Chapter-1

Introduction
INTRODUCTION

Amperometry is an offshoot of the technique of D.C. polarography and very well suited for trace level determination of metals. In fact, it is the only extended application of polarography discovered by Jaroslav Heyrovsky in 1922. Professor Heyrovsky was awarded Nobel Prize in 1959 for this method of analysis. Overriding merits of this technique were realized soon after its discovery and during the last fifty years, it has developed into a major branch of electrometric titrations, which is based on measurement of flow of electrons as an expression of chemical effect. In recent years the importance of low concentration has tremendously increased both in science and technology. Quantitative determination of very dilute solutions is now required in all fields of activity including research, manufacture and utilization. In view of this situation present work was undertaken with the aim of evolving new amperometric methods for trace determination of various metal ions species. Amperometric titrations have a very wide field of applicability. In fact, amperometric determinations are more rapid and reproducible. Moreover, it is unimportant whether the electrode reaction is reversible or irreversible. Amperometric determinations are more precise and accurate in comparison to polarographic estimations.

Precision, accuracy and reproducibility of a few tenth of a percent are commonly attainable with solutions of concentrations $10^{-4}$M or greater while more dilute solutions up to $10^{-5}$M have often been estimated within the inaccuracy limit of $\pm 2\%$, which compares favourably with that obtained with other sophisticated methods in vogue for analysis of very dilute solutions.

AMPEROMETRY

Amperometry is an electroanalytical technique based upon the measurement of the current flowing through the working electrode of an
electrochemical cell. It is very simple and low cost technique, suitable for developing country like India. In Heyrovsky method, dropping mercury electrode (d.m.e.) is the polarisable electrode while saturated calomel electrode (S.C.E.) is almost employed as the non polarizable (reference) electrode. Virtually every element in one form or other and a large number of organic compounds are amenable to polarographic analysis. In addition, the method has helped in the development of organic electro-synthesis and the study of reaction kinetics and phenomenon of adsorption. Polarography involves transfer of electrons between the d.m.e. and the ions, atoms or molecules present in the solution that surrounds it in the cell. Oxidation of the electro-active species at the d.m.e. gives anodic wave while reduction yields cathodic wave. Organic compounds like hydroquinones, mercaptans and some inorganic anions are known source of anodic waves while most of the metal cations and organic functional groups yield reduction (cathodic) waves. Anodic waves are less common as only a small range of oxidation potentials can be covered with the d.m.e. before oxidation of electrode itself commences. Polarographic behaviour of any species is unique for a given set of experimental conditions, making the technique unique for selective analysis. Conventional amperometric technique consists of an electrometric titration, which uses the polarographic wave as the basis. The current flowing at the d.m.e. is measured as a function of the potential imposed over it. When a potential is reached at which the electro-active species in the solution is reduced or oxidized, the current begins to rise very sharply with increasing potential until it is limited by the rate of arrival of the species at the d.m.e. surface by the process of diffusion alone (the whole exercise being carried out in quiet solution in the presence of sufficient concentration of some indifferent electrolyte, called supporting electrolyte). From now as the current - potential curve level off upto the point where hydrogen evolution takes over. The basis for D.C. amperometry employing
d.m.e. is the Ilkovic equation given below:

\[ i_d = 607 n D^{1/2} c m^{2/3} t^{1/6} \]

Where

\( i_d \) = Average diffusion current in microampere during the life of a mercury drop.
\( n \) = No. of electrons involved in the electrode reaction at the d.m.e.
\( D \) = Diffusion coefficient of the electro-active species in cm\(^2\)/sec.
\( c \) = Concentration of electro-active species in millimoles/litre.
\( m \) = Rate of flow of mercury from the d.m.e. expressed in mg/sec.
\( t \) = Drop time or time in seconds taken by a drop of mercury to fall from the capillary.

It is obvious that with all other factors remaining constant, the diffusion current is directly proportional to the concentration of the electro-active species.

Polarography can be used as the basis of an electrometric titration method (amperometry) provided the diffusion current, is yielded by the titrant, the substance being titrated, both or a reaction product of the two. Sometimes, if none of these is polarographically active, the titration can still be accomplished with the help of an electrometric indicator that gives a wave. Charlot and Tremillon\(^2\) have published an extensive review of the literature on the use of such indicators. All amperometric titrations are performed by measuring the current after the addition of each of a fairly small number of aliquots of reagent. If the titration is performed at a potential where the reduction of dissolved oxygen would contribute to the measured current, it is usually necessary to remove any oxygen added with the reagent by bubbling inert gas through the cell for an appropriate length of time after each addition. The reaction between the titrant and the substance being titrated may result in the progressive precipitation, oxidation, reduction or complexation and thus bring about a change in the concentration of the depolarizer. The end point in
such titrations is found graphically and the curve is a plot of limiting current corrected for dilution by the reagent and if necessary, for any residual current, as a function of the volume of titrant. The applied e.m.f. is kept constant throughout the process. Ideally, the titration curve consists of two straight lines intersecting each other at the equivalence point.

Sometimes an amperometric curve is obtained which looks almost linear. The reason being that there is no chemical reaction between the substance being titrated and the titrant but one gives cathodic and the other, anodic wave and the limiting region of both are present at the titration voltage. As the titration advances, the other gradually compensates one type of current, yielding the first linear segment of the curve that intersects the zero line (or residual current line) at the equivalence point (null point). After this as the titration proceeds further, the same linear segment forges ahead on the other side of the zero line with only slight, or sometimes almost invisible change of slope. In such cases, at times, a strictly linear curve with absolutely no change in slope at the null point may be obtained. But this is a very rare situation and happens only when the diffusion coefficients of the two species are identical.

The above electrometric titration method was first suggested by Heyrovsky and Berezicky in 1929 and later developed by Majer and Spalenka, who also suggested the name polarographic titration or polarometric titration. However, Kolthoff and Pans proposed the term "amperometric titration" to replace one suggested by Majer and Spalenka, as the method involved measurement of current. The latter term is now almost universally accepted though some workers, especially in the Czech, republic still favour the name polarometric titration.

IMPORTANCE OF AMPEROMETRY

1. Amperometric titrations have a wide field of applicability and different types of amperometric titrations can be accomplished successfully e.g.
   
a) Precipitation titrations
b) Acid base titrations

This is because the reading near the equivalence point have no special significance, hence slight soluble reactions can also be determined. Readings are recorded in the regions of excess titrant or excess reagent where solubility or hydrolysis is suppressed by the mass action effect. The point of intersection of two lines gives equivalence point.

2. It is highly sensitive technique and used for very dilute solutions upto ppm level.

3. The titrations can usually be carried out rapidly since the end point is found graphically.

4. This technique requires simple manual assembly and no prior calibration. Recording of whole polarogram is not necessary.

5. It does not require determination of the capillary characteristics and also the temperature need not to be adjusted or known as long as it is kept constant. Additionally,

a) relatively high solubility of the product

b) low solubility of the complex or

c) A slow reaction in the vicinity of equivalence point do not affect the accuracy of estimation as the null point is obtained from the $I$ vs vol. and the measurements of current near this point are of little significance in locating it just as in other electrometric titrations. All the titrations can often be carried out under conditions where visual or potentiometric methods are not possible and it is unimportant whether the electrode reaction is reversible or not. These titrations have also been used to study co-precipitation, adsorption and to determine solubility product and stoichiometry.6.

6. Foreign salts may frequently be present without any interference and indeed they are added as the supporting electrolyte in order to eliminate the migration current.
Amperometry has one limitation that one can determine the species (metal or otherwise) only up to ppm level. This limitation is due to the fact that the metal current (the variation in whose magnitude can be followed titrimetrically by gradually adding the titrant which may be a redox, precipitating or complexing agent) becomes almost negligible at desired lower concentrations. But even this limit can possibly be removed and the sensitivity of the method can be increased up to ppb or even ppt level, if catalytic waves of metals given in presence of some substance (catalysts) and often characterized by very high magnitude of current proportional to the concentration of metal are exploited for titrations.

**VARIOUS ELECTRODES USED IN AMPEROMETRY**

In amperometric titrations generally d.m.e. is used as an indicator electrode.

**ADVANTAGES OF SUCH ELECTRODE:**

1. Each drop behaves exactly in the same way as the preceding one and the average current measured with the galvanometer is accurately reproducible from drop to drop for a given applied potential.
2. A jerk or shock that causes one drop to behave erratically does not affect the following one; the d.m.e. is thus much less sensitive to mechanical disturbance than is a stationary microelectrode.
3. No chance of poisoning, as fresh electrode is formed after approximately every three second.
4. It adopts the applied e.m.f. instantaneously so is ideally polarizable.
5. Mercury is a noble metal so there is no reaction with constituent of electrolytic solution.
6. Dropping mercury electrode (d.m.e.) has small dimension hence electrolysis is possible in small volume of the solution and very small number of cations reduced or anions oxidized in electrolysis,
so that same solution can be used for hours, even days.

