Review

The fabrication of potentiometric membrane sensors and their applications

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Ionophore-incorporated PVC-membrane sensors are well-established analytical tools routinely used for the selective and direct measurement of a wide variety of different ions in complex biological and environmental samples. The key ingredient of such plasticized PVC-members is the involved ionophore, defining the selectivity of the electrodes complex formation with the cation of interest. In the past few years, the development of new ion-selective electrodes for various ions has been reported in the literature.

Key words: Ion-Selective Electrode, potentiometric membrane sensor, sensor.

INTRODUCTION

Among the benefits of using a liquid membrane is its high selectivity. In addition, specific molecular recognition can be achieved with the aid of suitable ion carriers for the transport mechanism. Owing to their relative high efficiency, they are being looked into for industrial applications. Liquid membranes require stability in order to be effective.

Depending on the nature of the used membrane material, the ion-selective electrodes (ISEs) can be divided into three groups: glass membrane, crystal or solid membrane, and polymeric or liquid membrane. Many ISEs are commercially available and routinely applied in various fields.

The basic observation in a potentiometric measurement is that of the potential (E), arising between the two electrodes in approximately zero current flow conditions. This is a very simple and practical electroanalytical method, making the application of these devices trouble-free and useful.

In a complete potentiometric cell, the sensing electrode should be used in conjunction with a reference electrode, or the so-called "external reference electrode". The indicator or the sensing electrode consists of a transducer, which is normally an Ag wire coated with AgCl (internal reference electrode), and a sensing material which is placed in the membrane. In the case of an ISE, the measured potential differences of the resulting electrochemical cell (ISE versus the outer reference electrode potentials) present a linear dependence with the activity logarithm of a given ion in the solution. During the potentiometric measurements, the current is about 10^{-6} μA, produced with the employment of a high-input-impedance millivolt-meter. The essential component of any potentiometric ion-selective sensor is definitely its ion-selective membrane, or in fact, the sensing material. The sensing material in the element exhibits the selectivity with which the sensor responds to the analyte in the presence of other ions in the sample. If an ion can pass through the boundary between the organic and the aqueous phases, it will be sensed by the sensing material in the ion-selective membrane. Then, an electrochemical equilibrium will be reached with the formation of different potentials in the two phases. The sensing material can exchange only one type of ion between the two phases and this is the reason why this material is the selectivity source of the sensor. The resulting potential difference, formed between the phases, will then be governed only by the activity of this specific ion in the two solution phases, and also in the membrane phase. Figure 1 shows a schematic diagram of an ion-selective potentiometric cell assembly (Ganjali et al., 2006a).

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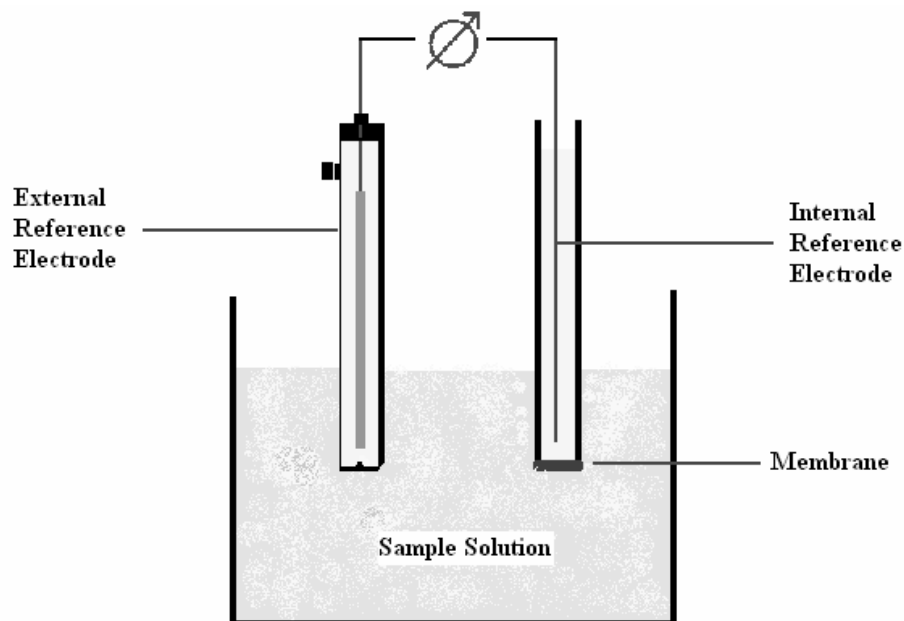
Figure 1. A schematic diagram of an ion-selective potentiometric cell assembly.

The ISEs operation has been proved to be due to the phase-boundary processes. This is in contrast with the approach based on a carrier mechanism across the electrode membrane. From a physical point of view, it does not make any sense to assume that the basis of the electrode potential formation is a simple ion-exchange reaction between the solution and the electrode surface or the bulk of the electrode membrane, as it is found in many textbooks. An electromotive force can only be the result of the free charges accumulation, which may not be the consequence of a simple ion-exchange.

The phase boundary potential across the sample membrane interface is the result of the ion-selective charge separation at that interface. In accordance with this charge separation, only the membrane surface processes affect the potential (Lindner et al., 1989).

The potentiometric measurements of ISEs are carried out in general with the following cell assembly:

Internal reference electrode internal solution (known concentration) membrane test solution (unknown concentration) External reference electrode

An ion analyzer, comprising a high-input-impedance millivolt-meter, is used for the potential measurements at $25.0 \pm 0.1°C$.

The properties of an ISE are characterized by parameters like:

(1) Measuring range
(2) Detection limit
(3) Response time
(4) Selectivity
(5) Lifetime
(6) Reproducibility

Measuring range

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. For many electrodes, this range can extend from 1 Molar down to 10^{-6} or even 10^{-7} Molar.

Detection limit

The detection limit of an ISE is calculated using the cross-section of the two extrapolated linear parts of the ion-selective calibration curve, according to the IUPAC recommendation. In practice, the values of the detection limit for most selective ISEs are in the order of 10^{-5} - 10^{-6} M.

Response time

The span of time between the instant of the ISE insertion and a reference electrode into, and their consequent contact in, a sample solution (or the instant when a change is induced in the concentration of the target ion), and the first instant at which the E slope fluctuations against the time curve become equal to ± 0.1 mV min^{-1}, is regarded as the response time of that electrode.

Selectivity

Selectivity is the most important characteristic of these devices. It describes the ISE specificity toward the target ion in the presence of other ions, also called as "interfering ions".

There are a number of different methods for the determination of the potentiometric selectivity coefficients (K_{XY}). Among them, however, four methods have been more widely accepted (Ganjali et al., 2006a), namely: 1. The Separate Solution Method (SSM). 2. The Mixed Solution Method (MSM). a. Fixed Interference Method (FIM). b. Fixed Primary Method (FPM). 3. The matched potential method (MPM). 4. The Unbiased Selectivity Coefficients.

Lifetime

The average lifetime for most of the reported ISEs is in the range of 4 - 10 weeks. After this time, the slope and the detection limit of the sensor will decrease and increase, respectively. It is accepted that the loss of plasticizer, carrier or ionic site from the polymeric film, as a result of leaching into the sample, is the primary reason for the limited lifetime of the carrier-based sensors.

Reproducibility

A prerequisite for the validity of the Nernst equation is a thermodynamic equilibrium between the adjacent aqueous and the organic phases. This condition is fulfilled when the phase transfer kinetics and the involved complex formation are fast with respect to the involved diffusion processes. In electrochemical terms, the exchange current must be large, compared with the current flowing through the membrane.

POLYMERIC (LIQUID) MEMBRANE ISEs

One of the most common classes of electrodes with mobile charged sites is the one based on ionophores. Ionophores are (organic or inorganic) compounds that bind to cations and anions. Because of the recent theoretical advances regarding the comprehension of the response mechanism of this sensor type, the focus remains on the discovery and the development of novel ionophores for the attainment of highly selective potentiometric membrane sensors.

ISE membrane components

The polymeric membrane is used to separate the test solution from the inner compartment, containing a solution of the target ion. Any polymeric membrane ion-

selective sensor consists of some components. The nature and the amount of each component illustrate great effects on the nature and the characteristics of the sensor. These components are: 1. The polymeric matrix. 2. The ionophore (membrane - active recognition). 3. The membrane solvent (Plasticizer). 4. The ionic additives.

The polymeric matrix

The application of polymers as homogeneous membrane matrices was first suggested for use with charged carriers in 1967 (Moody et al., 1970; Shatkay, 1967). In practice, typically 33% (w/w) PVC as the polymeric matrix, 66% plasticizer for homogenizing the matrix and 1% ionophore are used to prepare a sensing membrane (Moody et al., 1970). The first polymeric ISE membranes, where the polymer was considered to provide the required physical properties, like elasticity and mechanical stability, were prepared with valinomycin, as a neutral ion carrier, in silicone rubber (Pick et al., 1973) or PVC (Pick et al., 1973; Fiedler and Ruzicka, 1973), without the addition of lipophilic ionic sites. However, it is now understood that the Nerstian response of these ISEs was influenced by the probable presence of the ionic impurities in the used PVC (Horvai et al., 1986; Van den Berg et al., 1987; Lindner et al., 1988), and also in the other membrane components (Bühlmann et al., 1995).

The ionophore (membrane-active recognition)

The ionophore or the membrane-active recognition can be an ion exchanger or a neutral macrocyclic compound, having molecule-sized dimensions and containing cavities or semi-cavities to surround the target ions. The ionophore, also named "ion carrier" is the most significant component of any polymeric membrane sensor with reference to the selectivity and sensitivity, since the molecular-level phenomenon that is sensed by the ISE is the binding between the ionophore and the target ion. The different selectivities of an ISE toward the other ions, hence, may be considered to originate from the difference in the binding strength between any chosen ionophore, to be used in the sensor, and the various ions.

