CHAPTER 2

DISCUSSION OF METHODS
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PHYSICO-CHEMICAL METHODS:

These methods are used to investigate the nature of the complex formed.

The old method of investigation was to isolate the complexes, purify them and then subject them to analysis. Chromium thiocyanate complexes\(^1\) were studied by the above method. Such a method suffers from limitations. Physico-chemical methods capable of detecting and estimating the ions in solution are numerous, and it is possible to use any property of a complex system as an index property for its detection and determination.

The Electrometric method based on pH determination has been extensively used\(^2\) since the work of J. Bjerrum\(^3\). Weakly acidic ligands release hydrogen ions and these can be detected by lowering of pH. pH titration curves can be drawn to find out the ligand number coordinated to the metal.

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Various metal and amalgam electrodes are used to determine the concentration of a metal ion (M) in equilibrium with a ligand and its complex using potentiometric titration by the equation:

\[ E = E^0 + \frac{R \Delta}{nF} \log_a [M] \]

An outstanding use of the method and the mathematical analysis of such data are given by Laden⁴.

Half wave potential is a value characteristic of a substance and is independent of its concentration. A complexed ion resists electrolytic reduction and hence its half wave potential is more negative. This shift is used to detect the presence of complexed ions and to calculate the stability constants. Heyrovsky⁵ was the pioneer to use this method to calculate stability constants. Rigorous determinations in this field were made only after 1950⁶⁷.

Solubility, ligand-ligand partition and ion-exchange methods are used to determine the stability constants of the complexes along with kinetic indicator ion methods using radio active tracers.

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Many physico-chemical properties of solutions of complex compounds differ from the sum of the properties of the starting reagent solutions. This deviation from additivity is connected with the amount of the complex formed, its composition and properties. Colligative properties can be utilized to count the complex units formed. Conductivity determinations are of importance in demonstrating complex formation. Werner\(^7\) used this method as a strong evidence in favour of his theory of complex formation. Work on amino acid chelates by Ley\(^8\) is another classical example. Dey\(^9\), Nayer and Pandey\(^10\) have used it to demonstrate the existence of complex formation.

Changes in colour have been used as criteria of complex formation since very early times\(^11\). Considerable changes in the absorption spectra are now universally considered to be strong evidence in favour of chelate formation and identification of colour is used to detect and estimate the amount of chelate\(^11\).

Recent developments in instrumentation have extended the field of measurement of colour intensity to

7. Werner and Mislate, Z. Physik Chem. 12 35 (1893) 14 56 (1896) 21 225
the near ultra violet and infra red regions and also
increased the accuracy of measurement. It is now capable
of at least as much accuracy as any other method\(^{12}\) provided
precautions are taken properly\(^{13}\). Where molar extinctions
are large and there is considerable difference in the
absorptions of the complex and the constituents
spectrophotometric method is far superior to any other
method. In case of nickel-picolinate system Green\(^{14}\) was
able to demonstrate spectrophotometrically the formation
of a chelate and to calculate the stability constant of
the 1:3 chelate, the existence of which is missed by
isolation or pH titration. He pointed out the errors
in pH titrations. Spectrophotometric methods can very
well be used for the study of complexes.

It is known that T-sulfonamidine gives coloured
complexes with Cu(II)\(^{15}\) in presence of pyridine and with
Ce(IV)\(^{16}\). The chelates have absorption spectra differing
considerably from those of the constituents and were
studied using spectrophotometric method.

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12. Bale Davis, Discussions Faraday Society
Morgan Monk) No. 24, 94 (1957).
To confirm the results, precipitation studies were undertaken. T-sulfonamidine Cu(II) complex was precipitated by Bilman and Chernin. It had the metal ligand ratio as 1:2. They have reported the ligand to be specific for copper precipitation. They were the first to use sulfonamidine compound as the precipitating agent.\(^{17}\)

Job's method of continuous variation is the known technique that utilizes the additive property (as absorbance) to determine the composition of the complex. This method is applicable to systems where only one complex is formed, but Vosbergh and Cooper\(^{19}\) have extended it to systems where more than one complex coexists.

Woldbye\(^{21}\) has, however, criticized the method pointing out that it is extremely unlikely that only one complex will exist in solution where more than one ligand molecules combine with a metal ion to give a complex. The method of continuous variation often does not give correct results when hydrolysis, mixed complex formation or competitive reactions occur.\(^{22}\) Since the photometric systems presented here are dependent on three components

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and possible mixed complex formation the method of continuous variation was not applied. The slope ratio method to establish the empirical formula of the coloured complex was discussed by Harvey and Manning\textsuperscript{23}. This method is a modification of the continuous variation method in which the ends of the curves are used where there is a large excess of one or the other of the reactants\textsuperscript{24}.

Yoe and Jones worked out the mole ratio method\textsuperscript{25}. A series of the solutions containing a constant concentration of the metallic ion or the ligand and a gradually increasing concentration of the other is prepared. The absorbances of the solutions are plotted against the concentration ratios. For a stable coloured complex the curve rises and breaks sharply to a constant absorbance at the mole ratio of the components in the complex. If both interactants are colourless or if only one of the interactants is coloured and it is taken in a constant concentration while the other is varied, the curves of similar type are obtained. The less stable is a complex, the lesser is the sharpness of the break. However, a continuous curve which becomes approximately parallel to the mole ratio axis is obtained.

