Chapter 1

INTRODUCTION

In many fields such as earth science, biology, environment and electronics, the knowledge about elemental distributions and chemical speciation is important. The determination of metal levels especially the toxic ones both in the environment and in biological materials are increasingly demanded by the society. A number of techniques are available for the determination of metals. One of the most common and extensively used methods is the titrimetric analysis. The main advantage is that the method is precise but, a major drawback is that they are normally less sensitive and laborious. A major breakthrough was the application of potentiometric, coulometric and amperometric methods in titrimetric analysis.

Another 'wet' method used is the gravimetric analysis. It is a macroscopic method usually involving relatively large samples compared with any other quantitative analytical method and a very high level of accuracy is achieved. It is concerned with the weighing of a substance that has been precipitated from solution or volatized and absorbed. The need for trace level analysis led to the development of chromatographic methods, spectrophotometric methods and electroanalysis. Chromatography is mainly a separation technique. Ion chromatography is a technique used to separate and concentrate rare earths and transuranic ions. Gas chromatography which involves the separation of a mixture into its constituents by passing a moving
gas phase over a stationary sorbent is also used in the determination of cations. Spectrophotometry specifically refers to the use of a spectrophotometer. Quantitative applications of absorption / emission spectroscopy depend on the use of Beer's law, which relates absorbance to concentration. A number of techniques have evolved based on absorption / emission spectroscopy from simple spectrophotometric methods involving the use of a spectrophotometer, flame emission spectroscopy (FES), atomic absorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS) to the highly precise inductively coupled plasma atomic emission spectroscopy (ICP AES). Electroanalytical measurement is another technique used for trace level analysis.

One of the major research work carried out in our laboratory is the development of new techniques for the determination of metal ions in trace levels by the spectrophotometric and the electroanalytical methods.

1.1 Electroanalysis

Electroanalysis can be defined as the application of electrochemistry to solve real-life analytical problems. Each analytical technique has a specific purpose and a range of applications. Electroanalytical measurements have a number of important benefits such as:

1. selectivity and specificity
2. selectivity results from the choice of electrode material
3. high sensitivity and low detection limit
4. results can be furnished in real time or close to real time
5. portable sensors with dedicated instrumentation can be fabricated for use outside the laboratory
6. miniaturized sensors for application in cases where other probes may not be usable

One important criterion for any electroanalytical measurement is that the medium between the electrodes making up the electrical circuit has to be sufficiently conducting. Thus, electroanalysis is complementary to other analytical techniques. Electrochemical monitoring has many advantages; the detection limits achieved in electroanalysis make it a better alternative to the existing analytical techniques. Also, the advantage of distinguishing oxidation states is highly important. The electrochemical approach can give a rapid answer, without digestion, as to the labile fraction of a given element in a particular oxidation state, and the experiment can be performed on-site in the field. In cases where existing analytical techniques cannot be applied as they require complex and large equipment, electroanalysis provides a ready solution.

1.2 Electroanalytical Measurements

There are essentially three types of electroanalytical measurements and three kinds of controlling or measuring devices to implement them. The three types of electroanalytical technique are as follows:

1. conductimetry
2. potentiometry
3. amperometry and voltammetry

1.2.1 Conductimetry

In conductimetry, the concentration of charge is obtained through measurement of solution resistance and is therefore not species-selective. Conductimetric detectors can, however, be useful in situations where it is
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necessary to ascertain, for example, whether the total ion concentration is below a certain permissible maximum level or for use as an on-line detector after separation of a mixture of ions by ion chromatography. Such situations can arise in electroremediation.

1.2.2 Potentiometry

The equilibrium potential of an indicator electrode is measured against a selected reference electrode using a high-impedance voltmeter, i.e., effectively at zero current. Thus, the current path between the two electrodes can be highly resistive. At an inert redox indicator electrode such as platinum the potential measured is a mixed potential, a function of all species present in solution and their concentrations. In ion-selective electrodes, careful choice of electrode material can give good selectivity to one particular species, in many cases, with only minimal interference from other ions. Detection limits of the order of 100 nanomoles per litre of the total concentration of the ion present in a particular oxidation state, although down to 10 picomolar differences in concentration can be measured.

1.2.3 Voltammetry and amperometry

In voltammetry, the current is registered as a function of applied potential, more information and lower detection limits can usually be gained. Several species that react at different applied potentials can be determined almost simultaneously in the same experiment without the need for prior separation. Very low detection limits of down to the picomolar level can be reached using state-of-the-art instrumentation and preconcentration of the analyte on the electrode surface.
In amperometry, a fixed potential is applied to the electrode, which causes the species to be determined to react and a current to pass. Depending on the potential that is applied, the magnitude of the current is directly proportional to the concentration. Detection limits in the micromolar region can be obtained.

1.3 Chemical Sensors

A chemical sensor is a device which responds to a particular analyte in a selective way through a chemical reaction and can be used for the qualitative and quantitative determination of the analyte. There are two parts to a chemical sensor – a region where selective chemistry takes place and the transducer. The chemical reaction produces a signal such as a colour change, emission of fluorescent light, a change in electrical potential at the surface, a flow of electrons, the production of heat, or a change in the oscillator frequency of a crystal. The transducer responds to this signal and translates the magnitude of the signal into a measure of the amount of the analyte.

