Analytical chemistry is a scientific discipline that develops and applies methods, instruments and strategies to obtain information on the composition and nature of matter in space and time. The principal objective of the analytical chemistry is to obtain as much chemical information and of as high quality as possible from objects and systems by using as little material, time and human resources as possible and with minimal costs and risks. There is an escalating need and desire for us to monitor all aspects of our environment in real time and this has been brought about by our increasing concerns with pollution, our health and safety. There is also a desire to determine contaminants and analytes at lower and lower levels and one could say that the aim of all modern analytical chemistry is to lower the detection limits and to improve the accuracy and precision at those limits. Thus analytical chemistry is directly concerned with solving the analytical problems derived from chemical information needs in a variety of economic and social areas including industry, the environment, food science and technology, pharmaceutical analysis and clinical analysis. A qualitative analysis in analytical chemistry yields information about the identity of atomic or molecular species or the functional groups in the sample. Where as a
quantitative analysis provides numerical information as to the relative amount of one or more of these components. The quantitative execution of chemical reactions is the basis of traditional or classical methods of chemical analysis: gravimetry and titrimetry.

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).

Electroanalysis is another analytical technique used for the trace level analysis and can be defined as the application of electrochemistry to solve real life analytical problems. Electroanalytical chemistry encompasses a group of quantitative and qualitative analytical methods based on the electrical properties of a solution of the analyte when it is made a part of an electrochemical cell. These techniques are capable of producing low detection limit and a wealth of characterization.
information describing electrochemically accessible systems. 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

The principal criterion of an electroanalytical technique is that the species which is desired to be measured should react directly (or indirectly through coupled reaction) at, or be adsorbed onto the electrode. Electroanalytical measurements can only be carried out in situations in which the medium between the two electrodes making up the electrical circuit be sufficiently conducting. Thus, electroanalysis is complementary to other forms of analysis.

In comparison with other analytical techniques, electroanalytical methods have certain advantages such as the ability to distinguish the oxidation state of the element, provides 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.
1.1. Types of Electroanalysis

There are essentially four types of electro analytical measurements that can be performed:

1. Conductometry,
2. Potentiometry,
3. Amperometry
4. Voltammetry.

1.1.1. Conductometry

In conductometry concentration of the species is obtained through measurement of solution resistance and therefore not species selective. It is useful in situations where it is necessary to ascertain 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.

1.1.2. Potentiometry

This technique makes use of measurement of equilibrium potential of working electrode with reference to a standard electrode using high-impedance voltmeter under zero current condition. By the careful choice of the working electrode, ion selective electrodes, selective species determination can be achieved with minimal interference from other ions. Detection limits of the order of 100 nanomoles per liter of the total concentration of the ion present in a particular oxidation state, although down to 10 picomolar differences in concentration can be measured.
1.1.3. Amperometry

In this technique, a fixed potential is applied to the working electrode, which causes the oxidation or reduction of the species to be determined and produces current. If this potential is conveniently chosen, then the magnitude of the current is directly proportional to concentration. Detection limit in the micro molar region can be obtained.

1.1.4. Voltammetry

In voltammetry a varying potential is applied at the surface of an electrode and measures the resulting current with a three electrode system. This method can reveal the reduction potential of an analyte and its electrochemical reactivity. This method in practical terms is nondestructive since only a very small amount of the analyte is consumed at the two-dimensional surface of the working and auxiliary electrodes. 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.

An overview of analytical chemistry development demonstrates that electrochemical sensors represent the most rapidly growing class of chemical sensors. Electrochemical sensors and detectors are very attractive for on-site monitoring of analyte in the sample matrix. They are inherently sensitive and selective towards electroactive species, fast and accurate, compact, portable and cost effective. Such devices hold a leading position among sensors presently available and have found a vast
range of important applications in the fields of clinical, industrial, environmental and agricultural analysis\textsuperscript{10-11}.

