Chapter I of the thesis describes the oxidimetric determination of hydrazine and some of its organic derivatives in hydrochloric acid medium using sodium vanadate, chloramine-T, potassium periodate, potassium bromate, sodium hypochlorite, potassium chlorate and ceric sulphate as oxidising agents. In visual titrations iodine monochloride has been used as a catalyst and indicator in the extraction end-point method using chloroform as the organic liquid. In potentiometric titrations, platinum wire electrode was used as an oxidation-reduction electrode and it was coupled with saturated calomel electrode. At the equivalence point there was a sharp jump in potential in each titration.

Hydrazine and its organic derivatives were also determined indirectly using sodium vanadate, chloramine-T, potassium dichromate and potassium ferricyanide as volumetric reagents. An excess of the sodium vanadate solution added to each hydrazine derivative was back titrated potentiometrically with standard ferrous ethylenediamine sulphate solution. In case of chloramine-T, potassium dichromate and potassium ferricyanide, the excess of the oxidising agent was back titrated iodometrically with standard sodium thiosulphate solution.

Hydrazine sulphate, semicarbazide hydrochloride,
bensalazine, bensalsemicarbazone, aminoguanidine hydrochloride, chloral hydrazine, \( \text{o-hydroxybenzalsemicarbazone} \), \( \text{p-methoxy-benzalsemicarbazone} \), ethylmethylketonesemicarbazone, phenylhydrazine hydrochloride, \( \text{2:4-dinitrophenylhydrazine} \), \( \text{p-chlorobenzalsemicarbazone} \), cinnamylsemicarbazone, bis-phenylhydrazide of adipic acid, nitroaminoguanidine, acetonesemicarbazone, \( \text{o-nitrobenzalsemicarbazone} \), \( \text{o-chlorobenzalsemicarbazone} \), \( \text{m-nitrobenzalsemicarbazone} \), \( \text{\text{a-formylphenylhydrazine}} \), benzoylehydrazine, \( \text{\text{a-acetylphenylhydrazine}} \), \( \text{\text{a-propionylphenylhydrazine}} \), \( \text{4-hydroxy-3-methoxybenzalsemicarbazone} \), \( \text{3:4-methyleneedioxy-benzalsemicarbazone} \), \( \text{4-phenylsemicarbazide hydrochloride} \) and succinhydrazide were determined by the above mentioned methods. Hydrazino group in each compound is oxidised with a four-electron change.

\[
\text{NaHg}^+ \rightarrow \text{N}_2 + \text{H}_2 + 4\text{e}^-
\]

Chapter II deals with the use of perbensoic acid and iodine monochloride as volumetric reagents for the determination of some common reductants. Potassium ferrocyanide, arsenious oxide, tartar emetic, sodium sulphite, stannous chloride, hydrazine sulphate and sodium thiosulphate were titrated with 0.05 \( \text{M} \) perbensoic acid (in chloroform) solution at pH 4.0 to 4.6 in sodium acetate and acetic acid buffered solutions using iodine as a catalyst. In visual titrations appearance of faint violet colour in the chloroform layer indicated the end-point. In potentiometric titrations a sharp jump in potential was observed at the equivalence point in each titration.
The standard solution of perbenzoic acid in chloroform was also used as an oxidant for the indirect determination of hydrazine sulphate, ascorbic acid, sodium thiosulphate, tartar emetic, hydroquinone, sodium sulphite and arsenious oxide. The excess of perbenzoic acid added to each of the substances was back titrated iodometrically with standard sodium thiosulphate solution.

Chapter II further gives the use of iodine monochloride as volumetric reagent for the determination of arsenious oxide, tartar emetic, ascorbic acid, hydrazine sulphate, phenyl-hydrazine hydrochloride, aminoguanidine hydrochloride, 4-phenyl- semicarbazide hydrochloride, semicarbazide hydrochloride, hydroquinone, thallous nitrate, \( \alpha \)-formylphenylhydrazine and \( \beta \)-acetylphenylhydrazine in 1.0 N to 2.0 N hydrochloric acid and excess of mercuric chloride. The mercuric ions complexed with iodide ions which were formed due to the reduction of iodine monochloride and thus a sharp end-point was obtained in visual titrations. Some of the above mentioned reductants were also titrated with the iodine monochloride by a potentiometric method.

Chapter III describes some complexometric determinations with ethylenediaminetetra-acetic acid (disodium salt). Schwarzenbach and coworkers\(^1\) made a detailed study of physicochemical properties of ethylenediaminetetra-acetic acid (EDTA) and its salts regarding their ability to form complex compounds with various cations, and thus laid the foundation of a new
branch of volumetric analysis, 'complexometry'. They recommended EDTA as an analytical reagent in complexometric titrations because it forms very stable complexes with most cations. EDTA molecule contains a sufficient number of ligand groups to permit bonding with all coordination positions of a metal ion, and for this reason forms complexes with many metals.

Mainly metallochrome indicators have been used to detect the end-point in complexometric titrations. As the metallised indicator colour is different from the unmetallised indicator colour, a change in colour is observed when all the metal ions are complexed and pH of the solution changes. A number of organic and inorganic compounds give colour reactions with metal ions, but a few of them can be used as pH sensitive indicators in complexometry.

During the past few years a number of methods have been developed for the estimation of iron (III) with ethylenediamine-tetra-acetic acid using various metallochrome indicators. According to Flaschka, no known indicator for iron (III) gives satisfactory end-points and detection by instrumental means or a back titration procedure may give better results. However, the direct titration has the advantage of speed and of relatively high selectivity.

During the course of this study it has been found that p-anisidine-thiocyanate mixture serves as a very good indicator in the complexometric estimation of iron (III) with EDTA. It
fulfills almost all the requirements of a good metal indicator as its colour reaction with ferric iron is very sensitive and a sufficiently strong colour persists in the solution near the end-point. Violet colour due to the metal-indicator complex sharply changes to pale yellow at the end-point when whole of iron (III) is complexed with EDTA. Good results have been obtained with this indicator and it can safely be recommended for the titration of iron (III) at pH 2 to 3 and of copper (II) at pH 4.0 with EDTA.

Acetylacetone and N-benzyolphenyldroxylamine form red coloured complexes with iron (III) and on titration with EDTA the colour sharply changes from red to pale yellow. Very satisfactory results have been obtained with these indicators.

The stability constants (log K) for complexes of EDTA with iron (III) and copper (II) are reported to be 35.1 and 18.8 respectively. It is rather difficult to estimate each of the metals in a mixture by complexometry. A method has been developed for the estimation of copper (II) and iron (III) in a mixture. When potassium thiocyanate-ether is used as an indicator, copper present in the mixture does not interfere and red colour in the ethereal layer due to ferric thiocyanate disappears when whole of the ferric iron is complexed with EDTA (disodium salt). Total iron (III) and copper (II) in the mixture has been determined with EDTA (disodium salt) using p-anisidine-thiocyanate as indicator. Difference in the amounts
of EDTA (disodium salt) used in these two sets of titrations is equivalent to cupric copper present in the mixture of copper (II) and iron (III).

A number of metallic salts do not interfere in these complexometric determinations.

REFERENCES