The membrane solvent (Plasticizer)

Plasticizers are additives that increase the plasticity or fluidity of the material, to which they are added. Solvent polymeric membranes, used in ion sensors, are usually based on a matrix containing about 30 - 33% (w/w) PVC and 60 - 66% from a membrane solvent. Films with such a high plasticizer amount demonstrate optimum physical properties and ensure relatively high mobilities of their constituents. In order to give a homogeneous organic phase, the membrane solvent must be physically com-

patible with the polymer, that is, display plasticizer properties. For various reasons, it also has an influence on the selectivity behavior. Some of the common plasticizers are as follows: Benzyl acetate (BA), Bis(2-ethylhexyl) phthalate (dioctyl phthalate) (DOP), Bis (n-octyl) sebacate (DOS), Dibutyl phthalates (DBP), Dibutyl sebacate (DBS) and 2 Nitrophenyl phenyl ether (o-NPPE).

Ionic additives

Ionic additives are ion exchangers, which themselves induce a selective response when no or only an insufficient ionophore amount is present. Therefore, their concentration must be adjusted carefully. Although the neutral-carrier-based ISE membranes may work properly, even when they contain only a very small amount of ionic sites, the addition of a lipophilic ion salt is advisable and beneficial for various other reasons, as well. The original motive for adding a tetraphenyl borate salt to the membrane of a cation-selective electrode is to reduce the anionic interference observed in the presence of lipophilic anions like thiocyanate (Morf et al., 1974). At the same time, the electrical resistance of the membrane is lowered, illustrating a great importance for the microelectrodes (Ganjali et al., 2006a).

METHODS OF PREPARATION OF THE LIQUID MEMBRANE ISEs

Preparation of ISEs liquid membranes by dipping method

A typical procedure to prepare the PVC membrane is to mix thoroughly 30 - 35 mg of the powdered PVC, 60 - 65 mg plasticizer, the suitable ionophore amount (usually 1 - 10 mg) and 1 - 5 mg anionic additive in 5 mL THF. The resulting mixture is transferred into a glass dish of 2 cm in diameter. A Pyrex tube (3 - 5 mm o.d.) is dipped into the mixture for about 5 s, so that a transparent membrane (about 0.3 mm thickness) is formed. The tube is, then, removed from the mixture, kept at room temperature for at least 12 h and filled with an internal filling solution (usually 1.0×10^{-3} M of $M^{n+}Cl_n$). The electrode is, finally, conditioned for 12 - 48 h by soaking in a 1.0×10^{-2} M, $M^{n+}Cl_n$. A silver/silver chloride electrode is used as the internal reference electrode.

Preparation of ISEs liquid membranes by casting method

For this preparation, 30 - 35 mg from the powdered PVC, 60 - 65 mg plasticizer, the suitable amount of the ionophore (usually 1 - 10 mg) and 1 - 5 mg of an anionic additive in 10 mL THF are completely mixed. The result-

ing homogeneous mixture is poured into a glass ring with an inner diameter of 20 - 50 mm, resulting in a smooth glass plate. THF is evaporated at room temperature. A transparent membrane (with an average thickness of 0.2 - 0.3 mm) is formed. A disc with a 10 mm diameter is cut out from the PVC membrane and glued to the one end of the Pyrex glass tube with the help of Araldite. Afterwards, the tube is filled with the internal filling solution (usually 1.0×10^{-3} M of $M^{n+}Cl_n$) and is, eventually, conditioned for 12 - 48 h by soaking in a 1.0×10^{-2} M $M^{n+}Cl_n$. The internal reference electrode is usually an Ag/AgCl wire (1.0 mm diameter).

Sol-gel membrane preparation

Sol-gel is prepared by the reaction of proper amounts of 1,4-butanediol and (3-isocyanopropyl) triethoxysilane (stoichiometric ratio NCO/OH = 1) in THF. The reaction mixture is refluxed for 24 h under a N_2 atmosphere. After the THF evaporation, the highly viscous sol-state precursor is dissolved in N,N-dimethylformamide with the optimum ionophore amount, to which some hydrochloric acid milliliters were added. The mixture is poured onto the flat surface of the poly (ethylene terephthalate) film. The hydrolysis is carried out at 40°C for 4 days to attain transparent gel membranes, which contain the ionophore. Before use, the membrane is vacuum dried at 40ºC for 24 h (Kim et al., 1997).

ION SELECTIVE MEMBRANE SENSORS FOR MAIN GROUP CATIONS

Polymeric carrier-based ion-selective electrodes, which are selective towards the alkali and alkaline earth metal ions such as sodium, potassium and lithium, have been the focus of numerous studies. All of these cations can be determined by the spectroscopic methods. Potentiometric detectors based on ion-selective electrodes are suited, because they offer advantages such as high selectivity, sensitivity, good precision, simplicity, portable, non-destructive analysis, ability to monitor ion activity without extensive preparation of sample and low cost. Because of the importance of developing new ionophores in construction of liquid membrane ion-selective electrodes, many cyclic and acyclic macromolecules have been introduced as ionophores.

Sodium selective membrane sensors

Potentiometric ion-selective membrane electrodes for the Na^+ ions are steadily replacing flame photometry and the other analytical techniques for monitoring the sodium ion concentration in various matrices (Ma and Hassan, 1982). Such determinations are normally conducted with the sodium glass membrane electrode. Nevertheless, the

Table 1. Some of Sodium ion selective sensors with biological or environmental applications.

| Entry	Application	Reference
1	Determination of Na$^+$ in erythrocytes	Malon et al., 2005
2	For protein solutions	Yamamoto et al., 1996
3	Rat blood	Heidrich et al., 1998
4	In wood pulp suspension	Vazquez et al., 2001
5	Intracellular measurements in plant cells	Carden et al., 2001
6	Newborns and Prematures	Kau et al., 1995
7	Determination of Sodium in Blood-Plasma	Teltingdiaz et al., 1990
8	In Effluent Water	Klimovitskaya et al., 1990
9	In physiological Fluids	Shibata et al., 1992
10	In Processed Foodstuffs	Binsaad and Devi, 1991
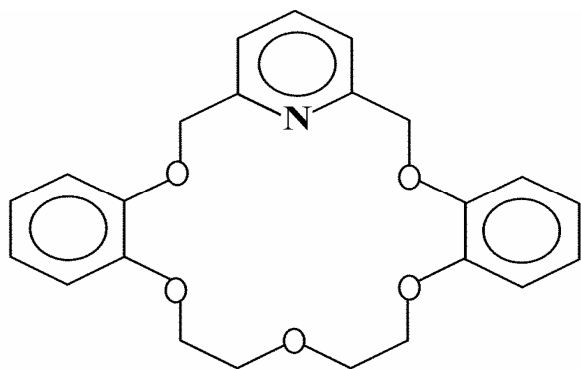
Figure 2. Dibenzopyridino-18-Crown-6 (Tavakoli, 2004).
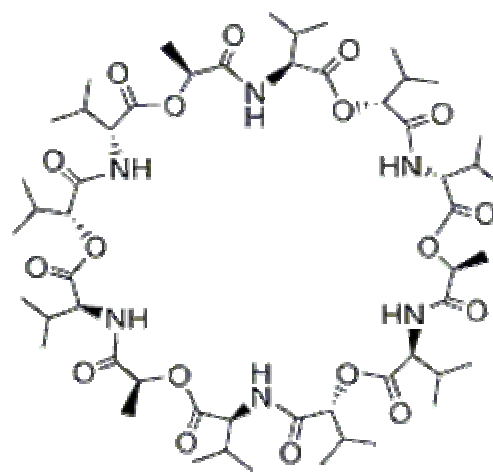

Figure 3. Valinomycin structure.

utilization of glass membranes presents several difficulties, such as the contamination of the glass membrane surface, high resistance, interferences from the hydrogen ions and technical problems in the design of various configurations and shapes of the cell assembly (Moody et al., 1989). Nowadays, there is a continuing search for alternative and improved sensors.

There are about 50 reports concerning the sodium selective sensors in the literature. Among them, the following sensors (Table 1) were applied for biological and environmental applications. Crown ethers are a good choice as a sensing material for using in the PVC membrane. An interesting application of crown ethers is their potential use as ion-selective components (ion-carriers) in liquid membrane electrodes. Crown-bridged calix [4]quinines (Yamamoto et al., 1996), Dibenzopyridino-18-Crown-6 (Figure 2) (Tavakoli, 2004) are good examples for sodium ionophore.

Potassium selective membrane sensors

Potassium is a vital element in biological fluids of the human body. The daily monitoring of its concentration may be one of the most important indices in the early dia-

gnosis of heart disorder, myocardial infarction, insult and other diseases (Goldberger and Goldberger, 1970).

In the past, a K$^+$-selective electrode with a plasticized polyvinyl chloride (PVC) membrane, illustrating valinomycin (Figure 3), was introduced for these purposes (Carden et al., 2001). This valinomycin electrode exhibited a unique selectivity. Nonetheless, it was poorly available and rather expensive. The invention of an ISE to substitute this naturally occurring antibiotic, displaying enhanced electrode properties and higher sensitivity, is a significant issue. Table 2, shows some Potassium ion selective sensors with biological or environmental applications.