7. With Hg-electrode, it is possible to reach more negative potential in comparison to any metal electrode, before evolution of hydrogen begins. Consequently, a large numbers of reactions can be studied.

Workers have also put some other electrodes in the service. Latinen and Kolthoff in 1941 introduced a rotating platinum electrode (r.p.e.) consisting of a thin metal wire being rotated at a constant speed of 600rpm or more has been widely used, mechanical mixing also help in bringing the electro active species to the electrode surface, besides diffusion. Consequently, limiting currents are much higher, about twenty times, in comparison to those obtained with d.m.e. This fact is quite attractive from the point of view of amperometry though the utility of r.p.e. is still restricted due to following limitations:

1. Limiting currents are not very reproducible and often influenced by the previous history of the electrode.
2. High currents obtained with the electrode, make it particularly sensitive to traces of oxygen in the solution.
3. Hydrogen over-voltage for this electrode is low and greatly restricts the range of potentials for study. In fact, potentials more negative than -1.0V (Vs S.C.E.) cannot be applied even in almost neutral solutions. Hydrogen evolution begins at much more positive potentials in acidic solutions.

Harris and Lindsey gave first account of vibrating platinum electrode, which is a type of micro electrode in 1948. Other workers have also used rotating micro electrodes made of gold, tantalum, graphite, glassy carbon and certain other materials. All these solid micro-electrode suffer from one or other serious drawbacks. Impracticability of any general theoretical treatment of the limiting currents obtained with them has also seriously hampered their
application as common analytical tools.

BRIEF SURVEY OF REVIEW LITERATURE ON AMPEROMETRIC WORK

Appreciable amount of review literature on amperometric work is available. A book entitled Amperometric titrations have been published by J.T. Stock in 1965 is a comprehensive work. Another very useful work a monograph captioned Amperometric titrations with thio organic reagents were published by A.L.J. Rao and Bikram S. Brar in the year 1983. A number of review articles have made appearances from time to time in distinguished journals. Some of them, which are more important, are mentioned below.


Amperometry has found widespread application in industry. Maschler has discussed the suitability of the technique in industrial applications in 1974. A paper about the use of the technique in studying the biological reactions appeared in 1975. Chatten has published another communication discussing the use of several electrochemical techniques including amperometry in the
pharmaceutical analysis in 1983.

**SELECTION OF THE LIGAND**

It was decided to employ organic sulphur compounds for achieving the above-mentioned objective. This was done in view of the acknowledged characteristics of these compounds as avid complex formers\(^{11,22,23}\) and their susceptibility to undergo oxidation by some of the metal ions\(^{24}\). Sulphur (thio) compounds are being increasingly employed in the field of analytical chemistry for developing new methods of quantitative estimation due to their ability to form complexes with a large number of metal ions\(^{22,23}\). Such interactions are expected to bring significant changes in the polarographic characteristics of the metal ion, providing a sound base for the development of new amperometric methods. Organic sulphur compounds containing \(-\text{SH}\) group are also known to give anodic wave at d.m.e.\(^{25-30}\) and the possibility of exploitation of these for the purpose is an additional point in favour of the selection of such compounds as an amperometric reagent. In view of this the author of this thesis has selected one such compound, thioglycolic acid abbreviated as TGA in this thesis for achieving the objective.

Success has been achieved in developing very sensitive new amperometric methods for the estimation of as many as thirteen metal species, viz.

- 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)

Interference of various foreign ions in each case has been investigated and the selectivity of the methods established. The new methods have been proved to be very efficient on the basis of convenience, accuracy, speed and the concentration range of the analyte and it is thought that these will help the workers, desirous of determining very low concentration of the metal ion a lot.
SURVEY OF RELEVANT LITERATURE

Before we undertake a systematic study of the problem selected for research, it would be pertinent to list the important coordination properties and other relevant information regarding the chemistry of the metals, which constitute the main focus of this study, and to give a survey of the work already done by other researchers in the field. Since the work done up to 1962 has already been included in the book *Amperometric Titrations* by J.T. Stock\(^1\), we can confine our survey of the relevant literature on amperometric determinations only to the work done after this date. Since the d.m.e. has been predominantly adopted by various researchers and since the present study also relies on this very electrode, particular mention of the electrodes has generally been made in the survey only where special type of electrodes other than d.m.e. were used by the workers concerned.

GALLIUM

Gallium, the element No. 31 whose ground state configuration is \([\text{Ar}]\) 3d\(^{10}\) 4s\(^2\) 4p\(^1\), is a silver white metal. The only oxidation state of importance is +3 state. It forms colourless Ga\(^{3+}\) ions. The hydroxide, Ga(OH)\(_3\) precipitates at pH~3, but dissolves in weekly alkaline medium (pH 8-9). Its main use is in the semiconductor technology; the compounds GaAs, GaP and GaSb are semiconductors. Gallium has inexplicably low melting point of 29.8°. This has given it the longest liquid range (B.P. = 2070°) of any known substance and hence finds use as a thermometer liquid and substitute for mercury in vacuum pumps. Gallium(III) may form 4- and 6-coordinate complexes with usual stereochemical arrangement of ligands. The most important octahedral complexes are those containing chelate rings. Coordination with dicarboxylic acids commonly involves both such groups.

About two dozens papers have appeared on amperometric determination
of gallium. Sulphur containing organic reagents such as thiomalic acid\textsuperscript{31}, mercaptoquinoline\textsuperscript{32,33}, methyl thymol blue\textsuperscript{34} and xylenol-orange\textsuperscript{35} have been used for the purpose.

Some other organic reagents like N-benzoyl-phenylhydroxylamine\textsuperscript{36}, N-cinnamoylphenyl-hydroxylamine\textsuperscript{37,38}, N-3-styryl-acryloyphenylhydroxylamine\textsuperscript{39}, uranil-N, N-diacetic acid\textsuperscript{40} and 4(2-pyridylazo)naphthol\textsuperscript{41} have been used for the amperometric estimation of gallium.

EDTA has been used to determine gallium in sulphur containing semiconductors\textsuperscript{42}. Amperometry has also been exploited to study the reactions between gallium and oxalic acid\textsuperscript{43} and between gallium and tartaric acid\textsuperscript{44}.

One inorganic compound, \(K_4[Fe(CN)_6]\), has also been employed for determination of gallium in alunite and other aluminium containing rocks\textsuperscript{45}. Sommer\textsuperscript{46} has used this compound as titrant for determination of gallium in the oxidation products of GaAs at vibrating platinum electrode.

Rotating tantalum electrode has also been utilized for the amperometric determination of metal species and EDTA has been found to be a successful reagent\textsuperscript{47} in a direct method. Another method for the determination of gallium involves addition of excess of EDTA and amperometric back titration with electrogenerated mercury(II)\textsuperscript{48}. Microgram amount of gallium has been determined by similar back titration of EDTA with bismuth(III) at a rotating mercury electrode\textsuperscript{49}.

Gallium has also been determined by addition of EDTA and its back titration with zinc at a gold amalgam cathode\textsuperscript{50}.

Graphite electrode has also been found useful for the amperometric determination of gallium. A method has been developed involving the reagent N-benzoylphenylhydroxyl amine\textsuperscript{51} for determining gallium in gallium arsenide or phosphide while N-3-styrylaerylophenylhydroxylamine\textsuperscript{52} and N-cinnamoyl-p-totylhydroxylamine\textsuperscript{53} have been used for determining this metal in alloys.
Oxidation of N-cinnamoylphenylhydroxylamine at graphite electrode has led to the use of this reagent as amperometric titrant for gallium. Gallium has also been determined by the addition of resorcinol methyleneiminodiacetic acid, pyrocatecholmethylene iminodiacetic acid, or hydroquinone-2-methylene-iminodiacetic acid, followed by back titration at a graphite electrode with nickel ion.

ARSENIC

Arsenic, the element No. 33 possesses the ground state electronic configuration of [Ar] 3d\(^{10}\) 4s\(^2\) 4p\(^3\). It occurs in its compounds in the oxidation states +3 and +5. Arsenic (+3) and (+5) are amphoteric, but with much more acidic than basic character. The sulphides are characteristically capable of yielding soluble complexes (thio-salts). (+5) arsenic forms heteropoly acids.

Arsenic of AsX\(_3\) compounds (X=hal., R, H etc.) can act as donor of lone pair and can sometimes also expand its coordination number to 4 or 5 by accepting electrons from donor molecules, +5 arsenic usually acquires coordination No 6 with octahedral symmetry. Arsenic compounds are widely applied in agriculture as means against vermins and in medicine. As\(_2\)O\(_3\) finds use in analytical chemistry as mild reducing agent.

Some methods have been evolved for the amperometric determination of As(V). Thiomalic acid has been employed to determine As(V) in 0.1M KCl medium. Various derivatives of 2,6-dimercaptothiopyron-4-one have been used to determine this metal species in iron and steel.

