1.1 INTRODUCTION

The foundations of quantitative chemical analysis can be traced back to the development of titrimetric analysis in which titrations end-points depended on the change in colour of the species being analyzed or of that of a specially added chemical indicator. These colour changes arise due to molecular and structural changes in the substances being examined, leading to changes in the ability to absorb light in the visible region of the electromagnetic spectrum. In various ways absorption spectroscopy in the visible region has long been an important tool to the analyst. Many important and sensitive colour tests have been developed for the detection and determination of a wide range of chemical species, both inorganic and organic in nature, and were used long before the development of visible and ultraviolet spectrometers.

Today, ultraviolet UV-visible spectroscopy is applied to many thousands of determinations which have been developed over the years. It has proved particularly useful in biochemical analysis, and is of vital importance in the clinical laboratory attached to most modern hospitals where various components of blood and/or urine samples, in particular, are determined and monitored on a twenty-four-hour basis. It plays a part in environmental studies of pollutants, in forensic-science work on drugs, and in maintaining the quality of the food that we eat. In all of these areas uv-visible spectroscopy is an essential tool in the identification and quantification of a very broad range of chemical and biological substances. The equipment for these purposes ranges from very simple colour comparators through to large computer-controlled automatic scanning instruments, which cover the whole of the uv-visible region of the electromagnetic spectrum. In all instances, however, these studies involve measurement of radiation intensity at the spectral wavelengths which are characteristic of the substances under investigation.
1.2 The Electromagnetic Spectrum

Electromagnetic radiation is a type of energy that is transmitted through space at enormous velocities. It takes many forms; light is the most easily recognized, but it also includes X-rays, and ultraviolet, radio and microwave radiation. In order to characterize many of the properties of electromagnetic radiation it is necessary to ascribe the wave nature to its propagation. The various types of radiation can then be defined in terms of their wavelengths or frequencies. The wavelength, $\lambda$, is defined as the linear distance between successive maxima or minima of a wave, and the frequency, $v$, as the number of waves per second. The unit of frequency is usually the hertz (Hz), which is equivalent to one cycle per second. Multiplication of the wavelength (in meters per cycle) by the frequency (in Hz) gives the velocity of the radiation (in meters per second) as follows:

$$c = v \lambda$$

Where $c$ is the velocity of light in a vacuum and the numerical value $3 \times 10^8$ ms$^{-1}$. It is therefore possible to calculate the wavelength of radiation, given its frequency and vice versa, so that:

$$\lambda = \frac{\text{velocity of light (} c \text{) }}{\text{frequency (} v \text{) }}$$

Another expression which is very important in all forms of spectroscopy relates the frequency of the electromagnetic radiation to its energy. The energy (in joules, J) is proportional to the frequency of the radiation as follows:

$$E = h v$$

where $h$ is a constant, known as the Planck constant. It has the numerical value $6.624 \times 10^{-34}$ J s.

The electromagnetic spectrum covers an immense range of wavelength or energies. The visible region of the electromagnetic spectrum is defined in terms of the wavelength range to which the human eye responds. The usual range of wavelength quoted is from 380 nm at the blue/violet end to 750 nm at the long...
wavelength, i.e. red end of the spectrum. Some sources, however, quote wavelengths down to 360 nm as the short-wavelength limit and as high as 780 nm as the long-wavelength limit. The ultraviolet region extends from about 380 to 100 nm. Below 200 nm, however, oxygen in the air makes it difficult to record the absorption of the ‘accessible ultraviolet’ region is usually taken to be from 200 to 400 nm. The lower limit is determined mainly by instrumental factors, such as the lack of detector sensitivity, and the reduced transmittance of radiation by the optical components, as well as the increased absorption of radiation by common solvents at low wavelengths.

The wavelength of the electromagnetic radiation decreases its energy increases, and so red light is at the low-energy end of the visible spectrum and blue light is at the high-energy end.

The visible and the accessible part of the ultraviolet region covering the total wavelength range from about 200 to 800 nm.

1.3 **Advantages:**
(a) Colorimetric methods are usually rapid in comparison with volumetric and gravimetric methods.
(b) Often they require a minimum of sample preparation, with sometimes only dissolution and colour development.
(c) Usually only a small amount of sample is required – in many methods a few milligrams will suffice.
(d) The simplest of equipment is required, particularly in the case of the visual comparison technique.
(e) Highly trained technicians are not required, even non-technical personnel can be trained to do simple visual comparisons of colour intensity.

