PREFACE

This thesis deals with studies on some new redox titrimetric methods in aqueous as well as nonaqueous media.

The highlight of the present investigation is the development of a new oxidimetric titrant, bromamine-T for use in aqueous media. Bromamine-T is the sodium salt of N-bromo-p-toluene sulphonamide and is the bromine analogue of the well-known and established oxidimetric titrant, chloramine-T. Although the compound bromamine-T had been known for a long time and had been occasionally used as a brominating agent in organic bromination reactions, its use as an oxidimetric titrant has been developed for the first time in the present investigation. Analytical methods using bromamine-T have been developed for the titrimetric determination of about 19 typical, yet diverse, reductants. These studies, it is hoped, would serve to establish the status of bromamine-T as an oxidimetric titrant.

In addition to the introduction of bromamine-T as a new oxidimetric titrant, the present investigation is also concerned with extended applications of some other already-
known halogen-bearing oxidants. These include bromine monochloride, dibromamine-T, dichloramine-T and iodosobenzene dichloride.

Pioneer work on bromine monochloride was done by Schulek and coworkers.¹ In the present studies, new excess back titration methods using bromine monochloride have been developed for the determination of 17 reductants. Dichloramine-T, dibromamine-T, and iodosobenzene dichloride were introduced as oxidimetric titrants by earlier workers in our laboratories. In the present investigation this work has been extended to several additional reductants.

Interest in redox titrimetry led us to make a brief survey of this field. In the course of a literature survey, our attention was drawn to the work of Baur and Bricker² who introduced hexammine cobalt(III) tricarbonato cobaltate(III) as an oxidimetric titrant. This complex acts as an oxidant by virtue of the easy decomposibility of the tricarbonato cobaltate(III) anion in acid medium leading to the in situ production of the highly potent oxidant, the hexaquo Co(III) ion. This interesting oxidant seems to have attracted only scanty attention since its discovery. The original authors (Baur and Bricker) had studied only three systems with this oxidant. In the present studies we have extended the use of this oxidant to 5 other systems. This work is included in
The work described in this thesis has been published/is under publication as detailed below.

1. Interhalogens as oxidimetric titrants--Oxidimetric determinations with Bromine monochloride, (Indian Journal of Chemistry, 14A (1976), pp. 115-117.


3. Novel redox titrants in nonaqueous or partially aqueous media--Part VII--Visual indicator redox titrations and excess-back titrations using some purely organic compounds as oxidimetric titrants in mixed aqueous organic solvent media--Paper read at the 27th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, held between 1st and 5th March, 1976 at Cleveland, U.S.A.

4. Determination of Anthranilic acid and Anthranilates of Zn, Mn, Co, Ni, Cu and Cd using Dichloramine-T and Dibromammine-T (under publication).

5. Iodosobenzene dichloride as an oxidimetric titrant--Determination of Iron(II), Ferrocyanide, Hydrazine,
Antimony(III), Hydroquinone and Anthranilic acid (under publication).

6. Hexammine Cobalt(III) tricarbonato Cobaltate(III) as an oxidimetric titrant--Determination of Antimony(III) Arsenic(III), Thallium(I), Ferrocyanide and Ascorbic acid (under publication).