Arsenic in organic compounds has been determined by decomposition with H\(_2\)SO\(_4\)-HNO\(_3\), oxidation to the +5 state, addition of KI and Na\(_2\)S\(_2\)O\(_3\) and amperometric titration with electogenerated iodine. KI has been employed to determine As(V) in ores and in presence of Sb(V) while diantipyrylmethane has been used to determine it in ferrotungsten. The
formation and composition of thorium arsenates has been studied by amperometric titration.\(^{52}\)

As(III) has attracted a large number of researchers. Arsenic (III) in 20% ethanolic 0.1M Na$_2$SO$_4$ has been titrated with tartaric acid,\(^{63}\) in citrate buffers with chloroamine T,\(^{64}\) and in anhydrous AcOH with lead acetate.\(^{65}\) N-bromosuccinimide has been used as amperometric titrant for arsenic(III) by Nagai et al,\(^{66}\) and also by Zhdanov and Akhmedov.\(^{67}\) Khadeev and Mukhamedzhanova\(^{68}\) have employed hexamine cobalt(III) tricarbonatocobaltate in this capacity. The formation and composition of lanthanum arsenites\(^{69}\) and reaction between UO$_2$(NO$_3$)$_2$ and various alkali arsenites\(^{70}\) have also been studied amperometrically. Arsenic(III) has also been titrated with KMnO$_4$\(^{71-74}\), Ce(IV)\(^{71,75}\) and electrogenerated chromium (VI)\(^{76}\) too have been employed to titrate arsenic(III). Electrogenerated iodine has been reported to be a successful titrimetric agent for As(III)\(^{77-79}\). Zakharov et al\(^{59}\) have determined As(III) in bicarbonate medium with iodine while Ramadan et al\(^{80}\) have chosen non-aqueous medium.

Puri et al\(^{81}\) have used K-morpholine-4-carbodithioate for determination of As, Sb, and Pb in 0.1M HOAc-NaOAc and NH$_4$OH-NH$_4$Cl buffer. Hahn and Wagenkuecht\(^{82}\) have determined submilligram quantity of arsenic by conversion into molybdenum heteropoly acids and amperometric titration with nitron. Titration with KBrO$_3$ has been carried out to determine arsenic in oxidation products of gallium arsenide\(^{46}\) and in water.\(^{83}\)

RPE has been employed for amperometric determination of As(III) with ICl,\(^ {84}\) IBr,\(^ {85}\) K$_3$[Fe(CN)$_6$]\(^ {86}\) and hypobromite.\(^ {87}\) Titration of arsenic(III) with electrogenerated hypobromite has been discussed.\(^ {88}\) Arsenic(III) has been titrated with K$_2$Cr$_2$O$_7$\(^ {89-90}\) when the RPE potential is 0.25V vs NHE and by using a Pt indicator electrode at 0.2V vs SCE.\(^ {91}\) Titration at zero potential, using RPE, with manganese(III) has been performed to determine submilligram
amount of As(III) in H₃PO₄. Arsenic(III) has also been titrated with KI₂ and KIO₄. A kinetic method has been reported for determination of As(III), based on the oxidation of bromide by potassium periodate in acid medium with amperometric recording of the reaction rate. The titration of arsenic(III) with iodine has been run at a gold electrode and at a platinum-graphite electrode system.

Several methods require the use of arsenic solution as titrant. Thus, chlorine in water has been estimated with PhAsO⁻ and with sodium arsenite at a gold electrode. Titration with phenylarsenoxide has been exploited to evaluate active chlorine in bleaching agents. Chloranins, ClO₂ and other active chlorine species have been determined by a succession of amperometric titrations with Na₃AsO₂. This titrant has also been pressed into service to titrate dodecylamine hydrobromide and Pb(IV) which is relatively stable in H₂SO₄/H₃PO₄ medium. Na₃AsO₂ has been employed to determine KMnO₄ in alkaline medium by addition of K₄[Fe(CN)₆] and OsO₄ catalysed RPE titration of the resulting hexacyanoferrate(III) and also for successively titrating Ag(I) and Cd(II) with the help of an electrometric indicator, p-aminophenol. Tetrafluoroborate in alkaline solution has been determined by addition of CH₂Cl₂ and amperometric titration with Ph₄AsCl. Oxidation of N,N-bis(β-aminoethyl) dithiocarbamic acid by alkaline hexacyanoferrate(III) has been studied by addition of the oxidant and then amperometric back titration with arsenite. Addition of hexacyanoferrate(III) and amperometric back titration with arsenite has been carried out to determine 2-mercapto-5-anilino-1,3,4-thiadiazole and P₂S₅. P₂S₅ has also been determined by addition of NaBrO and amperometric back titration with arsenite. Amperometric titration with arsenite has been employed to standardize solution of copper(III). Titration of Ce(IV) with arsenic(III) has been found to be more selective then titration with hexacyanoferrate(III), hydroquinone or ascorbic acid.
A platinum-graphite electrode system has been used in the titration of iodine with arsenic(III)\textsuperscript{115}.

**SELENIUM**

Selenium, the element No. 34 possesses the ground state electronic configuration of [Ar] 3d\textsuperscript{10} 4s\textsuperscript{2} 4p\textsuperscript{4}. It is obtained in -2 (selenide) oxidation state in association with strongly electropositive elements. Besides, it can also exists in +4 and +6 states. Se(IV) compounds are most stable. Selenium compounds are, in general, more easily reduced and less easily oxidized than the corresponding tellurium compounds. Strong oxidants can convert SeO\textsubscript{2} to selenic acid, H\textsubscript{2}SeO\textsubscript{4}, a crystalline soild. Selenium, like sulphur can make frequent use of d\pi orbitals to form multiple bonds. The commonest, coordination number that Se(IV) can acquire is 6 with octahedral geometry while Se(VI) can acquire both, 4 (tetrahedral) and 6 (octahedral) coordination numbers.

Some selenium compounds are poisonous and are used in agriculture to combat pests.

More then two dozen papers on the amperometric determination of selenium(IV) have appeared since 1963. Sulphur containing ligands have been employed by a number of workers for the purpose. Agrawal and coworkers have used thiomalic acid\textsuperscript{56}. Deshmukh and Nandi\textsuperscript{116} developed a method in which Se(IV) is titrated with methyl dithiobiuret. Se(IV) has been amperometrically titrated with 2,4-dithiobiuret to determine it in industrial materials\textsuperscript{117} and in technological samples\textsuperscript{118}. Chaudhuri et al\textsuperscript{119} have exploited potassium-dithiohydroxymethylaminomethane, Deshmukh and Rao\textsuperscript{120}, potassium-ethylxanthate, Tarayan and Shaposhnikova\textsuperscript{121}, thionalide, Danilenko and coworker\textsuperscript{122}, unithiol, Pavlichenko et al\textsuperscript{123}. Calcium carboxymethyl-dithiocarbamate and Lavale and Dave\textsuperscript{124}, chromotropic acid for the same purpose.
Selenium in semiconductor and other selenium containing materials has been estimated with 2,6-dimercapto-3,5-diethyl-4-oxo-4H-thiopyran\textsuperscript{125}, pyridyl-dimercaptothiopyrone or the dipropyl derivatives\textsuperscript{126} and 3-methyl-5-phenyl derivative\textsuperscript{127} while various derivatives of 2,6-dimercaptothiopyran-4-one\textsuperscript{128} have been employed to determine selenium in ores.

Some inorganic compounds have also been found useful for titrating selenium(IV). KMnO\textsubscript{4}\textsuperscript{129} is one such reagent and Pb(OAc)\textsubscript{4}\textsuperscript{130} is another. The titration of H\textsubscript{2}SeO\textsubscript{3} with Pb(OAc)\textsubscript{2} has also been examined\textsuperscript{131}.

Selenium in industrial products such as converter dust has been evaluated by addition of either hydrazine and back titration with iodine, or KI and titration of iodine with hydrazine\textsuperscript{132}. Titration with electrogenerated iodine has been carried out to determine selenium in urine by a method that terminate with the back titration of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}\textsuperscript{133} while addition of KMnO\textsubscript{4} and back titration with electrogenerated iron(II) has been exploited to determine selenium and tellurium on metallurgical dusts and sludges\textsuperscript{134}.

Amperometric determination of selenite and selenate in simple solution or in a binary mixture has been successfully carried out with ascorbic acid\textsuperscript{135}. This reagent has also been employed for determination of Se(IV) in steels\textsuperscript{136,137}.

N-bis(β-aminoethyl)-dithiocarbamic acid\textsuperscript{138} has been used at r.p.e. to determine selenium in pyrites.

Use of electrodes other than d.m.e. has also been recommended for titrating selenium with suitable inorganic compounds. A method has been developed for the determination of H\textsubscript{2}SeO\textsubscript{3} by amperometric titration with Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} at a rotating Pt electrode\textsuperscript{139}. Microgram amounts of selenium(IV) have been determined by addition of KI and titration with this reagent at a Pt-platinized platinum electrode system\textsuperscript{140}. RPE titration with AgNO\textsubscript{3} has been used for the simultaneous determination of H\textsubscript{2}SeO\textsubscript{3} and KI, KBr or KCl\textsuperscript{141}. 