Depending on the transducer type, chemical sensors are categorized into the following groups.

1. *Electrochemical sensors*

These include potentiometric sensors (ion-selective electrodes or ISEs) and voltammetric and amperometric sensors.

2. *Optical sensors*

In this class of sensors, a spectroscopic measurement is associated with the chemical reaction. They are referred to as optodes.
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3. Mass sensitive sensors

These make use of the piezoelectric effect. They rely on a change in mass on the surface of an oscillating crystal which shifts the frequency of oscillation. The extent of frequency shift is a measure of the amount of material adsorbed on the surface.

4. Heat sensitive sensors

They are also known as calorimetric sensors; here, the transducer monitors the heat of a chemical reaction involving the analyte.

1.4 Potentiometric sensors

The glass electrodes\textsuperscript{13-15} for pH measurements were the first developed potentiometric sensors that has been known since 1930s. The membrane in a pH electrode is the sodium silicate glass made by fusing a mixture of Al\textsubscript{2}O\textsubscript{3}, Na\textsubscript{2}O and SiO\textsubscript{2}. Increasing the Al\textsubscript{2}O\textsubscript{3} content in the glass results in an increasing response to other monovalent cations. In 1937, Kolthoff and Sanders\textsuperscript{16} made the first silver halide disc electrodes. In the early 1960s, Pungor\textsuperscript{16} published his first paper on AgI-based electrodes and he along with his co-workers developed the first commercial solid state ion selective electrode. Concepts from medicine and physiology also spurred the development of potentiometric sensors. In 1964, Moore and Pressman\textsuperscript{16} observed that neutral macrocyclic antibiotics induce ion permeation in mitochondria, leading to the development of neutral carrier electrodes. In 1966, a major break came from the discovery by Frant and Ross that a slice of a single crystal of lanthanum fluoride attached to the end of an electrode barrel could be used to sense the fluoride ion in aqueous solution\textsuperscript{17}. Ross and Frant teamed up and formed the Orion Research Inc. and both of them are considered as the founding fathers of ion selective electrodes.
powdered type of membranes using a sparingly soluble salt was another development as it does not require the need to grow a single crystal. An example is the silver sulphide disc\textsuperscript{18}. The liquid membrane type of sensors\textsuperscript{19} was first produced in 1967 and the major break through occurred in 1970 when a polymer film with sensing properties was produced by immobilizing the electroactive component into poly(vinyl chloride)\textsuperscript{20}. A number of PVC plasticized membrane sensors have been developed using different types of electroactive species (ionophores). Ruzicka \textit{et al}\textsuperscript{21} were the first to introduce liquid state electrode based on carbon in 1970. The development of sensors using spectral grade graphite powder, nujol oil and metal salts of low solubility in a plastic body was described by Mesaric and Dahmen\textsuperscript{22} in 1973. In 1980, Heineman \textit{et al} described the first use of a polymer film chemically modified carbon paste electrode (CMCPE)\textsuperscript{23}.

Research in the field of development of potentiometric sensors is gaining more and more attention and a number of potentiometric sensors have been developed for the cations like alkali, alkaline earth, transition metals, lanthanides etc; for anions like Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, perchlorate etc.; for drugs like terazosin, diclofenac etc\textsuperscript{24-33}.

\subsection*{1.4.1 Technique}

Potentiometric sensors make use of the development of an electrical potential at the surface of a solid material when it is placed in a solution containing ions which can exchange with the surface. The magnitude of the potential is related to the number of ions in the solution and the measurement of the cell potential is made under a ‘zero current’ condition. Species recognition is achieved through a chemical equilibrium reaction at the sensor surface.
Consider a metal rod dipped into its metal salt solution. The metal comprises of a periodic network of positive ions and a pool of mobile electrons.

\[
\text{metal} \quad M \leftrightarrow M^{n+} + n\, e^- \\
\Delta E \left\{ \text{interface} \right\} \\
M^{n+}_{\text{aq}} \\
\text{metal solution}
\]

A few $M^{n+}$ ions at the surface distribute into the aqueous solution in the region of the surface and become hydrated ($M^{n+}_{\text{aq}}$) which leaves an equivalent number of free electrons on the metal side of the solution/metal interface as depicted in the Figure 1.1. Thus there is a charge separation, which gives rise to an electrical potential difference.

1.4.2 Classification

Based on the physical state of the substances forming the electrode membrane\(^{18,34}\), potentiometric sensors are classified into

1. Ion-selective electrodes with solid membranes

The membrane can be either homogeneous (a single crystal, a crystalline substance or a glass which is considered to be a solid with regard to the immobility of the anionic groups) or heterogeneous, where a crystalline substance is built into a matrix made from a suitable polymer.
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2. Ion-selective electrodes with liquid membranes

In this case, the sensor membrane is represented by a water-immiscible liquid in which is dissolved a substance capable of exchanging the ion in solution for which the sensor is selective.

Another classification based on the membranes used in potentiometric sensors are

1. Glass membranes

These are selective to ions such as H\(^+\), Na\(^+\) etc.

2. Sparingly soluble inorganic salt membranes

This type consists of a section of single crystal or the pressed powdered disc of an inorganic salt which is seen to show selectivity to certain ions.

3. Polymer-immobilized ionophore membranes

In these, an ion-selective complexing agent or ion-exchanger is immobilized in a plastic matrix such as poly(vinyl chloride).

