected.

$$I_0 = I_a + I_t \quad \text{............... (8)}$$

Lambert (1760) investigated the relation between $I_0$ and $I_t$. Beer (1852) extended the experiments to solutions. Spectrophotometry and colorimetry are based upon Lambert’s and Beer’s laws [47]
Chapter I

Introduction of Separation Science and Technology

Analytical and Environmental Research Laboratory

Figure 1.1 Basic Structure of Spectrophotometer

a) Lambert’s laws

This law states that when monochromatic light passes through a transparent medium, the rate of decrease of intensity with the thickness of the medium is directly proportional to the intensity of the light. Mathematically the Lambert’s law may be stated as follow.

\[ KI = \frac{dI}{dt} \]  \hspace{1cm} (9)

Where, I is the intensity of the incident light of wavelength \( \lambda \), t is the thickness of the medium, and k is the proportionality factor. Integrating (4) and putting, \( I = I_0 \) when \( t = 0 \), we obtain,

\[ \ln \frac{I_0}{I_t} = kt \]  \hspace{1cm} (10)

Or stated in other terms

\[ I_t = I_0 e^{-kt} \]  \hspace{1cm} (11)

Where, \( I_0 \) is the intensity of the incident light falling upon an absorbing medium of thickness t, \( I_t \) is the intensity of the transmitted light, and k is a constant called the absorption coefficient for the wavelength and the absorbing medium used. On changing the equation (4) from natural to common logarithms, we get

\[ I_t = I_0 \cdot 10^{-0.4343 \cdot kt} = I_0 \cdot 10^{-kt} \]  \hspace{1cm} (12)
Where, $K = k / 2.3026$ and is usually termed the absorption coefficient [44].

**b) Beer’s law**

The light absorption and the light transmission for monochromatic light as a function of the thickness of the absorbing layer only. In quantitative analysis, however, it is concerned with solutions. Beer (1852) studied the effect of concentration of the coloured constituent in solution upon the light transmission or absorption. He found the same relation between transmission and concentration as Lambert had discovered between transmission and thickness of the layer equation (4), i.e. the intensity of a beam of monochromatic light decreases exponentially as the concentration of the absorbing substance increases arithmetically. This may be written in the Form,

$$I = I_0 e^{-kt} = I_0 10^{-0.434kc} = I_0 10^{-kc} \quad \text{……………….. (13)}$$

Where, $c$ is the concentration of the absorbing substance, and $k$ and $K$ are constants.

Combining equation no (5) and (6),

We get,

$$I = I_0 10^{-c\varepsilon} \quad \text{……………….. (14)}$$

Or

$$\log \frac{I_0}{I} = \varepsilon c t \quad \text{……………….. (15)}$$

This is the fundamental equation of colorimetry and spectrophotometry, and is often spoken of as the Beer-Lambert Law. The value of $\varepsilon$ will clearly depend upon the method of expression of the concentration. If $(c)$ is expressed in gram moles per liter and $(t)$ in centimeters then, $(\varepsilon)$ is the molar extinction coefficient (also termed molar absorbtivity or molar absorbency index). The latter is equal to the reciprocal value of the thickness in centimeters of a 1 molar solution $(c = 1)$ at which
It = 0.1 I_o, since It = I_o \cdot 10^{-\epsilon} \text{ when, } t = 1 \text{ and } c = 1.

1.9.1 Deviation from Beer’s law

From Beer’s law, it follows that, if we plot absorbance (A) against concentration (C), a straight line passing through the origin should be obtained. But there is usually a deviation from a linear relationship between concentration and absorbance and an apparent failure of Beer’s law may ensure. Deviations from the law are reported as positive or negative according to whether the resultant curve is concave upwards or concave downward.

Deviations from the law can arise due to the following factors

1. The Beer’s law will hold over a wide range of concentration provided the structure of the coloured ion or of the coloured non-electrolyte in the dissolved state does not change with concentration. If a coloured solution is having a foreign substance whose ions do not react chemically with the coloured components, its small concentration does not affect the light absorption whereas its large concentration may affect light absorption and may also alter the value of the extinction coefficient.

2. Deviation may also occur if the coloured solute ionizes, dissociates or associates in solution.

3. Deviation may also occur due to the presence of impurities that fluoresce or absorb at the absorption wavelength. This interference introduces an error in the measurement of absorbance of radiation penetrating the sample.

4. Deviations may occur if monochromatic light is not used.

5. Deviations may occur if the width of the slit is not proper and, therefore, it allows undesirable radiations to fall on the detector. These undesirable radiations might be absorbed by impurities present in the sample which would cause an apparent change in the absorbance of the sample. The magnitude of this deviation becomes
appreciable at higher concentrations.

6. Deviation may occur if the solution species undergo polymerization.

7. The Beer’s law cannot be applied to suspensions but the latter can be estimated colorimetrically after preparing a reference curve of known concentration [44].

1.10 Experimental setup and instruments

Separating funnels for batch extraction, special glass apparatus for continuous extraction, automatic shakers used for discontinuous counter-current distribution. The instruments required for the whole solvent extraction and determination process are very simple like, separating funnels, digital.

![Digital pH meter](image1)

![Separating Funnel](image2)

![Digital Flame photometer](image3)

![Spectrophotometer](image4)

**Figure1.2** Experimental Setup and Instruments.
References

Chapter I  

Introduction of Separation Science and Technology


43. Starry J., the Solvent Extraction of Metal Chelates, London (1964).