Beryllium selective membrane sensors

The design and the construction of a potentiometric sensor for the beryllium ion are very difficult. This difficulty is caused by its extraordinary high charge density and its hydration energy, inhibiting the transfer of the beryllium ions from the aqueous solution to the orga-

Table 2. Some of Potassium ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In Biological Buffers	Cabral, 1992
2	Determination of K^+ in erythrocytes	Malon and Maj-Zurawska, 2005
3	In Barley Root-Cells	Walker et al., 1995
4	Rat blood	Heidrich et al., 1998
5	Measurements of net fluxes and extracellular changes of H^+, Ca^{2+}, K^+, and NH_4^+ in Escherichia coli	Shabala et al., 2001
6	In wood pulp suspension	Vazquez et al., 2001

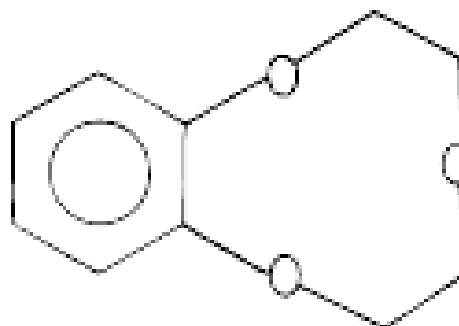**Table 3.** Some of magnesium ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In papillary muscle of guinea pig	Kim et al., 2006
2	In blood serum	Godlewska-Zylkiewicz et al., 1998
3	In plasma	Zoppi et al., 1996
4	Study of the Role of magnesium in patho-physiological	Altura and Altura, 1996
5	Water hardness determination	Amarchand et al., 1998
6	In erythrocytes	Malon and Maj-Zurawska, 2005
7	In undiluted serum, plasma or blood	Ben et al., 2005
8	Determination of Serum iMg	Schenck, 2005
9	In blood	MajZurawska, 1997
10	Determination of water hardness	Gupta et al., 2002
11	Human Blood-Serum	Spichiger et al., 1991
12	Determination of ionized magnesium in erythrocytes	Malon and Maj-Zurawska, 2001

nic phase. The first ISE for the beryllium ions was reported by Ganjali and his co-workers in 1998 using benzo-9-crwon-3 (Figure 4) as a sensing material. This ionophore presents a suitable cavity size and proper donor atoms for the beryllium ions (Ganjali et al., 1998). The other reports, associated to the beryllium ion, are also reported by the same research group (Ganjali et al., 2003a, b, 2004a, b; Shamsipur et al., 2001a).

Magnesium selective membrane sensors

The intracellular ionized magnesium, sodium and potassium were determined using a clinical potentiometric analyzer with ISEs. The results did not differ significantly compared with those of the other methods (magnetic resonance spectroscopy (NMR), atomic absorption spectrometry (AAS), flame emission spectrometry (FES), inductively coupled mass spectrometry (ICP-MS), zero-point titration (ZPT)). An appropriate composition of the ion-selective membrane for the intracellular calcium determination was found. The ionized magnesium determination in erythrocytes was successfully applied to the medical analysis of dialyzed and critically ill postoperative patients (Malon and Maj-Zurawska, 2005).

There are nearly 30 reports for magnesium ion sensors in the literature. In some cases, the developed sensors

Figure 4. Benzo-9-crwon-3.

were employed to biological or environmental uses (Table 3).

Calcium selective membrane sensors

Calcium is an important mineral as far as the bone and tooth health is concerned. The main minerals (calcium, magnesium, phosphorus, sodium, chloride and potassium) are either demanded in the greatest quantities or they are present in large amounts in the body. The three basic functions of the minerals are as constituents of the

Table 4. Some of calcium ion selective sensors with biological or environmental applications.

Entry	Application	References
1	Rain Solutions	Lauver et al., 1992
2	Study of Protein Effect	Covington and Zhou, 1992
3	In soil	Lemos et al., 2007
4	In natural and borehole water	Van Staden and Stefan, 1999
5	In coconut water	Chumbimuni-Torres and Kubota, 2006
6	In Serum	Cattrall and Fong, 1978
7	In natural waters	Alvares-Ribeiro and Machado, 1998
8	In erythrocytes	Malon and Maj-Zurawska, 2005
9	In tap water and in different plants	Saleh, 1991
10	In natural waters	Chen and Adams, 1998
11	Measuring Calcium in Plasma	Umemoto et al., 1994
12	In wood pulp	Vazquez et al., 2001
13	In Apple Juice	Cooke, 1975
14	To the detection of calcium release during bone resorption	Berger et al., 1999
15	In Pharmaceuticals and Serum	Veltsistas et al., 1994

Table 5. Some of lead ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In water samples	Rouhollahi et al., 1998
2	In river waterl	Hara and Kusu, 1992
3	In polluted waters	Srivastava et al., 1995
4	In some real samples	Ardakani et al., 2004a
5	In polluted water	Yan et al., 2004
6	In electroplating bath solutions, alloy sample, battery waste samples and effluent waters	Bhat et al., 2004
7	In mineral rocks and wastewater	Ardakany et al., 2003
8	In spring water samples	Riahi et al., 2003
9	Determination of anions such as sulfides, chromates and carbonates	Gholivand and Mohammadi, 2003a
10	In edible oil, human hair and water samples	Ganjali et al., 2002a
11	Lead in lubrication oil samples	Zareh et al., 2001
12	In the sample of solder	Kumari et al., 2001
13	Determination of the Bile Phosphates	Campanella et al., 1981
14	In minerals	Vlasov et al., 1999

skeleton, as soluble salts which help control the composition of the body fluids, and as essential adjuncts to the action of many enzymes and other proteins. There are more than 70 reports on Ca^{2+} selective electrodes. Most of them were used in biological and environmental analysis (Table 4).

Lead selective membrane sensors

Because of the increased industrial use of lead, on one hand, and its serious hazardous effect to human health, on the other hand (Lynarn et al., 1975); the electro-chemical properties and the preparation of the lead ion selective membrane electrodes have been extensively studied after the examination of different active materials (Table 5).
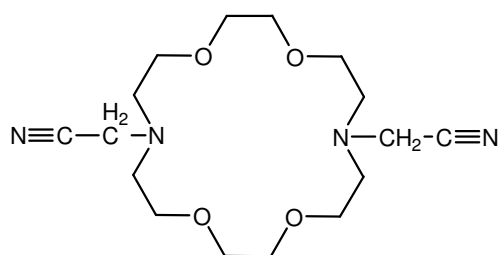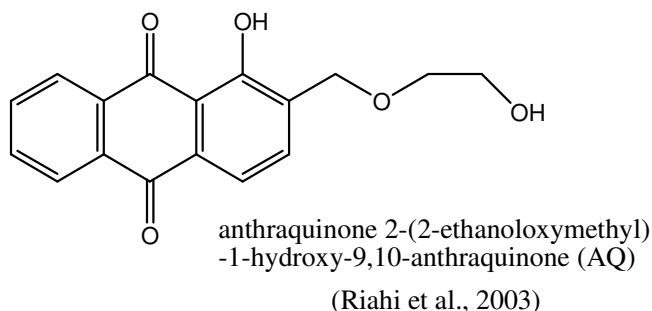
A lead ISE finds applications to the electroplating industries, the environmental monitoring, and the waste-water analysis and to the detection of some anions, like bromide, sulfide and sulfate. Figure 5 shows examples of suitable ionophore for Pb^{2+}.

TRANSITION METAL CATIONS

Generally, the transition metal ions can determine by using ion chromatography, high performance liquid chro-

Table 6. Some of reported chromium ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In real sample	Ganjali et al., 2003b
2	Determine Cr^{3+} in certified and real alloys and in effluents of electroplating shops	Akl et al., 2006
3	Electroplating industry waste Samples	Gupta et al., 2006a
4	In wastewater	Hassan et al., 2005
5	In real sample	Ganjali et al., 2006b
6	In waste water and alloy samples	Gholivand and Raheedayat, 2004
7	In some food materials and various types of plants	Khalil et al., 2004
8	Electroplating bath solutions	Sil et al., 2004

anthraquinone 2-(2-ethanoloxymethyl)
-1-hydroxy-9,10-anthraquinone (AQ)

(Riahi et al., 2003)

N,N'-dimethylcyanodiaza-18-cown-6 (DMCDA18C6)

(Ganjali et al., 2002a)

Figure 5. Some of the ionophore used for construction of Pb^{2+} Selective membrane sensor.

matography (HPLC) and inductively coupled plasma atomic absorption spectroscopy. However, as mentioned above, construction and application of ion selective electrode as a potentiometric sensor for determination of the ions in the real samples, offers interesting advantages such as simplicity, speed, relatively fast response, low cost, wide linear dynamic range and ease of preparation and procedures.

Chromium selective membrane sensors

Chromium exists in two states; Cr (VI) and hydrated chromium (III) species, despite the Cr trace amounts in the trivalent state. It is known to be an essential element in the human nutrition but its accumulation in the human body results in toxicity. Chromium is widely employed (Table 6) in various industries such as plating, tanning, paint and pigment production as well as metallurgy, which possibly contaminates the environment.

Furthermore, chromium in hexavalent state is 100 - 1000 times more toxic than the other. Chromium (VI) is also reported as mutagenic and carcinogenic for the human body, leading to lung cancer, skin allergy and probably to asthma and renal diseases. As a result, finding an effective method for the chromium determination is of great importance.