4. Gel-immobilized and chemically bonded enzyme membranes

These membranes use the highly specific reactions catalyzed by enzymes. The enzyme is incorporated into a matrix or bonded onto a solid surface.

1.5 Aspects of Sensors

1.5.1 Recognition elements

The key component of any sensor is the ionophore or electroactive component or the modifier which imparts the selectivity that enables the sensor to respond selectively to a particular analyte, thus avoiding interferences from other substances. Schiff bases, complexes, ion association complexes, calixarenes, crown ethers etc. have been tested for their use as ionophores.
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1.5.2 Performance factors

1. Selectivity
This is the most characteristic property of a sensor – the ability to discriminate between different substances and this is a function of the selective component.

2. Sensitivity range and detection limits.
This refers to the concentration range of the analyte for which the sensor behaves in a Nernstian manner. The lower level is the detection limit and the precise definition according to IUPAC convention is that it is the concentration of analyte at which the extrapolated linear portions of the calibration graph intersects the baseline – a horizontal line corresponding to zero change in response for several decades of concentration change.

3. Nature of solution
Conditions such as pH and the non aqueous content are taken into consideration.

4. Response time
The response time is the average time for the sensor to reach a potential within ±1 mV of its final equilibrium value. The practical response time of the sensor is calculated by measuring the time required to achieve 95% of the equilibrium potential from the moment of addition of $1.0 \times 10^{-5}$ M $M^{n+}$ solution.

5. Working lifetime
The lifetime of a sensor refers to the period of time during which the sensor can be used for the determination of the analyte and it is determined by the stability of the selective material.
1.5.3 Areas of application

The applicability of the sensors for continuous real time monitoring of certain analytes in the environment or in the online and offline processes in the industry are of great importance. In addition to pollution applications, farming, gardening, veterinary science and mining are all areas where sensors are needed for environmental monitoring.

1.6 A brief review on important potentiometric sensors for metal ions.

As part of the present investigations, potentiometric sensors have been developed for the following metals – Mn$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Pb$^{2+}$. A brief review on the potentiometric sensors for the titled metal ions is presented below.

1.6.1 Manganese

There are only few reports on manganese sensors in literature and so far none of them have been commercialized. Buchanan and Seago$^{36}$ reported the use of two electroactive components MnHPO$_4$ in MnCl$_2$ and MnCO$_3$ in MnCl$_2$ which were impregnated into silicone rubber matrix. Though the sensors fabricated responded to Mn$^{2+}$ test solutions; they were not ‘specific’ in their response to towards Mn$^{2+}$ ions; but rather it showed a response to the total free cations in solution. The use of an electrode with manganese(II) telluride-silver sulphide disc was explored by Hirata and Higashiyama$^{37}$. This sensor showed a non Nernstian response of 25 mV/pM and was selective relative to alkali-metal and alkaline-earth metal cations, but no other performance characteristics were described. The group of Lal$^{38}$ published their results where a membrane consisting of a cation exchange resin (Dowex 50 WX-4) in an epoxy resin matrix was proposed for Mn$^{2+}$ ion
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determinations, but the sensor gave a super Nernstian response. Midgley and Mulcahy\textsuperscript{39} reported the use of manganese(IV) oxide with a graphite/PTFE substrate in the fabrication of a solid type manganese sensor. The results show that the sensor gave a near Nernstian response to Mn\textsuperscript{2+} ions but the main practical problem was the slow response time of ~20 min and also, the pH had to be precisely controlled (maintained at pH 4.0 acetate medium). Agarwala and Chattopadhyaya\textsuperscript{40} studied the response characteristics of sensor fabricated with tetrapyridine Mn(II) thiocyanate precipitate as the ionophore which had a good working pH range of 2.3 – 8.8, but the response was only near Nernstian. Sun and Qi\textsuperscript{41} fabricated a sensor using permanganate ion while Dong\textsuperscript{42} determined the Mn\textsuperscript{2+} ions in solutions using a crystal ion-selective electrode. Singh \textit{et al}\textsuperscript{33} reported the use of a pentaazaamacroyclic manganese complex in the construction of a PVC-plasticized membrane sensor. Unfortunately, most of the developed manganese sensors have some problems like narrow working concentration range, high response time, poor selectivity and high detection limit.