1.2. Chemical Sensor

A chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal\textsuperscript{12}. The chemical information, mentioned above, may originate from a chemical reaction of the analyte or from a physical property of the system investigated. There are two parts to a chemical sensor—a region where the selective chemistry takes place and then a transducer. The chemical reaction produces a signal such as a colour change, the emission of fluorescent light, a change in the electrical potential at a surface, a flow of electrons, the production of heat, or a change in 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 analyte. Depending on the type of transducer used, chemical sensors are classified into the following groups

1.2.1. Electrochemical sensor

Electrochemical devices transform the effect of the electrochemical interaction between the analyte and the electrode into a useful signal. Such effects may be stimulated electrically or may result in a spontaneous interaction at the zero-current condition. These include potentiometric sensors (Ion selective electrode-ISE, Ion selective field effective transistor-ISFETs), voltammetric and amperometric sensors including solid electrolyte gas sensor.
1.2.2. Optical sensors

In optical sensors there is a spectroscopic measurement associated with the chemical reaction. Optical sensors are often referred to as optodes and use of optical fibers is a common feature. Absorbance, reflectance and luminescence measurements are used in the different types of optical sensors.

1.2.3. Mass sensitive sensor

This type of sensor makes use of the piezoelectric effect and include devices such as the surface acoustic wave sensor and are particularly useful as gas sensors. They rely on a change in mass on the surface of an oscillating crystal which shifts the frequency of oscillation. The extent of the frequency shift is a measure of the amount of material adsorbed on the surface.

1.2.4. Heat sensitive sensors

These are often called calorimetric sensors in which the heat of a chemical reaction involving the analyte is monitored with a transducer such as a thermistor or a platinum thermometer.

Compared to optical, mass and thermal sensors, electrochemical sensors are especially attractive because of their remarkable detectability, experimental simplicity and low cost.

1.3. Potentiometric Sensor

In potentiometric sensors, the analytical information is obtained by converting the recognition process into a potential signal, which is proportional (in a logarithmic fashion) to the concentration (activity) of species generated or consumed in the recognition event. An ion-selective
membrane is the key component of all potentiometric ion sensors\textsuperscript{13}. It establishes the preference with which the sensor responds to the analyte in the presence of various interfering ions from the sample. If ions can penetrate the boundary between two phases, then an electrochemical equilibrium will be reached, in which different potentials in the two phases are formed. If only one type of an ion can be exchanged between the two phases, then the potential difference formed between the phases is governed only by the activities of this target ion in these phases. When the membrane separates two solutions of different ionic activities (\(a_1\) and \(a_2\)) and provided the membrane is only permeable to this single type of ion, the potential difference \((E)\) across the membrane is described by the Nernst equation:

\[
E = \text{constant} + \frac{RT}{nF} \times \ln \left( \frac{a_2}{a_1} \right)
\]

If the activity of the target ion in phase 1 is kept constant, the unknown activity in phase 2 (\(a_1 = a_x\)) is related to \((E)\) by:

\[
E = \text{constant} + \frac{RT}{nF} \times \ln \left( \frac{a_x}{a_1} \right) = \text{const} + S \times \log \left( a_x \right)
\]

where \(S=59.16/n \text{ [mV]}\) at 298 K and \(n\) is the charge of the analyte. The potential difference can be measured between two identical reference electrodes placed in the two phases. In practice the potential difference i.e. the electromotive force is measured between an ion selective electrode and a reference electrode, placed in the sample solution. The potential measurements are made at zero current condition.

The glass electrodes\textsuperscript{14-18} 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 $\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}$ and $\text{SiO}_2$. Increasing the $\text{Al}_2\text{O}_3$ content in the glass results in an increasing response to other monovalent cations. In 1937, Kolthoff and Sanders$^{19}$ made the first silver halide disc electrodes. In the early 1960s, Pungor$^{19}$ published his first paper on AgI-based electrodes and filed a patent on heterogeneous selective membranes with his co-workers, which were the basis for the first commercial solid-state ISEs. Concepts from medicine and physiology also spurred the development of ISEs. In 1964, Cyril Moore and Berton C. Pressman observed that neutral macrocyclic antibiotics induce ion permeation in mitochondria, leading to the development of neutral carrier electrodes. Wilhelm Simon, an eminent organic chemist at ETH in Zurich (Switzerland), used extracts of poisonous mushrooms containing the dicsipetide valinomycin dissolved in a liquid ion-exchanger membrane. Although the response was slow, an electrode that measured $\text{K}^+$ in the presence of a 5000-fold excess of the $\text{Na}^+$ was soon developed and patented. His studies on the structure selectivity relationships of many synthetic ionophores, plasticizers, and additives allowed him to fabricate novel ISEs$^{20}$. In 1966, Frant and Ross$^{21}$ were reported the first potentiometric sensor for fluoride based on single crystal electrode. This pioneering work lead to the emergence of a new breed of potentiometric chemical sensors. Ross and Frant teamed up and formed the Orion Research Inc. and both of them considered as the founding father of ion selective electrodes.