Iron selective membrane sensors

Iron is one of the most important elements in the biological systems, playing a significant role in the oxygen transport, storage and in the electron transport. Regarding its industrial use, iron and its compounds have numerous important industrial applications (Table 7)

Cobalt selective membrane sensors

Cobalt is a component of Vitamin B12, and this is the only known function of cobalt. Toxic intake is 500 mg, and the total mass of the element in an average (70 kg) person is 1.5 mg. Cobalt is widely distributed in the body, with high concentration in liver, bone and kidney. Some of reported cobalt ion selective sensors with biological or environmental applications are seen in Table 8, while Figure 6 shows 9-tertbutyl-3,9,15,21-tetraaza-4,5;13,14-dibenzo-6,12-dioxabicyclo [15.3.1] henicosa-1(21),17,19-triene-2,16-dione (Shamsipur et al., 2004a) as an excellent neutral ion carrier in construction of a selective Co^{2+} sensor.

**Nickel selective membrane sensors**

Nickel is a silvery white metal that takes on a high polish. For many decades, nickel was regarded as a potentially

Table 7. Some of reported Iron selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In blood and in grape molasses which is traditional syrup made of grapes	Ekmekci et al., 2007
2	Analysis of sodium diclofenac in pharmaceutical formulations	Santos et al, 2006
3	Determination of iron(III) in vitamin formulations	Teixeira et al., 1998
4	In some rocks	Saleh, 1999
5	Analysis of alloys, electroplating bath solutions and pharmaceutical samples	Sil et al., 2005
6	In tap water samples	Fakhari et al., 2001
7	In pharmaceuticals	Mahmoud, 2001
8	In water, alloys, rocks and pharmaceuticals	Hassan and Marzouk, 1994

Table 8. Some of reported cobalt ion selective sensors with biological or environmental applications.

Entry	Application	References
1	Determination of phosphate in waste waters and fertilisers	De Marco et al., 1998
2	In real samples	Gupta et al., 2006b
3	In wastewater of the electroplating industry	Singh et al., 2006a
4	In wastewater of the electroplating industry	Ganjali et al., 2004c
5	In waste water samples	Shamsipur et al., 2002a
6	In sea water	Ashtamkar and Thakkar, 2002
7	Determination of nitrite ion	Ganjali et al., 2003d
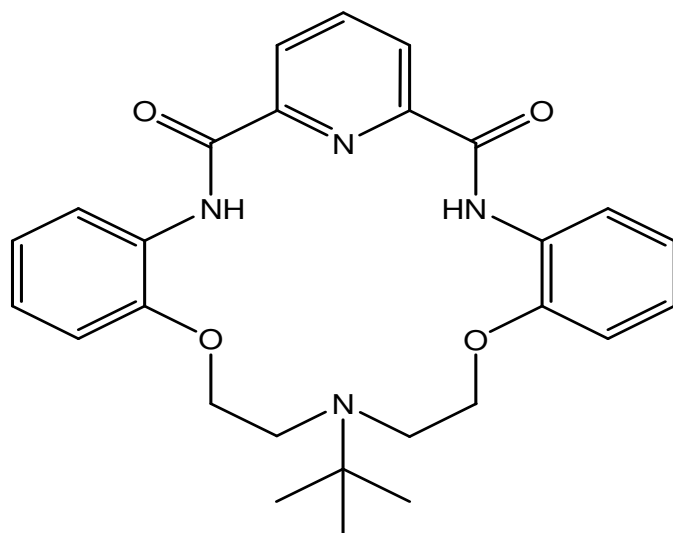
Figure 6. 9-tertbutyl-3,9,15,21-tetraaza-4,5;13,14-dibenzo-6,12-dioxabicyclo [15.3.1] henicosa-1(21),17,19-triene-2,16-dione (Shamsipur et al., 2004a) as an excellent neutral ion carrier in construction of a selective Co^{2+} sensor.

toxic element, since its concentration in various foods was higher than that needed for living organisms. More recently, it is now considered a possible essential element for plants, although deficiencies can occur under certain circumstances. However, nickel can be toxic at high concentrations and can be a problem in some soils. Table 9 shows some reported nickel ion selective sensors with biological or environmental applications
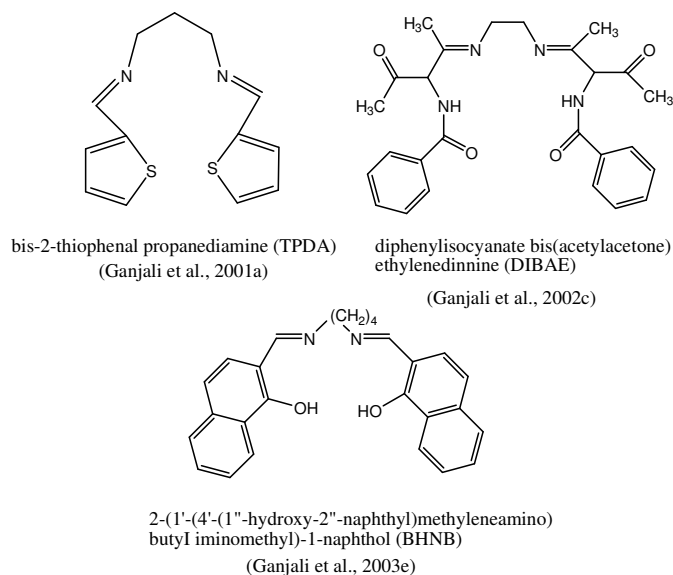
Copper selective membrane sensors

Due to the vital importance of copper in many biological systems and the urgent need for a copper-selective electrode for potentiometric monitoring of Cu^{2+} in environmental, medicinal and different industrial samples, there has been increasing interest in the development of novel membrane sensors for the detection of copper ion, during the past decade. Figure 7 shows the structure of some suitable ionophore for copper ions. Generally, symmetric Schiff base are good choice for this puropose. Table 10 shows some of the copper ion selective sensors with biological or environmental applications

Zinc selective membrane sensors

Zinc is one of the transition metals, which is used in paint, electroplating, pharmaceutical and chemical industries, and thus occurs widely in the environment. Table 11 listed some of these ISEs which are applied to determination of the zinc in real samples.
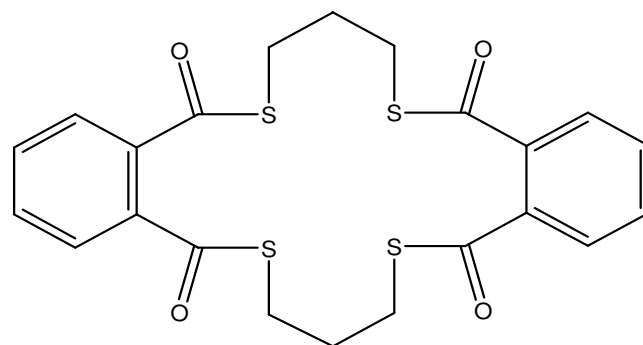
Table 9. Some of reported nickel ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	in some Indian brand chocolates	Gupta et al., 2007a
2	in some water samples	Yari et al., 2006
3	effluent samples, chocolates and hydrogenated oils	Kumar et al., 2006
4	in industrial waters	Pleniceanu et al., 1997
5	in industrial waters	Pleniceanu et al., 1996
6	in silicate rocks	Hassan et al., 1995
7	metallic alloys (Ni-Cr and Ni-Ge) and stainless steel (AISI 316L) sample	Teixeira and Fatibello, 1996
8	in real sample	Ganjali et al., 2000a
9	in real sample	Ganjali et al., 2000b
10	in industrial waters	Pleniceany et al., 2005
11	in wastewater from the electroplating industry	Belhamel et al., 2005
12	in real samples	Gupta et al., 2002a
13	in edible oil and wastewater of nickel electroplating samples	Ganjali et al., 2002b
14	determination of nickel content of chocolate and milk powder samples	Mazloum et al., 2002
15	nickel in electroplating waste	Singh et al., 2001
16	in chocolates	Gupta et al., 2000
17	in industrial waters were also elaborated	Luca et al., 1992

bis-2-thiophenal propanediamine (TPDA)
(Ganjali et al., 2001a)

diphenylisocyanate bis(acetylacetone) ethylenedinnine (DIBAE)

(Ganjali et al., 2002c)

2-(1'-(4'-(1"-hydroxy-2"-naphthyl)methyleneamino) butyl iminomethyl)-1-naphthol (BHNB)

(Ganjali et al., 2003e)

Figure 7. Some of the ionophore used for construction of Cu²⁺ selective sensors.

Figure 8. 7,8: 16,17-dibenzo- 6,9,15,18-tetraoxo- 1,5,10,14-tetrathiacyclooctadeca-7,16- diene [Bz(2)Oxo(4)(18) dieneS(4), an example of the silver ionophore Singh et al., 2006c).

good example of silver ion carrier for construction of the silver ion sensors. Table 12 listed some of silver sensors with biological and environmental applications.

