CHAPTER I

GENERAL INTRODUCTION AND SCOPE OF WORK
A study of almost any problem in the field of chemistry requires analytical investigations. Analytical chemistry deals with the art and science of determination of composition of materials in terms of the elements or compounds, which they contain, and the consequent interpretation of the results obtained.

Although analytical chemistry came in existence long ago it has developed immensely during the last thirty years. This development has been possible because of the introduction of several instruments as tools of chemical analysis. Instruments have not only widened the scope of analytical chemistry but they have also made it possible to perform complete analysis of a sample in incredibly short time.

In the closing decade of nineteenth century spectroscopic was introduced, which gave a better approach to analytical goals, mostly in qualitative aspects. So far many years gravimetric and volumetric methods were the only methods for all kind of analysis. Gradually other techniques were developed i.e., nephelometric, colorimetric etc., mainly for those substances for which no other reliable methods were known.

Then electrical measurements were tried for the end points of titrations, which were well suited in most of cases. Round about the year 1930 vacuum tube, amplifier, photoelectric cell and other electrical devices started to serve analytical
chemistry with the result that different analytical techniques were invented and put to use. Hence a modern analyst has, at his disposal several instruments and it is expected of him to be acquainted with their uses. Normally any characteristic property can be used as a base for an analytical procedure, to get more fundamental or required information e.g., in case of light, Absorbance, Interference, Diffraction, Refraction; in case of electricity, Conductance, Potential, Current, Capacity charge etc.

It is, however, to be noted that the choice of an instrument for the analysis of a sample will necessarily depend on the physico-chemical properties of the sample itself. It is possible to make use of instruments both for quantitative as well as qualitative analysis. Only few instruments like polarograph, spectrophotometer, spectrograph, nuclear magnetic resonance technique give qualitative and quantitative information simultaneously. Most of the analytical methods are based on sound mathematical theories. Occasionally there are a few methods which remain purely empirical for a longtime, for it requires extensive studies to establish theories underlying them. In such a case the efficiency of a method is established by collecting extensive data, and by their scrutiny by independent workers. The procedure makes it possible for an analyst to know which property can be measured reliably.
A list can be made of physical properties which have been found applicable in chemical analysis.¹

1. **Extensive properties**: mass, volume.

2. **Mechanical properties**: specific gravity, surface tension, viscosity, velocity of sound in gases.

3. **Properties involving interaction with radiant energy**:
   (a) Absorption of radiant energy: X-rays, ultra-violet, visible, infra-red, microwaves.
   (b) Turbidity.
   (c) Emission of radiation (following excitation).
   (d) Raman effect.
   (e) Rotation of the plane of polarised light.
   (f) Refractive index.
   (g) Dispersion.
   (h) Fluorescence and phosphorescence.
   (i) Diffraction of X-rays and electrons.
   (j) Nuclear and magnetic resonance.

4. **Electrical properties**:
   (a) Half cell potentials.
   (b) Current voltage characteristics.
   (c) Electrical conductivity.
   (d) Dielectric constant.
   (e) Magnetic susceptibility.

5. **Thermal properties**:
   (a) Transition temperature.
   (b) Heat of reaction.
   (c) Thermal conductivity of gases.

6. **Nuclear properties**:
   (a) Radioactivity.
   (b) Mass spectroscopy.
Only a few physical properties can be measured directly. Most of the instruments involve observations of linear or angular displacement on some kind of scale. The function of an instrument is evidently to translate chemical composition into information directly observable by the operator. It may in general be said that an instrument acts either directly or indirectly as a comparator, in that the unknown is evaluated in terms of a standard.

Classical methods of chemical analysis usually consists of separation of different components by methods like:

1. precipitation, 2. electro deposition, 3. distillation,
4. solvent extraction, 5. chromatography, 6. ion-exchange, etc.

But the instruments have made possible analysis of even complex samples containing several components without the necessity of separation from each other. The application of flame photometry for analysis of water containing sodium, potassium, calcium etc., may be cited as an example to illustrate this.

Chemistry is an experimental science. Experimentation, therefore, constitutes an essential part of the subject. An experiment involves several steps, each step is susceptible to errors which may be determinate and/or indeterminate. Hence a single observation is of no value in the field of chemical analysis. It is imperative to perform an experiment several times in order to have an idea of the precision and accuracy involved. It is,
therefore, essential to repeat the experiment a large number of times and thus collect data in connection with it. Obviously one has to deal with a large number of figures about a particular property. It is possible to subject these figures to statistical analysis and thus draw an inference about the accuracy of the method involved. It is usually possible to determine a particular property by following two or more methods. Different methods may give various values for the property. In such cases it becomes difficult to say which method is the most accurate. Visual observation of the different values may not give a correct indication about the accuracy involved. Under these conditions statistical analysis can be taken recourse to, and the observed data can be interpreted.