The liquid membrane sensor$^{22}$ was first introduced in 1967 which provided the means for the direct determination of calcium ions. A 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{23}. Ruzicka et al\textsuperscript{24} were the first to introduce liquid state electrode based on carbon in 1970. In 1971, Henry Freiser\textsuperscript{25} introduced first coated wire electrode and it received considerable attention because of it dispensed with the inner reference solution. Pungor and his co-workers developed an iodide ion selective electrode by incorporating finely dispersed silver iodide into a silicone rubber monomer and then carrying out polymerization\textsuperscript{19, 26-27}. An enzyme ISE for amygdalin has also been proposed\textsuperscript{28}. 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{29} in 1973. In 1980, Heimen et al\textsuperscript{30} described the first use of a polymer film chemically modified carbon paste electrode (CMCPE).

Various on-line monitoring systems can benefit from the inherent specificity, wide scope, dynamic behavior and simplicity of potentiometric sensors\textsuperscript{31}. They have become widely used as detectors in high speed automated flow analyzers, such as air-segmented \textsuperscript{32-33} and flow-injection systems\textsuperscript{34}. In addition, the coupling of modern ion chromatography with potentiometric detection has been used with significant success\textsuperscript{34-35}. Miniaturization of ISE has also permitted their use as on-column detectors for capillary electrophoresis\textsuperscript{36}.

Rodwedder et al\textsuperscript{37} and Fatibello and co-workers\textsuperscript{38-41} have shown the use of coated graphite epoxy ion selective electrodes for the determination of cations using ion-pair formation with tricaprylylimethylammonium cation in a PVC matrix. Using a similar system with incorporation of saccharinate anion and toluidine, Rover et al\textsuperscript{42} have described the construction of a tubular ion selective electrode useful for determination of saccharin. A more sensitive system for saccharin determination has
been described by Alfaya et al\textsuperscript{43} using a thin film of silsesquioxane 3-n-propylpyridinium chloride polymer coated on a graphite rod. The successful use of thin film electrodes modified, by nickel(II) hexacyanoferrate, for potassium determination has been described by Stradiotto and co-workers\textsuperscript{44}.

Potentiometric sensors are simple to use, easily automated for rapid sampling, with low interferences from the matrix and can be applied to small volumes. These advantages make potentiometric sensors an ideal choice for both clinical and industrial measurements where speed, simplicity and accuracy are essential. Thus research in the field of potentiometric sensors attains considerable attention and a number of sensors have been reported for metal ions such as alkali, alkaline earth, transition, lanthanides, etc; for anions such as perchlorate ion, \textit{Cl}^{-} etc; for pharmaceutical compounds such as acetylsalicylic acid, mebendazole, diclofenac etc\textsuperscript{45-57}.

There are three basic types of potentiometric devices: ion-selective electrodes (IES), coated wire electrodes (CWES) and field effect transistors (FETS).

