Chapter 4

General Survey and Discussion of the Work
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The amperometric reagent employed for the determination of various mental species was thioglycolic acid (TGA). The polarographic behaviour and the coordinating properties of this acid have been discussed in detail in the ‘Introduction’ of this thesis. However, a few salient features deserve mention again to make it clear as to why the choice of TGA as an amperometric reagent was made by the author.

TGA possesses a sulphhydryl and a carboxylic group

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\text{HS-} \overset{}{\text{H}_2\text{C}} - \text{COOH}
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It is apparent that due to presence of ‘hard’ donor oxygen and ‘soft’ donor sulphur atoms, TGA can act as a very effective chelating ligand. Evidences are available in literature to suggest that TGA often involves both these for the purposes of co-ordination. This results in the formation of stable 5-membered ring. However, it may, depending upon the metal species, also act sometimes as a monodentate ligand. It is noteworthy that TGA is polarographically active and gives reversible, one electron, pH dependent anodic wave at d.m.e. This makes it doubly useful as an amperometric analytical reagent as not only the cathodic wave of different metal species but its own anodic wave too can be exploited for the purpose. It is obvious that this ligand offers greater chances of developing new amperometric methods (based on the variation of its anodic current as the titration advances) of estimating even those metal species which are not reducible at d.m.e. in certain media, without using any electrometric indicator.

TGA gave good results with the following metal species:

Ga(III), As(III), As(V), Se(IV), Se(VI), In(III), Sb(III), Te(IV), Tl(I), Tl(III), Pb(II), Th(IV) and U(VI)

The fundamental interaction found operating in all the titrimetric processes was complexation of the metal species except in case of Te(IV).
Method for Te(IV) seems to involve a two step reaction, the first step results in the reduction of Te(IV) to Te(II) by the reagent followed by the complexation in the second step.

Since TGA possess ‘soft’ (Sulphur) as well as ‘hard’ (Oxygen) donor atom, they should coordinate with a whole spectrum of metal species. This expectation stands fully justified as all the metal species selected, be it hard, soft or border line lewis acid except one i.e. Te(IV) seemed to enter into coordination with this acid coordination presumably occurred in general through deprotonated carboxylic and sulphhydryl groups simultaneously (chelation) as has been concluded by several workers on the basis of spectroscopic studies of solid complexes prepared. A thorough discussion of coordination of various metal species has already been given at the end of every individual section. Out of all these metal ions, Ga(III), As(III), As(V), In(III), Th(IV) and U(VI) are the hard lewis acids, Sb(III) and Pb(II) are the borderline species while all others i.e. Se(IV), Se(VI), Te(IV) Tl(I) and Tl(III) are soft lewis acid species.

All the metal species except Te(IV) could be estimated anodically while estimation of Te(IV) could be accomplished by anodically as well as cathodically.

A few generalization regarding coordination of metal species that can be made from above discussion are as following:

1. In overwhelmingly, large number of cases, only anodic titrations could be perfected as the cathodic titration led to either irregular/ scanty suppression of the reduction current of the metal species or no reaction at all. Only exception was Te(IV). This meant that the coordination was initiated only in presence of excess of the ligand. This indicated formation of rather weak complexes.

2. Formation of weak complexes could also be inferred from the observation that in most of the cases [except Se(IV) and Te(IV)] a large
amount of anodic current remained unneutralized at the null point, pointing towards possible large scale dissociation of the complex. This may be due to the overall low concentration of the ligand in the cell solution and the presence of a number of other ligand like Cl\(^-\), NH\(_3\), CO\(_3^{2-}\) etc, in the same which could offer stiff competition to TGA for coordinating with the metal species.

The new methods evolved are quite satisfactory. Their efficiency is better than or comparable with earlier reported amperometric methods. They also mostly compare favourably with common spectrophotometric methods, wherever they are not, atleast they score a point over such methods in terms of large concentration range that can be covered. Tolerance for foreign species in the cell solution is also good and lies within a reasonable limits.