A particular determination may be accurately made by the application of one method. Even in this case the expected accuracy is usually possible under clearly defined conditions. It may be noted that a particular method is useful under one set of conditions but it may not at all be reliable under another set of conditions. Thus while a method may appear of general application it may in fact not be so. It is the statistical analysis of the data obtained by following the same method under several different conditions, that will testify to the accuracy, or otherwise of the method.

The development and introduction of new analytical
methods take place considerably faster than their standardisation. This inevitably leads to the fact that in all analytical laboratories, even small ones, complex metrological problems arise constantly, the rational solution of these is impossible without the application of methods of mathematical statistics. It is already evident that an analyst must be as thoroughly familiar with the methods of modern mathematical statistics as the geodesist is with the method of least squares.

Modern mathematical statistics began to develop on the basis of theory of probability, at the end of the nineteenth and beginning of the twentieth century in connection with investigation in such fields of science and technology as agrobiology, medicine, machine-building, and instrument constructions, the chemical industry, metallurgy, etc.

A completely new branch of knowledge has been developed, quite recently, on the basis of theory of probability — Information theory. The original task of which was to study problems connected with the transmission of signals in radio engineering.

Investigations connected with chemical analysis form one of the new fields of application of mathematical statistics. A number of factors render it necessary to apply statistical methods in chemical analysis. First of all it should be pointed out here that the introduction of new alloys and materials, complex in constitution, into industry, and constant acceleration of the
process of production, necessarily require extensive application of new physical methods of analysis.

These are based on processes studied insufficiently, not lending them self to strict control and exact adjustment. The existence of multitude of new physico-chemical methods of analysis, side by side with the classical methods of chemical analysis, urgently raises the question of finding out rational criteria for comparing the results obtained by various analytical methods.

Absorptiometry and polarography are two of the methods which seem to be of general application in chemical analysis. A large number of research papers are found in the chemical literature. It may, however, be mentioned that the results obtained from these methods do not appear to have been subjected to statistical tests. The author has, therefore, undertaken this.

It seems appropriate to describe briefly polarography and absorptiometry in the following pages.

Polarography:

The first polarography measurements were made in 1920 by Professor Jareslav Heyrovsky at Charles University Prague. In 1925 Heyrovsky and Shikata invented the instrument known as polarograph which records automatically the current-voltage curves in the electrolysis of a suitable sample in very short time. In this way the Professor gave an experimental foundation to another
electrochemical method as an analytical technique. Even then its use was limited by the lack of any real understanding of the theory on which polarography was based. Theoretical aspects of polarography were developed by Ilkovic, Kolthoff and others. It must be understood that polarography is a complex science; it is complex experimentally as well as theoretically and our knowledge of it is not yet so complete that there is not often art to it as well. Polarography is a branch of electro analytical chemistry which deals with the measurement and interpretation of current voltage relationship during the electrolysis of solution between two electrodes one of which is very small.

When the concentration of a cation at the surface of the cathode is kept equal to that in the body of the solution by some mechanical or other way, no concentration polarisation exists, such an electrode is known as nonpolarised electrode. But if the cathode is very small and the solution is unstirred, as the applied potential is increased the concentration of cations decreases simultaneously at the surface of microelectrode until it becomes practically zero. A further increase of the applied potential can no longer increase the current which is now limited by the rate at which cations from the body of the solution reach the electrode surface, where they are immediately reduced. The cathode is then said to be concentration polarised and the current flowing through the cell depends on the concentration of cations in the body.
Residual current:

Mercury is unique in remaining electrically uncharged when it is dropping freely into a solution containing an indifferent electrolyte such as potassium chloride or potassium nitrate. If a current-voltage curve is determined for a solution containing ions with a strongly negative reduction potential (e.g. potassium ion) a small current will flow before the decomposition of the solution begins. This current increases almost linearly with the applied voltage and it is observed even when the purest air free solutions are used, so that it can not be due to reduction of impurities. It must, therefore, be considered a non-faradic or condenser current made appreciable by the continual charging of a new mercury drop to the applied potential. It is known that metals when dipped in an electrolyte are covered with an electrical double layer of positively and negatively charged ions. The capacity of the double layer and hence the charging current vary depending upon the potential which is imposed upon the metal. In practice it is usually found that indifferent electrolyte contain traces of impurities, so that small, almost imperceptible, currents are superimposed upon the condenser current. It is customary to include all these in the residual current. The current which passes increasingly even before the decomposition potential of the reducible substance is reached, is known as the residual current.

The total residual current at any potential may be defined as the sum of the current $i_d$ consumed by the reduction
of the impurities present. The residual current increases with the increasing pressure of mercury. It increases more rapidly than does the diffusion current with increasing pressure of mercury. Hence the relative importance of residual current and the accuracy with which it must be measured and corrected for, increases with the increase in mercury pressure.