Cadmium selective membrane sensors

Cadmium is an extremely toxic metal commonly found in industrial workplaces, particularly where any ore is being processed or smelted. The effect of its acute poisoning is manifested in a variety of symptoms, including high blood pressure, kidney damage, anemia, hypertension, bone marrow disorders, cancer and toxicity to aquatic biota. Due to its low permissible exposure limit (PEL), over-exposures may occur even in situations where trace

Silver selective membrane sensors

Because of the increased silver content of environmental samples with increasing use of silver compounds and silver containing preparations in industry and medicine the quick determination of trace quantities of Ag⁺ ion by simple methods is of critical importance in chemical, clinical and environmental analysis. Figure 8 shows a

Table 10. Some of reported copper ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In electroplating wastewater and various brands of Indian tea	Chandra et al., 2007
2	Kinetic-potentiometric assay of formaldehyde in pharmaceutical and industrial samples	Stergiou et al., 2007
3	The study of interactions between copper ions and human growth hormone (hGH) in biological systems	Shamsipuret al., 2007
4	Copper in black, red pepper and the waste water	Norouzi et al., 2006
5	In vegetable foliar and swimming pool water sample	Gupta et al., 2006c
6	In real samples	Ardakani et al., 2006a
7	In real samples	Singh et al., 2006b
8	In copper sulfide ores	Murzina et al., 1997
9	In seawater	De marco, 1994
10	In black tea samples	Ganjali et al., 2003e
11	Black tea leaves and multivitamin capsule	Sadeghi et al., 2006
12	In wastewater of copper electroplating samples	Zamani, et al. 2005a.
13	In wastewater	Zamani, et al. 2005b.
14	In black tea, and in wastewater	Ganjali et al. 2002c
15	In real samples	Shamsipur et al., 2002b
16	In real samples	Kupper and Schultze, 1997
17	In marine waters	DeMarco et al., 1997
18	In seawater	Mackey and DeMarco, 1997
19	In seawater	Eriksen et al., 1999
20	In sample of brass and a sample of Wilson's patient's urine	Fakhari et al., 2005
21	Real sample assays	Ardakani et al., 2004b
22	In real samples	Gupta et al., 2003
23	In milk powder samples	Firooz et al., 2002
24	In river water	Abbaspour and Kamyabi, 2002
25	In black tea	Poursaberi et al., 2001
26	In black tea	Ganjali et al., 2001a
27	In Real Samples	Sanchez-Pedreno et al., 1992a

Table 11. Some of reported zinc ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In real sample	Gupta et al., 2006d
2	In wastewater of industrial zinc electroplating companies	Zamani et al., 2006a
3	In vitamin preparations	Dumkiewicz et al., 2000
4	In wastewater	Gupta et al., 2005a
5	Environmental samples	Rakhman'ko et al., 2003
6	In real and synthetic samples	Gholivand and Mozaffari, 2003b
7	In some rock materials	Saleh et al., 2001
8	In a pharmaceutical sample	Fakhari et al., 2000

quantities of cadmium are found in the parent ore or smelter dust. Cadmium is used extensively in electroplating, although the nature of the operation does not generally lead to overexposures.

Mercury selective membrane sensors

The need for monitoring the toxic heavy metal ions such as Hg^{2+} (Figure 9) in the environmental samples causes

Table 12. Some of reported silver ion selective sensors with biological or environmental applications.

Entry	Application	References
1	In water samples	Yan et al., 2007
2	In various synthetic samples and also used for the determination of SCN⁻, CN⁻, S²⁻ and I⁻	Mittal et al., 2007
3	In waste from photographic films	Singh and Saxena, 2006c
4	In radiology film	Mashhadizadeh et al., 2006a
5	In water samples	Mahajan et al., 2005
6	The silver content of silver sulphadiazine (burning cream)	Ibrahim, 2005
7	In blood	Lee et al., 1999
8	Silver in electroplating wastewater samples	Badr et al., 2005
9	In real samples	Ardakani et al., 2004c
10	Silver content of a radiological film	Zare et al., 2004
11	In waste photographic solutions	Amini et al., 2003
12	In photographic emulsions and in radiographic and photographic films	Shamsipur et al., 2002c
13	In photographic waste solutions	Amini et al., 2002
14	In electroplating bath solutions, additives and brighteners	Sil et al., 2001
15	In photographic emulsion	Kataky et al., 2000
16	In electroplating wastewater	Liu et al., 2000
17	In wastewater	Shamsipur et al., 2003a

Table 13. Some of reported cadmium ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In different water samples and human urine	Singh et al., 2007a
2	In real samples	Gupta et al., 2007b
3	Cd^{2+} transport in yeast and plants	Plaza et al., 2005
4	In industrial waste water	Ito et al., 1997
5	In situ applications	Pineros et al., 1998
6	In waste water	Gupta and Kumar, 1999
7	In aqueous solutions	Mashhadizadeh et al., 2005
8	In real samples	Singh et al., 2005
9	In wastewaters	Gupta et al., 2002b

the development of new Hg^{2+}-ionselective electrodes a challenging problem (Table 14).

RARE-EARTH ELEMENTS

The greatest problem in the field of the ion-selective sensors worldwide was the fabrication of selective sensors for the lanthanides ions. The world researchers tried to construct a selective sensor for these ions with the employment of ionophores demonstrating cavity like crown ethers. Unfortunately, their efforts were not successful. The only way of constructing a lanthanide ISE was by using ionophores having a semi cavity, heteroatoms mostly S and N as donor atoms and high flexibility. Such an ionophore can easily form a template
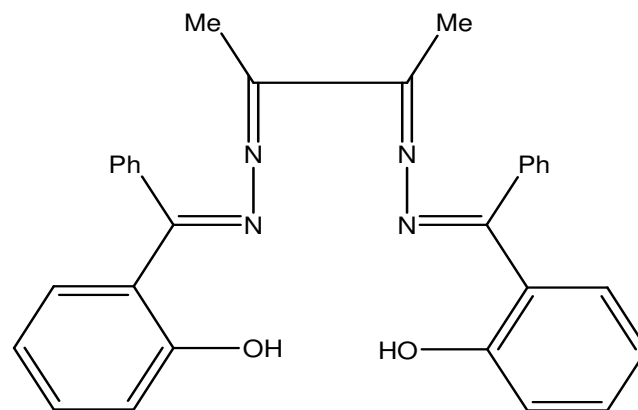

Figure 9. Bis(2-hydroxybenzophenone) Butane-2,3-dihydrazone, a good sensing material for mercury ion (Ganjali et al., 2007a).

Table 14. Some of reported mercury ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In different environmental and biological samples	Gupta et al., 2007c
2	In some binary and ternary mixtures.	Ganjali et al., 2007a
3	In wastewater and an amalgam sample	Mashhadizadeh et al., 2006b
4	In hazardous wastes	Hassan et al., 2006
5	In groundwater	Licht et al., 1991
6	In strong acid media and a wide variety of practical analytical systems	Radic and Komljenovic, 1991
7	In vegetables and in Azolla filiculoides	Ye et al., 2006
8	Ions in wastewater and microbial media	Othman, 2006
9	In some dental amulgum alloys	Saleh et al., 2006
10	Real sample analysis	Gupta et al., 2005b
11	In real sample	Javanbakht et al., 1999
12	Humic acids	Gismera et al., 2004
13	In aqueous solution	Mashhadizadeh et al., 2003
14	In a real sample	Lu et al., 2003
15	In some amalgam alloys	Hassan et al., 2000
16	In zinc amalgams	Ortuno et al., 1991
17	In high purity waters	Marshall and Midgley, 1979
18	In aqueous solution	Bohnke et al., 1978

regarding the cation size. Furthermore, it is able to form a complex with the strongest cation, due to the type, the number and the site of its donor atoms as well as its flexibility, the size and the charge density of the cation. The result of their efforts led to the synthesis of the proper ionophores and the potentiometric sensor cons-truction for 10 lanthanide members for the first time in the world.

The biological properties of the lanthanides, primarily based on their similarity to calcium, have been the research basis for the potential therapeutic applications of lanthanides, since the early part of the twentieth cen-tury. The lanthanides have similar ionic radii to calcium, but by virtue of possessing a higher charge, they present a high affinity for the Ca^{2+} sites in the biological molecules and a stronger binding towards the water molecules (Fricker, 2006; Wang et al., 2003; Evans, 1983).

With reference to the physiological effects of the Ln^{3+} ions, it should be mentioned that their property to block both the voltage operated and the receptor operated calcium channels. The Ln^{3+} cations can block the Na^+/Ca^{2+} synaptic plasma membrane exchange and inhibit the skeletal, smooth and cardiac muscle contrac-tion by blocking the Ca^{2+}-ATPase in the sarcoplasmic reticulum of the muscle. The Ln^{3+} ions themselves, being unable to cross the cell membranes, act by blocking the exterior face of the calcium channel. Although the Ln^{3+} cations cannot gain access to the intracellular organelles, they have been used as biochemical probes to study the calcium transport in mitochondria and other organelles (Evans, 1988; Yeung et al., 2003).

The lanthanides can substitute calcium in proteins, though it should be noted that the Ln^{3+} ions can also substitute other metal ions such as Mg^{2+}, Fe^{3+} and Mn^{2+}. Calcium dependent enzymes can either be inhibited by lanthanides, or in some cases be activated to a similar or greater extent than by calcium. It has been proposed that the stimulatory or inhibitory effect of the lanthanides may be a related to the role of calcium in the native enzyme (Fricker, 2006; Wang et al., 2003; Evans, 1983).

It is useful to recognize that only trace amounts of lanthanides are present in living organisms. Lanthanides do not take part in any metabolic process. The interest in lanthanides, with respect to the biochemical reactions, derives from their capability to unravel the interactions between the Ca^{2+} cation and the biologically important molecules. As it has been stated earlier, the absorption spectra, paramagnetism and luminescence of lantha-nides can be profitably employed for the investigation of the Ca^{2+} interactions with the biological molecules (Sastri et al., 2003).

Rare earths are found with non-metals, usually, in the 3+ oxidation state. There present limited tendency to vary the valence. (Also, europium has a 2+ valences and cerium 4+ valences). This series of elements has 15 members which are rather similar to each other. How-ever, the ionic radii, the charge density and the hydration energy of their ions are not similar (Table 15). Due to the radii of the lanthanum ions (from Ce^{3+} to Lu^{3+} in the range of 1.02 - 0.80 °A, respectively), these elements demon-strate different properties, such as their charge densities, their size and their hydration energy (from Ce^{3+} to Lu^{3+} with the range of 3370 - 3760 kJ/mol) (Greenwood and Earnshaw, 1984). Subsequently, it is possible to fabricate highly selective lanthanide ion sensors with the usage of

Table 15. Ionic radii and hydration energy data for the lanthanide ions.