1.6.2 Nickel

Extensive efforts have been made by researchers to develop sensors for the estimation of nickel especially as it is used in many catalytic processes and occurs in many industrial effluents. Morazzani-Pelletier and Baffier\textsuperscript{44} studied collodion and paraffin membranes embedded with nickel salts. Pungor \textit{et al}\textsuperscript{45} developed impregnated silicone rubber membrane electrodes incorporating nickel(II) dimethylglyoxime complex which showed response to Ni\textsuperscript{2+} ions. The silicone rubber membranes impregnated with nickel dimethylglyoximate, nickel acetylacetonate (dehydrate and anhydrous), nickel carbonate and nickel orthophosphate were prepared by
Buchanan and Seago\textsuperscript{36} and the results showed that the membranes containing the chelates nickel dimethylglyoximate and nickel acetylacetonate dihydrate failed to show response towards cations. Dobbelstein and Diehl\textsuperscript{46} studied the response of a sensor containing nickel dimethylglyoximate in epoxy polyester and phenol formaldehyde membranes. Hirata and Higashiyama\textsuperscript{37} demonstrated the use of sintered nickel selenide and telluride discs in the determination of Mn\textsuperscript{2+} ions over the concentration range 10\textsuperscript{-1} to 10\textsuperscript{-5} M. Though the sensors responded in a Nernstian manner, the selectivity was poor with strong interferences from silver, copper(II), mercury(II), iron(III), sulphide and chloride. Liquid membrane type sensors were reported with different ionophores like O,O' diisobutyl dithiophosphatonickel(II) in chlorobenzene by Materavo \textit{et al}\textsuperscript{47}; bis(tetraethylammonium) bis(dithiobenzophenazine) nickelate in nitrobenzene by Luca \textit{et al}\textsuperscript{48} and nickel diethyldithiocarbamate in chloroform by Smirnova \textit{et al}\textsuperscript{49}. Lal \textit{et al}\textsuperscript{50} reported the use of a nickel complex of 1,4,8,11-tetraazacyclotetradecane in araldite as the membrane disc for the fabrication of a liquid exchange type sensor. Hampton \textit{et al}\textsuperscript{51} suggested the use of 1,4,7,10-tetraoxacyclododecane as the electroactive component in the fabrication of a sensor for nickel but the characteristics like shelf life and pH range was not studied. Aswathi \textit{et al}\textsuperscript{52} reported a membrane sensor incorporating nickel bis(2-ethylhexyl) phosphate as ionophore. Bhatt and Thakkar\textsuperscript{53} constructed a sensor by incorporating a nickel(II) complex of isonitrosopropiophenone in styrene butyl methacrylate co-polymer which gave a non-Nernstian response to Ni\textsuperscript{2+} ions. Rao \textit{et al}\textsuperscript{54} investigated the responses of a membrane prepared by dissolving a 1:1 ratio of a chelating ion-exchange resin and PVC in THF. Gupta and co-workers\textsuperscript{55-58} published four reports where porphyrins, 5,7,12,14-tetramethyl dibenzotetraazaannulene, dibenzocyclaminickel(II) and
dibenzo-18-crown-6 were investigated as electroactive materials for preparing PVC based membrane sensors. Jain et al\textsuperscript{59,60} reported the use of different electroactive components; macrocyclic compounds in PVC and polystyrene binders and two nickel chelates of schiff bases in PVC membrane sensors for the determination of Ni\textsuperscript{2+} ions. Crown ethers such as 1,10-dibenzyl-1,10-diaza-18-crown-6 reported by Mousavi et al\textsuperscript{61} and dibenzodiaza-15-crown-4 reported by Shamsipur and Kazemi\textsuperscript{62} were used as neutral carriers in the construction of a PVC based membrane sensor. The group of Ganjali\textsuperscript{63,64} suggested two ionophores; a thiopyran derivative as the electroactive material in the construction of a PVC membrane sensor and a coated graphite PVC-membrane sensor based on benzylbis(thiosemicarbazone). A PVC-based membrane of 1,5-diphenylthiocarbazone was discussed in detail by Abbaspour and Izadyar\textsuperscript{65} while the group of Singh reported a polystyrene based 3,4,11,12-dibenzo-2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane\textsuperscript{66} and also 3,4:12,13-dibenzo-1,6,10,15-tetraazacyclooctadecane\textsuperscript{67} and dibenzo[e,k]-2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,5,7,9,11-hexaene\textsuperscript{68} in a PVC membrane matrix. A wire sensor coated with the PVC plasticized membrane containing 1,3,7,9,13,15,19,21-octaaazapentacyclooctacosane which was selective to Ni\textsuperscript{2+} ions was reported by Mazloum et al\textsuperscript{69}. Mashhadizadeh et al\textsuperscript{70,71} reported the response characteristics of two PVC membrane sensors based on two ionophores- a mercapto derivative and a schiff base. Singh and Bhatnagar\textsuperscript{72} reported the use of carboxylated and methylated porphine while Belhamel et al\textsuperscript{73} made use of a macrocyclic compound for the construction of a nickel sensor. The group of Yari\textsuperscript{74} discussed the results of the sensor fabricated using a dioxime derivative. However, most of the reported sensors
suffer from one or the other drawbacks like narrow working concentration range, high detection limit, high response time and poor selectivity.