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This reagent has also been employed to determine metallic selenium\textsuperscript{142} and H$_2$SeO$_3$\textsuperscript{143}.

**INDIUM**

Indium, the element No 49, is a soft silvery metal with a brilliant lustre and it gives out a high pitched cry when bent. Its ground state electronic configuration is [Kr] 4d$^{10}$ 5s$^2$ 5p$^1$. The most common oxidation state is +3. Metal is used as corrosion resistant coating and in the preparation of low melting alloys; indium compounds have been found to display semiconducting properties. Indium has been acclaimed as twenty first century metal and it is very gratifying to note that its first deposits in India have been discovered in the Tosham region of Haryana.

In(III) can form 4-, 5- and 6- coordinate complexes; a few 8-coordinate complexes have also been reported. Most important octahedral complexes are those containing chelate rings. It forms a large number of such complexes wherein two coordination positions are satisfied by two donor oxygen atoms of the same ligands resulting in ring formation.

Only a few methods of determining In(III) amperometrically are known. Organic compounds containing sulphur such as thiomalic acid\textsuperscript{31}, 8-mercaptotoquinoline\textsuperscript{144}, methyldimercaptotripyrone\textsuperscript{145}, sodiumdiethylthiocarbamate\textsuperscript{146,147}, potassiummorpholine-4-carbodithioate\textsuperscript{148}, methylthymol blue\textsuperscript{34} and xylenol orange\textsuperscript{35} have been used for the purpose.

Some organic reagents such as uranil-N, N-diacetic acid\textsuperscript{40}, 4-(2-pyridylazo)naphthol\textsuperscript{41,149}, 4(2-pyridylazo)resorcinol\textsuperscript{150} and N-(3-nitrocinnamoyl)-N-(4-bromophenyl)hydroxylamine\textsuperscript{151} have also been employed for the amperometric estimation of indium.

Indium(III) has also been determined by the addition of resorcinolmethyleneiminodiacetic acid, pyrocatecholmethyleneiminodiacetic acid, or hydroquinone-2-methyleneiminodiacetic acid, followed by back
titration at a graphite anode with nickel ion. Submilligram amounts of indium have been determined by back titration of excess of EDTA with electrogenerated Bi(III)\(^{152}\).

Rotating tantalum electrode has also been found efficient for determinations involving EDTA\(^{153}\).

Amperometric titration with \(\text{K}_4[\text{Fe(CN)}_6]\)\(^{154}\) at a platinum electrode has been recommended for determining indium in thin films that also contained arsenic or antimony while indium in catalyst has been estimated by amperometric titration with 8-mercaptoquinoline\(^{155}\) at r.p.e.

**ANTIMONY**

Antimony, the element No. 51, is a silvery brittle metal. Its ground state electronic configuration is \([\text{Kr}]\ 4d^{10}\ 5s^2\ 5p^3\) and it occurs in its compounds in the oxidation state +3 (antimonious compounds) and +5 (antimonic compounds). The antimonious compounds are the most stable. The \(\text{Sb}^{3+}\) ions hydrolyse at pH values as low as ~1, but the hydroxide, \(\text{Sb(OH)}_3\), dissolves at pH ~ 10, forming the antimonite ion \(\text{SbO}_2^-\). Antimony (V) is more acidic then antimony(III).

Antimony of \(\text{SbX}_3\) (\(X = \text{hal.}, \text{R}, \text{H etc.}\)) is a very weak donor of electrons, though can act as good acceptor when \(X\) is strongly electronegative.

Pentahalides form a large number of complexes wherein antimony acts as acceptor. The commonest coordination number is six with octahedral set up of ligands. These complexes have special importance in preparative chemistry.

Appreciable numbers of papers have appeared on amperometric determination of antimony since 1963. Some organic reagents containing sulphur such as thiomalic acid\(^{56}\), potassiumdithiohydroxymethylaminomethane\(^{123}\), calcium carboxymethylthiocarbamate\(^{156}\) and thionalide\(^{157,158}\) have been used for the purpose. Antimony in tin-lead solders has been
determined with amyldimercaptothiopyrone\textsuperscript{159}. While antimony in bronzes has been determined by titration with 2,4-dithiobiuret\textsuperscript{160}.

Antimony in organic compounds has been determined by decomposition with H\textsubscript{2}SO\textsubscript{4}-HNO\textsubscript{3}, oxidation of antimony to 5+ state, addition of KI and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} and amperometric titration with electrogenerated iodine\textsuperscript{61}.

Several methods have been reported for Sb(III). EDTA or DCTA\textsuperscript{161} and Pb(OAc)\textsubscript{4}\textsuperscript{162} have been recommended for titrating Sb(III) at d.m.e. Cyclohexanediaminetetraacetic acid\textsuperscript{163} has been employed to study chelate formation with antimony(III). Ce(IV)\textsuperscript{75}, KMnO\textsubscript{4}\textsuperscript{72} and K\textsubscript{3}[Fe(CN)\textsubscript{6}]\textsuperscript{164} have also been employed for amperometric determination of antimony(III). This species in 2M KOH-0.05M EDTA has been titrated with HgCl\textsubscript{2}\textsuperscript{165}. Titration of antimony(III) with ICl\textsubscript{3}\textsuperscript{166} in anhydrous AcOH has been described. Antimony(III) has been determined by titrating with electrogenerated Cr(VI)\textsuperscript{167}. Electrogenerated bromine\textsuperscript{168} has been used to titrate submilligram amounts of antimony(III) while electrogenerated iodine\textsuperscript{169} has been employed to determine total antimony and antimony(III) in glasses. Amperometric method has also been employed in the iodometric determination of antimony(III) in non-aqueous medium\textsuperscript{80}.

Ferrocene\textsuperscript{170} has been put into service as amperometric reagent for determination of antimony in alloys and DCTA for the purpose in gold antimony plating baths\textsuperscript{171}. KBrO\textsubscript{3} has been used to titrate antimony in alloys with gallium or indium\textsuperscript{154}. This reagent has also been used to determine antimony in spray-coated layer of stibnite\textsuperscript{172}.

Chloramine-T\textsuperscript{173,174}, KBrO\textsubscript{3}\textsuperscript{175} and K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{89,90} have been recommended for titrating Sb(III) at rotating platinum electrode while iodine\textsuperscript{98,99} has been employed with success at a platinum graphite electrode in this capacity.
TELLURIUM

Tellurium, the element No. 52, exists in the form of powder or light grey crystals with metallic lustre. Its ground state electronic configuration is [Kr] 4d^{10} 5s^{2} 5p^{4} and occurs in -2, +4 and +6 oxidation states in its compounds. Reducing agents, such as SnCl₂, SO₂, NH₂OH and hypophosphite reduce tellurium(IV) to the element. Tellurium can be oxidised to Te(IV) only by powerful oxidants. Te(IV) can acquire coordination number 5 (square pyramidal) or more commonly, 6 (octahedral) while Te(VI) most universally acquires coordination number 6 (octahedral); coordination number 8 has also been reported for Te(IV) though it remains to be confirmed.

Tellurium and its compounds (tellurides) are widely employed in semiconductor industry and electronics.

Some sulphur containing organic compounds have been pressed into service for amperometric determination of tellurium. Tellurium(IV) has been titrated with thiomalic acid, potassium methylxanthate, methylldithiobiuret, calciumcarboxymethyldithiocarbamate, thionalide, 2,6-dimercapto-3,5-diethyl-4-oxo-4H-thiopyran and potassium dithiohydroxymethyl-aminomethane. The last one can be used for the successive titration of selenium or tellurium and antimony. Tellurium in ferrous alloys and semiconductors has been estimated by conversion to Te(IV) and anodic titration with 2,4-dithiobiuret when elementary tellurium is precipitated. Amperometric titration with 8-mercaptoquinoline reduces Se(IV) to elementary selenium over a wide range of H₂SO₄ concentration; the analogous reduction of Te(IV) occurs only if the H₂SO₄ concentration is at least 4M. Reduction to Te(II), which combines with the titrant, occurs in less acidic media. These reactions have been used for successive determination of selenium and tellurium in technological samples. The simultaneous determination of selenium and tellurium by amperometric titration with 8-mercaptoquinoline has been the subject of a patent. Lavale
and Dave have employed chromotropic acid for the amperometric estimation of trace amount of tellurium.

Ascorbic acid has been employed as amperometric titrant for tellurium(IV) for the estimation of this element in steels.

Some inorganic compounds have also been found useful for the amperometric determination of tellurium. KMnO₄ is one such reagent and hydrazine another. Addition of KMnO₄ and back titration with electrogenerated iron(II) has been used to determine tellurium in metallurgical dusts and sludges while Na₂S₂O₃ has been employed to determine tellurium(IV) in tellurite-tellurate compounds. Microgram amounts of tellurium(IV) have been evaluated by addition of KI and titration with this reagent at a platinum-platinized platinum electrode system.