1.4 **Disadvantages:**
(a) The preparation of fundamental standards for colorimetry can be a problem, and for visual comparison methods these may have to be replaced at frequent intervals.
(b) Where coloured filters are used to simulate the standard a suitable source of illumination must be specified and be available.
(c) The presence of interfering ions can cause colour distortion and invalidate the visual comparison.
(d) The sensitivity of visual methods is not high; an absolute accuracy of ±5% may be expected routinely, which is much poorer than a good volumetric or gravimetric method of analysis.

1.5 **Instrument Components:**

There are five essential components required for most absorption spectrometers. These are as follows:
(a) A source or sources of radiation covering the required wavelength range.
(b) A means for selecting a narrow band of wavelengths.
(c) Facilities for holding the cells containing the sample solution and the blank in the radiation beam.
(d) A device or devices capable of measuring the intensity of the radiation beam transmitted through the cells.
(e) A display or output device to record the measured quantity in a suitable form.

1.6 **The general arrangement of components in a simple spectrophotometer:**

![Spectrophotometer Diagram](image)
1.7 Theory of spectrophotometry and colorimetry:

When light (monochromatic or heterogeneous) falls upon a homogeneous medium, a portion of the incident light is reflected, a portion is absorbed within the medium, and the remainder is transmitted. If the intensity of the incident light is expressed by $I_o$, 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:

$$I_o = I_a + I_t + I_r$$

For air-glass interfaces consequent upon the use of glass cells, it may be stated that about 4 per cent of the incident light is reflected. $I_r$ is usually eliminated by the use of a control, such as a comparison cell, hence:

$$I_o = I_a + I_t$$

(1)

Lambert (1760) investigated the relation between $I_o$ and $I_t$. Beer (1852) extended the experiments to solutions. Spectrophotometry and colorimetry are based upon Lambert’s and Beer’s laws.

1.8 Lambert’s laws:

This law states that when monochromatic light passes through a transparent medium, the rate of decrease in intensity with the thickness of the
medium is proportional to the intensity of the light. This is equivalent to standing that the intensity of the emitted light decreases exponentially as the thickness of the absorbing medium increases arithmetically, or that any layer of given thickness of the medium absorbs the same fraction of the light incident upon it. The law may be expressed by the differential equation as

\[
\frac{dI}{dt} = -kI
\]  

(2)

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 (2) and putting \( I = I_o \) when \( t = 0 \), we obtain:

\[
\ln \frac{I_o}{I_t} = kt
\]  

(3)

or stated in other terms,

\[
I_t = I_o \cdot e^{-kt}
\]

where \( I_o \) 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. By changing from natural to Briggsian logarithms we obtain:

\[
I_t = I_o \cdot 10^{\frac{-0.4343kt}{10}} = I_o \cdot 10^{-Kt}
\]  

(4)

where \( K = k / 2.3026 \) and is usually termed the extinction coefficient (Bunsen and Rosecoe, 1857). The extinction coefficient is generally defined as the reciprocal of the thickness (\( t \) cm.) required to reduce the light to 1/10 of its intensity. This follows from equation (4), since:

\[
\frac{I_t}{I_o} = 0.1 = 10^{-kt} \text{ or } Kt = 1 \text{ and } K = 1/t
\]

The ratio \( I_t/I_o \) is the fraction of the incident light transmitted by a thickness \( t \) of the medium, and is termed the transmission or transmittance \( I \). Its reciprocal \( I/I_o \) is the opacity, and the optical density \( D \) of the medium, sometimes designated the extinction \( E \) or absorbance \( A \), is given by:

\[
D = \log \frac{I_o}{I_t}
\]
Thus a medium with optical density 1 for a given wavelength transmits 10 per cent of the incident light at the wavelength in question.

### 1.9 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 (3)), i.e. the intensity of a beam of monochromatic light decreases exponentially as the concentration of the absorbing substances increases exponentially as the concentration of the absorbing substance increases arithmetically. This may be written in the form:

\[ I_t = I_o \cdot e^{-k'c} = I_o \cdot 10^{-0.4343k'c} = I_o \cdot 10^{-K'c} \]  

(5)

where \( c \) is the concentration, and \( k' \) and \( K' \) are constants. Combining (4) and (5), we have:

\[ I_t = I_o \cdot 10^{-ect} \]  

(6)

or

\[ \log \frac{I_o}{I_t} = cct \]  

(6’)