\textsuperscript{23} Harvey A. E., Manning D. L., \textit{J. A. C. S.} \textbf{72} 4480 (1950).
\textsuperscript{24} Holcomb H. P., Yoe J. H.; \textit{Anal. Chem.} \textbf{32} No 6 612 (1960).
when an excess of the variable component is added. The curves can be made to break sharply by carefully controlling the ionic strengths of solutions by the addition of an inert electrolyte. This is suggested as the modification of the mole ratio method by Harvey and Manning (loc cit). In case where ionic concentration is not adjusted extrapolation gives an idea of the break with clarity. Holcomb and Yee (loc cit) in the studies of uranyl complexes have ascertained the break by extrapolation of the graph. Extrapolation was used in the studies of Hafnium–chromotop–2R complexes and also in the studies of N–aryl hydroxamic acid.

The mole ratio method is used to find out the empirical formula of the coloured complexes of Copper(II) and Cerium(IV) with the sulfonamidines in the present study. The formula of copper sulfonamidine complex is also confirmed by precipitation studies conducted at pH 7.2 – 7.5. The observed weights of the precipitates are in good agreement with the theoretical i.e. calculated weights. Among the successful physico–chemical methods of determining the end point in titration, the use of monochromatic light

absorption is rather recent. Although preliminary investigations were carried out in the beginning of this century, Muller and Patridge\textsuperscript{28} pioneered in this field. Goddu and Hume have published a review in 1954\textsuperscript{29}. Bosridge\textsuperscript{30} has discussed the various aspects of this method in his mono-graph. The titrations are based on Lambert-Beer's law which is the fundamental law of photometry and photometric titrations. The standard solution is added to the sample in increments, while the absorbance of the light passing through the solution is measured. A graph between absorbance and the volume of the titrant added is plotted and the point of inflection of the graph gives the end point. Photometric titrations have been used to standardize E.D.T.A. with NcdV by Jack Powel etal.\textsuperscript{31}

The detailed discussion of the photometric titration is given along with the study of Cerium(IV) complexes. The present work incorporates the study of colour reactions of p-chloro and p-bromo-sulfonamidines with Cerium(IV) and copper(II) and the complexes formed by them.

Photometric titrations of cerium (IV) with the ligands were used to determine the empirical formula of the complexes formed with cerium (IV) by the ligands. Titrations give that 1:2 complex is formed by Ce(IV) with both the reagents. This observation is confirmed by Yoe and Jones mole ratio method (loc. cit).

West has given a detailed discussion about the interferences caused by any foreign ion or substance and has recommended various precautions to be taken during investigation. If the substance interferes, it may reduce or increase the absorbance. If the foreign substance is colour-less it rarely interferes.\(^3\)\(^2\),\(^3\)\(^3\),\(^3\)\(^4\).

Shape of the absorption curve is a good criterion of identifying and is much used in the analysis of complex compounds. The absorption spectrum reveals the presence of chemically similar impurities in a sample of supposed purity. This method provides the proper wave length and is applicable to simultaneous determination of more than one component.\(^3\)\(^5\). There is no difficulty in determining two components where absorption spectra do not overlap.

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When the curves overlap interference is caused. This is demonstrated by Skoog et al.\textsuperscript{36} in the studies of quinoxaline 2,3 diol as a colorimetric reagent for nickel. Cobalt forms a complex with the reagent and the absorption curve overlaps the nickel curve sufficiently to cause interference when the procedure is followed and when nickel cobalt concentrations are approximately equal.

A common analytical problem is the determination of a single absorbing constituent in the absence of other constituents with interfering absorptions. Some times no interfering absorption exists because of the nature of the sample. However some interferences can be removed by suitable treatment of the sample\textsuperscript{37}. From the absorption curves the best wave length for determination is to be decided. A region may be chosen where the effect of the other ions may be absent or minimum. To determine two substances present together in solution the absorbances of the solution are measured at two wave lengths provided the absorbances of the two components present are known separately. Interferences caused by commonly alloying materials with copper and cerium were investigated on


\textsuperscript{37} Biffen, F. M., Seaman, W.—In chap. \textbf{Visible and U.V. Spectrophotometry of Modern Instruments in Chemical Analysis.}
similar lines in the present study.

Organic compounds are of use in the quantitative analysis, in separation, and determination of elements. Because of group reactivity, organic reagents react with metals. Organic reagents have an increasing analytical significance since their use greatly increases the specificity and the sensitivity of analytical reactions, introducing a simplification and rationalization of analytical methods in micro-chemical analysis. An organic compound is designated as a reagent only if it reacts with a material which is to be detected or determined. The question is not of reacting materials but of important analytical aids, which are admitted in carrying out analytical processes. Such materials include substances that are employed as indicators or spotting test reagents.

Ferroin\textsuperscript{38} gives colour with iron and is used for the estimation of iron and also as indicator in titration of ferrous ion\textsuperscript{39}. N-Phenyl anthraquinoneacid is also used as indicator in iron titrations and cerate titrimetry.


Since p-chloro and p-bromo sulfonamido- N-anilines give an intense colour with Ce(IV), it was thought that these reagents could be used as internal indicators in ceric titrimetry. A study was undertaken and it was found that these reagents serve as excellent indicators for this purpose and can replace ferroin and N-phenyl anthraquinonic acid. These reagents are easy to prepare and are much less costly than ferroin and N-phenyl anthraquinonic acid and do not need any blank.

No present day worker who discovers organic reagents that lead to coloured organic metallic reaction products would omit trials to discover the applicability of his compounds as spot test reagents. All spot test reagents give coloured organometallic reaction products. In the present study the sulfonamidines have been tried as spot test reagents for copper(II) and cerium(IV).