A graphite anode has been employed in amperometric titrations of tellurium(IV) with unithiol and with the 3-methyl-5-phenyl derivative of 2,6-dimercaptothiopyran-4-one to determine selenium and tellurium in semiconductor alloys. Sodium diethylthiocarbamate has been employed to titrate tellurium(IV) or Se(IV) plus Te(IV) at r.p.e. Tellurium and mixture of selenium and tellurium have also been titrated with sodium hexyl- and cyclopentylthiocarbamates.

Sometimes new methods developed have involved the use of the metal species as titrant. Milligram amounts of uranium(VI) have been titrated with Na₂TeO₃. Same titrant has also been employed successfully for copper(II).

THALLIUM

Thallium, the element no. 81, is a bluish white metal, tarnishes readily in air and reacts with steam or moist air to give TIOH. Its ground state electronic configuration is [Xe] 4f⁴ 5d¹⁰ 6s² 6p¹. It can take +1 and +3 valence states. The unipositive state is quite stable while Tl⁺ ions, which are colourless, exist
only in strongly acidic medium. In crystalline salts, Tl\(^+\) ion is usually 6- or 8-coordinate. Thallium compounds are highly toxic.

Tl(III) forms a number of 4-, 5- and 6-coordinate complexes; tendency for chelation is prominent. This being a very soft species, has a strong tendency to coordinate with sulphur. With the exception of those with halide, oxygen and sulphur ligands, Tl(I) gives rather few complexes. In solution, Tl(I) may form mostly 2-coordinate (linear) or 4-coordinate (tetrahedral) complexes, though a few 6-coordinate complexes have also been reported. Tl(I) has also strong affinity with sulphur donor atom.

Thallium compounds are used in photography and medicine and in the manufacture of optical glasses with high refractive index. Thallous sulphate is used as a rodent poison.

The natural tendency of Tl(III) to establish a strong coordinate bond with sulphur has been exploited by a large number of workers for determining this species amperometrically with the help of ligands containing sulphur. The reported methods involved the use of a variety of electrodes. The number of methods based on d.m.e. is appreciable. Usatenko and Kutsenko, have employed N-(phenylsulfonyl) thiobenzamide\(^{189}\), diethyldithiocarbamate\(^{190}\), potassiumethylxanthate\(^{191}\) and dimercaptothiopyrones\(^{192}\) while Kutsenko et al\(^{193}\) have used bis(methoxy carbonyl) dimercaptothiophosphate. Rao et al\(^{194}\) have successfully titrated thallium individually as well as in mixture with Na-1, 2,4-triazole-3-thiolate. Successful titration of Tl(III) has also been accomplished with thiomalic acid\(^{195}\), potassium-dithiohydroxy-methylaminomethane\(^{156}\), N-bis (β-aminoethyl) dithiocarboxic acid\(^{196}\), thiosalicylic acid\(^{197}\), 8-mercaptoquinoline\(^{33,197-199}\), 4-methyl-8-mercaptoquinoline\(^{200}\), thiounithiol\(^{201}\) and mercaptounithiol or unithiol\(^{202}\), unithiol has been successfully tried at the rotating platinum electrode as well\(^{203}\) and has featured in a patent\(^{204}\). This electrode has also been used by Nashivan'ko and coworkers\(^{205}\) for determination of Tl\(^{3+}\) with diethylthiourea in industrial materials (alloys,
metals and ores containing thallium).

Methods of amperometric determination of Tl(I) have also been reported in rather large number. A number of oxoions have been pressed into service. Gupta\textsuperscript{206} has reported the estimation of Tl(I) with Na\textsubscript{2}WO\textsubscript{4} while very precise end points have been reported in the amperometric titration of Na\textsubscript{2}WO\textsubscript{4} and polytungstates with Tl\textsubscript{2}SO\textsubscript{4} and reverse by Saxena and Sharma\textsuperscript{207}. Saxena and Mittal\textsuperscript{208,209} have employed the technique of amperometry for studying the stoichiometry of the compounds formed by the interaction of Tl(I) and some vanadates in different media. Titrations involving thallium(I) sulphate and alkali polymolybdates have also been reported by these workers\textsuperscript{210}. Formation and composition of thallium(I) thiomolybdate has been studied by titrations involving TiNO\textsubscript{3} and Na\textsubscript{2}MoS\textsubscript{4}\textsuperscript{211}, Gaur and Jain\textsuperscript{212-214} have used K\textsubscript{2}CrO\textsubscript{4} and K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{215} for the purpose and have recommended the methods for determining Tl(I) in the presence of cadmium and lead. The a.c. amperometric titration of Tl(I) in 20% ethanolic KNO\textsubscript{3} with K\textsubscript{2}CrO\textsubscript{4} appears to be somewhat more accurate than the d.c. method\textsuperscript{216}. Deshmukh and Choudhary\textsuperscript{163} have determined Tl(I) with Pb(OAc)\textsubscript{4}.

Amperometric titration with KBrO\textsubscript{3}\textsuperscript{217-219} as well as KIO\textsubscript{3}\textsuperscript{217} have also been employed to determine Tl(I). Titration of KIO\textsubscript{3}\textsuperscript{218} involves the use of platinum graphite electrode. This very electrode has also been used for the cerimetric titration of Tl(I)\textsuperscript{220} while graphite electrode with a silicon resin base has been employed in the amperometric titration of Tl(I) with NaBPh\textsubscript{4}\textsuperscript{221}. Songina et al\textsuperscript{222} have titrated thallium with KMnO\textsubscript{4} in alkaline medium.

Some organic reagents have also been put to good use for the amperometric determination of Tl(I). Pitre and his coworkers have employed methylthymolblue\textsuperscript{34}, xylenolorange\textsuperscript{35} and 4(2-pyridylazo)naphthol\textsuperscript{41} while ammoniumdithiocarbamate\textsuperscript{223}, potassiummorpholine-4-carbodithioate\textsuperscript{148}, thioacetamide\textsuperscript{224-225}, dithioterphtallic acid\textsuperscript{226}, methyldithiobiuret\textsuperscript{116} and thiomalic acid\textsuperscript{21} have been used by various other workers for the determination of Tl(I).
Several methods require the use of thallium solution as titrant. Thus, potassium has been determined by precipitation as tetra-phenylborate, followed by dissolution in acetone and titration with TlNO₃. Thallium sulphate has been used for titrating hydrazine sulphate in NaHCO₃-KI medium. Ethanolamines have been determined by addition of an alkaline solution of BaCl₂ and permanganate, the excess of the latter was then titrated with Tl(I). Zirconium can be determined by addition of EDTA and back-titration of the excess with Tl(III).

LEAD

Lead, the element No. 82, is a soft, ductile, malleable metal of grey colour. Its ground state electronic configuration is [Xe] 4f¹⁴ 5d¹⁰ 6s² 6p². It is widely distributed on the earth's crust. The oxidation states are +2 and +4; tetravalent lead compounds are far less stable than their divalent counterparts. In fact, Pb⁴⁺ ion has no real existence. Pb(II) forms numerous complexes which are mostly octahedral. The metal finds use in cable covering and storage batteries etc.

Some amperometric methods have been evolved for the determination of Pb(IV). Lead(IV), which is relatively stable in H₂SO₄/H₃PO₄ medium, has been titrated with NaAsO₂ while Solomatin et al. have recommended the use of ferrocene as titrant for it. Arsenic (III) and Vanadium(IV) have been successfully titrated with Pb(OAc)₄. Pb(IV) generated in HOAc medium has also been used to titrate ethylthioglycolate and thiosalicylic acid.

More than four dozen papers on the amperometric determination of lead(II) have appeared since 1963. EDTA, the versatile complexing agent, has been used by a number of workers for the purpose. Ozaki et al. have developed a method in which lead(II) solution as dilute as 0.01mM can be titrated with this reagent in KNO₃-ascorbic acid medium. Savic and coworkers have reported the use of glycerol as a masking agent in the
amperometric titration of lead with EDTA in presence of Iron(III). Zhdanov and Muminov have described two EDTA methods for separate determination of copper and lead. Sierra and coworkers have employed photoredox indicators such as thionine, iodine, phenosafranine, brilliant cresyl blue and toluidine blue in the amperometric titration of lead with EDTA. Toluidine blue has also been used as photoredox indicator in the titration of lead with DCTA. Some other workers have also used EDTA or its related compounds in different ways for carrying out amperometric determination of lead. Optimum conditions have been determined for the amperometric estimation of lead with triethylenetetraminehexacetic acid (TTHA).

A strong tendency of Pb(II) to enter into coordination with sulphur ligands has been exploited by a large number of workers. Rao et al have used N-methyl-aniline carbodithioate, potassium-morpholino-4-dithiocarboxylate and potassium-ethylxanthate for the purpose. Potassium ethylxanthate has also been used at r.p.e. by Deshmukh and coworkers. Deshmuck et al have also employed ethoxythiosemicarbazide, potassiumdithiotrihydroxymethylaminomethane, potassiumthiocarbonate and N-bis(β-aminoethyl)-dithiocarbamic acid. The last reagent has been used by other workers as well. Thioacetamide has been employed to titrate lead in presence of zinc. Berzina et al have employed 8-mercaptoquinoline while this reagent and its methyl derivatives have been used for amperometric titration of lead by Kreicberga et al. Agrawal et al have developed a sensitive method of estimation with thiomalic acid. Successful titration of Pb(II) has been accomplished with sodiumdiethylthiocarbamate, pentamethylene-dithiocarbamate, dithioloterephthalic acid, propanethiol and unithiol also, unithiol has been tried at graphite electrode. Lead(II) in presence of polyethylene glycol has been titrated with sodiumtetr phenyl borate.