This is the fundamental equation of colorimetry and spectrophotometry, and is often spoken of as the Beer-Lambert Law. The value of \( c \) will clearly depend upon the method of expression of the concentration. If \( c \) is expressed in gram moles per litre and \( t \) in centimeters then \( c \) is the molecular 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:

\[ I_t = 0.1 I_o, \text{ since } I_t = I_o \cdot 10^{-c} \text{ when } t = 1 \text{ and } c = 1. \]
1.10 **Deviation from Beer’s law:**

Beer’s law will generally hold over a wide range of concentration if the structure of the coloured ion or of the coloured non-electrolyte in the dissolved state does not change with concentration. Small amounts of electrolytes, which do not react chemically with the coloured components, do not usually affect the light absorption; large amounts of electrolytes may result in a shift of the maximum absorption, and may also change the value of the extinction coefficient. Discrepancies are usually found when the coloured solute ionizes, dissociates, or associates in solution, since the nature of the species in solution will vary with the concentration. The law does not hold when the coloured solute forms complexes, the composition of which depends upon the concentration. Also discrepancies may occur when monochromatic light is not used. The behavior of a substance can always be tested by plotting \( \log \frac{I_0}{I} \), \( E \) or \( \log T \) against the concentration: a straight line passing through the origin indicates conformity to the law.

For solutions which do not follow Beer’s law, it is best to prepare a calibration curve using a series of standards of known concentration. Instrumental readings are plotted as ordinates against concentrations in, say, mg per 100 ml or as 1000 ml as abscissae. For the most precise work each calibration curve should cover the dilution range likely to be met with in the actual comparison.

1.11 **Solvent Extraction:**

Solvent extraction has become a very powerful method of separation for various reasons. One amongst them is, it is very simple, rapid, selective and sensitive. This method does not need any kind of sophisticated instrument excepting a separating funnel. The organic chemists have rendered yeoman’s service to analytical chemists by synthesizing an array of ligands with different functional groups containing varying donor atoms. The solvent extraction domain is dominated by the extraction by chelation or compound formation. It
has received maximum attention due to an array of reagents available for the purpose of separations in solvent extraction.

Ion exchange is another method which is quite effective for the purpose of separations at macro and microgram concentrations. On account of discovery of plate theory one could easily predict and design the column from optimum conditions of sorption and carryout the separations. The efficiency of ion exchange separation could be easily improved by increasing column height or in other words increasing the number of theoretical plates (HETP) while in solvent extraction, efficiency of separation could be accomplished by multiple extractions or counter current extractions.

Liquid ion exchanger, the name implies combines the advantages of both solvent extractions as well as of ion exchange techniques. The greatest advantage of liquid ion exchanger is that one could regenerate the resin and use it again and again. Therefore the process becomes economical. This is one of the reasons why most of industrial processes for recovery of metals from minerals prefer the use of liquid cation exchanger like LIX 64N or liquid anion exchangers like Alanine 336 or Amberlite LA-1.

1.12 Historical Developments:

The solvent extraction method has made great strides in last four decades. A number of monographs have been published [1-5] dealing with various aspects of solvent extraction. Some of them put emphasis on the theory of chelaets extraction [2-5] while others have dwelt on rigorous treatment of extraction equilibria [4-6] or on the mechanism of extraction. Few of them have ramification with aspects of solvent extraction [1, 2]. The chemical engineering aspects pertaining to design and development have been covered by worthwhile monographs [7-9]. The handbook [10] 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 [11] by the author.
1.13 Separation Methods:

The separation science plays a significant role in analytical chemistry. In the past many methods have been developed using large number of sophisticated instruments. It facilitated quantitative analysis of metals from milligram ($10^{-3}$) to auto level ($10^{-18}$). The methods were rapid and sensitive. They included absorption spectroscopy, fluorescence technique, plasma spectroscopy including atomic absorption method and numerous electroanalytical and radiochemical methods. However, inspite of these methods being so sensitive and selective, for the purpose of quantitative analysis the demand grew for analysis of extra pure materials specially those free from interfering components. Some methods could not furnish reliable results if in case nanogram ($10^{-9}$) impurities were present. This led to search for reliable methods for the purpose of isolation and purification of compounds before one could undertake the task of instrumental quantitative analysis. Many separation methods are described in authoritative monographs [12-24]. Each of them is important in a true sense. An account of various separation methods [12-16] like chromatography, reversed osmosis, electrophoresis, and dialysis are available in the monographs [17-24]. They indicate how an excellent instrumental method of analysis can be used if supplemented by an efficient separation technique. All colorimetric methods [17-22] need preliminary separation of impurities. In the presence of such impurities it would influence the process of analysis. Some books [23, 24] present information on the specialized methods for the isolation and determination of rare metals or the radioactive isotopes. Only few methods were an exception to this rule of pre-separation as is atomic absorption spectroscopy or inductively coupled plasma atomic emission spectroscopy which generally do not need preliminary treatment of sample solution for separation. Amongst separation methods so far utilized, solvent extraction occupies the most favoured position.
1.14 Basic Principles of Solvent Extraction:

The solvent extraction process was generally governed by Gibb’s phase rule which states that:

\[ P + F = C + 2 \]  
\[ (7) \]

Where \( P \) = nos. of phases, \( F \) = degree of freedom, \( C \) = components

In solvent extraction processes, there are two phases viz. organic and aqueous phase \((p = 2)\) while the degree of freedom at constant temperature and pressure was one degree of freedom \((F = 1)\) and finally one encounters one component namely solute \((C = 1)\) which freely partitions between organic and aqueous phase.

So we have,

\[ (2 + 1) = (1 + 2) \]  
\[ (8) \]

However, solvent extraction was best explained thermodynamically in terms of the Nernst equation. If \( C_1 \) = concentration of solute in organic phase and \( C_2 \) = concentration of the solute in the aqueous phase, then the ratio which is constant is

\[ K_D = \frac{[C_1]_{\text{org}}}{[C_2]} \]  
\[ (9) \]

Where, \( K_D \) was designated as ‘distribution coefficient’. If one considers total concentration of all components in two phases \( C_1, C_2, \ldots, C_n \sum C \) i.e. organic as well as aqueous phase we have then overall distribution ratio as

\[ D = \frac{\text{Total conc. in the organic phase}}{\text{Total conc. in the aqueous phase}} = \text{Distribution ratio} \]  
\[ (10) \]

If there was no association, dissociation or polymerization present in the organic phase then \( K_D \) will be equivalent to \( D \) in idealized conditions.
However, for all practical purposes, we use a term designated as (%E) percentage extraction. If $V_o$ = volume of organic phase, $V_w$ = volume of aqueous phase, $E$ = % extraction and $D$ = distribution ratio, then

$$D = \frac{V_w}{V_o} \times \frac{E}{(100 - E)}$$  \hspace{1cm} (11)

Whenever the volumes of organic aqueous phases are equal viz. $V_o = V_w$, we get a simplified version of $D$ as:

$$D = \frac{E}{(100 - E)}$$  \hspace{1cm} (12)

Usually when $E = 100\%$, $D$ tends to be infinity ($\infty$) and one could give (%E) in terms of distribution ratio ($D$) as

$$D = \frac{V_o (C)_{org}}{V_o (C)_{org} + V_w (C)_{w}} \times 100$$  \hspace{1cm} (13)

If $C_o$ = concentration in org. phase and $C_w$ = concentration in aq. Phase. This on simplification reduces to

$$%E = \frac{100D}{D + \frac{V_w}{V_o}}$$  \hspace{1cm} (14)

1.15 Classification of Extraction Processes:

The present day classification of extraction is based upon the process of extraction or mechanism involved in extraction as [4]:

(a) Extraction by chelation or compound formation

(b) Extraction by solvation

(c) Extraction by ion-pair formation or ion association

(d) Synergistic solvent extractions involving two extractants
(a) **Extraction by chelation or compound formation**

If the extraction proceeds by the formation of chelate or close ring structure we call it chelate extraction. For instance, extraction of uranium(VI) with oxine was an example of extraction by compound formation or chelation in a solvent like chloroform.

\[ \text{UO}_2^{2+} + \text{oxine} \rightarrow \text{UO}_2/2 \text{(extractable in the organic solvent)} \quad (15) \]

This kind of extraction was usually termed as extraction by chelation. For instance, extraction of copper with dithizone, or the extraction of nickel with dimethyl glyoxime, or the extractions of molybdenum with dithiol are examples of chelate extraction.

(b) **Extraction by solvation**

The process of extraction depended upon the dielectric constant of solvent. The extracted species gets solvated into organic phase. Usually chelate extraction system uses non-polar solvents having low or negligible dielectric constant. Such solvents include aromatic hydrocarbons or chlorinated aliphatic hydrocarbons, but when one uses solvent containing oxygen, phosphorus or nitrogen, it leads to the process of solvation. Extraction of iron(III) with ethylacetate or diethylether from hydrochloric acid e.g.

\[ \text{Fe}^{3+} + 4\text{Cl}^- \rightarrow [\text{FeCl}_4]^- \quad (16) \]

The extracted species in the latter case is shown in bracket.
\[ \{\text{H}^+ (\text{C}_2\text{H}_5)_2\text{O}, \text{(FeCl}_4^-) (\text{C}_2\text{H}_5)_2\text{O}\}_{\text{org}}. \]  

In such case the extractability depends on the basicity of donor atom namely oxygen. It also depends upon electron density around donor atom lie oxygen e.g. in diethylether (I) (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}O and \(\beta\beta\)'-dichlorodiethyl ether (II) CCl\textsubscript{3}CH\textsubscript{2}OCH\textsubscript{2}Cl\textsubscript{3}, electron density of oxygen in first (I) is higher, promoting better extraction. The extractions of uranium (VI) with TBP or of zinc with TOPO are all extractions by solvation process.