1.6.3 Copper

A variety of potential ion carriers have been used in the construction of sensors for Cu$^{2+}$ ions and a commercial solid state membrane sensor based on CuS-Ag$_2$S has been introduced by Orion Research Inc.$^{75}$ but it suffers interferences from Hg$^+$, Hg$^{2+}$, Ag$^+$ and Fe$^{3+}$ ions. Chatterjee and Mitra$^{76}$ prepared clay membranes while Buchanan and Seago$^{36}$ tested the response of silicone rubber membranes impregnated with anhydrous and hydrated CuHPO$_4$ in Cu(NO$_3$)$_2$ but these sensors gave a sub-Nernstian response to Cu$^{2+}$ ions. The group of Hirata$^{77,78,37}$ investigated the response of different types of sensors – a copper(I) sulphide ceramic sensor, silicone rubber membranes impregnated with copper(I) sulphide and copper(I) selenide and telluride sensors, to Cu$^{2+}$ ions. Sharp and Johansson$^{79}$ prepared solid-state sensors from ion-radical salts of 7,7,8,8-tetracyanoquinodimethane. Neshkova and Sheytanov$^{80,81}$ developed two solid-state sensors with homogeneous membranes of CuAgSe and Cu$_{2-x}$Se which showed response to Cu$^+$ ions and not Cu$^{2+}$ ions. Kamata $et$ $al^{82,83}$ reported the use of acyclic neutral ionophores with dithiocarbamate groups in the fabrication of a copper sensor. The group of Jain$^{84,85}$ reported two types of sensors - a polystyrene based heterogeneous ion-exchanger membrane of cerium(IV) phosphomolybdate and PVC membrane sensors based on copper chelates. Sun $et$ $al^{86}$ produced a novel copper sensor based on molecular deposition technique of copper phthalocyanine tetrasulphonate and bipolar pyridine salt on 3-mercaptopropionic acid modified Au electrode. Chen and Alexander$^{87}$ reported the use of tungsten oxide as the ionophore in the fabrication of a...
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copper sensor. Gismera et al\textsuperscript{88,89} fabricated copper sensors based on copper complexes containing thiohydrazone and thiosemicarbazone ligands and also based on dithiosalicylic and thiosalicylic acids. The group of Shamsipur\textsuperscript{90-92} reported the use of a 23-membered macrocyclic diamide, naphthol-derivative schiff base and mixed aza-hioether crowns containing a 1,10-phenanthroline sub-unit; in the fabrication of copper sensors. K. C. Gupta and D'Arc\textsuperscript{93,94} published their results on copper sensors containing a copper(II) salicylaniline schiff base complex in styrene-co-acrylonitrile copolymer while Saleh\textsuperscript{95} reported a copper sensor based on a cephaloridine antibiotic as ionophore in a PVC matrix. Chattopadhyaya and co-workers\textsuperscript{96,97} successfully estimated the copper content in gun metal by using a heterogeneous coated wire Cu\textsuperscript{2+} ion selective electrode based on Cu(II)-cupron complex as ionophore and also used thiopentone-Cu(II) complex as the ionophore in a PVC membrane sensor for the determination of Cu\textsuperscript{2+} ions. Park et al\textsuperscript{98} developed five novel 1,3-alternate calix[4]azacrown ethers having 2-picoly, 3-picoly and benzyl unit on the nitrogen atom as ionophores for copper-selective PVC membrane sensors and Gholivand and Nozari\textsuperscript{99} used 2,2'-dithiodianiline as the neutral carrier in the fabrication of a copper sensor. Tymecki et al\textsuperscript{100} discussed the thick-film graphite electrodes produced by screen-printing and it was shown that CuS-doped graphite sensors show stable and improved response to copper ions. Su et al\textsuperscript{101} reported a copper sensor based on 2'-picoly sym-dibenzo-16-crown-5 ether as membrane carrier with a super Nernstian response to Cu\textsuperscript{2+} ions. Ganjali and co-workers\textsuperscript{102-104} reported a graphite sensor coated with PVC plasticized bis-2-thiophenal propanediamine membrane and two PVC membrane sensors incorporating a bis-thiophenalpropanediamine and diphenylisocyanate bis(acetylacetone) ethylenediimine as the electroactive species. Firooz et
constructed a coated wire copper sensor based on phenylglyoxal-α-monoxime ionophore while the group of Abbaspour\textsuperscript{106,107} reported a carbon paste electrode modified with 3,4-dihydro-4,4,6-trimethyl-2(1H)-pyrimidine thione and a PVC membrane sensor incorporating dithioacetal as ionophore for the potentiometric determination of Cu\textsuperscript{2+} ions. Coated wire and coated disc copper sensors based on Cu(II) complex with cyclized salophen were reported by Al-Saraj \textit{et al}\textsuperscript{108,109} for the determination of Cu\textsuperscript{2+} ions in aqueous solutions. Sadeghi \textit{et al}\textsuperscript{110} reported the use of a series of schiff base derivatives inorder to characterize their abilities as copper ion carrier in PVC membrane sensors. Yoshimoto \textit{et al}\textsuperscript{111} studied the response of the sensor based on hydrotris(3-isopropylpyrazolyl)methane in a poly(vinyl chloride) matrix. V. K. Gupta and co-workers\textsuperscript{112-114} fabricated three PVC plasticized membrane sensors based on ethambutol-copper complex, bis(acetylacetone)propylenediimine and porphyrins as ionophores. A comparison between the response characteristics of sol-gel and coated wire copper sensors based on thiosemicarbazone was studied by Ardakani \textit{et al}\textsuperscript{115}. Singh and Bhatnagar\textsuperscript{116} explored the response of PVC plasticized membrane sensor based on a schiff base complex derived from 2,3-diaminopyridine and o-vanillin, to Cu\textsuperscript{2+} ions. The group of Michalska\textsuperscript{117,118} reported the use of conducting polymers in the construction of an all-plastic, disposable copper sensor. Fakari \textit{et al}\textsuperscript{119} fabricated a series of PVC membrane sensors based on different salens as carriers for the determination of Cu\textsuperscript{2+} ions in solutions. Two novel copper PVC membrane sensors were constructed by Hassan \textit{et al}\textsuperscript{120} which were based on cyclic tetrapeptide derivatives. Singh \textit{et al}\textsuperscript{121} studied the characteristics of two plasticized membrane sensors based on 3-(2-pyridinyl)2-H-pyrido[1,2-a]-1,3,5-triazine-2,4(3H)-dithione and acetoacetanilide. Szigeti\textsuperscript{122} explored the response characteristics of the sensor
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fabricated using \( N,N,N',N' \)-tetracyclohexyl-3-thioglutaric diamide as ionophore for the potentiometric determination of \( Cu^{2+} \) in drinking water while Oliveira et al\(^{123} \) reported a new copper sensor incorporating a new thiophosphoril-containing macrocycle as neutral carrier. However, most of the reported sensors have limitations in that they exhibit inferences to some common ions, work over a narrow concentration range and show non-Nernstian response, limited pH range and high response time.