1.3.1. Ion-selective electrodes

Ion-selective electrodes are part of a group of relatively simple and inexpensive electroanalytical tools which are commonly referred to as potentiometric chemical sensors since selective chemistry take place at the electrode producing an interfacial potential. Species recognition is achieved with a potentiometric chemical sensor through a chemical equilibrium reaction at the sensor surface. Thus the surface must contain a component which will react chemically and reversibly with the analyte.
Ion selective electrodes allow the specific and quantitative determination of an almost unimaginable number of substances, ranging from simple inorganic ions through amino acids to complex organic molecules. The wide range of applications, low material requirements and simplicity of analytical procedure have not only brought ion-selective electrodes in to the lime light of analytical chemistry, but have promoted their use as tools for physiologists, medical researchers, biologists, geologists, environmental protection specialists, etc.58

1.3.2. Coated-wire electrodes

Coated-wire electrodes (CWEs) were first introduced in the mid of 1970's by Freiser.25, 59 In the classical CWE design, a conductor is directly coated with an appropriate ion-selective polymer membrane (usually poly(vinyl chloride, poly(vinylbenzyl chloride) or poly(acrylic acid)) to form an electrode system that is sensitive to electrolyte concentrations. The CWE response25, 59 -60 is similar to that of classical ISE, with regard to detectability and range of concentration. The great advantage is that the design eliminates the need for an internal reference electrode, resulting in benefits during miniaturization, for example. This is particularly useful for the in vitro and in vivo biomedical and clinical monitoring of different kind of analytes.

1.3.3. Ion-selective field effect transistors (ISFET)

Ion-selective field effect transistors (ISFET) work as an extension of CWE. ISFET incorporate the ion-sensing membrane directly on the gate area of a field effect transistor (FET). The FET is a solid-state device that exhibits high input impedance and low-output impedance and therefore is capable of monitoring charge buildup on the ion-sensing
membrane. The construction is based on the technology used to fabricate microelectronic chips\textsuperscript{61-63} and the great contribution is that it is possible to prepare small multisensor systems with multiple gates, for sensing several ions simultaneously, while their small size permits the in vivo determination of analytes.

1.4. Classification

Based on the physical state of the substance forming the electrode membrane, potentiometric sensors are classified into

1.4.1. Ion selective electrodes with solid membranes

The membrane can either be 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.

1.4.2. Ion selective electrodes with liquid membranes

In this case the electrode membrane is represented by a water immiscible liquid, in which a dissolved substance capable of exchanging the ion in the solution for which the electrode is selective. This substance is either an associate of this ion with an oppositely charged ion, soluble in the membrane or it is a complex of the ion for which the electrode is selective.

According to the type of membrane used, potentiometric sensors are again classified into

1.4.3. Glass membrane

These are selective for ions such as H\textsuperscript{+}, Na\textsuperscript{+}, and NH\textsubscript{4}\textsuperscript{+}. The glass electrode for pH measurements were the first potentiometric sensor
developed based on glass membrane and has been known from 1930s. The membrane in a pH electrode is essentially a sodium silicate glass made by fusing a mixture of Al₂O₃, Na₂O and SiO₂.

1.4.4. Sparingly soluble inorganic salt membranes

This type consist of a section of a single crystal of an inorganic salt such as LaF₃ or a pressed powder disc of an inorganic salt or mixtures of salt such as Ag₂S/AgCl. Such membranes are selective for ions such as F⁻, S²⁻ and Cl⁻

1.4.5. Liquid membrane sensor

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

1.4.6. Gel-immobilized and chemically bonded enzyme membranes

These membranes use the highly specific reactions catalysed by enzymes. The enzyme is incorporated into a matrix or bonded onto a solid substrate surface. These are the first examples of biosensors as they make use of biochemical process.

1.5. Ion recognition elements

The most significant component of the sensor is the ionophore or ion carrier which enables the sensor to respond to a particular ion selectively in the presence of other ions. The ionophores can be of an ion exchanger or a neutral macro cyclic compound having molecule-sized dimensions and containing cavities or semi-cavities, Schiff’s bases, crown ethers etc.
1.6. Performance Factors

1. Working concentration range and detection limit

The linear range of the electrode is defined as that part of the calibration curve through which a linear regression would demonstrate that the data points do not deviate from linearity by more than 2 mV. According to the IUPAC recommendation\textsuperscript{64}, the detection limit of an ISE is calculated using the cross-section of the two extrapolated linear parts of the calibration curve.

