Chapter-9

ANALYSIS OF BINARY MIXTURES
Over the classical methods of analysis, Instrumental methods of analysis have several advantages. They are less time consuming, more sensitive and permit micro quantities to be determined more accurately. Examples of these methods are emission and absorption spectroscopy, polarography, mass spectroscopy and X-ray diffraction. With these methods, analysis which formerly required several hours may be performed in minutes, trace constituents can be detected and determined. Mixtures whose components could hardly be differentiated in any other way can be analysed completely. Among the modern instruments of analysis, the polarography deserves a place of distinction.

Polarographic analysis can be used directly for the determination of any substance – solid, liquid, or gaseous, organic or inorganic, ionic or molecular– that can be dissolved in a solvent of reasonable dielectric constant and either reduced or oxidized at a mercury electrode.

Extensive research has been carried out on the polarographic behaviour of elements during the past few years resulting into a widespread application of polarography to various fields. Not only polarography is one of the most fruitful techniques of research in physical, inorganic, and organic chemistry but also more widely used in the fields of biochemistry, pharmaceutical chemistry and others.

Polarography has also been used to study topics as hydrolysis, solubility, complex formation, adsorption, the stoichiometry and kinetics of chemical reactions, the mechanisms of electrode reactions and of chemical
reactions accompanying them, standard and formal potentials, molecular dimensions, the effects of structure on reactivity and many others of interest and importance. The determination of oxygen in gases and solutions is another uniquely valuable application of polarographic analysis.

Polarographic analysis is not limited to aqueous solutions, and can be applied to solutions in certain non-aqueous solvents. The essential condition is that the solvent be sufficiently polar so that ionic solutions can be prepared. The use of non-aqueous solvents is particularly necessary with many water-insoluble organic substances. It is even possible to obtain polarographic waves in molten salt media.

In the field of inorganic analysis it has been applied to the determination of nearly all the elements. Reliable procedures are available for the analysis of most common types of alloys and ores. In many instances these methods are not only more rapid but also more reliable than classical techniques.

Although with the development of modern instrumentation greatly increased resolution between closely following waves and direct analysis of more adverse ratios of depolarizers is possible, the role of complexation remains important because of its simplicity. Complexation has an important role in that a suitable complexing electrolyte may improve the shape of a wave or bring it to a more readily accessible region of applied potential. What is often of greater importance is that in the chosen medium, the wave for the required species may appear well separated from neighbouring waves for
other depolarizers. Under noncomplexing conditions the waves may be so close together as to be almost superimposed so that measurement of individual wave heights is impossible. Complexation often be used to reverse the order of appearance of the waves and make measurement of the minor component comparatively easy. Sometimes a particular medium can serve for the effective separation of a number of metals. It is in this line that the present investigation has been selected to separate number of metal ions which will constitute in one way or the other either an alloy or ore. Trimethoxy benzaldehyde-amino methyl propanediol (TMBAMPD) Schiff base has been used as a complexing agent for the detection and quantitative determination of some metal ions in the presence of one or more ions.

According to the Ilkovic equation, with all other factors being constant,

\[ id \propto C \]

This relation is the foundation of quantitative polarographic analysis and its general validity is well established.

**Methods of quantitative polarographic analysis**

Principally all the polarographic methods for quantitative analysis are based on an emperical comparision of the diffusion current of the unknown with that obtatined with a known concentration of the substance in question under identical conditions. The most important conditions that must be maintained constant for comparative purpose are (1) The composition of the medium (2) characteristics of the dropping electrode (3) Temperature and (4) Concentration of the maximum suppressor.
Polarographic methods may be classified into two categories (1) those which strictly involve comparison of the diffusion current due to the unknown, and known concentration of the same ion in question and (2) those which require the measurement of the characteristics of the dropping electrode and the diffusion current and then substituting these values in the Ilkovic equation, provided $D$ or $I_d$ values are known. Accordingly these methods are termed as comparison methods and absolute method, respectively.

**Comparison methods**

The most direct comparison technique is to record the polarograms of the known, under similar conditions that the unknown is recorded. Maximum accuracy results, if the concentration of the comparison standard is about the same as that of the unknown. In the analysis of complex materials i.e. traces of metals in certain alloys, it is necessary to add to the comparison solution approximately the same amount of undesired substances that are present in the unknown.

It is not necessary to measure the capillary characteristics (m and t) in comparison methods but it is essential that the characteristics of the dropping electrode remain constant during the analysis. This may be checked by measuring the drop times at regular intervals.

Another advantage of the comparison method is that the temperature need not be controlled at any fixed value but should be exactly the same for the unknown and the comparison standard. Various comparison methods are discussed below.
I. The standard curve method

When a large number of samples are to be analysed, this method is usually preferred. In this a number of solutions, identical in composition with the solution to the finally prepared from the unknown but containing known concentrations of the substances being determined that cover the whole range of interest, records their polarograms, and measures their wave heights. These data are used to construct a standard curve that is then used to obtain the concentrations of unknown solutions from their wave heights.