1.6.4 Mercury

Literature reports on mercury sensors are sparse and one is yet to achieve an efficient commercial mercury(II) sensor. One of the earliest report of a mercury sensor was by Ruzicka and Tjell\(^{124} \) which was a liquid membrane electrode based on the mercury(II) complex of dithizone. Baiulescu et al\(^{125-127} \) reported the use of \( Hg^{2+} \) chelate of diketohydrindylidine diketohydrindamino in chloroform, palladium dithizonate and PAN chelate of \( Hg^{2+} \) dissolved in chloroform in the fabrication of three liquid membrane sensors. Szczepaniak and Oleksy\(^{128} \) published their results of a liquid membrane sensor based on \( N(O,O-diisopropylthiophosphoryl) \) thiobenzamide. But, these sensors suffered interferences from \( Ag^+ \) and \( Fe^{3+} \) ions. Lai and Shin\(^{129} \) reported the use of 1,4-dithia-12-crown-4 as a neutral carrier in the fabrication of a PVC membrane sensor which gave a discrimination of both \( Ag^+ \) and \( Fe^{3+} \) ions, but while Nernstian slopes were observed for \( Hg(NO_3)_2 \) solution, the use of a chloride salt led to nearly complete disappearance of an emf response. In the case of the sensor fabricated using the ionophore hexathiacyclooctadecane, which was reported by Masuda and Sekido\(^{130} \), there was serious interferences from \( Fe^{3+}, Bi^{3+} \) and \( Pb^{2+} \), the effect of \( Ag^+ \) was not mentioned. The group of Brzózka\(^{131,132} \)
reported the use of two \(N,N'\)-substituted 1,10-diaza-18-crown-6 ethers for the fabrication of a PVC membrane sensor which exhibited a high discrimination for most of the tested ions except \(\text{Ag}^+\) ions. Srivastava et al\(^{133}\) constructed a solid membrane sensor using polytungstoantimonate as the electroactive phase using which they were able to estimate the metal ions in polluted waters. The group of Siswanta\(^{134,135}\) used non cyclic thioethers, sulphoxides and sulphone as ionophores. Their experiments revealed that sulphoxides and thioethers were better ionophores for the mercury sensor as they had a preference for \(\text{Hg}^{2+}\) to \(\text{Ag}^+\) ions. The sensor fabricated using \(N\)-hydroxyl amide derivatives gave a twice Nernstian response which could be attributed to the fact that they are charged \(\text{Hg}^{2+}\) ion carriers and that at an appropriate pH, a response mechanism could prevail or alternatively, they could be responding to monocation mercury acetate\(^{136}\). Gupta et al\(^{137,138}\) explored the response characteristics of the PVC membrane sensors fabricated using pentathia-15-crown-5 and a diamine donor ligand while the group of Shamsipur\(^{139,140}\) studied the responses of PVC membrane sensors based on hexathia-18-crown-6-tetraone and dibenzodiactathia-18-crown-6-dione. Yang and co-workers\(^{141}\) reported the use of two ionophores, 7,16-dithenyl-1,4,10,13-tetraoxa-7,16-diazaacyclooctadecane and 7,16-di-(2-methylquinoly)-1,4,10,13-tetraoxa-7,16-diazaacyclooctadecane, for the fabrication of PVC membrane mercury sensors. Jain et al\(^{142}\) fabricated a PVC membrane sensor incorporating 1-(2-nitro-4-methyl phenyl)-6-methyl-6-methoxy-1,4,5,6-tetrahydro-pyrimidine-2-(3H)-thione as the electroactive ingredient which gave a sub Nernstian response to \(\text{Hg}^{2+}\) ions. Marco et al\(^{143}\) reported the use of a chalcogenide glass ISE for the determination of ultra trace level of \(\text{Hg}^{2+}\) ions in saline media. Perez-Marin\(^{144}\) and co-workers fabricated a PVC membrane sensor incorporating 1,3-diphenyl thiourea. The
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construction, performance and application of coated wire sensors based on three carriers, 2-mercaptobenzimidazole, 2-mercaptobenzothiazole and hexathiacyclooctadecane, were reported by Mazloum et al.\textsuperscript{145} while the group of Hassan\textsuperscript{146} explored the response behaviour of a PVC membrane sensor based on ethyl-2-benzoyl-2-phenylcarbamoyl acetate. A new tetrazolium-triiodomercurate modified carbon paste sensor was tested by Abbas and Mostafa\textsuperscript{147} and it gave a near Nernstian response and was applied for the direct determination of Hg\textsuperscript{2+} ions in spiked waste water, metal amalgams and dental alloys. Mahajan et al.\textsuperscript{148,149} explored the use of a thiosemicarbazone and p-tert-butyl calix[4]crown with imine units as ionophores in the fabrication of two PVC membrane sensors for the determination of Hg\textsuperscript{2+} ions. Two PVC membrane sensors based on a mercapto compound and bis[5-((4-nitrophenyl)azo salicylaldehyde)] were reported by the group of Mashhaizadeh\textsuperscript{150,151} which gave near Nernstian slopes for Hg\textsuperscript{2+} ions. Lu et al.\textsuperscript{152} reported the use of a calixarene derivative containing a thiazole azo group as the electroactive component in the fabrication of a mercury sensor. A peculiar twice Nernstian response was observed at pH 6.5 and a typical response at pH 4.0. Singh et al.\textsuperscript{153} reported a polystyrene-based membrane incorporating 2,3,4,9,10,11-dipyridine-3,10-diaza-1,5,8,12-tetrathiacyclotetradeca-2,9-diene as ionophore. Gismera et al.\textsuperscript{154} constructed a carbon paste sensor chemically modified with tetraethylthiuram disulphide with super Nernstian responses to Hg\textsuperscript{2+} as well as Cu\textsuperscript{2+} ions. Ye and co-workers\textsuperscript{155} fabricated a sensor incorporating N,N-dimethylformamide-salicylacetylhydrazone as neutral carrier. Khan and Inamuddin\textsuperscript{156} reported the use of polyaniline Sn(IV) phosphate composite for the fabrication of a mercury sensor. However, most of the reported sensors suffer from one or
the other drawbacks like narrow working concentration range, high detection limit, high response time and poor selectivity.