Ion	Radii (A°)	$\Delta H_{hydration}$ (kJ/mol)
Ce^{3+}	1.02	3370
Pr^{3+}	1.00	3413
Nd^{3+}	0.99	3442
Pm^{3+}	0.98	3478
Sm^{3+}	0.97	3515
Eu^{3+}	0.97	3547
Gd^{3+}	0.94	3571
Tb^{3+}	0.89	3605
Dy^{3+}	0.88	3637
Ho^{3+}	0.86	3667
Er^{3+}	0.85	3691
Tm^{3+}	0.85	3717
Yb^{3+}	0.81	3739
Lu^{3+}	0.80	3760

suitable ionophores, having a semi-cavity and a relatively high flexibility.

Lanthanide complexation

The tendency of a metal ion to form complexes depends strongly on a number of factors. For the rare earth ions, these factors are different from those of the transition metals. The trivalent rare earth ions have the electronic configuration $4f^n\ 5s^2\ 5p^6$, where (n) varies from 0 to 14. The figure representing the square of the radial wave functions for the 4f, 5s, 5p and 6s electrons of Gd^+ versus the electron-nucleus distance shows clearly that the 4f orbitals are inner orbitals with respect to the 5s and 5p orbitals. The outer $5s^2$ and $5p^6$ subshells shield the inner 4f electrons from the outer interactions, which determine most of the lanthanide (III) ion properties. The Ln^{3+} ions are essentially spherical and present an environment very similar to that of the alkali and alkaline earth ions towards the complex formation. Since the 4f orbitals are not available for chemical bonding and are sufficiently shielded, the crystal field stabilization energy is of the order of 100 cm^{-1}, being considerably smaller as compared with ~ 30,000 cm^{-1} in the case of the d-transition elements. Hence, the lanthanide complexes will be mostly ionic in nature and the geometrical arrangement of the ligands will not be dictated by bonding requirements to a great extent, but by steric requirements.

With the exception of scandium, the ionic radii are quite large and, in fact, their values are among the largest ones considering all the trivalent ions. These large radii indicate that the ionic potential (charge to radius ratio) is relatively low, which results in a very low polarizing ability. This is reflected in the predominantly ionic character in the metal-ligand bonds. Another major effect of the large ionic radii is the influence on the coordination number of the rare earth complexes. These two factors lead to rare earth complexes having a coordination number greater than six.

The first step in the study of metal complexes is the synthesis or preparation of the complex of interest, followed by the physicochemical characterization of the complex. Lanthanides scarcely behave like transition metal cations and, therefore, different precautions are required for their handling. The fundamental characteristics and the behavior of the lanthanides in solution are useful for embarking on the synthesis of lanthanide complexes. Some lanthanide properties, which are of direct interest for practical purposes, will be recalled here:

The 4f valence electrons of the lanthanides are situated in the inner orbitals and are not directly available for bonding. The lanthanides form essentially electrostatic bonds and, hence, their complexes are labile. As a consequence, it is difficult to predict the conformation and isolate the optical isomers of a lanthanide complex.

The lanthanides exhibit a wide range of coordination numbers (for example, 3 to 12). The stoichiometry and the conformation of a lanthanide complex often depend on the preparation method. The lanthanide contraction can affect the stoichiometry and the structure of the complexes of light and heavy lanthanides. In some cases, the isolation of the lanthanide complexes is possible either with members in the beginning or at the end of the lanthanide series.

Lanthanides interact strongly with the negatively charged groups, because of the electrostatic nature of the coordination bonds. For example, the poly dentate inorganic anions, like the nitrate (NO_3^-) and sulphate (SO_4^{2-}) ions, form stable lanthanide compounds preventing the formation of the lanthanide complexes with poorly coordinating ligands.

Lanthanide cations hydrolyze readily to form hydroxy lanthanides and form ultimately insoluble hydroxides. For that reason, careful pH control of the lanthanide salt solutions is necessary. The lanthanide complexes, formed and isolated from aqueous solutions, yield solid complexes with water of hydration. The complete dehydration of the complexes may result in the partial decomposition of the complexes and the final formation of the hydroxy lanthanide species.

Lanthanides form many types of complexes in both aqueous and non-aqueous solutions, having been studied extensively. In the early stages, the researchers' attention was focused on the development of efficient ligands for the lanthanides separation with the ion-exchange technique. The second thrust was the study of complexes in non-aqueous solutions, which can be used in the solvent extraction separation of lanthanides.

In the aqueous solutions, the most common complex is the aquo ion, $[M\ (H_2O)\ n]^{3+}$, when the counter anion is an innocent or non-complexing anion. The "n" value is

known and is not constant in the lanthanide series. However, this value is usually 9 for the elements from La to Nd, whereas for the elements from Tb-Lu n is proposed to be 8. For the ions from Nd^{3+} to Tb^{3+}, the steric factors play a critical role with an equilibrium mixture of the 8-coordinated and 9-coordinated aquo ions. This equilibrium is gradually shifting toward the 8-coordination. The solution chemistry of the lanthanides in both the aqueous and non-aqueous solutions is complicated by the concentration effects, leading to both inner and outer sphere anion coordination (Sastri et al., 2003).

METABOLISM AND TOXICITY OF LANTHANIDES

Metabolism

As it has been already discussed, the abundance of rare earths in the earth's crust is over 100 ppm. In addition, the migration potential of rare earths under natural environmental conditions is not high, owing to the formation of insoluble hydroxides and carbonates. The migration potential depends upon the concentrations of $LnOH^{2+}$, $Ln(OH)_4^-$, $LnCO_3^+$ and $Ln(CO3)_3^{3-}$. In areas rich in lanthanide ores, the soils may contain as much as 1 mg per gram of dry soil. Lanthanides probably find their way to the formation of atmospheric dusts. Industrial exposure results in the inhalation of atmospheric dusts, fumes and external contamination of existing wounds. This group of elements has a limited ability to traverse through the food chain. Even though some soils may contain high lanthanide levels (Robinson et al., 1958), the concentration in the ground waters is very low. Some plants absorb relatively large amounts, while others do not. The poor absorption by vertebrates limits the lanthanides assimilation from food and this is observed by the low concentrations detected in the mammalian organs (Gladney, 1980). The surface binding of the trivalent lanthanides to microorganisms is strong (Sobek and Talburt, 1968). It is likely that lanthanides are not transported into bacteria, algae or yeast. Their poor intestinal absorption may be due to: (i) the insoluble nature of salts, (ii) the binding to digesta and (iii) the lanthanides inability to make use of the Ca^{2+} transporting mechanism. The absorption efficiency varies from 1 to 100 % when administered orally or intravenously. Most of the distribution is in the liver and skeleton. Lanthanide sequestering may also occur in the spleen, lung and endocrine glands (Takada, 1978). The excretion of the lanthanide complexes occurs through urine. The lighter lanthanides preferentially accumulate in the liver, while the heavier ones prefer to accumulate in the bones (Durbin et al., 1956). This trend is particularly evident when the lanthanide citrate complexes are administered. When the lanthanides are introduced as chelate complexes, the body absorption is complete and the excretion

rates also increases (Hart, 1956). The excretion depends upon the stability of the chelate complex. If there is no exchange with the physiological ligands, the excretion is rapid and complete.

Toxicity

The toxic and pharmacological aspects of lanthanides have been reviewed (Haley, 1965; Venugopal and Luckey, 1978; Arvela, 1979). Many studies have been conducted regarding the lanthanides effect on microorganisms. Lanthanides inhibit the growth of bacteria, fungi and yeast. As a matter of fact, Ln^{3+} concentrations as low as 10^{-4} to 10^{-5} M are required for inhibition. On the other hand, 10^{-5} M Ln^{3+} concentrations were found to stimulate bacterial growth. It appears that the inhibition mode is the suppression of the bacterial respiration (Sastri et al., 2003).

The lanthanides toxicity is dependent on the chemical form and the administration mode. Concerning the administration mode, the oral administration is not effective, because of the poor absorption from the gastrointestinal tract. The respective LD_{50} values were in the range of several grams per kilogram of the body weight. At high doses, the rats' growth was suppressed. Gastric hemorrhage and slight structural changes in the hepatocytes have been observed (Sastri et al., 2003).

With respect to the subcutaneous injections, they led to minimal lethal doses in the range of 100 - 1000 mg/kg. The appearance of granulomas and calcification is the consequence of the intradermally injected lanthanides, while calcification and sterility are the consequences of their intratesticular injection. The intraperitoneally injected lanthanides are also toxic with LD_{50} values varying from 50 to 500 mg/kg. The intravenously injected lanthanides are the most toxic ones with LD_{50} values across the range of 10 - 100 mg/kg. The pharmacological response after the intravenously (I.V.) injected lanthanides include calcification hypotension, hypoglycemia and increased clotting times. Another response is the rare earth fatty liver produced by the lighter lanthanides, resulting in massive hepatic accumulation of triglycerides (Sastri et al., 2003).

The lanthanide elements cause internally peritonitis, adhesions, ascites as well as ocular irritation, conjunctivitis, embryotoxicity and, sometimes, ulceration. Ulcers can be additionally caused by the contact of the abraded skin with the lanthanides. Chronic exposure to lanthanide fumes result in emphysema, pneumonitis, bronchitis and pulmonary fibrosis (Sastri et al., 2003).