**Diffusion current**:

When the excess of supporting electrolyte is present in the solution the electrical force on the reducible ions is nullified. This is due to the ions of added electrolyte which carry particularly all the current due to migration. The potential gradient is compressed or shortened to a region so very close to the surface, that it is no longer operative to attract electro-reducible ions. Hence, now the only possible way to pass the current is by diffusion of the reducible ion towards the electrode due to concentration gradient formed. Under these conditions the limiting current is almost solely a diffusion current.

Taking under consideration the various factors which govern the diffusion current Ilkovic in 1934 established the now well known relation:

\[ i_d = 607 n D^{1/2} cm^{-1/2} t^{1/2} \]

where,

- \( i_d \) = The average diffusion current in micro amperes during the life of the drop.
\[ n = \text{Number of faradays of electricity required per mole of the electrode reaction (or number of electrons consumed in the reduction of one mole of the electroactive species).} \]

\[ D = \text{The diffusion coefficient of the reducible or oxidisable substance expressed in cm}^2 \text{ sec}^{-1}. \]

\[ c = \text{It is concentration of the reducible or oxidisable substance in milimoles per litre.} \]

\[ m = \text{Rate of flow of mercury from the dropping electrode expressed in mg per second.} \]

\[ t = \text{Drop time in seconds.} \]

The constant 607 is a combination of natural constants including faraday's. It is slightly temperature dependent and the value 607 is for 25°C. The Ilkovic equation has got its importance because it accounts quantitatively for the many factors which influence the diffusion current, particularly the linear dependence of the diffusion current on the concentration of the electroactive material. This is of great importance in quantitative polarographic analysis. Its general validity is well established. The diffusion current \( i_d \) depends upon several factors such as temperature, viscosity of the medium, composition of the base electrolyte, molecular or ionic state of electro active species, dimensions of capillary and pressure on the mercury droplet, etc.

**Polarographic maxima:**

Current-voltage curves obtained with the dropping mercury cathode frequently exhibit pronounced maxima which are reproducible. They can usually be eliminated by the addition of
certain appropriate suppressors. These maxima vary in shape from sharp peak to rounded bump, which gradually decreases to the normal diffusion current as the applied voltage is increased. In order to measure the true diffusion current these maxima must be eliminated. Surface active substances which are used for suppressing them are dye stuffs, sodium methyl red, gelatine, Triton X-100, and other colloids.

The function of any such maximum suppressor is probably to form an adsorbed layer on the aqueous side of mercury solution interface which resist compression. This prevents the streaming movement of the diffusion layer (which is believed to be responsible for the current maximum) at the interface.

Half wave potential:

Each electro active material in polarography is characterised by its half wave potential. This is the potential at the point of inflection of the current-voltage curve, one half the distance between the residual current and the final limiting current plateau. It may also be defined as the potential on the polarographic wave where the current is equal to one half of the diffusion current. The half wave potential $E_{1/2}$ is related to the standard oxidation potential by the equation:

$$E_{1/2} = E^0 + \frac{2.303RT}{nF} \log \left( \frac{D_{\text{red}}}{D_{\text{ox}}} \right)$$

$D_{\text{red}}$ and $D_{\text{ox}}$ are the diffusion coefficients of the appropriate reducing and oxidising species.
Nevertheless the half wave potential is a characteristic property of the given oxidation reduction system, and it can be used for its identification. It is quite clear from the above equation that the value of the half wave potential is independent of the concentration of the oxidant in bulk solution.

**Limiting current:**

As the applied voltage is increased the current flowing through the polarographic cell increases up to a certain value. Any further increase in the applied potential (beyond this point), does not have any effect on this value. The current acquires a limiting value and then it becomes constant. This region is called the limiting current plateau, because it represents the limiting or maximum rate at which the particular ion species can be discharged under the given experimental conditions. As the concentration of the reducible ion in the bulk of the solution increases so does the limiting current.

Polarography found use in analytical chemistry immediately after its invention by Heyrovsky and Shikata in 1925, but its use was quite limited. It was after ten years of its invention that polarography was introduced in the study of coordination chemistry. Among the quantitative data obtainable by the polarographic means are dissociation constants of complexes, coordination number of the metal ion, the degree of stabilization and various oxidation states.

A number of factors may affect the electrolysis and
alter the recorded curve. In this discussion most important factor is presence of complexes. Normally a complexed ion resist the electrolytic reduction more than the corresponding uncomplexed ions. The half wave potential is more negative for complexes. The pH of the solution may affect the half wave potential either by altering the nature of the complex or by varying the product of electrolysis.