1.6.5 Lead

Hirata and Higashiyama\textsuperscript{157,37} reported a new lead sulphide-silver sulphide-copper(I) sulphide electrode, selenide and telluride electrodes for Pb\textsuperscript{2+} ions but they were susceptible to interference from Hg\textsuperscript{+}, Hg\textsuperscript{2+}, Ag\textsuperscript{+}, and Cu\textsuperscript{2+} ions. A liquid membrane sensor was reported by Linder \textit{et al}\textsuperscript{158} where \textit{N},\textit{N}-dioctadecyl-\textit{N}',\textit{N}'-dipropyl-3,6-dioxaoctanediameide was used as the ionophore to detect PbX\textsuperscript{+} (X= OH\textsuperscript{−}, Cl\textsuperscript{−}, NO\textsubscript{3}−, CH\textsubscript{3}CO\textsubscript{2}−). Vlasov and co-workers\textsuperscript{159} reported the use of chalcogenide glass sensors based on PbS-Ag\textsubscript{2}S-As\textsubscript{2}S\textsubscript{3} for the online detection of Pb\textsuperscript{2+} in river water but there was deviation in response characteristics on continuous usage. The group of Gupta and Jain\textsuperscript{160-165} reported a series of sensors for the determination of Pb\textsuperscript{2+} ions based on different ionophores- bismuth tungstate, 15-crown-5, 4-t-butyl calix[4]arene, 3,4,4a,5-tetrahydro-3-methyl pyrimido-[1,6-a] benzimidazole-1(2H) thione, tetrapyrazole and calix[4]arene receptors and \textit{N},\textit{N}'-dibenzyl-1,4,10,13-tetraoxa-7,16-diazyacyclooctadecane. Sheina \textit{et al}\textsuperscript{166} fabricated a PVC membrane sensor based on a Pb\textsuperscript{2+} chelate of N-benzoyl-N-phenyl hydroxamine, but the sensor showed interferences in the presence of Hg\textsuperscript{2+}, Cu\textsuperscript{2+} and Fe\textsuperscript{3+}. The group of Malinowska and Brzozka\textsuperscript{167-171} fabricated lead sensors where a group of cyclic amides and oxamides, di and tetrathioamide functional calix[4]arene derivatives, calix[6]arene thiophosphorylated were tested as potential carriers. A change in the ion-selectivity was seen in the thioamide calix[4]arene derivative where the sensor showed a response to perchlorate ion in the absence of lipophilic salts but, on the addition of potassium tetrakis[3,5-bis(trifluoromethyl)-phenyl]
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borate, the sensor gave a near Nernstian response to \( \text{Pb}^{2+} \) ions. Kamata and Onoyama\(^{172} \) suggested the use of methylene bis(diisobutyl dithiocarbamate) as the ionophore for the fabrication of a lead sensor but this sensor showed serious interferences in the presence of \( \text{Cu}^{2+} \), \( \text{Fe}^{3+} \), and \( \text{Zn}^{2+} \) ions. They rationalized that the response characteristics of the sensor was attributed to the size of the 'C' cavity of the ionophore. Sheen and Shih\(^{173} \) fabricated a lead sensor based on mono benzo-15-crown-5-phosphomolybdic acid and they observed a very good pH range of 3.0 - 9.0. Anuar and Hamdam\(^{174} \) reported a near Nernstian response for the sensor fabricated using polyhydroxamic acid with silicone rubber as the supporting material while Attiyat \textit{et al.}\(^{175} \) reported a silver wire coated sensor using benzo-18-crown-6 as ionophore. Bakker \textit{et al.}\(^{176} \) compared the response of a \( \text{Pb}^{2+} \) ion selective electrode with a \( \text{Pb}^{2+} \) optode fabricated with the same solvent polymeric membrane phase. The group of Shamsipur\(^{177-185} \) fabricated a large number of sensors for lead based on different ionophores – dibenzopyridino 18-crown-6, 9,10-anthraquinone derivatives, 5,5'-dithiobis-(2-nitrobenzoic acid), 4'-vinylbenzo-15-crown-5 homopolymer, bis(anthraquinone) sulphide derivatives, ethaneamine \( 2,2'\text{-[1,2-ethylenebis(oxy)]N,N'\text{-bis(2-thienylmethylene), 18-membered thia crown derivative, piroxicam, anthraquinone derivative. Yang et al.}\(^{141,186} \) studied the response characteristics of sensors fabricated using the ionophores dithiophene diazacrown ether derivatives, \( 7,16\text{-dithenoyl}-1,4,10,13\text{-tetraoxa}-7,16\text{-diazacyclooctadecane and 7,16-di-(2-thiopheneacetyl)-1,4,10,13\text{-tetraoxa}-7,16\text{-diazacyclooctadecane}. Cadogan and co-workers}\(^{187} \) reported near Nernstian slopes for lead sensors fabricated with calixarene phosphine oxide derivatives as ionophore. Abbaspour and Tavakol\(^{188} \) presented a PVC membrane sensor based on benzyl disulphide as ionophore but only the