II. The Standard sample method

This method consists of measuring the wave height of a standard sample at the same time that the unknown is analysed. The intent of the standard sample method is to minimize the effects of fluctuations in the capillary characteristics, temperature and other experimental variables. In the analysis of technical materials one naturally prefers to use a standard whose composition is closely similar to that of the unknown, since this gives a more perfect compensation for any errors in the chemical steps that precede the polarographic measurements. It may be stressed that proportionality between wave height and concentration should never be taken for granted, it must always be carefully checked during the development of any analytical method.

III. Standard addition method

This method is convenient only for an occasional analysis. The polarogram of the unknown is recorded, at first and then a known volume of the standard solution of the same ion is added to the unknown solution and the polarogram is recorded again. From the increase in the wave height...
caused by the known addition, the concentration of the unknown may be computed.

IV. The Pilot-ion method

The pilot-ion method, depends on the fact that the ratio of the heights of two diffusion-controlled waves is practically independent of experimental variables. Standard solutions are prepared that contain known concentrations of both the substance being determined and another substance, called the 'pilot-ion' despite the fact that it need not be ionic, and the ratio of their wave heights is measured. The ratio of wave heights is independent of dilution over the whole range in which the wave heights of both substances are proportional to their respective concentrations. Therefore, it is sufficient to know the amount of the pilot ion added. The pilot ion method should not be used in determinations of substances yielding kinetic or catalytic waves. If a known concentration of the pilot ion is added to the solution being analyzed, the concentration of the substance being determined is easily calculated from the ratio of wave heights and the previously established calibration figure.

Absolute method

Lingane introduced this method to eliminate the calibration experiments which are essential in the comparative methods. The concentration of any substance is simply determined by substituting its diffusion current and the characteristics at the dropping electrode into the Ilkovic equation

\[ i_d = 607 n c D^{1/6} m^{2/3} t^{1/6} \]

Lingane suggested that the quantity \( 607 n D^{1/6} \) is constant for a given substance in a given supporting electrolyte and is independent of the
concentration of the diffusing ion and characteristics of the dropping electrode and named it as diffusion current constant'. This in turn is given by the relation.

\[ I_d = \frac{i_d}{cm^{1/2}} t^{1/6} \]

If \( I_d \) values are once calculated in a given medium, the concentration of the unknown may be evaluated by substituting the values of \( i_d \), \( m \) and \( t \). The measurement of \( m \) and \( t \) is much similar and quicker, requiring no standard solution of the substance to be determined.

Using the polarographic technique, very minute quantity of the elements may be determined accurately (10^{-6} molar). In view of the small concentrations involved and the small volumes of solutions that can be used, the precision and sensitivity of polarography can be compared very favourably with other microanalytical methods.
Section(i): Analysis of Cadmium and Copper

Copper containing 0.7 and 1.0% cadmium [565] is very ductile and has found wide use in the telegraphic, telephonic and power transmission wires since cadmium imparts good tensile strength, hardness and high annealing temperature and does not seriously impair the conductivity. It is most useful as trolley wire where its high strength, high conductivity and resistance to wear are of prime importance. Even 0.15% of cadmium in copper stabilizes the work-toughening the metal under exposure to heat [566]. Copper and cadmium from the monomer constituents in the zinc alloys and zinc ores. Approximately, 2.0% copper and 1.0% cadmium are involved in Dow metal. Very small percentage of these elements exist in lead and tin base alloys as impurity.

Preliminary studies [Chapter-IV&VI;Section-(ii)] gave half-wave potential values for copper and cadmium in presence of 0.1M ligand, 0.1M KNO3 and 0.002% Triton-x-100 at pH 8.0 as -0.3147 V. vs S.C.E. and -0.6620 V. vs S.C.E. respectively. Half-wave potential difference between the two metals was more than 0.2v, which was the minimum requirement to carry out simultaneous determination of one metal ion in presence of the other. Synthetic solutions of cadmium and copper in different proportions were prepared and polarograms were recorded (Fig.113). The amounts of these metal ions in the synthetic mixtures were determined by comparing the wave heights with their respective calibration plots (Fig.35&98) obtained under similar conditions. The results were tabulated (Table 67).
TABLE - 67

Determination of Copper and Cadmium

\[
\begin{align*}
[3,4,5-\text{TMBAMPD}] &= 0.1 \text{ M} \\
[\text{KNO}_3] &= 0.1 \text{ M} \\
\text{pH} &= 8.0 \\
\text{Triton - x - 100} &= 0.002\% 
\end{align*}
\]