Shome and coworkers have exploited thiosalicylamide for the determination of lead in zinc and gasoline and 1, 5-bis (benzylidene)-
thiocarbohydrazone\textsuperscript{268} for the determination in gun metal and ores. Sodiumpiperdinethiocarbamate\textsuperscript{269,270} has been used to determine lead in steels while mercaptothiopyrone\textsuperscript{271} derivative has been employed for its determination in ores and antimony alloys\textsuperscript{272}.

Some inorganic compounds have also been found useful for titrating lead. Sodiumtripolyphosphate\textsuperscript{273} is one such reagent and sodium tellurite\textsuperscript{189} is another. Amperometry has been exploited to study the formation and composition of lead polyvanadates\textsuperscript{274}. Chaudhuri et al\textsuperscript{275} have used \( \text{P}_2\text{S}_5 \) titrant for the amperometric determination of lead. \( \text{P}_2\text{S}_5 \) has also been used to determine milligram amount of lead at r.p.e\textsuperscript{276}. Titration with \( \text{K}_4[\text{Fe(CN)}_6] \) has been carried out to determine lead in presence of barium\textsuperscript{277} and thallium\textsuperscript{213}. This reagent has also been employed at a platinum wire-platinum foil electrode system\textsuperscript{278}. \( \text{K}_2\text{Cr}_2\text{O}_7 \) has been used by many workers\textsuperscript{179-181} in different ways. Several hexacyanoferrate(II)-lead titrations have also been reported\textsuperscript{282-284}.

Several methods require the use of lead(II) solution as titrant. Sulphate in galvanic baths\textsuperscript{285}, soil extracts\textsuperscript{286} and vanadium catalyst\textsuperscript{287} has been amperometrically titrated with lead nitrate or lead acetate. Lead acetate has been used to titrate nitrate in anhydrous AcOH\textsuperscript{288-290}, molybdate in acetate buffered \( \text{H}_2\text{O}_2 \)\textsuperscript{291}, fatty acids in aqueous PrOH medium\textsuperscript{292}, sulphate in lake suspensions\textsuperscript{293} and \( \text{H}_2\text{SeO}_3 \)\textsuperscript{131} while lead nitrate has been exploited to determine molybdenum in high alloy steels\textsuperscript{294}, in alloys with nickel\textsuperscript{295}, in alloys with nickel and rhenium\textsuperscript{296} and in molten LiCl-KCl\textsuperscript{297}, tungsten in high-alloy steels\textsuperscript{298}, \( \text{SO}_3 \) in cement\textsuperscript{299}, \( \text{CO}_2 \) in aqueous solution\textsuperscript{300}, sulphur in organic substances\textsuperscript{301} and spent sulphite liquor\textsuperscript{302}, calcium in soil extracts\textsuperscript{303} and sulphuric acid in mixtures with p-choloro-benzenesulphonic acid\textsuperscript{304}. The same titrant has also been used for the rapid and accurate determination of thiomolybdate\textsuperscript{305} and tungstate\textsuperscript{306}.
Amperometric titrations of chromate or dichromate\textsuperscript{284} in KNO\textsubscript{3}, sodium tartrate\textsuperscript{307}, 30\% ethanolic 0.1 M NaClO\textsubscript{4}, molybdate and tungstate\textsuperscript{308} and dilute EDTA solution\textsuperscript{309} with Pb(II) have been reported. Anions such as phosphate and sulphite have been titrated with lead(II), electrogenerated from lead amalgam at r.p.e\textsuperscript{308}.

THORIUM

Thorium, the element no. 90, is a white metal, which tarnishes in air. It has valence shell electronic configuration of 6d\textsuperscript{2}7s\textsuperscript{2}. In aqueous solutions, thorium ions exist in one valence state (+4) only. Due to high m.p. and high atomic weight, it is used as one of the components of refractory alloys. The element has gained enormous importance because of possibility of its use in fast breeder reactors.

Several organic reagents including a thio acid (thiomalic acid)\textsuperscript{310} have been used for the amperometric determination of thorium. Mukherji\textsuperscript{311} has carried out the determination in presence of nitrate by using benzene-phosphonic acid. 8-hydroxy-quinoldinic acid\textsuperscript{312}, m-nitro-benzoic acid\textsuperscript{313}, ethyl-cyanoglyoxalate-2-carboxyphenylhydrazone\textsuperscript{314}, methyl thymol blue\textsuperscript{315} and \(3\times3'\)-bis[N,N' -dicarboxymethyl]-O-cresolsulfo-thalein-(DACS)\textsuperscript{316} have also been used by different workers for the determination. A number of maleanilic acids have been employed for the titration by Sharma and Arya\textsuperscript{317}. These workers\textsuperscript{318} have also used phthalanilic acid for the purpose and have recommended the method for determining thorium in monazite. Another method for determining thorium in monazite involving molybdate as titrant has been evolved by Burastero and Martres\textsuperscript{319}. Similarly, the use of thoron has been suggested by Tserkovnitskaya and Yeh\textsuperscript{320} for this purpose.

Several new methods for the direct amperometric estimation of Th(IV) at d.m.e. have come to light since 1962. A number of oxo-ions have been pressed into service. Deshmukh and Asthana\textsuperscript{321} have titrated Th\textsuperscript{4+} solution in
60-70% EtOH medium containing 0.9M ammonium acetate with Na₂SeO₃. Saxena and Sharma have employed the technique of amperometry for studying the stoichiometry of the compounds formed by the interaction of Th⁴⁺ salt and some vanadates. Similarly Saxena and Prasad have studied the interaction of Th(NO₃)₄ and sodium meta, pyro and ortho-arsenates. Gupta has carried out the titration of thorium with sodium tungstate in 1 M LiCl medium.

EDTA has been employed by several workers for developing new methods of amperometric determination of thorium. Mukherji has used this strong complexing reagent for determining thorium in presence of nitrate. Perez et al. have developed new version of the method involving the use of a photoredox indicator, azure B. Thionine blue has also been employed as photoredox indicator for the purpose. Cu(II) has been shown to be an attractive indicator for the EDTA titration of thorium by Dean and Harris. Fe(II) complex of the ligand has been employed by Goldstein, Manning and Zittel for the determination of Th(IV) at pH 2.5. An indirect method actually involving the amperometric estimation of EDTA itself left after the formation of Th-EDTA complex, with Bi(NO₃)₃ at tantalum electrode has also been proposed. The formation of 1:1 complexes of thorium with EDTA, NTA, CDTA and TTHA have been exploited for the determination of metal species by Vydra and Stulik. A method employing Th(NO₃)₄ as titrant against fluoride has also been proposed.

Electrodes other than d.m.e. have been frequently used by workers for determining thorium. Thorium-EDTA titration itself has been carried out at rotating tantalum anode, while rotating mercury electrode has been employed by Freese et al. Khadeev and Masalova have carried out the determination of the metal species with the help of two platinum electrodes using K₄Fe(CN)₆ or citric acid as titrant. Two indicator electrodes have been employed by the same workers for proposing a method involving the use of
complexone III also. Complexone III has also been employed by Palei and Udal'tsova$^{337}$ for the determination involving platinum electrode again. This electrode has been recommended by Vasilenko and Mazharovskaya$^{338}$ also for the amperometric titration of Ce(IV), Th(IV) and La(III) with N-benzoylphenylhydroxylamine.

**URANIUM**

Uranium, the element no. 92, is a soft, silver white and dense metal. The element, well known for its use in the field of nuclear energy, is a member of actinide family, of the elements and possesses the valence shell electronic configuration as $5f^{2}6d^{1}7s^{2}$. The most common oxidation state, $+6$ involves the loss of all the valence electrons. However, uranium may also exist in lower oxidation states of $+3$, $+4$ and $+5$. The author has selected dioxo ion (uranyl ion-$\text{UO}_2^{2+}$) for the amperometric study of $+6$ state of this metal. Coordination number 6 is very common for hexavalent uranium.

Appreciable numbers of papers have appeared on amperometric determination of uranium. It seems the metal has caught the imagination of a number of workers because of its extreme importance in the field of nuclear energy. Direct titration of U(VI) has been carried out at d.m.e. with organic reagents like thiomalic acid$^{339}$, bromo-pyrogallol red$^{340}$, arsenazo III$^{340}$, 2', 3', 4'-trihydroxychalcone$^{341}$, complexone III$^{342}$ and 8-hydroxyquinoldinic acid$^{343}$. Sodium tellurite$^{187}$, sodium tellurate$^{344}$, sodium orthovanadate$^{345}$ and alkali arsenites$^{346}$ have also been used for the purpose.