The polarographic method is unique among electrometric methods. Only a small fraction of the solution is electrolysed. A further advantage is that quite a small concentration of the material is required for investigation. In fact it is possible to obtain the same current-voltage curve over and over again from a sample. The polarographic method can be applied advantageously to the study of complex metal ion by virtue of the fact that the half wave potentials of metal ions are shifted usually to a more negative value by complex formation. By measuring the shift as a function of concentration of the complexing agent both the formula and the dissociation constant of the complex can be determined.

Quantitative reliable information can only be obtained when the reduction-oxidation of the metal ion complex take place reversibly at the polarised electrode i.e., dropping mercury electrode.

Under the usual analytical conditions the accuracy of the polarographic method is of the order ± 1 percent in the concentration range $10^{-2}$ - $10^{-4}$ molar and of the order ± 5 percent in the
concentration range $10^{-4} - 10^{-5}$ molar. By observing certain precautions it is possible in favourable cases to obtain some what greater accuracy. The lower limit of the polarographic detection is in the neighbourhood of $10^{-6}$ molar. In view of the small concentration involved and the small volume of the solution that can be used, the precision and sensitivity of polarography compare very favourably with other micro analytical methods.

A great variety of organic compounds is reducible at the dropping electrode, consequently polarographic analysis has become a valuable tool in organic chemistry and related fields such as biology and biochemistry. It is also very useful in the analysis of alloys and other inorganic substances. It is not limited to aqueous solutions and can be applied to solutions in certain non-aqueous solvents. The essential condition is that the solvent should be sufficiently polar, so that the ionic solution can be prepared.

The use of non-aqueous solvents is particularly necessary with many water insoluble organic substances. It is also possible to obtain polarographic waves in molten salt media. A new electrometric titration technique "Amperiometric titration" has been developed as a branch of polarography. The method is particularly useful for titrating relatively small concentrations of substances. It is being used to advantage in many cases where reversible indicator electrodes are not available for titrating by the potentiometric method.
SPECTROPHOTOMETRY:

Spectrophotometry is an improved form of colorimetry. There are two fundamental laws governing the theory and practice of absorptiometry. They are Lambert's law and Beer's law.

Lambert's law states that layers of equal thickness of a homogeneous absorbing medium absorbs equal proportion of the penetrating radiations i.e.,

\[ \log \frac{I_0}{I} = K_b \]

where \( K_b \) is a constant depending upon the wave length of the radiations and the nature of the medium and \( b \) is the thickness of the medium.

Beer's law states that intensity of a beam of parallel monochromatic radiations decreases exponentially as the concentration increases:

\[ \log \frac{I_0}{I} = K'c \]

where \( K' \) = constant depending upon the wavelength, the nature of the medium and the thickness of the medium. The two laws are combined to give single law:

\[ \log \frac{I_0}{I} = a'bc \]

where \( a' \) = absorption coefficient, 
\( b \) = thickness of medium, and 
\( c \) = concentration of medium.

When applied to solutions contained in cells, the relationship becomes:

...
\[
\log \frac{I_{\text{solvent}}}{I_{\text{solution}}} = a_{bc}
\]

But, we may expect deviation from the Lambert's Beer's law in systems of weak acids, weak bases and other systems involved in ionization equilibria, or dissociation or association equilibria. Kortum and Sciler point out further that the Beer's law is only a limiting law and should be expected to apply only at low concentrations. They show that it is not \( a^1 \) which is constant, independent of concentration, \( \frac{a^1}{(n^2 + 2)^2} \) where \( n \) is the refractive index at low concentrations, \( n \) is practically constant, but at higher concentrations, \( n \) may vary appreciably. An increase in temperature has a bathochromic effect on ions in solutions, that is the absorption bands are shifted to longer wavelengths. The temperature of solution must be carefully controlled, if this effect is large. An instrument which passes a wider band of radiant energy than a narrower (i.e., nearly monochromatic) band can be expected to cause apparent deviation. Fundamentally this departure is due to the fact that with all radiant energy measuring devices, it is the intensities of various components wavelength which are additive (or nearly so), and which act to effect the measuring device, whereas Beer's law would require that the logarithm of intensities to be additive. The wider the band passed by the filter or monochromator, the greater will be the apparent deviation from Beer's law.

It has been shown above that both polarography and spectrophotometry are useful tools in chemical analysis. An
analyst has rarely to deal with a single substance. He is usually required to analyse mixtures and complex materials. The accuracy of an analytical method depends on the presence of other substances in the system. In the absence of other substances one can expect the required accuracy in an analysis. But the presence of foreign substances are likely to vitiate this accuracy.

The author has, therefore, planned to investigate the dependence of the accuracy of an analysis following the polarographic and, or the spectrophotometric method. Sulphates of the metals have been used in the experiment. Only nitrates of nickel and cobalt are used in spectrophotometer for one set. Several mixtures have been analysed polarographically and spectrophotometrically. The result of the analyses have been subjected to statistical tests. The thesis also contains a chapter on the polarographic studies in the complexes of cobalt.
REFERENCES