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selectivity coefficients were calculated for some metal ions; no other parameters were studied. Xu and Katsu\textsuperscript{189} reported near Nernstian values for the sensor fabricated with tetrabenzyl pyrophosphate as ionophore but the sensor using diphenyl phosphinic anhydride gave a non Nernstian response. Mousavi \textit{et al}\textsuperscript{190,191} developed PVC membrane sensors based on 1,10-dibenzyl-1,10-diaza-18-crown-6 and capric acid while the group of Zareh\textsuperscript{192} studied the effect of the presence of 18-crown-6 on the response of 1-pyrrolidine dicarbodihtioate based lead sensor and it was observed that the response of the sensor with the immobilized 18-crown-6 was Nernstian. The lead sensor based on a calixarene carboxyphenyl azo derivative as reported by Lu \textit{et al}\textsuperscript{193} showed good Nernstian responses but the selectivity studies done were poor as the method adopted was the separate solution method. Hassan \textit{et al}\textsuperscript{194} fabricated three new PVC plasticized membrane sensors based on three newly synthesized pyridine carboximide derivatives as neutral ionophores which displayed near Nernstian responses. The group of Ardakany and Ensafi\textsuperscript{195-197} fabricated a highly selective lead (II) coated wire sensor based on a schiff base, a sol-gel and PVC membrane sensor based on bis(thiophenal)-4,4'-methylenedianiline and a PVC membrane sensor based on 1-phenyl-2-(2-quinolyl)-1,2-dioxo-2-(4-bromo) phenyl hydrazone. Bhat \textit{et al}\textsuperscript{198} fabricated a coated wire sensor based on 4-\textit{tert}-butylcalix[6]arene which was effectively used for the direct determination of Pb\textsuperscript{2+} ions in real samples. The lead sensor reported by Agarwal \textit{et al}\textsuperscript{199} was based on a heterogeneous membrane of chelating inorganic ion exchange resin (\(\alpha\)-nitroso-\(\beta\)-naphthol sorbed zirconium (IV) tungstophosphate) embedded in a PVC matrix and was used for the direct determination of Pb\textsuperscript{2+} ions in soil samples. Jeon \textit{et al}\textsuperscript{200} fabricated a PVC membrane sensor based on a schiff base complex of \(N,N'\)-bis(salicylidene)2,6-pyridinediamine but Cu\textsuperscript{2+} ions was observed to be
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an interferent. Carbon paste sensors modified with dithiodibenzoic and mercaptobenzoic acids were studied by Gismera et al\textsuperscript{201} of which the dithiodibenzoic acid based CMCPE sensor exhibited a more sensitive and selective response to Pb\textsuperscript{2+} ions. However, most of the reported sensors have limitations in that they exhibit inferences to some common ions, work over a narrow concentration range and show non-Nernstian response, limited pH range and high response time.

1.7 Scope of the present investigation

The present investigation purports to fabricate sensors for the determination of the transition metal ions such as Mn\textsuperscript{2+}, Ni\textsuperscript{2+}, Cu\textsuperscript{2+}, Hg\textsuperscript{2+} and Pb\textsuperscript{2+} at trace levels. Three different types of sensor fabrication has been adopted viz. PVC membrane sensor, CPE-PVC membrane sensor and CMCPE type of sensor and fourteen sensors have fabricated.

For all these sensors, the principal analytical parameters have been studied, including the linear response range, calibration slope, detection limit, effect of pH and non aqueous media, shelf life and selectivity. The usefulness of developed sensors has also been studied. The developed sensors have been applied for the analysis of metal ions in real samples by direct potentiometry and as an indicator electrode in potentiometric titrations. It is hoped that all the fourteen sensors developed can be used for the determination of the respective metal ion with high accuracy and precision.