Some indirect methods have also been evolved. Cheery$^{347}$ reduced U(VI) to U(IV) in strong $\text{H}_3\text{PO}_4$ medium with Fe(II) and then titrated U(IV) with dichromate. A slightly modified version of this method has also been proposed$^{348}$. In yet another modified version$^{349}$ of this method, it was the excess of the reducing species Fe(II), instead of U(IV), which was determined amperometrically at the platinum electrode. Graphite electrode was employed
by Rozhdestvenskaya et al\textsuperscript{350} for developing an indirect method involving the reduction of U(VI) to U(IV) with formamidinesulphonic acid and then titrating U(IV) with EDTA using Hg(II) as indicator.

Direct methods of determination of U(VI) at indicator electrodes other than d.m.e. have also been reported. Cr(II) and Ti(III) compounds have been used by Gallai and Kalenchuk\textsuperscript{351} and Gallai and Sheina\textsuperscript{352} respectively for this purpose at rotating or vibrating platinum electrodes. Vibrating d.m.e. has been preferred by Carr and Meites\textsuperscript{353} for titrating U(VI) with Cr(II).

Uranyl sulphate solution itself has been used as titrant for determining Na\textsubscript{3}PO\textsubscript{4} contents in steel degreasing solution\textsuperscript{354}.

Several methods have been reported for U(IV). Fe(III) has been recommended for titrating U(IV) at d.m.e. as well as at r.p.e.\textsuperscript{355} while Mohr's salt has been employed with success for titrating a mixture of U(IV) and U(III)\textsuperscript{356}. Silverman and Skoog\textsuperscript{357} as well as Zanello and Cospito\textsuperscript{358} have employed KMnO\textsubscript{4} while Zittel and Miller\textsuperscript{359} have used Ce(HSO\textsubscript{4})\textsubscript{4} for the purpose.

Amperometric methods have also been evolved for the quantitative analysis of the mixtures of the metal species containing metal ions covered in this thesis as components. 8-mercaptoquinoline appears to be very good reagent for this type of analysis. It has been recommended for the successive titration of Hg(II), Cu(II) and Mo(VI)\textsuperscript{360} and Hg(II) and Ag(I)\textsuperscript{360}. Usatenko and Suprunovich\textsuperscript{361} have evolved a procedure for the determination of copper, zinc and iron in aluminium alloys by using this reagent as titrant. This titrant has also been used to evaluate copper and zinc in brass and bronze\textsuperscript{362} and iron and molybdenum in chrome nickel steel\textsuperscript{363}. The reagent and some of its methyl derivatives have earned recommendation for determining bivalent ions of lead, cadmium and copper in the three component mixture also without using
Many researchers have used EDTA for the analysis of mixtures. Mixtures of Zn(II) with either Fe(II) or Cd(II) have been evaluated at d.m.e. The method has found application in the analysis of zinc ores. Binary mixtures of Pb(II) and Mg(II) has been evaluated using thionine blue as photoredox indicator. EDTA has also been used for sequential titrations based on pH change-potential change method for evaluating the following mixtures:

1. Hg(II), Zn(II) and Cd(II) or Pb(II)
2. Pb(II) and Bi(II)
3. Cu(II), Hg(II) and Bi(III)
4. Hg(II), Zr(IV), Bi(III) and Ni(II)

EDTA has also been employed for the analysis of following binary and ternary combinations of metal ions at rotating tantalum electrode:

1. Mg(II), Zn(II) and Bi(III)
2. Hg(II) and Cu(II)
3. Hg(II) and Zn(II)
4. Cd(II) and Bi(II)
5. Cd(II) and Tl(I)
6. In(III) and Cd(II)
7. In(III) and Pb(II)
8. Ga(III) and In(III)
9. Binary combinations of
   (i) Hg(II) and Cu(II), Zn(II), Cd(II), In(III), Pb(II) and Bi(III)
   (ii) Tl(III) or Bi(III) with Ga(III)

10. Binary and ternary combinations containing
(i) Tl(III) with Ag(I), Zn(II) and Pb(II)\(^{380}\)
(ii) Cu(II), Mg(II), Zn(II), Pb(II), Th(IV) and Ni(II) with Zr(IV)\(^{381}\)
11. Ga(III), In(III) and Cd(II)\(^{382}\)
12. Ga(III), Bi(III) and Cu(II)\(^{383}\)
13. Bi(III), Hg(II) and Cu(II), Zn(II) or Pb(II)\(^{384}\)
14. Zn(II), Zr(IV) and Mo(VI)\(^{385}\)
15. In(III) and Zn(II)\(^{386}\)
16. Hg(II) and Cd(II), Zn(II) or Pb(II)\(^{387}\)
17. Sc(III), Zn(II) and Mg(II)\(^{388}\)
18. Mg(II), Cd(II) and Bi(III)\(^{389}\)

EDTA has also been employed for the successive titrations of Hg(II) and Ag(I) or Cu(II) or Mo(VI) in the mixture\(^{361}\). This has also been used for estimating Zn(II), Cd(II) and Mn(II) in a mixture with the help of oxalate as masking agent\(^{390}\). Back titration of excess EDTA with Zn(NO\(_3\))\(_2\) has been used in the analysis of mixture of Ni(II) and Cr(III)\(^{391}\), Zn(II) and V(V)\(^{392}\) and certain metal ion mixtures containing molybdenum\(^{393}\). A direct method of analysing the mixture of molybdenum and iron again involving this reagent, has also been recommended\(^{394}\). A vibrating graphite electrode has been employed in the amperometric titration of Pb-Cu mixture with EDTA\(^{395}\). EDTA has also been employed in the quantitative analysis of mixtures of Ni(II) with Zn(II), Cd(II) or Pb(II) at a rotating Nb-Zn-Ni alloy electrode\(^{396}\).

Organic sulphur compounds have also been pressed into service for the quantitative evaluation of mixtures. The reported methods involve the use of a variety of electrodes. Sodium diethyldithiocarbamate has been used to titrate mixtures of copper(II) with lead(II) or Tl(I)\(^{397}\) and Se(IV) plus Te(IV)\(^{185}\). Tellurium and selenium plus tellurium have also been titrated with sodium hexyl- and cyclopentylthiocarbamates, which are more stable in acid solution than the diethyl compounds\(^{186}\). Conditions have been developed for the
simultaneous determination of lead and copper with K-morpholino-4-dithiocarboxylate. Diethyldimercaptothiopyrone has been used for the analysis of mixture of bismuth with mercury or thallium. Potassium dicarboxymethyldithiocarbamate has been employed for the successive titrations of silver and indium and mercury with indium while potassiummethylxanthate for the successive titrations of copper and lead. Mixtures of copper and lead have also been titrated with 1-methyl-2,4-dithiobiuret, Pentamethylene dithiocarbamate has been used for the determination of lead in its binary mixtures with Hg, Ag, Cu. Amperometric titration with ammonium dithiocarbamate has been carried out for the simultaneous determination of Tl(I) and lead(II) in their mixtures.

A few reagents, which do not contain sulphur have also been found helpful in the amperometric determinations of mixtures. Binary mixture of copper, cadmium, lead or cobalt have been titrated with 1,2-cyclohexane-N,N,N',N-tetracetate in ethylaminoacetate medium while binary mixtures of Tl with La, Ni and Se and ternary mixtures of Tl with Sc and Y, In and La, and In and Ni have been titrated with complexon III.

Some inorganic compounds have also been pressed into service for the quantitative evaluation of mixtures. KI and Na₂S₂O₃ have been recommended for the mixtures of Ag(I) and Hg(II) involving a two stage operation. Ag(I) and Cd(II) have been successfully titrated in a mixture with sodium arsenite by using p-aminophenol as electrometric indicator.

Iron compounds have also been employed for the quantitative determination of mixtures. K₄Fe(CN)₆ has been used for the analysis of mixtures of lead and thallium or molybdenum and tungstun while hexacyanoferrate(III) with KIO₃ has been recommended for determining As(III) and Sb(III) in presence of each other.
Mixtures of bismuth and antimony and that of arsenic (III) and antimony (III) have been analysed by titration with KI^{409} and KBrO_{3}^{410} respectively. Cr(II) has been recommended by Gallai et al^{411} for evaluating the mixtures of Cr(VI) and Mo(VI); the titration curves show two breaks.

**THIOGLYCOLIC ACID (TGA)**

**General Properties**

Thioglycolic acid (mercaptoacetic acid or TGA) formulated as HSCH_{2}COOH and abbreviated as TGA in this thesis, have molecular weight 92.12, density 3.18 and the boiling point 123°C. It is soluble in water. It was developed in the 1940’s for use as a chemical depilatory and is still used as such, especially in the calcium thioglycolate salt form. TGA, besides being the basis for the permanent wave solution, ammonium thioglycolate, is used in a wide variety of applications including the making of polyvinyl chloride and leather processing. TGA has the ability to break down the disulphide bonds in the cortex of hair to either rearrange or to help break down the hair shaft entirely, its primary purpose.