Rare-earth ion sensors

So far, voltammetry, mass spectroscopy, Rutherford back-scattering techniques, higher order derivative spec-

trometry, ICP-MS, NAA (Neutron Activation Analysis) and spectrofluorometric methods have been applied to the rare-earth elements analysis (Holzbrecher et al., 1994; Bauer et al., 1995; Perina et al., 1998; Biju and Rao, 2001). These methods are either time-consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories.

On the contrary, the potentiometric electrodes can offer several advantages such as fast and ease of preparation and procedures, simple instrumentations, relatively fast responses, very low detection limit, wide dynamic ranges, reasonable selectivity and low costs. This has led to the increase of the available electrodes and microelectrodes over the last few years (Ganjali et al., 2007b).

Although the neutral carrier-type ISEs have been successful for the determination of a wide variety of metal ions, including the alkali, alkaline-earth, transition and some other heavy metal ions, there is only a limited number of reports on the design of highly selective electrodes. These reports refer to eleven lanthanide ions, based on different noncyclic and macrocyclic ionophores. Some of them are: (2-mercaptoanil)diacetyl (Ganjali et al., 2004d), aza-crown (Gupta et al., 2003), dicyclohexano-18-crown-6 (Mittal et al., 2004a), 1,3,5-trithiacyclohexane (Shamsipur et al., 2002a), N-N Schiff's base (Ganjali et al., 2005a), bis(thiophenal)phenylen-1,3-diamine (Ganjali et al., 2004e), 1-phenyl-3-methyl-4-octadecanoyl-5-pyrazolone (Ito and Goto, 2001), 4-methyl-2-hydrazinobenzothiazole (Ganjali et al., 2006c), 5,14-N,N'-hydroxyphenyl-4,15-dioxo-1,5,14,18-tetraaza hexacosane (Khalil, 2003), 3-hydroxy-N'-(pyridin-2-ylmethylene)-2-naphthohydrazide (Ganjali et al., 2006m), N-(2-pyridyl)-N'-(2-methoxyphenyl)-thiourea (Ganjali et al., 2006d), N'-(1-pyridin-2-ylmethylene)-2-furohydrazide (Zamani et al., 2006b), gliclazide (Ganjali et al., 2003f), 1, 3, 5-trithiacyclohexane (Shamsipur et al., 2002d) and bis(5-nitro-2-furaldehyde)butane-2,3-dihydrazone (Ganjali et al., 2006e) for lanthanum, 1,3,5-trithiane (Shamsipur et al., 2000, 2001b), azomethine (Gaber, 2003), N′-[(2-Hydroxyphenyl) methylidene]-2-furohydrazide (Zamani et al., 2007a), 2-aminobenzothiazole (Akhond et al., 2004) for cerium, bis(thiaalkylxanthato)alkanes (Chowdhury et al., 1996), glipizide (Ganjali et al., 2004f; 2003g), 3-{[2-oxo-1(2H)-acenaphthylenyliden]-amino}-2-thioxo-1,3-thiazolidin-4-one (Zamani et al., 2007b), Tin (IV) Boratophosphate (Mittal et al., 2004b), and 4,5,6,7-tetrathiocino[1,2-b:3,4-b']diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione (Et4todit) (Shamsipur et al., 2003b) for samarium, omeprazole (Ganjali et al., 2003h), S-N Schiff's base (Ganjali et al., 2003i, 2005b), and N-(2-pyridyl)-N'-(4-nitrophenyl) thiourea (Ganjali et al., 2007c) for gadolinium, 2-{[(6-aminopyridin-2-yl)imino]methyl}-phenol (Ganjali et al., 2006n; Norouzi et al., 2006b) for Neodymium, N-(2-pyridyl)-N'-(2-methoxyphenyl)-thiourea (Ganjali et al., 2005c), 1-phenyl-3-(2-thiazolyl)-2-thiourea (Singh et al., 2007b), (3-hydroxy-N′-[(2-hydrox yphenyl) methylene]-2-naphthohydrazide (Ganjali et al., 2006f),

cefixime (Ganjali et al., 2003j), 6-methy-4-{[1-(1H-pyrrol-2-yl)methylidene]amino}-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-one (Zamani et al., 2007c) for ytterbium, N,N-diethyl-N-(4-hydroxy-6-methylpyridin-2-yl)guanidine (Ganjali et al., 2004g), S-N hexadentates schiff's base (Ganjali et al., 2007d), 4-(2-hydroxybenzylideneamino)-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-one (Zamani et al., 2007d) for europium, bispyrrolidene Schiff's base (Ganjali et al., 2005d) and 4-Amino-3-{2-[4-amino-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazin-3(2H)-yliden]hydrazono}-6-methyl-3,4-dihydro-1,2,4-triazin-5(2H)-one (Zamani et al., 2006c) for terbium, bis-pyrrolidene Schiff's base (Ganjali et al., 2004h) and asymmetrical Schiff's base (Ganjali et al., 2006g) for dysprosium, N'-(2-hydroxy-1,2-diphenylethylidene) benzohydrazide (Ganjali et al.,2006h) and pyridine-2-rbaldehyde-2-(4-methyl-1,3-benzo thiazol-2-yl) hydrazone (Ganjali et al., 2007e) for erbium, N-(1-thien-2-ylmethylene)-1,3-benzothiazol-2-amine (Ganjali et al., 2006i) and N,N′-bis(2-quinolinecarboxamide)-1,2-benzene (Ganjali et al., 2006j) for holmium, hydrazide derivative (Ganjali et al.,2006k, 2007g) for presidium, thiophene-2-carbaldehyde-(7-methyl-1,3-benzothiazol-2-yl)hydrazone (Ganjali et al.,2005e) for thulium, and finally, an asymmetrically S–N Schiff's base for lutetium (Ganjali et al., 2006l, 2007f). Table 16 shows some of these ionophores.

ANION SELECTIVE SENSORS

Anion selective electrodes, just like cation selective ones, are an important group of ion selective electrodes. The number of anion selective electrode is lower than that of the cationic sensors, due to reasons like the relative larger size of anions, their various shapes, and their high hydration energies; however, there have been a relatively large number of sensors for anionic species by researchers during the past decade.

For an anion-selective electrode, a strong interaction between the ionophore and the anion is required in order to form a complex anion in a selective fashion. Potentiometric response of the membranes doped with these complexes is believed to be based on the coordination of analyte anion axial ligand to the metal center of the carrier molecule. Table 17 shows some of the suitable ionophores for anion selective electrodes.

Fast determination of low level of anion by a simple method is of critical importance in water, food, feed and environmental analyses. Tables 18 to 26 show some of application of the anion selective electrodes in biological or environmental samples.

Carbonate selective membrane sensors

The carbonate ion is a polyatomic anion with the empirical formula CO_3^{2-}. In aqueous solution, carbonate, bicar-

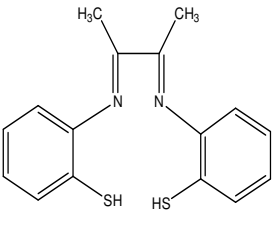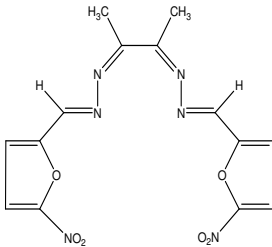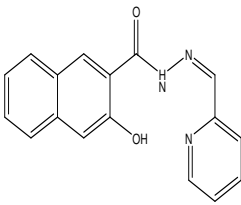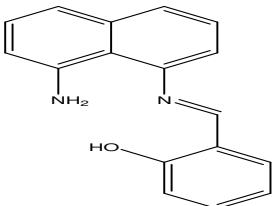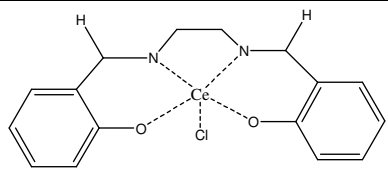**Table 16.** Structures of some of lanthanide ionophores.
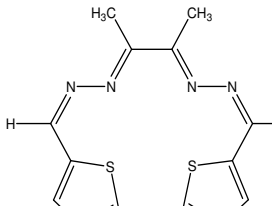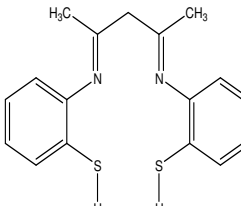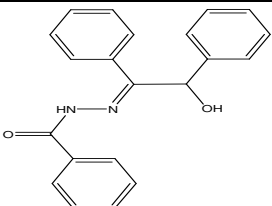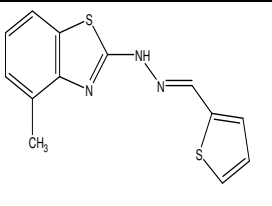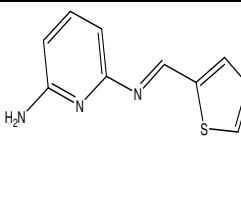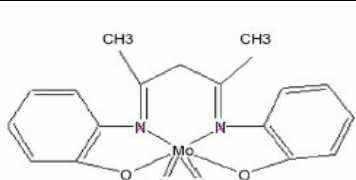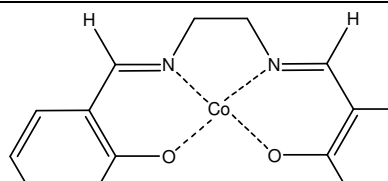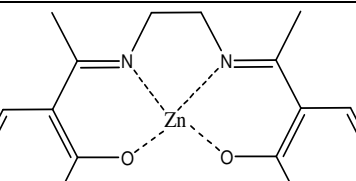
La(Ganjali et al., 2004d)	La(Ganjali et al., 2006e)	La(Ganjali et al., 2006m)
Nd(Ganjali et al., 2006n)	Eu(Ganjali et al., 2007d)	Gd(Ganjali et al.,2003i)
Er(Ganjali et al., 2006h)	Tm(Ganjali et al.,2005e)	Lu(Ganjali et al.,2006l)

Table 17. Structures of some of lanthanide ionophores.