<table>
<thead>
<tr>
<th>Amount taken (mg)</th>
<th>Amount found (mg)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Cadmium</td>
<td>Copper</td>
</tr>
<tr>
<td>0.6354</td>
<td>2.8102</td>
<td>0.6279</td>
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<tr>
<td>0.7942</td>
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<tr>
<td>1.2708</td>
<td>1.6861</td>
<td>1.2708</td>
</tr>
<tr>
<td>1.5885</td>
<td>1.1240</td>
<td>1.5764</td>
</tr>
</tbody>
</table>
Fig: 113 Polarograms of (a) 0.40, 1.00 (b) 0.50, 0.80 (c) 0.80, 0.60 and (d) 1.00, 0.40 mM Copper and Cadmium respectively in 0.1M TMBAMPD and 0.1M KNO₃ at pH 8.0
Section(ii): Analysis of Cadmium and Nickel

Cadmium-Nickel alloys [566] containing 1-2% nickel are used for bearing metals and have good frictional properties. Owing to their relative high melting points and resistance to corrosion they are suitable for bearings of high compression type engines, motor cars etc.

The half-wave potentials of cadmium and nickel in presence of 0.1M concentration of Schiff base TMBAMPD, 0.1M KNO₃ as supporting electrolyte at pH 8.0 were -0.6620 V.vs S.C.E. and -1.0411 V.vs S.C.E respectively [chapter-IV & VI; Section (ii)]. As the half-wave potentials of these metals differed by more than 0.2V, this advantage was taken to carry out quantitative determinations in binary mixtures. Synthetic solutions of these metal ions were prepared and polarograms were recorded (Fig.114). The diffusion currents of these metal ions in different combinations were compared with the calibration curves of the corresponding individual metal ions recorded under the same conditions (Fig.35&108). The results obtained were accurate within the limits of experimental error (Table 68).
TABLE - 68

Determination of Cadmium and Nickel

\[[3,4,5\text{-TMBAMPD}] = 0.1\text{M}\]
\[[\text{KNO}_3] = 0.1\text{M}\]
\[\text{pH} = 8.0\]
\[\text{Triton - x - 100} = 0.002\%\]

<table>
<thead>
<tr>
<th>Amount taken (mg)</th>
<th>Amount found (mg)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>Nickel</td>
<td>Cadmium</td>
</tr>
<tr>
<td>1.1240</td>
<td>1.1742</td>
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<tr>
<td>1.6861</td>
<td>1.4678</td>
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<tr>
<td>2.2481</td>
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<tr>
<td>2.8102</td>
<td>2.0549</td>
<td>2.8035</td>
</tr>
</tbody>
</table>
Fig: 114 Polarograms of (a) 0.40, 0.80 (b) 0.60, 1.00 (c) 0.80, 1.20 and (d) 1.00, 1.40 mM Cadmium and Nickel respectively in 0.1M TMBAMPD and 0.1M KNO₃ at pH 8.0
Section(iii): Analysis of Copper and Nickel

The alloys of copper and nickel are often known as cupro - nickel [566] which contain 10 to 30% nickel have found wide use because of resistance to corrosion, especially in Marine environments. One of the oldest uses of copper - nickel have been in the field of coinage where alloys containing up to about 25% nickel have been in use for several thousand years. The strong, ductile nickel - copper alloys (e.g. 70/30 nickel - copper alloy) have a long history of commercial use because of their ability to resist attack in many corrosive media. These two elements are also present in steel and in many minerals. Their determination in a single run is, therefore, of considerable interest.

Polarograms for copper and nickel ions were recorded separately in 0.1M KNO₃, 0.1M Schiff base and 0.002% Triton-x-100 at pH 8.0 [Chapter VI; Section (ii)]. The half-wave potentials of these two metals were found to be \(-0.3147 \text{ V vs S.C.E.}\) and \(-1.0411 \text{ V vs S.C.E.}\) respectively. Synthetic mixtures of copper and nickel in different proportions were prepared and polarograms were recorded (Fig.115). The concentration of these ions in different combinations were calculated by comparing the diffusion currents with their individual calibration plots constructed under similar experimental conditions (Fig. 98 & 108). The results were tabulated (Table 69).
TABLE - 69
Determination of Copper and Nickel

\[
\begin{align*}
[3,4,5-TMBAMPD] & = 0.1 \text{ M} \\
[K\text{NO}_3] & = 0.1\text{M} \\
pH & = 8.0 \\
\text{Triton} - \times 100 & = 0.002\%
\end{align*}
\]

<table>
<thead>
<tr>
<th>Amount taken (mg)</th>
<th>Amount found (mg)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Nickel</td>
<td>Copper</td>
</tr>
<tr>
<td>0.6354</td>
<td>1.1742</td>
<td>0.6279</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
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</tr>
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<td></td>
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<td>-0.75</td>
</tr>
</tbody>
</table>
Fig: 115 Polarograms of (a) 0.40, 0.80 (b) 0.60, 1.00 (c) 0.80, 1.20 and (d) 1.00, 1.40mM Copper and Nickel respectively in 0.1M TMBAMPD and 0.1M KNO₃ at pH 8.0