2. Effect of PH

The pH plays a very important role in the response of the potentiometric sensors. It can influence the formation of protonated and unprotonated species of the same substance, it can favor the redox processes at the electrode or the electrode can become pH selective under certain conditions\textsuperscript{65}.

3. Response time

The dynamic response time is an essential parameter for a sensor\textsuperscript{66}. The response time of an electrode is evaluated by measuring the average time required to achieve a potential within $\pm 1$ mV of the final steady-state potential, upon successive measurement of the potential of the respective ion, each having a ten-fold difference in concentration\textsuperscript{67,68}.

4. Selectivity

Selectivity is the most important characteristics of the sensors. It describes the sensors specificity towards target ion in the presence of other ions.
5. Life time

The life time of the 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. After this time, the slope and the detection limit of the sensor will decrease and increase, respectively. The reason for the limited lifetime of the carrier-based sensors may be due to the loss of plasticizer, carrier or ionic site from the polymeric film, as a result of leaching into the sample.

1.6.1. Application

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

1.7. A Brief Review on Important Potentiometric Sensors for Lanthanides

As part of the investigations, potentiometric sensors have been developed for the following lanthanides-La$^{3+}$, Sm$^{3+}$, Pr$^{3+}$, Nd$^{3+}$ and Gd$^{3+}$. A brief review of potentiometric sensors for these metal ions are presented blow.

1.7.1. Lanthanum

A variety of potential ion carriers have been used in the construction of sensors for lanthanum. Ito and Goto$^{60}$ tested the response of the lanthanum sensor impregnated with 1-phenyl-3-methyl-4-octadecanoyl-5-pyrazolone. Shamsipur et al$^{70}$ developed lanthanum selective sensor using 13,5-trithiacyclohexane as electroactive element.

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5,14-N,N'-hydroxyphenyl-4,15-dioxo-1,5,14,18-tetraaza hexacosane was made use of as ion carrier for La\(^{3+}\) by Khalil. Liquid membrane sensor was reported with monoazo-12-crown-4 by Gupta et al. The sensor responded to lanthanum in the concentration range \(3.16 \times 10^{-5}\) to \(1.0 \times 10^{-1}\), but working pH range was only 3-7. Mittal et al explored the use of dicyclohexano derivative of 18-crown ethers as ionophore for lanthanum. Ganjali et al reported a PVC membrane sensor and coated graphite electrode for La\(^{3+}\) based on bis(2-mercaptanil)diacetyl. The sensors showed linear response to lanthanum, but are susceptible to interference from Na\(^{+}\) and Cr\(^{3+}\). Akhond et al suggested the use of 2,2'-dithiodyridine as electroactive element in the fabrication of La\(^{3+}\) selective sensor. Singh et al studied the response characteristics of membrane sensor based on hexaaaza macrocycle, 8,16-dimethyl-6,14-diphenyl-2,3,4,10,11,12-dipyridine-1,3,5,9,11,13,16-hexaene as membrane carrier which showed linear response to lanthanum in the range \(1.0 \times 10^{-1}\) - \(7.94 \times 10^{-7}\) M and have good working pH range. 1,10-diaza-4,7,13,16-tetraoxacyclo octadecane-N,N'-diacetic acid was explored as an ion carrier in the construction PVC membrane sensor by Suyanta et al. Even though sensor was selective to lanthanum, other rare earth ions were found to be interfering with its working. PVC membrane sensors incorporating gliclazide, bis (thiophenal) phenylen-1,3-diamine, bis(2-methylbenzaldehyde)butane-2,3-dihydrazone, 4-methyl-2-hydrazinobenzo thiazole,3-hydroxy-N'(pyridine-2-ylmethylene)-2-naphtho hydrazide, N-(2-pyridyl)-N'(2-methoxyphenyl) -thiourea, octadentates Schiff's base, and \(1-[9\{2-[2-2-hydroxy-1-naphtyl]-3-(2-\{[(E)-1-(2-hydroxy-1-naphtyl)methylidine]amino\}ethyl]-1-imidazolidyl\}imino)methyl]-2-naphthol\) as ionophores were fabricated by Ganjali et al. Among them sensor based \(1-[9\{2-[2-2-hydroxy-1-naphtyl]-3-(2-\)}
{(E)-1-(2-hydroxy-1-naphtyl)methylidene)amino}ethyl)-1-imidazolidyl} imino) methyl]-2-naphthol) exhibited good detection limit of $4.5 \times 10^{-10} \text{M}$, but analytical application sensor was not reported.

1.7.2. Samarium

Chowdhury et al$^{86}$ reported the first samarium selective sensor impregnated with bis(thiaalkylxanthato)alkanes, but sensor showed interferences in the presence of Cu$^{2+}$ and Fe$^{2+}$. A liquid PVC membrane sensor was reported by Ganjali et al$^{87}$ where the glipizid was used as the ionophore to detect Sm$^{3+}$. Shamsipur et al$^{88}$ fabricated a PVC membrane and coated graphite sensor for samarium based on 4,5,6,7-tetrathiocino[1,2-b:3,4-b]diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione. Coated graphite sensor was found to have better concentration range and detection limit compared to the PVC membrane sensor, but the working pH range was only 4 - 6.5. Mittal et al$^{89}$ fabricated samarium selective sensor incorporated with Tin (IV) boratophosphate but the sensor gave a super Nernstian slope. Mittal and Sharma$^{90}$ studied the response characteristics of sensor fabricated with Zirconium(IV)boratophosphate as ionophore which had good life time of 6 months. The use of Spiro[oxirane-pyrazolidinedione] derivative as ionophore for samarium was reported by Saleh et al$^{91}$ and the sensor was applied in the determination of acetylsalicylate and carbonate in some drugs. Zamani et al investigated the response characteristics of membrane sensor impregnated with 3-\{[2-oxo-1(2H)-acenaphthylidencyan] amino\}-2-thioxo-1,3-thiazolidin-4-one to Sm$^{3+}$ ions$^{92}$. The first asymmetric potentiometric Sm (III) micro-sensor was reported by Ganjali et al$^{93}$. 2-((2-thioxothiazolidin-4-one) methyl) phenol was employed as ionophore.
and sensor showed linear response in the range of $1.0 \times 10^{-9}$ to $1.0 \times 10^{-4}$ M with slope of 18.27.

1.7.3. Neodymium

There are only a limited number of reports on the design of highly selective electrodes for neodymium based on different non cyclic and macrocyclic ionophores. Shamsipur et al.\textsuperscript{94} reported the construction of a neodymium sensor based on 5-Pyridino-2,8-dithia[9](2,9)-1,10-phenanthrolinephane. The sensor exhibited linear response in the concentration range $1.0 \times 10^{-6}$ to $1.0 \times 10^{-2}$ with a fast response time and was applied to the recovery of Nd\(^{3+}\) ion from tap water samples. The working pH range of the sensor was found to be very low. P. Norouzi et al.\textsuperscript{95} developed a membrane sensor based on N-(2-Furylethylene) pyridine-2,6-diamine which showed nenstian response to neodymium ions in the concentration range $1.0 \times 10^{-5}$ to $1.0 \times 10^{-2}$ M. The sensor was applied to direct monitoring of Nd\(^{3+}\) in various binary mixtures. 2-{{[(6-aminopyridin-2-yl)imino]methyl}-phenol based sensor was developed by Ganjali et al.\textsuperscript{96} which showed Nernstain response to Nd\(^{3+}\). Behmadi et al.\textsuperscript{97} demonstrated the use of benzylbis (thiosemicarbazone) in the determination of Nd\(^{3+}\) over the concentration range $1.0 \times 10^{-2}$ and $1 \times 10^{-6}$ M. The sensor was employed for the monitoring of Nd\(^{3+}\) from soil and sediment samples. Sensors based on two neutral ionophores, N,N′-bis((1-H-pyrrol-2-yl)methylene) cyclohexane-1,2-diamine and 3,3′-(cyclohexane-1,2-diylibis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(5-hydroxymethyl)pyridine-2-ol) are described for quantification of neodymium (III) by Gupta et al.\textsuperscript{98}. Sensor based on 3,3′-(cyclohexane-1,2-diylibis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(5-hydroxymethyl) pyridine-2-ol) showed enhanced selectivity for Nd\(^{3+}\).
1.7.4 Praseodymium

Only four reports have been published in literature for praseodymium. Ganjali et al produced a novel PVC membrane sensor for praseodymium based on hydrazide derivative. Zamania and coworkers reported the use of N, N-bis(α-methylsalicylidene) diethylenetriamine and N,N2-bis-(2-oxo-1,2-diphenylethylidene) ethane dihydrazide as electroactive components for the determination of Pr3+ ions. Both the sensors showed linear response in the concentration range 1.0 × 10^{-6} to 1.0 × 10^{-2} M. The sensor based on N, N-bis (α-methyl salicylidene) diethylenetriamine was applied for the determination of Pr3+ from soil and sediments while with N1,N2-bis-(2-oxo-1,2-diphenylethylidene)ethanedihydrazide based sensor used for the recovery of praseodymium from different water samples and the determination of fluoride ions in mouthwash samples. Gupta et al developed two PVC membrane sensor by incorporating 1,3-diphenylpropane-1,3-diylidenebis(azan-1-ylidene) diphenol and N,N'-bis(pyridoxylideneiminato)ethylene as ion recognition element. Sensor based on N, N'-bis (pyridoxylideneiminato)ethylene exhibited enhanced selectivity for praseodymium.

1.7.5 Gadolinium

Ganjali and coworkers reported three sensors for the determination of gadolinium based on different ionophores such as omeprazole, (2-[{3-{(2-sulfanlylphenyl)imino}-1-methylbutyridene} amino] phenyl hydrosulfide and bis(thiophenal)pyridine-2,6-diamine. Among them sensor based on bis(thiophenal)pyridine-2,6-diamine showed enhanced response in the concentration range 1.0 × 10^{-6} to 1.0 × 10^{-1} M. Zamania et al fabricated membrane sensor based on 6-methyl-4-
(thienyl)methylidene-amino)3-thioxo-3,4-dihydro-1,2,4-triazin-5-(2H)-one and was applied to the determination of concentration of Gd (III) ions in soil and sediment samples. Faridbod et al\textsuperscript{107} developed a PVC membrane, sensor based on N-(2-pyridyl)-N'-(4-nitrophenyl) thiourea. The sensor showed linear response in the concentration range $1.0 \times 10^{-8}$ to $1.0 \times 10^{-3}$ M, but with a sub Nernstian slopes. Sharma et al\textsuperscript{108} studied the response characteristics of sensor fabricated with Zirconium (IV)tungstophosphate (inorganic ion exchanger) as the ionophore which had a good working pH range of 4 – 10, but the slope was found to be super Nernstian of 30 mv/decade.

1.8. Scope of the Present Work

In many fields such as earth science, biology, environment and electronics, the knowledge about elemental distributions and chemical speciation is important\textsuperscript{109}. The determination of metal levels especially the toxic ones both in the environment and in biological materials are increasingly demanded by the society. Among the different methods available for the trace level determination of metal ions, electroanalytical techniques, especially electrochemical sensors holds a leading position as they have reached the commercial stage and which have found a vast range of important applications in the fields of clinical, industrial, environmental and agricultural analyses. In continuation to our works in the area of low level monitoring of metal ions\textsuperscript{49, 110-113}, the present work focused on the fabrication of potentiometric sensors for the determination of lanthanides such as La\textsuperscript{3+}, Pr\textsuperscript{3+}, Nd\textsuperscript{3+}, Sm\textsuperscript{3+} and Gd\textsuperscript{3+}. It is to be noted in this context, that only a very few sensors are developed so far for the determination of lanthanide ions. This fact enhances the importance of the present work. Total of ten sensors have been fabricated for these
metal ions and that includes PVC membrane and CMCPE type sensors. Response characteristics such as working concentration range, slope, detection limit, pH range and selectivity were studied in case of all the sensors. The developed sensors have been applied for the determination of metal ions in real samples and also applied as an indicator electrode in the potentiometric titrations. It is hoped that all the ten sensors developed can be used for the determination of the respective metal ion with high accuracy and precision.