Summary
The brief summary of thesis entitled “New Amperometric Methods for Trace Determination of Coinage and Platinum Metal Ions” is presented. Thesis has been divided into 5 chapters. The chapters are:

1. Introduction
2. Method, apparatus and chemicals
3. Amperometric determination of coinage metals
4. Amperometric determination of platinum metals
5. General survey and discussion of the work.

CHAPTER 1: INTRODUCTION

This chapter opens with an introduction to the technique of amperometry and a brief history of its evolution. Mention has been made of electrodes other than d.m.e., used in this type of work and a short description of variation of the technique known as “dead spot end point technique” is given. This has been followed by a brief survey of review literature on amperometric work. Objective and scope of the present work have been defined and this precedes a survey of literature published on the amperometric determination of various metals ion selected by the author (mentioned earlier) for studies. Then a brief description of the general, coordination and polarographic properties of organic ligands (TGA, TDPA and TSH) chosen has been given along with a survey of the reported work on the complexation reactions of these ligands.

CHAPTER 2: METHOD, APPRATUS AND CHEMICALS

This chapter deals with the methodology of the work and also includes a description of the dropping mercury electrode assembly and other apparatus and instruments used for investigations. Source compounds of various metal ion species determined as well as the methods employed for the standardization of solutions have been mentioned. A list of source compounds of the species, whose interference in the titrimetric methods evolved has been checked, is also given.

CHAPTER 3: AMPEROMETRIC DETERMINATION OF COINAGE METALS
This chapter has been divided into three sections. These are as follows:

SECTION I: AMPEROMETRIC DETERMINATION OF COPPER

Amperometric determination of copper with TGA was achieved in 0.1M NH₃+0.1M NH₄Cl medium. Metal species as well as organic acid, both are polarographically active in this medium and give their characteristic cathodic and anodic waves. Metal-ligand molar ratio was found to be 1:2 in both the cases i.e. cathodic and anodic titrations. Emergence of violet colour in the cell solution was noted during both types of titrations. Complexation with thioglycolic acid seems to be the basis of the new amperometric methods of estimation. Efficiency of TGA was found to be very good, and this enabled estimation of Cu(II) solutions as dilute as 3.18ppm with great accuracy. Interference of foreign ions has also been checked.

SECTION II: AMPEROMETRIC DETERMINATION OF SILVER

Amperometric determination of silver with TGA was performed in 0.1M KNO₃ medium. TGA as well as Ag(I) gave their waves in this medium. KNO₃ instead of KCl was used in the agar-agar salt bridge employed in these titrations. Both cathodic and anodic titrations were carried out successfully. Brownish colour appeared during cathodic titration while during anodic titration milkiness appeared. The metal-ligand ratio found was 2:1 in both of the cases. Complexation of Ag(I) with TGA has been suggested as the fundamental basis of the titrimetric methods evolved. The new amperometric method was quite efficient. Solution as dilute as 5.39 ppm could be estimated with high degree of accuracy. Tolerance limit of foreign ions was also checked for the new amperometric method.

SECTION III: AMPEROMETRIC DETERMINATION OF GOLD

Amperometric determination of gold with TGA was successfully carried out in three mediums, 0.1M KCl, 0.1M NH₃ + 0.1M NH₄Cl and acetate buffer of pH 3.7. Cathodic as well as anodic titrations were performed in all these three mediums because both metal ion and TGA were polarographically active in these mediums. In case of 0.1M NH₃ + 0.1M NH₄Cl medium, 0.005% solution of gelatine was used to suppress maxima. Near the end point of these titrations different colours appeared in different mediums. In case of 0.1M NH₃ + 0.1M NH₄Cl medium dirty yellow colour appeared, in 0.1M KCl medium colour changed yellow to milky while in acetate buffer
of pH 3.7 medium yellow colour changed to purple near the end point. Metal-ligand ratios were found to be 1:1 in each case. Cathodic titrations were more sensitive in comparison to anodic ones as more dilute solutions could be estimated with high degree of accuracy. Interference of foreign ions has also been checked in all these amperometric methods.

CHAPTER 4: AMPEROMETRIC DETERMINATION OF PLATINUM METALS

This chapter has been sub-divided into six sections, described below:

SECTION I: AMPEROMETRIC DETERMINATION OF RUTHENIUM

This section involves the amperometric determination of Ru(III) with TGA in 2.5M NaCl in 7% acetic acid medium. In this medium both, metal ion and TGA, were found polarographically active. The metal species-TGA molar ratio obtained at the null point was 1:0.64. No indication of any chemical interaction between the metal species and organic acid was observed in this medium. Titration curve obtained was a straight line with slight change in the slope after it intersected the residual current line. Positive evidences were gathered to show that the phenomenon of compensation of the cathodic current of Ru(III) by the anodic current of TGA was responsible for the appearance of the null point. The new method enabled the estimation of Ru(III) solution as dilute as 5.05 ppm quite accurately. Tolerance limit of foreign ions was also worked out successfully.

SECTION II: AMPEROMETRIC DETERMINATION OF RHODIUM

This section is sub-divided into two parts:

a) Amperometric Determination of Rhodium with TGA

This part deals with the amperometric study of Rh(III), which was carried out with the help of thioglycolic acid (TGA) in 0.1M NH₃+ 0.1M NH₄Cl supporting electrolyte. Only anodic titrations were successful in this medium. Rh(III):TGA molar titrimetric ratio 2:1 was obtained. In cathodic titrations no suppression in cathodic current was observed. Solutions as dilute as 5.15 ppm were determined quite accurately. Interference of foreign ions was also checked.
b) Amperometric Determination of Rhodium with TDPA.

This part involves the amperometric study of Rh(III), which was carried out with the help of thiodipropionic acid (TDPA) in 0.1M NH$_3$+ 0.1M NH$_4$Cl supporting electrolyte. Cathodic and anodic titrations were successfully carried out in this medium. Metal–ligand molar ratio was found to be 1:1 in cathodic as well as in anodic titrations.

SECTION III: AMPEROMETRIC DETERMINATION OF PALLADIUM

Successful amperometric estimation of Pd(II) has been carried out with the help of TGA in 0.1M KCl medium. Both anodic and cathodic titrations were performed in this medium. Titration potentials have been selected in the limiting region of the anodic wave of TGA and in the limiting region of cathodic wave of metal ions. At the end point colour of solution changed to golden yellow. The molar ratio of 1:2 was obtained for Pd(II)- TGA. Cathodic titrations were found to be more sensitive, as solutions as dilute as 1.06 ppm could be estimated accurately than anodic ones in which the estimation limit was 10.64 ppm. Tolerance limit of foreign ions was also carried out.

SECTION IV: AMPEROMETRIC DETERMINATION OF OSMIUM

This section is sub-divided into two parts.

a) Amperometric Determination of Osmium with TGA

This part deals with the amperometric determination of Os(VIII) with TGA in 0.1M KCl and 0.1M NaOH mediums. In case of 0.1M KCl medium, 0.005% gelatine solution was added to suppress maxima. Anodic as well as cathodic titrations were carried out successfully. Metal to ligand molar ratio of 5:1 was found in both the mediums and in both type of titrations. Titrating solution changes from yellow to colourless near the null point in case of 0.1M NaOH medium. The new methods enabled the estimation of Os(VIII) solution as dilute as 3.80 ppm quite accurately in case of 0.1M NaOH medium while in 0.1M KCl medium this limit was 5.71 ppm. Interference of various foreign ions was also worked out in the new amperometric methods.

b) Amperometric Determination of Osmium with TDPA

(v)
This part deals with the amperometric determination of Os(VIII) with TDPA (thiodipropionic acid) in 0.1M NaOH medium. Anodic as well as cathodic titrations were carried out successfully. Metal-TDPA molar titrimetric ratio of 1:1 was obtained in both types of titrations. Solutions as dilute as 4.76 ppm were determined quite accurately. Tolerance limit of foreign ions was also worked out successfully.

SECTION V: AMPEROMETRIC DETERMINATION OF IRIDIUM

This section is sub-divided into two parts:

a) Amperometric Determination of Iridium with TGA

This part involves the successful amperometric determination of Ir(III). TGA was used as an amperometric reagent. 0.1M NaClO₄ solution was used as supporting electrolyte. Only cathodic titrations were performed successfully in this medium. Metal-ligand ratio found to be 1:1. Tolerance limit of foreign ions was also checked for the new amperometric method.

b) Amperometric Determination of Iridium with TSH

This part deals with the amperometric studies of Ir(III), which was carried out with the help of thiomalic acid (TSH) in 0.1M NaClO₄ supporting electrolyte. Cathodic as well as anodic titrations were performed. Metal–ligand molar ratio of 1:1 was obtained in cathodic and anodic titrations. Interference of various foreign ions was also worked out in the new amperometric method.

SECTION VI: AMPEROMETRIC DETERMINATION OF PLATINUM

This section involves the amperometric studies of Pt(IV) which was carried out in acetate buffer medium of pH 4.99 with the help of TGA. Only cathodic titrations were performed in which TGA solution was used as titrant. As Pt(IV) wave shows maxima, 0.005% gelatine solution was added in the titrating solution to suppress this maxima. Pt(IV):TGA molar titrimetric ratio 1:2 was obtained. Complexation of metal ions with organic acid was the basis of new amperometric method. The method seems to be quite efficient, as solution as dilute as 9.75 ppm can be estimated successfully. Tolerance limits for foreign ions have also been worked out.

CHAPTER 5: GENERAL SURVEY AND DISCUSSION OF THE WORK
This chapter deals with the general survey of the work embodied in various sections and attempts to find out a correlation. The chapter starts with an account of the coordinating and polarographic properties of organic sulphur compounds (TGA, TDPA and TSH) and proceed to classify the new titrimetric methods evolved for estimating the coinage and platinum metal species amperometrically into three distinct categories namely (i) complexation; (ii) current compensation and (iii) reduction of the metal species. Since each of the organic sulphur compound possesses ‘soft’ as well as ‘hard’ donor atoms, their complexation reactions with the various metal species have been discussed in the light of such characteristics. In the end, certain generalized conclusions have also been drawn.
List of Publications

1. New Amperometric Methods for the Trace Determination of Cu(II), Ag(I) and Au(III).
   Satyender P. Khatkar, Dayawati, Ritu Langyan

2. Amperometric Trace Determination of Os(VIII) with Thioglycolic Acid.
   Ritu Langyan, V.B. Taxak and S.P. Khatkar
   International Discussion Meet on Electrochemistry and its Applications, Editor,

3. New Amperometric Methods for Trace Determination of Ru(III) and Ir(III).
   Ritu Langyan and S.P. Khatkar
   (Communicated)

4. New Amperometric Methods for the Trace Determination of Pd(II) and Pt(IV).
   Ritu Langyan and S.P. Khatkar
   (Communicated)

5. New Amperometric Methods for the Trace Determination of Rh(III) and Ir(III).
   Ritu Langyan and S.P. Khatkar
   (Communicated)

6. Amperometric trace determination of Rh(III) and Os(VIII).
   Ritu Langyan and S.P. Khatkar
   (Communicated)