Many sulphur containing organic ligands have been used in amperometry for the trace determination of metal ions. Organic sulphur compounds containing –SH group are also known to give anodic wave at d.m.e.^{25-30}. TGA in this report has often been used as a complexing agent^{412-414} and an analytical reagent^{415-418}. This acid has also been used in grafted onto silica gel^{419}, in preparation and characterization of glass embedding^{420}. However, its capacity to act as an amperometric reagent has by and large remained unexplored. Complexing properties of thioglycolic acid are especially interesting in view of the fact that it contains both hard oxygen donor atoms of carboxylate group and soft sulphur atom of the sulphydryl group. This combination enables it to form rather stable complexes with a large number of
metal ions. Both of these can take part in coordination and thus it can act as mono or bidentate ligand. TGA seems to be capable of forming complexes with a large number of metal ions and a survey of literature justifies this expectation.

**Polarographic Behaviour**

Polarographic behaviour of this acid has been studied in detail by several workers. It has been found to give a diffusion controlled, reversible, one electron anodic wave, the half wave potential of which is dependent on pH; as 0.2M acetate buffer\(^{421}\) (pH - 4.6), 0.05M sodium phosphate\(^{421}\) (pH - 6.8) and 1M ammonia - 0.2 ammonium chloride\(^{422}\) have \(E_{1/2} = -0.26\text{V}, \ -0.38\text{V}\) and \(-0.56\text{V}\) respectively. The pH dependence is complex, owing to the diprotic nature of TGA\(^{422}\). Kolthoff and Belcher\(^{423}\) gave standardization of TGA by titration with iodine solution and diluted to give 0.05, 0.025, 0.0125 and 0.01M solutions. Leussing and Kolthoff\(^{424}\) have shown that a mercury compound is formed during the anodic oxidation of thioglycolic acid. The electrode reaction has been suggested as follows:

\[
\text{TGA} + \text{Hg} \longrightarrow [\text{Hg} (\text{TGA})_2] + 2\text{H}^+ + 2\text{e}^-
\]

The dissociation constants of the acids were determined at a temperature of 20.0° and an ionic strength of 0.1 at several concentration of buffer. The average values of the dissociation constant of thioglycolic acid is \(3.89 \times 10^{-4}\). The first and second successive formation constants of the thioglycolate complexes were calculated\(^{425-428}\).

The agreement of the values of stability constants obtained at the different metal ion concentrations indicates that the amount of hydrolysis was negligible in the region between pH values of 2 and 4. The logarithms of the stability constants were calculated by Bjerrum’s graphical method\(^{429}\). The error limits\(^{430}\) are ±5% for \(K_1\), ± 10% for \(K_2\). This corresponds to the errors: ± 0.02
for log $K_1$, ± 0.05 for log $K_2$. Stability constant for thioglycolic acid reported as log $K_1$=2.88 and log $K_2$=2.40.

**Complexation Reactions**

Rieger *et al.*\(^{431}\) reported ESR spectrum of vanadyl ion in the presence of lactic or glycolic acid ($H_2A$) indicates the existence of at least 6 different species over the pH range 1-7. By studying the behaviour of the ESR intensities in the vanadyl-lactic acid system as a function of pH and ligand to metal ratio, the observed species are identified as the aquovanadyl ion and 1:1 complex VO(HA)$^+$, which give virtually indistinguishable ESR spectra. V.M. Bhuchar\(^{432}\) described polarographical method for the determination of Cr, U, W, or Ni by complexing with thioglycolic acid. The large scale electrolysis of Zn(II), Cd(II), Hg(II), Cu(II), Ni(II), Co(II), Fe(II), Mn(II), Cr(II), Cr(III), Bi(III), In(III) and Sb(III) at Hg electrodes in the presence of mercaptoacetic acid, 3-mercaptopropionic acid, cysteine and thiourea was carried out and the products were investigated\(^{433}\). Khadikar and Kakkar\(^{434}\) prepared Cr(III) complexes with salicylic acid, thiosalicylic acid, thioglycolic acid, m-(mercaptoacetamido) phenol, and p-(mercaptoacetamide) chlorobenzene.

Thioglycolic acid\(^{435}\) metal chelates were prepared by treating thioglycolic acid or its derivatives with a base and then with an aqueous solution of a metal compound. Addition of a base preferably NH$_4$OH increased the yield of chelates. Maslowska *et al.*\(^{436}\) give a review with 89 references on the biological role, chemical compounds structure, properties, stability constants and thermodynamics functions, reactions and mechanisms of formation, as well as analytical and industrial applications of the complexes of Mn(II), Fe(II, III), Co(II, III), Ni(II), Cu(II), and Zn(II) with thioglycolic acid.

Murray and Newman\(^{437}\) have reported a number of solid complexes, most of which are extremely unstable in air, were isolated from reactions between aqueous Fe(II) and ligand thioglycolic acid. The 1:1 and 1:2
Fe-ligand stoichiometries were obtained. Spectroscopic and magnetic measurements were used to deduce possible structures and in most cases polymeric structures are indicated. A photometric study of the equilibrium in the system [Fe(CN)\textsubscript{5}NO\textsuperscript{2-}] - thioglycolate\textsuperscript{438} indicated the formation of a colored 1:1 complex. Roy and Dipali\textsuperscript{439} have reported a method based on the complexation of Fe with TGA to form a colorless Fe\textsuperscript{2+}-TGA complex, oxidation to a red Fe\textsuperscript{3+}-TGA complex in the pH range 4.2-5.0 in air and final titration of complex with EDTA to a colorless end point.

Hori and Kiichi\textsuperscript{440} have reported Co(II) complexes with TGA and studied their properties. Babkin and Geinrikhs\textsuperscript{441} have reported reduction of cobalt on a mercury cathode in solutions of thioglycolic acid and thiosemicarbazide. Anzenbacher and Kalous\textsuperscript{442} have reported polarographic study of anodic peaks of cobalt in thioglycolic acid medium. Joanna and Jozef\textsuperscript{443} have reported co-ordination of Co(II) with thioglycolic acids using potentiometry at 20° in aqueous solution of ionic strength 0.1M NaClO\textsubscript{4}. Formation of 1:1 and 1:2 (M:L) complexes was observed. The electrochemical catalytic process was studied in solutions of Co(II) and Ni(II) complexes with thiosemicarbazide and thioglycolic acid in different alkaline buffer media\textsuperscript{35} by oscillographic study of potential on a dropping Hg electrode\textsuperscript{444}.

King\textsuperscript{445} has reported Zn complex of thioglycolic acid and its exposure to sunlight. Nepal and Dubey\textsuperscript{446} have studied stability constants of Mn(II), Fe(II), Co(II), Cu(II) and Zn(II) complexes with thiomalic acid, thioglycolic and thiolactic acid potentiometrically.

Martin and Spence\textsuperscript{447} have reported the oxidation of thioglycolic acid by Mo(V) and Mo(VI) in phosphate buffer at pH 4.60-7.50. At pH 6.00 Mo(V) forms a strong dimeric complex with TGA in which the ratio of Mo(V) to TGA is 1:2.
Dzintarnieks and Busev\textsuperscript{448} have determined solvation of anionic internal complexes of molybdenum with thioglycolic acid during extraction by isoamyl alcohol and 1,2-dichloroethane in the presence of diphenylguanidinium. Ordonez and Garrido\textsuperscript{449} have investigated the ionization constant of thioglycolic acid.

Saxena \textit{et al}\textsuperscript{450} have reported the precise nature of complexation of Cd, Pb and Tl with thioglycolic acid and glutamic acid investigating by polarographically. Domingo and Molina\textsuperscript{451} found that in weakly acid aqueous media, thioglycolic acid forms in the presence of Cd(II) ions, a weakly solution, 1:1 complex assumed to be the title salt. Mittal and Mohan\textsuperscript{452} have reported polarographic reduction of Cd(II) in 20\% dioxane containing thioglycolic acid was a reversible diffusion-controlled, 2-electron process and half-wave potential can be explained by the formation of complex [CdL\textsubscript{3}]\textsuperscript{4+}.

Qazi and Dubey\textsuperscript{453} have studied complexes of Hg(II) with TGA. All the complexes contain tetrahedrally coordinated ion, [Hg(TGA)\textsubscript{2}]\textsuperscript{2-}. Equilibrium constants for TGA-Hg(II) system in aqueous solution have been earlier reported by Stricks and Kolthoff\textsuperscript{454}. The metal bisthioglycollatomercurates were analysed for sulphur, mercury and metal-ion contents using standard method\textsuperscript{455-457}.

To the best of the knowledge of the author, no amperometric work involving this acid has been reported on these following elements viz:

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).

\textbf{AMPEROMETRIC DETERMINATION}

Thioglycolic acid seems to be an excellent ligand which has the additional advantage of being polarographically active. It is a pity that these properties of the ligand have not been fully exploited for developing amperometric methods of determining metal ions.