I⁻(Ganjali et al., 2002d)	HPO_4^{2-}(Ganjali et al., 2006b)
NO_2^-(Ganjali et al., 2003d)	SO_4^{2-}(Ganjali et al., 2003p)

bonate, carbon dioxide, and carbonic acid exist together in a dynamic equilibrium. In strongly basic conditions, the carbonate ion predominates, while in weakly basic conditions, the bicarbonate ion is prevalent (Table 18).

Thiocyanate selective membrane sensors

Thiocyanate is administered as a drug in the treatment of thyroid conditions. Thiocyanate is present in low concen-

Table 18. Some of reported carbonate ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In drinking water	Arribas et al., 1991
2	In bovine serum	Sokalski et al., 1996
3	In human blood	Zeng and Tang, 2001
4	In Serum and Plasma	Scott et al., 1984
5	In Serum and Plasma	Rechnitz et al., 1977

Table 19. Some of reported thiocyanate ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In waste water	Gui et al., 2006
2	In saliva and urine samples	Ardakani et al., 2006b
3	In determination of urinary and salivary thiocyanate concentration	Shamsipur et al., 2004
4	In human biological samples (urine and saliva)	Vlascici et al., 2006
5	In biological samples	Segui et al., 2006
6	In waste water and human saliva	Dai et al., 2005a
7	In wastewater and human saliva	Chai et al., 2005
8	In wastewater	Xu et al., 2005
9	Human urine samples	Shahrokhian et al., 2005
10	In urine samples	Shamsipur et al., 1999
11	In urine samples	Amini et al., 1999
12	In wastewater and human saliva	Dai et al., 2005b
13	In urine and saliva of smokers and nonsmokers	Shamsipur et al., 2004a
14	In saliva and urine samples	Ardakani et al., 2004d
15	In waste water	Wang et al., 2004
16	In waste water	Yuan et al., 2003
17	In saliva and urine samples	Poursaberi et al., 2001
18	In Serum	Below et al., 1990
19	In Waters	Korenaga et al., 1979

Table 20. Some of reported chloride ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In the liverwort *Conocephalum conicum* L	Trebacz et al, 1994
2	In Ant malpighian mubules	Dijkstra et al., 1995
3	In biological applications	Brasuel et al., 2003
4	In natural-waters	Akaiwa et al., 1982

trations in human serum saliva, and urine. If the content of thiocyanate ion is a little higher in the body than normal, the proteinialysis will be affected and it may even result in coma. Table 19 shows some of reported thiocyanate ion selective sensors with biological or environmental applications.

Chloride selective membrane sensors

The need for chloride ion determination in clinical analysis and environmental monitoring has led to a number of methods for the measurement of this analyte. Many conventional methods, such as volumetric and coulometric titrimetry that are based on coprecipitation with Ag^+ or $Hg(II)$, are time-consuming and/or require use of reagents. The use of ion-selective electrodes, on the other hand, is simple and even allows in vivo measurements. Table 20 shows some of reported chloride ion selective sensors with biological or environmental applications.

Table 21. Some of reported bromide ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In real samples	Singh et al., 2006d
2	In canine serum bromide concentration	Kimber and Gaskill, 2006
3	In aqueous solution	Wang et al., 1997
4	In sea water	Ilcheva et al., 1991
5	In Natural-Waters	Akaiwa et al., 1982
6	Determination of hyoscine bromide	Ganjali et al., 2003k
7	In serum	Katsu et al., 1995

Table 22. Some of reported iodide ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In various pharmaceutical preparations	Hassan et al., 1997
2	In common iodinated salts	Sanchez-Pedreno et al., 1992b
3	In various geothermal water samples	Koh et al., 1991
4	In urine and serum	Almeida et al., 1997
5	Iodine content in the salts	Zeng and Tang, 2001
6	Determination of iodide in Jialing river and spring in Jinyun Mountains	Chai et al., 2004
7	In lake water samples	Shahrokhian et al., 2002
8	In real samples	Ganjali et al., 2002d

Table 23. Some of reported nitrate ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In drinking water	Watts et al., 2006
2	In environmental samples (water, fruits, vegetables and others)	Deniz et al., 1997
3	In natural waters	Lapa et al., 1997
4	In Lake Waters	Simeonov et al., 1979
5	In upland soils	Ito et al., 1996
6	In tomatoes	Perez et al., 2004
7	In the river water	Le Goff et al., 2003
8	In agricultural drainage waters	Le Goff et al., 2002
9	In water monitoring	Schwarz et al., 2000
10	Environmental application	Bendikov et al., 2005

Bromide selective membrane sensors

Bromide is present in typical seawater (35 PSU) with a concentration of aroud 65 mg/l, which is around 0.2% of all dissolved salts. Bromide is needed by eosinophils (white blood cells of the granulocyte class, specialised for dealing with multicellular parasites), which use it to generate antiparasitic brominating compounds by the action of esoinophil peroxidase, an enzyme which preferentially uses bromide. Table 21 shows some of reported bromide ion selective sensors with biological or environmental applications.

Iodide

Iodide (>6 mg/day) can be used to treat patients with hyperthyroidism due to its ability to block the release of thyroid hormone (TH), known as the Wolff-Chaikoff Effect, from the thyroid gland. In fact, prior to 1940, iodides were the predominant antithyroid agents. In large doses, iodides inhibit proteolysis of thyroglobulin. This permits TH to be synthesized and stored in colloid, but not released into the bloodstream. Table 22 listed some of iodide selective sensors with biological or environmental applications.

Table 24. Some of reported nitrite ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	in water, sausage, flour, wheat, cheese and milk	Ganjali et al., 2004i
2	real samples such as sausage, milk, flour and cheese	Shamsipur et al., 2003c
3	in sausage and milk samples	Ganjali et al., 2003l

Table 25. Some of reported perchlorate ion selective sensors with biological or environmental applications.

Entry	Application	References
1	In water samples and human urine	Rezaei et al., 2007
2	In mineral water, urine samples	Soleymanpour et al., 2007
3	In direct determinations of glucose, mannitol, ephedrine, serine, and threonine	Negash et al., 1995
4	In urine and water	Ardakani et al., 2005
5	In water and human urine	Shamsipur et al., 2003d
6	In water and human and cattle urine	Sanchez-Pedreno et al., 2002
7	In cattle urine	Ganjali et al., 2007h
8	In water samples	Ganjali et al., 2003m

Table 26. Some of reported phosphate ion selective sensors with biological or environmental applications.

Entry	Application	Reference
1	In two fertilizer samples (NPK)	Ganjali et al., 2006o
2	In waste waters and fertilisers	De Marco et al., 1998
3	In rich biological polyanions	Esson and Meyerhoff, 1997
4	In natural waters	DeMedina et al., 1996
5	In waste water samples	Ganjali et al., 2006p
6	In fertilizer samples	Ganjali et al., 2003n
7	In waste water samples	Ganjali et al., 2003o
8	In hydroponic nutrient solutions	De Marco and Phan, 2003

Chromate selective membrane sensors

There is a report on chromate ion selective electrode in which the proposed sensor has been used to determination of chromate ion in waate water samples (Ardakani et al., 2004e).

Nitrate selective membrane sensors

Nitrate and nitrite are ubiquitous within environmental, food, industrial and physiological systems. Various distillation, gravimetric and especially spectrophotometric analytical methods are used for nitrate pollution studies in water and soil sample. Table 23 shows some of reported nitrate ion selective sensors with biological or environmental applications.

Perchlorate selective membrane sensors

Low levels of perchlorate have been detected in both drinking water and groundwater. There is a little information about the health effect of low level long-term exposure to perchlorate. It is known that the perchlorate salts have been used to treat patients with hyperactive thyroidglands and to carry out diagnostic tests and as thyreostatic drugs and growth promoters in cattle fattening. Table 25 shows some of reported perchlorate ion selective sensors with biological or environmental applications.

Phosphate selective membrane sensors

Phosphate levels in freshwaters have increased in the past 50 years, which may have a negative effect on

aquatic ecology and water quality. Recent studies show that leaching of PO_4^{2-} as small as 10 µg L^{-1} from agricultural land can contribute to eutrophication. Thus, due to the increasing use of phosphate fertilizers in agricultural industries, monitoring of phosphate ions is very important. Fast determination of low level of phosphate ion by a simple method is of critical importance in water, food, feed and environmental analyses. Ion chromatography and spectrophotometric methods such as molybdenum blue, complex of molybdophosphate with basic dye compounds and indirect lanthanum chloranilate methods are the main methods for the monitoring of phosphate ions in real samples.

Sulphate selective membrane sensors

There is a report for sulphate ion in which the electrode was applied to the direct determination of sulfate and indirect determination of zinc in a zinc sulfate tablet (Ganjali et al, 2003p).

CONCLUSION

This review summarized the most considerable ISEs practical applications concerning the anionic and cationic determination in the scientific branches of biology, pharmacology, medicine and the environment. Rapidity and simplicity in operation and preparation, low cost, comparatively fast responses, very low detection limit, wide dynamic ranges and satisfactory selectivity were among the ISEs advantages. As a conclusion, ISEs consist of promising analytical tools, given their above-mentioned advantages and the current environmental and biological monitoring needs.

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