(c) Extraction by ion-pair formation or ion association

The third most important from the point of theme of this monograph is extraction by ion pair formation. Such ion pair formation result in formation of uncharged species which readily was extracted as follows: If \(R = \) extractant, \(M = \) metal and \(X = \) anion.

\[
\begin{align*}
R_2\text{NH} + \text{HX} & \iff \{R_2\text{NH}_2^+\text{X}^-\} + \text{H}^+; \\
M^{n^+} + \text{HX} & \iff \text{MX}_n^- + \text{H}^+; \\
\{R_3\text{NH}^+\text{X}^-\} + \text{MX}_n^- & \iff \{R_2\text{NH}_2^+\text{MX}_n^-\} + \text{X}^-.
\end{align*}
\]

The ion-pair was formed with basic extractant. However with acidic extractant like \(\text{H-DEHP}\), extraction proceed as

\[
2\text{H-DEHP} + \text{ZnCl}_2 \iff \{(\text{Zn}^{2^+} (\text{DEHP})_2\} + 2\text{HCl}
\]

Once again an ion-pair is formed and in first case anionic species was extracted so we call it as liquid anion exchange process while in latter case a cationic species was formed to give rise to liquid cation exchanger.

(e) Synergistic solvent extractions involving two extractants

The term synergism was coined by Blake et. al. [1] in 1958 in their report that, when dialkyl hydrogen phosphate, \((\text{RO})_2\text{PO} .\text{OH}\), is used in conjugation with certain neutral organophosphorus reagents. e.g. TBP, the
extracting power of mixture extracts the sum of extracting power of its component. This phenomenon of greatly enhanced the extraction of or synergism due to its mixture of extractant has attracted considerable attention in recent years. A significant effort has been devoted to the study of synergistic extraction over the last few decades as the very nature synergism offers interesting possibilities and their practical applications. The chemistry of synergistic system generally, and also of those making use of chelating extractants, is highly diverse as the variety of extracting agents and their possible combination are numerous. The mechanisms of synergistic extraction of metals as well as the influence of different factors (metals, extractants, anion of the amine salt, diluents, ionic media and ionic strengths in the aqueous phase) on the extraction processes were discussed. The large number of papers that described synergistic metal extraction with combination of acidic chelating extractants and lipophilic anion exchangers are now available. The synergistic extraction of Co(II), Ni(II), Cu(II), Ag(I), Au(III) is of greater interest because of the high extraction efficiency of these metals. In the presence of chelating agents and a neutral or a basic donor was enhanced.

Considerable work has been done in this synergistic extraction area. Irving and Edgington [1] postulates that the conditions for synergistic extractions are

(a) One of the active reagents (HX) should be able to neutralize. The charge on metal ions, preferable by forming a chelate.

(b) The solvent (S) should be displace any residual coordinated water from the neutral metal complex, rendering its less hydrophilic.

(c) The solvent (S) should not itself be hydrophilic and coordinated less strongly than HX.

(d) The maximum coordination number of metal and the geometry of ligands should be favorable.

Synergistic extraction system proceeds with use of two extractants e.g. TTA and TBP for extraction of uranium (VI).
These postulates were valid for UO$_2$(TTA)$_2$TBP systems. From the infra-red studies it has been concluded that the complexes contains TTA as both a unidentate and bidentate ligand. The extraction mechanism is given as,

\[
[\text{UO}_2(\text{H}_2\text{O})_4](\text{NO}_3^-) + 2\text{HTTA} \rightleftharpoons [\text{UO}_2(\text{TTA})_2(\text{H}_2\text{O})] + 2\text{NO}_3^- + 2\text{H}^+ + 3\text{H}_2\text{O} \\
[\text{UO}_2(\text{TTA})_2(\text{H}_2\text{O})] + \text{TBP} \rightleftharpoons [\text{UO}_2(\text{TTA})_2(\text{TBP})] + \text{H}_2\text{O}
\]
References:


