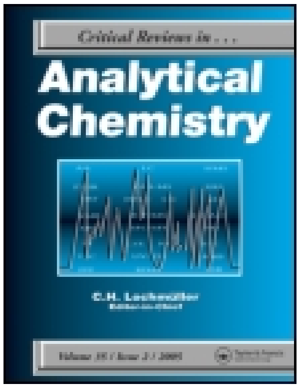

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Electrochemical Analysis of Some Toxic Metals by Ion-Selective Electrodes

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Electrochemical Analysis of Some Toxic Metals by Ion–Selective Electrodes

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An overview of potentiometric sensors that are capable of detecting toxic heavy metal ions in environmental samples is presented and discussed. Notwithstanding the tremendous work performed so far, it is obvious that still several limitations do exist in terms of selectivity, limits of detection, dynamic ranges, applicability to specific problems, and reversibility. A survey on important advances in potentiometric sensors with regard to high selectivity, lower detection limit, fast response time, and on-line environmental analysis is presented in this review article. [*Supplemental materials are available for this article. Go to the publisher's online edition of* Critical Reviews in Analytical Chemistry *to view the free supplemental file.*]

Keywords Cations, drugs, potentiometric sensors, sensors, chemical sensors

INTRODUCTION

Electroanalytical chemistry can play a very important role in the protection of our environment, in particular, chemical sensors. A useful definition for a chemical sensor is "a small device that as the result of a chemical interaction or process between the analyte and the sensor device, transforms chemical information of a quantitative, or qualitative type into an analytically useful signal." Chemical sensors have a chemical or molecular target to be measured. Most of these devices fall into two major categories (in accordance with the nature of the electrical signal): amperometric and potentiometric. In contrast to amperometric sensors, where current is monitored as a function of time, 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. Such devices rely on the use of ion selective electrodes (ISE) for obtaining the potential signal. A perm-selective ion-conductive membrane (placed at the tip of the electrode) is designed to yield a potential signal that is primarily due to the target ion. Such response is measured under conditions of essentially zero current. Potentiometric sensors are very attractive for field operations because of their high selectivity, simplicity, and low cost. The inherent selectivity of these devices is attributed to highly selective interactions between the membrane material and the target ion.

Recognition of the detrimental effects of heavy metals on humans and higher animals (Foulkes, 1990) has, in part, inspired work to develop compounds that selectively respond to specific heavy metal ions for use as ion sensors (Prasanna de Silva et al., 1997). Potentiometric sensors based on plasticized poly(vinyl chloride) (PVC) membranes doped with neutral carriers have been extensively developed for many ions (Bakker et al., 1997; Bühlmann et al., 1998; Mashkovskii, 1993). For example, crown and *bis*-crown ether ionophores can be incorporated into polymer membranes, the recognition coming from the size of the host cavity or through specific metal-ligand interactions; an alternative with similar properties are calixarenes and porphyrins derivatized to bind metal ions. There is much effort in improving selectivity relative to interfering species through chemical recognition principles.

Since it is not possible to cover all the literature due to limited time and space, we have chosen to detail a representative sample of work from the latest literature highlighting new developments in potentiometric sensors with high selectivity and lower detection and fast response time towards specific heavy metal ions and drug molecules. For a quick view, see Table 1 for characteristics of heavy metal selective sensors (please see the supplementary table file on the journal's website).

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TOXIC HEAVY METALS

Besides the fact that some heavy metal ions are essential to many organisms in small doses, high doses affect the ecosystem and human health, and in the case of very toxic metals even small doses can be hazardous to human health. An extensive survey on metals in the environment has been given by Merian (1991). Heavy metals, by definition, are metals with a density >5 g cm^{-3}. Heavy metals are prevalent in municipal and industrial effluents; they modify the structure and productivity of ecosystems (Magdaleno et al., 1997).

Several analytical methods are in use to determine heavy metal levels in various matrices. Of those, potentiometric sensors have attracted substantial interest and are especially advantageous for field, in situ, and remote applications.

In recent years, the importance of controlling the level of environmental pollution in natural waterways and potable water has generated increasing interest in the development of novel potentiometric sensors for the detection of heavy metals.

Cobalt

In 1997 Jain et al. (1997a) developed Co(II) selective electrodes with comparative analysis. The electrodes were based on macrocycles, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchlorate (I), 3, 5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchiorate (II), and 5,10,15,20-tetraphenylporphyrin(III). The best performance was observed with the membrane having the composition III-PVC-STB-DBP in the ratio 3:8:1:8, which works well over a wide concentration range (8.0×10^{-6}–1.0×10^{-1} mol L^{-1}) with a Nernstian slope of 29.0 mV per decade of activity between pH 2.8 and 7.3. This electrode shows a fast response time of 20 s and was used over a period of four months with good reproducibility ($s = 0.4$ mV) but shows interference from Na^+, Ni^{2+}, and Fe^{3+} ions. In 2001, a cobalt-selective solid contact electrode was prepared on the basis of titanium ditelluride and reported by Velikanova et al. (2001). The electrode exhibits the slope of the electrode function –(29 ± 1) mV/pC and provides the determination of 1×10^{-5}–1×10^{-1} M cobalt (II) in the pH range 4.5–6.5. The electrode was used for the potentiometric indication of the titration end point in the determination of cobalt (II) in lanthanum-strontium cobaltite $La_{0.5}Sr_{0.5}CoO_3$. The intercalant concentration range providing optimal ion-selective properties was determined. In addition to these, PVC-based Co(II)-selective electrodes based on other neutral carriers, namely benzosubstituted macrocyclic diamide (Shamsipur et al., 2001), 2-mercapto-4-methylphenyl)-2-benzamido-3-phenyl-thiopropenolate (Mashhadizadeh et al., 2002), and Schiff base (Mashhadizadeh et al., 2003), have been reported.

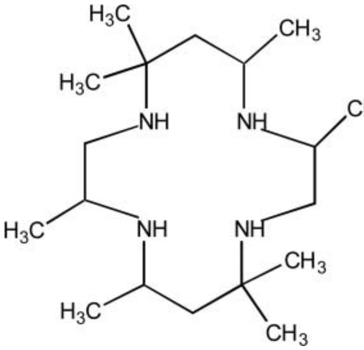
Gupta et al. (2004) reported PVC-based membranes of 5,10,15,20-tetrakis(4-methoxyphenyl) porphyrinatocobalt (TMOPP-Co) as electroactive material with sodium tetra phenyl borate as anion excluder and several plasticizers. However, membranes without plasticizers showed best results in terms of the working concentration range (1.9×10^{-5}–1×10^{-1} M) with a slope of 30.5 mV/decade over the pH range 1.9–5.8.

Ganjali et al. (2004) reported a Co(II) membrane sensor fabricated from PVC matrix containing a new oxime compound (oxime of 1-(2-oxocyclohexanediol) as a neutral carrier and the reported sensor exhibited a linear potential response in the concentration range 1×10^{-1}–1×10^{-6} M of Co^{2+}. The electrode displayed a Nernstian slope of 29.8 mV/decade in the pH range 3.5–8.0.

In 2006, Singh et al. (2006e) developed a Co(II)-selective sensor based on 2,4-dimethyl-1,5,8,11-tetraazacyclotrideca-1,4-diene [$Me_2(13)dieneN_4$] as an ion carrier. The sensor exhibited a Nernstian response for Co^{2+} ions over a wide concentration range (7.94×10^{-6}–1.0×10^{-1} M) at pH 2.5–7.0, and a response time of 10 s, and it could be used for three months without any significant divergence in potential. The proposed membrane sensor exhibited good selectivity for Co^{2+} over a wide variety of other metal ions and in mixtures containing up to 25% (v/v) nonaqueous content. The sensor was successfully used as an indicator electrode in the potentiometric titration of Co^{2+} with EDTA and the direct determination of Co^{2+} in real samples. In the continuity of development of cobalt-selective sensors, Singh and coworkers further developed cobalt-selective sensors with improved working range (Singh et al., 2006c, 2007b; Gupta et al., 2008d).

Gupta et al. (2006a) fabricated a new PVC membrane electrode for Co^{2+} based on N,N′-bis(salicylidene)-3,4-diaminotoluene, using sodium tetraphenylborate (NaTPB) as an anionic excluder and dioctylphthalte (DOP) as a solvent mediator. The electrode exhibited a linear potential response in the concentration range of 7.9×10^{-8} to 1.0×10^{-1} M with a slope of 30 ± 0.2 mV/decade. The detection limit of the proposed sensor is 5.0×10^{-8} M, and it can be used over a period of five months. The proposed sensor revealed good selectivity over a wide variety of other cations including alkali, alkaline earth, heavy, and transition metals and could be used in the pH range of 2.0–9.0. This electrode was successfully applied for the determination of Co^{2+} in real samples. Zamani et al. (2007) constructed an authentic PVC membrane cobalt(II) ion-selective electrode using N′-[1-(2-thienyl)ethylidene]-2-furohydrazide (NTEF) as membrane carrier. The sensor has a fast response time, comparatively good selectivity with respect to alkali, alkaline earth, some transition, and heavy metal ions. It was used more than 10 weeks without demonstrating any considerable potential divergence. Moreover, the suggested sensor exhibited a Nernstian response for Co(II) ions over a wide concentration range (from 1.0×10^{-6} to 1.0×10^{-1} M). It was used for direct cobalt determination in wastewater and tap water samples.

Wardak (2008) developed plastic sensor for Co^{2+} ions based on 2-amino-5 (hydroxynaphtyloazo-1′)-1,3,4 thiadiazole (ATIDAN). The electrode exhibited a low detection limit of 1.5×10^{-6} mol L^{-1} and an almost theoretical Nernstian slope in the activity range 4.0×10^{-6}–1×10^{-1} mol L^{-1} of cobalt ions. The



SCH. 1. 3,10-*c*-*meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane.

response time of the sensor is less than 10 s, and it can be used over a period of six months without any measurable divergence in potential.

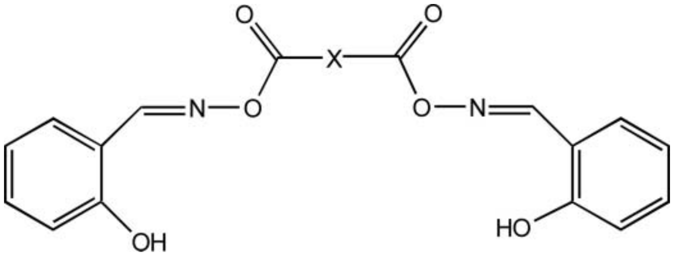
A bridge-modified 4-tert-butylthiacalix[4]arene (I) was employed as electroactive material in the preparation of a cobalt-selective sensor by Gupta et al. (2008f). The potential response of this membrane was linear to Co^{2+} ions in the concentration range 5.3×10^{-6} to 1.0×10^{-1} M with a near-Nernstian slope of 30.0 mV/decade of activity and a detection limit of ~0.3 ppm. This membrane also showed a lowest response time of 10 s and worked satisfactorily in partially nonaqueous medium. The sensor possessed excellent selectivity for Co^{2+} over a large number of mono-, bi-, and trivalent cations and could be used in the determination of cobalt content in wastewater and beer samples.

Kumar and Shim (2009) used a new PVC-based membrane containing *p*-(4-*n*-butylphenylazo)calix[4]arene (I) as an electroactive material along with sodiumtetraphenylborate (NaTPB) and dibutyl(butyl)phosphonate in the ratio 10:100:1:200 (I:DBBP:NaTPB:PVC) (w/w) to fabricate a new cobalt(II)-selective sensor. It exhibited a working concentration range of 9.2×10^{-6} to 1.0×10^{-1} M, with a Nernstian slope of 29.0 ± 1.0 mV/decade of activity and response time of 25 s. This sensor showed a detection limit of 4.0×10^{-6} M. Its potential response remains unaffected by pH in the range 4.0–7.2. The sensor has a lifetime of about three months. It can be used for the determination of cobalt ion concentration in real samples.

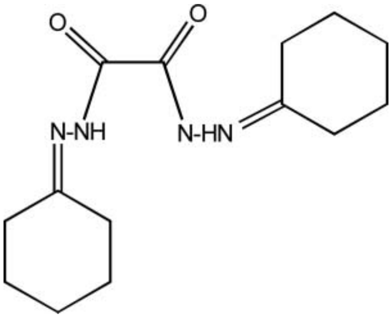
Chromium

Chromium (III) is an essential nutrient for humans, and its shortage may cause heart conditions, disruption of metabolism, and diabetes. But the uptake of too much chromium (III) can cause health effects as well, for instance, skin rashes. The main human activities that increase the concentration of Cr(III) are steel, leather, and textile manufacturing industries. A literature survey revealed that among the reported ISEs, very limited studies were carried out for Cr^{3+} ions. Singh et al. (1999) reported a PVC-based membrane of 3,10-*c*-*meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane diperchlorate with sodium tetraphenyl borate (STB) as an anion excluder (see Scheme 1), and dibutyl phthalate (DBP), dibutyl butylphosphonate (DBBP), tris(2-ethylhexyl) phosphate (TEP), and tributyl phosphate (TBP) as plasticizing solvent mediators were prepared and investigated as a Cr(III)-selective electrode. The best performance was observed with the membrane having the ligand-PVC-DBP-STB composition 2:10:7:1, which worked well over a wide concentration range (1.77×10^{-6}–0.1 mol L^{-1}) with a Nernstian slope of 20 mV/decade of activity between pH 3.0 and 6.5. This electrode showed a fast response time of 15 s and was used over a period of four months with good reproducibility ($s = 0.4$ mV). The selectivity coefficients for mono-, di-, and trivalent cations indicate excellent selectivity for Cr(III) ions over a large number of cations. The practical utility of the membrane sensor has also been observed in solutions contaminated with detergents, i.e., cetyltrimethylammonium bromide and sodium dodecyl sulfate. Above all, the membrane sensor has been used very successfully to analyze some food materials for the determination of Cr(III) ion.

A PVC-based membrane of 4-dimethylaminoazobenzene with a Nernstian potentiometric response (with slope of 19.5 ± 0.6 mV/decade) for Cr(III) over a wide concentration range (1.66×10^{-6}–1.0×10^{-2} M) was reported by Abbaspour and Izadyar (2001). The potential of the reported electrode was independent of pH in the range 3.0–5.5. A plasticized Cr(III) ion sensor by incorporating 2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene (TTCT) ionophore was reported by Ganjali et al. (2003) that exhibited a good response over a wide concentration range 1×10^{-1}–1×10^{-6} M with a slope of 19.5 mV/decade. The TTCT-based electrode showed a fast response time (15 s) and can be used in aqueous solutions of pH 3–5.5. Shamsipur et al. (2005) synthesized Schiff bases and studied their ability as Cr^{3+} ion carrier in PVC-membrane electrodes. The polymeric membrane (PME) and coated glassy carbon (CGCE) electrodes based on 2-hydroxybenzaldehyde –O,O′-(1,2-dioxetane-1,2-diyl)oxime exhibited Nernstian response for Cr^{3+} ion over a wide concentration range (1.5×10^{-6}–8.0×10^{-3} M for PME and 4.0×10^{-7}–3.0×10^{-3} M for CGCE) and very low limits of detection (1×10^{-6} M for PME and 1×10^{-7} M for CGCE) (see Scheme 2).



SCH. 2. 2-Hydroxybenzaldehyde –O,O′-(1,2-dioxetane-1,2-diyl)oxime.

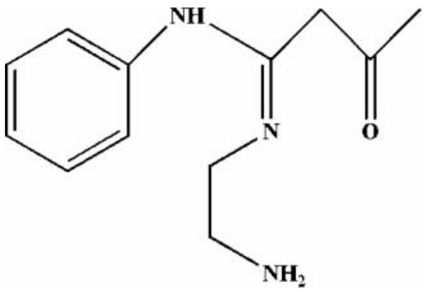


SCH. 3. OABCH.

Gohlivand et al. (2004) reported a PVC membrane sensor based on oxalic acid bis (cyclohexylidene hydrazide) (OABCH) as membrane carrier Cr(III)-selective electrode (see Scheme 3). The electrode reveals a Nernstian behavior (slope 19.8 ± 0.4 mV decade^{-1}) over a wide Cr(III) ion concentration range of 1.0×10^{-7}–1.0×10^{-2} mol dm^{-3} with a very low limit of detection (i.e., down to 6.3×10^{-8} mol dm^{-3}). The potentiometric response of the sensor is independent of the pH of the test solution in the pH range 1.7–6.5. The electrode possesses advantages of very fast response, relatively long lifetime, and especially good selectivity to a wide variety of other cations. The sensor was used as an indicator electrode in the potentiometric titration of chromium ion and in the determination of Cr(III) in wastewater and alloy samples.

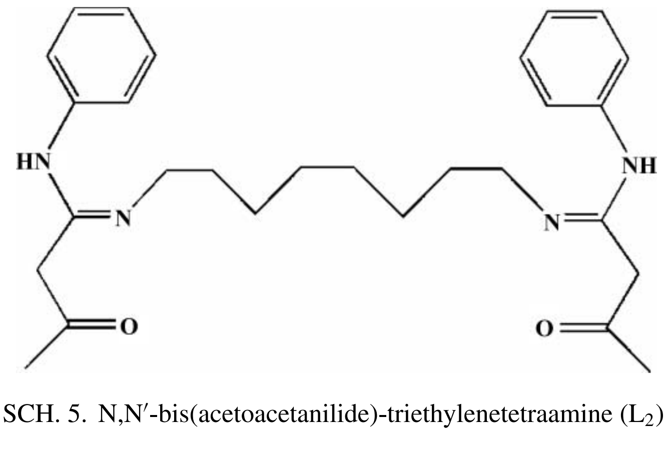
Gupta et al. (2006d) used tri-o-thymotide (I) as an electroactive material in a PVC matrix for fabrication of a chromium (III)-selective sensor. The membrane containing tri-o-thymotide, sodium tetraphenyl borate (NaTPB), dibutyl phthalate (DBP), and PVC in the optimum ratio 5:1:75:100 (w/w) exhibits a working concentration range of 4.0×10^{-6} to 1.0×10^{-1} M with a Nernstian slope of 20.0 ± 0.1 mV/decade of activity in the pH range of 2.8–5.1. The detection limit of this sensor is 2.0×10^{-7} M. The electrode exhibits a fast response time of 15 s, shows good selectivity towards Cr^{3+} over a number of mono-, bi-, and trivalent cations, and can also be used in partially non-aqueous medium (up to 15%, v/v). Ganjali et al. (2006) prepared a highly selective and sensitive plasticized membrane sensor for chromium (III) ions, based on SNS as membrane carrier. The sensor showed a linear dynamic range of 1.0×10^{-6} to 1.0×10^{-1} M with a Nernstian slope of 19.9 ± 0.3 mV decade^{-1} and a detection limit of 7.0×10^{-7} M (∼40 ppb). It has a fast response time of <12 s and can be used for at least eight weeks without any considerable divergence in its potentials. The proposed sensor could be used in a pH range of 3.0–6.6. It was also used in the determination of Cr(III) in the wastewater of chromium electroplating and leather industries, showing satisfactory results. The sensor was also applied for monitoring the chromium ion level in wastewater of chromate industries.

Further, Singh et al. (2007a) used chromium chelates of Schiff bases, N-(acetoacetanilide)-1,2-diaminoethane (L_1) (see Scheme 4) and N,N′-bis(acetoacetanilide)-triethylenetetraammine (L_2) (see Scheme 5), as neutral ionophores for preparing PVC-based membrane sensors selective to Cr(III). The best performance was obtained for the membrane sensor having a composition of L_1:PVC:DBP:NaTPB in the ratio 5:150:250:3 (w/w). The sensor exhibited Nernstian response in the concentration range 8.9×10^{-8} to 1.0×10^{-1} M Cr^{3+} with a limit of detection of 5.6×10^{-8} M. The proposed sensor manifested advantages of relatively fast response (10 s) and good selectivity over some alkali, alkaline earth, transition, and heavy metal ions. The potentiometric response of the proposed sensor was independent of pH of the test solution in the range of 2.0–7.0. The proposed electrode was used in direct determination of chromium (III) in different water and food samples.



SCH. 4. N-(acetoacetanilide)-1,2-diaminoethane (L_1).

Abedi et al. (2007) developed a new greatly selective and sensitive PVC membrane sensor as a Cr(III) ion selective electrode, using an ionophore named 1,3-diamino-2-hydroxypropane-N,N,N′,N′-tetraacetic acid (DPTA). The sensor displayed a linear dynamic range between 7.0×10^{-7} and 1.0×10^{-1} M, with a near-Nernstian slope of 19.8 ± 0.3 mV/decade and a detection limit of 2.0×10^{-1} M. The potentiometric response of the proposed electrode was pH independent in the range of 2.5–6.8. The sensor possessed the advantages of short conditioning time, fast response time (<10 s), and, especially, good selectivity towards transition and heavy metals and some mono-, di-, and, trivalent cations. The electrode could be used for at least 10 weeks without any considerable divergence in the potentials. It



SCH. 5. N,N′-bis(acetoacetanilide)-triethylenetetraamine (L_2).

was effectively used in the Cr(III) determination in wastewater of the chromium electroplating industry.

A new PVC membrane, containing synthesized p-(4-acetanilidazo)calix[4]arene as a membrane carrier, was used to fabricate a chromium (III) selective electrode by Kumar and Shim (2008). This electrode exhibited a near-Nernstian slope of 19.8 ± 0.2 mV/decade of activity in the working concentration range of 9.8×10^{-7}–1.0×10^{-1} M. It displayed a stable potential response in the pH range 2.8–5.7. The electrode exhibited a fast response time of less than 14 s and could be used for at least 12 weeks without any considerable divergence in potentials. This electrode showed very good selectivity over most of the common cations and could be employed successfully for the determination of Cr(III) ion activity in real samples.

A highly Cr^{3+}-selective ionophore, based on 5-amino-1-phenyl-1H-pyrazole-4-carboxamide (APC) as a carrier, was synthesized in order to obtain a Cr^{3+} ion-selective electrode by Zamani et al. (2009b). The demonstrated characteristics of the sensor included a linear dynamic range between 1.0×10^{-6} and 1.0×10^{-1} M with a near-Nernstian slope of 19.6 ± 0.4 mV/decade, a detection limit of 5.3×10^{-7} M, and a very good selectivity for Cr^{3+} over other cations in a wide pH range (3.2–6.3). Furthermore, the newly designed electrode presented a fast response time of 10 s with a lifetime of at least two months. The developed sensor provided satisfactory results after its application in Cr^{3+} determination in biological samples and also in wastewater of the chromium electroplating industry.

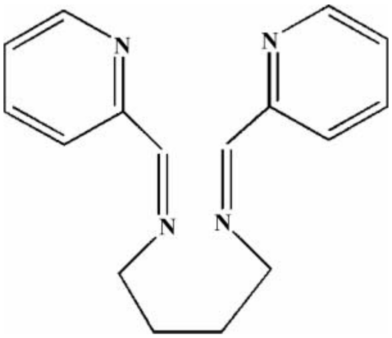
More recently, in 2010, a new chromium carbon paste electrode sensor based on a carbon paste electrode containing 1-[(2-hydroxy ethyl) amino]-4-methyl-9H-thioxanthen-9-one (AMTX) as new carrier was prepared (Ghaedi et al., 2010). The best performance characteristics for the electrode was obtained with carbon:NaTPB:Nujol:AMTX in the mass ratio of (400:1.43:57.2:3 mg) (86.65:0.31:12.39:0.65%). At the optimum value of all variables, the response of the electrode was linear in the range of 3.2×10^{-7} to 1.0×10^{-1} mol L^{-1} with a Nernstian slope of 20.51 mVdecade^{-1} of Cr^{3+} ion concentration with detection limit of 1.6×10^{-7} mol L^{-1}. The electrode response was independent of pH in the range of 4.8–6.3, while the response time of the electrode was ~8 s.

Cadmium

Cadmium exists in industries as an inevitable by-product of zinc, lead, and copper extraction. After being applied, it enters the environment mainly through the ground, because it is found in manures and pesticides. Health effects that can be caused by cadmium are diarrhea, stomach pains, reproductive failure, damage to the central nervous system, and possibly DNA damage or cancer development. In humans, long-term exposure is associated with renal dysfunction. Cadmium may also produce bone defects (osteomalacia, osteoporosis) in humans and animals. In addition, the metal can be linked to increased blood pressure and effects on the myocardium in animals, although most human data do not support these findings.

Shamsipur and Mashhadizadeh (2001) reported a Cd^{2+}-selective PVC-based membrane electrode exhibiting a wide concentration range (1×10^{-1}–4×10^{-7} M) with a slope of 29 mV/decade. The limit of detection was 0.01 ppm and it can be used in the pH range 2.5–8.5. Pretsch and coworkers (Alina et al., 2001) determined selectivity behavior for two membranes based on the ionophore N, N, N′, N′-tetradodcecyl-3,6-dioxaoctanedithioamide (ETH 5435), and the best lower detection limit of 10^{-10} M or 11 ppt Cd^{2+} was achieved at pH 7 with an ionic background of 10^{-4} M $NaNO_3$. A new PVC membrane electrode for Cd^{2+} ions based on [1,1′-bicyclohexyl]-1,1′,2,2′-tetrol as membrane carrier was prepared by Javanbakht et al. (2000). The electrode exhibited a Nernstian response over a wide concentration range (1×10^{-1}–1×10^{-5} M) with a slope of 27.8 mV/decade. The limit of detection was 9×10^{-6} M and it can be used in the pH range 4.0–7.0. Gupta et al. (2002c) reported PVC-based membrane containing dicyclohexano-18-crown-6 (I) as active material along with sodium tetraphenyl borate (NaTPB) as an anion excluder and dibutyl phthalate as solvent mediator in the ratio 20:4:150:150 (w/w) (I:NaTPB:DBP:PVC); it exhibits good properties with a Nernstian response of 29.0 ± 1.0 mV/decade of activity and a working concentration range of 2.1×10^{-5}–1.0×10^{-1} M. The working pH range of the sensor is 1.9–7.0. The sensor works satisfactorily in mixtures having 10% (v/v) nonaqueous content without showing any considerable change in working concentration range or slope. It has been successfully used as an indicator electrode for the potentiometric titration of Cd^{2+} against EDTA as well as for its determination in wastewater. Another Cd^{2+} ion-selective electrode based on poly (styrene-*co*-acrylonitrile) copolymer (SAN) has been prepared by Gupta et al. (2000) using 8-hydroxyquinoline as an electroactive ionophore and dibutylphthalate as a plasticizing agent. The Cd^{2+} ion-selective electrode in the presence of sodiumtetraphenylborate (NaTPB) as an anion excluder exhibited a linear response within 4.46×10^{-4}–1.0×10^{-1} mol dm^{-3} activities of Cd^{2+} ions at a pH variation of 3.20 to 6.80. The observed response time of the prepared electrode was 12 s. The electrode has shown a reproducible Nernstian slope of 29 mV decade^{-1} activities of Cd^{2+} ions over a period of six months. The selectivity of the prepared electrode for Cd^{2+} ions in the presence of a number of interfering cations is found to be high within the working range of the electrode. However, Pb^{2+}, Cu^{2+}, and Mg^{2+} ions have shown interference when the activities of the Cd^{2+} ions in the solution were less than 1×10^{-6} mol dm^{-3}. Singh et al. explored different macrocyclic ionophores such as 3,4,11,12-dibenzo-1,6,9,14 tetraaza-cyclohexadecane (Singh et al., 1999) and thia containing ligands (Singh et al., 2007c) for fabrication of Cd(II) selective electrodes.and investigated them as Cd^{2+} selective sensors.

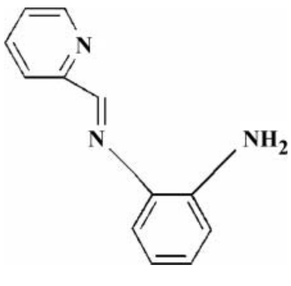
Mashhadizadeh et al. (2005) dveloped cadmium (III) selective sensors based 5-[((4-methyl phenyl)



SCH. 6. N,N′-[bis(pyridin-2-yl)formylidene]butane-1,4-diamine.

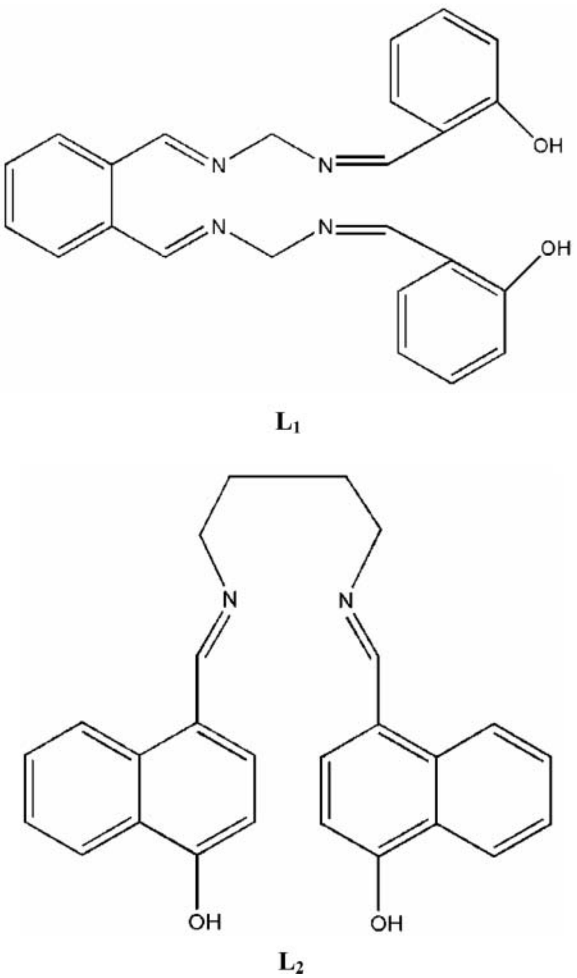
azo)-*N*-(6-amino-2-pyridin) salicylaldimine] S_1 and 5-[((4-methyl phenyl) azo)-*N*-(2-diamino-2-cyano-1-ethyl cyanide) salicylaldehyde] S_2 respectively. The electrodes based on S_1 and S_2 exhibit a Nernstian or near-Nernstian response for cadmium ion over a wide concentration range of 1.5×10^{-1}–7.5×10^{-7} with a slope of 28 mV/decade of activity and 2.0×10^{-1}–4.0×10^{-7} with a slope of 22 mV/decade of activity, respectively. Gupta et al. (2007c) developed cadmium-selective membrane sensors as a comparative analysis based on N,N′-[bis(pyridin-2-yl)formylidene]butane-1,4-diamine (see Scheme 6) and N-(2-pyridinylmethylene)-1,2-benzenediamine (see Scheme 7). The sensors shows wide concentration range of 7.9×10^{-8}–1.0×10^{-1} M with slope of 30.0 mV decade^{-1} activity and 1.3×10^{-6}–1.0×10^{-1} M with a slope of 28.0 mV decade^{-1} activity respectively.

Gupta et al. (2008e) fabricated Cd^{2+}-selective sensors from PVC matrix membranes containing t-butyl thiacalix[4]arene (I) and thiacalix[4]arene (II) as electroactive materials. The addition of sodium tetraphenylborate and the plasticizer 2-nitrophenyl octyl ether was found to improve the performance of the sensors substantially. The sensor showed a linear potential response for Cd^{2+} over a wide activity range of 3.2×10^{-6} to 1.0×10^{-1} M with Nernstian compliance (29.5 mV decade^{-1} of activity) in the pH range 4.5–6.5 and a fast response time of ∼8 s. The sensor exhibited adequate shelf life (∼3 months) with good reproducibility (S.D. ± 0.2 mV). The sensor could be successfully used for the quantification of cadmium in river water samples.



SCH. 7. N-(2-pyridinylmethylene)-1,2-benzenediamine.

The same authors (Gupta et al., 2009a) tried to further improve the working parameter of the cadmium-selective sensor and for first time developed a nano level monitoring membrane sensor based on two neutral ionophores, 2,2′-(1Z,1′Z)-(1E,1′E)-(1,2-phenylenebis(methan-1-yl-1-ylidene))bis (azaan-1-yl-1-ylidene) bis(methylene) bis(azan-1-yl-1-ylidene) bis(methan-1-yl ylidene) diphenol (L_1) and 4,4′-(1E,1′E)-(butane-1,4-diylbis (azan-1-yl-1 ylidene)) bis(methan-1-yl-1-ylidene)dinaphthalen-1-ol (L_2), for quantification of cadmium ions (see Scheme 8). The best performance was obtained with the electrode having a membrane composition (w/w) of (L_1) (2.6%):PVC (31.6%):DOP (63.2%):NaTPB (2.6%). The proposed electrode exhibited Nernstian response in the concentration range 5.0×10^{-9} to 1.0×10^{-1} M Cd^{2+} with limit of detection of 3.1×10^{-9} and performs satisfactorily over wide pH range (2.0–8.5) with a fast response



SCH. 8. 2,2′-(1Z,1′Z)-(1E,1′E)-(1,2-phenylenebis(methan-1-yl-1-ylidene))bis (azaan-1-yl-1-ylidene) bis(methylene) bis(azan-1-yl-1-ylidene) bis(methan-1-yl ylidene) diphenol (L_1) and 4,4′-(1E,1′E)-(butane-1,4-diylbis (azan-1-yl-1 ylidene)) bis(methan-1-yl-1-ylidene)dinaphthalen-1-ol (L_2).

time (11 s). The electrode was found to work satisfactorily in partially nonaqueous media up to 40% (v/v) content of methanol, ethanol, and acetonitrile and could be used for a period of 2.5 months. The analytical usefulness of the proposed electrode was evaluated by its application in the determination of cadmium in cigarette samples.

A PVC membrane with 4-hydroxy salophen as an ionophore along with sodium tetraphenyl borate (NaTPB) as an anion excluder and dibutyl phthalate as a solvent mediator in the ratio 28.7:3.3:63.2:4.7 (w/w) (PVC-NaTPB-DBP-ionophore) developed by Ensafi et al. (2009) exhibited good properties with a Nernstian response of 30.1 ± 1.0 mV/decade of activity for Cd(II) ions and a working concentration range of 1.0×10^{-6}–1.0×10^{-1} mol L^{-1} Cd(II). The limit of detection was 8.4×10^{-7} mol L^{-1} Cd(II). The sensor had a fast response time of 20 s and could be used for at least eight weeks without any divergence in potential. The electrode could be used in the pH range of 2.8–8.1. The practical utility of the sensor was demonstrated by using it successfully for the direct determination of Cd(II) in water and in wastewater samples.

Shamsipur et al. (2009) synthesized and characterized a new sulfur-containing macrocyclic diamide, 1,15-diaza-3,4,12,13-dibenzo-5,11-dithia-8-oxa-1,15-(2,6-pyrido)cyclooctadecan-2,14-dione, L, and used it as an active component for fabrication of PVC-based polymeric membrane (PME), coated graphite (CGE), and coated silver wire electrodes (CWE) for sensing Cd^{2+} ion. The electrodes exhibited linear Nernstian responses to Cd^{2+} ion in the concentration range of 3.3×10^{-6} to 3.3×10^{-1} M (for PME, LOD = 1.2×10^{-6} M), 2.0×10^{-7} to 3.3×10^{-1} M (for CWE, LOD = 1.3×10^{-7} M), and 1.6×10^{-8} to 1.3×10^{-1} M (for CGE, LOD = 1.0×10^{-8} M). The CGE was used as a proper detection system in flow-injection potentiometry (FIP) with a linear Nernstian range of 3.2×10^{-8} to 1.4×10^{-1} M (LOD = 1.3×10^{-8} M). The optimum pH range was 3.5–7.6. The electrodes revealed fairly good discriminating ability towards Cd^{2+} in comparison with a large number of alkali, alkaline earth, transition, and heavy metal ions. The electrodes were found to be chemically inert, showing a fast response time of <5 s, and could be used practically over a period of about two to three months.

Most recently, Tyagi et al. (2010b) used a highly electroactive material, $Mo_2[(OAc)_2(H_2\text{-calix[4]arene})]$, as a neutral carrier for Cd^{2+} ions. The membrane was fabricated by using ionophore $[Mo_2(OAc)_2(H_2\text{-calix[4]arene})]$:poly(vinyl chloride) (PVC):dibutylphthalate (DBP):sodium tetraphenyl borate (NaTPB) in the ratio of 40:300:470:5 and tetrahydrofuran (THF) as solvent. The membrane electrode performed in the concentration range of 9.9×10^{-8}–1.0×1021 M (2.34×10^{-5}–23.64 mg/mL) having the Nernstian slope of 30.0 ˆ 1.0 mV, and the best detection limit was observed at 9.8×10^{-8} M (2.31×10^{-5}mg/mL). The proposed membrane electrode had a response time of 12 s and a useful working pH range of 1.0–7.0; it was used over a period of 10 months and worked satisfactorily in the test solution having 30% (v/v) nonaqueous content. The electrode sensor has distinguishing ability for Cd^{2+} ion with regard to several alkali, alkaline earth, transition, and heavy metal ions.

Lead

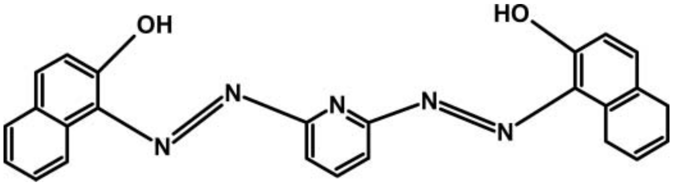
Lead is ubiquitous in the environment and is hazardous. The recognized potential for human safety hazards presented by lead in the environment necessitates monitoring of its concentration in industrial effluents. The use of ion-selective electrodes for the detection of lead has received much interest, and many ligands have been investigated as sensing agents in electrodes based on ionophore-doped PVC membranes.

Mousavi et al. (2000b) constructed a PVC membrane lead (II) ion-selective electrode using 1,10- dibenzyl-1,10-diaza-18-crown-6 (DBzDA18C) as membrane carrier. The sensor showed Nernstian response for Pb(II) ions over a wide concentration range (1×10^{-2}–5×10^{-5} M) and exhibited good selectivity with respect to alkali, alkaline earth, and some transition and heavy metal ions. It was employed as an indicator electrode in potentiometric titration of EDTA with lead ions and used for direct determination of lead in wastewater. Tavakkoli et al. (1998) studied four different 9,10-anthraquinone derivatives and characterized their abilities as lead ion carrier in PVC membrane electrodes. The electrode based on 1,8-dihydroxy-2,7-bis(prop-2′-enyl)-9,10-anthraquinone exhibited a Nernstian response for Pb^{2+} ions over a wide concentration range (2×10^{-3}–2×10^{-6} M). It was used as an indicator electrode in potentiometric titration of sulfate ions with a lead ion solution. A lead (II) ion-selective PVC membrane electrode containing 2,2′-dithiodibenzoic acid as a carrier was prepared and reported by Gohlivand and Raheedayat (2004). The electrode exhibited a Nernstian response for lead (II) cations over a wide concentration range (5×10^{-6}–1×10^{-2} M) with a slope of 29.9 mV/decade. Its selectivity to Pb^{2+} in the presence of alkali, alkaline earth, and some transition and heavy metal ions is satisfactory in the pH range of 4.0–6.5. A novel selective membrane electrode containing N,N′-dimethylcyanodiaza-18-crown-6 (DMCDA18C6) for determination of ultra trace amount of lead was prepared by Ganjali et al. (2003). The electrode exhibited a Nernstian response for lead (II) cations over a wide concentration range (1×10^{-7}–1×10^{-2} M) with a limit of detection of 14.5 ppb. The proposed sensor was used as an indicator electrode in potentiometric titration of Pb(II) ions and in the determination of lead in edible oil, human hair, and H_2O sample. An ion-selective electrode for lead based on piroxicam as a suitable ionophore is described by Sadeghi et al. (2002). The electrode responds to Pb^{2+} in a linear range from 1×10^{-5} to 1×10^{-1} M with a slope of 30 mV/decade and a detection limit of 4×10^{-6} M. The proposed electrode could be used in a pH range of 4.0–8.0. Another lead ion-selective electrode was prepared by Lu et al. (2002) with polymeric membranes based on a calixarene derivative containing carboxyphenyl azo groups. The electrode gave good Nernstian responses of 29.4 mV/decade for lead in the activity range 10^{-6}–10^{-2} M. The limit of detection reached $10^{-6.1}$ M and exhibited high selectivity towards alkali, alkaline earth, and transition metal ions. Four different fatty acids (C7, C10, C14, and C18) were studied to characterize their abilities as lead (II) ion carrier in PVC membrane electrodes by Mousavi et al. (2001). The electrodes based on capric acid [$CH_3(CH_2)_8COOH$] showed good Nernstian response for Pb^{2+} ions. The optimum composition of the membrane was 30 wt.% PVC, 60 wt.% NPOE as plasticizer, 5 wt.% ionophore, and 5 wt.% potassium tetrakis (*p*-chlorophenyl)borate as lipophilic salt. The electrode exhibited a Nernstian slope of 29 mV/decade of Pb^{2+} over a concentration range (1×10^{-5}–1×10^{-2} M). Membranes of 4-tert-butylcalix[4]arene as an electroactive material, sodium tetra-Ph borate (NaTPB) as an anion excluder, and di-Bu phthalate (DBP) as solvent mediator in a PVC matrix were tried by Jain et al. (1995b) for developing a lead-selective sensor. The best performance was exhibited by the membrane having the composition 2:1:100:200 (I: NaTPB: DBP: PVC). This sensor works well in the concentration range 1.1×10^{-5}–1.0×10^{-1} M with a Nernstian slope (30.0 ± 1.0 mV/decade of activity). The working pH range of the sensor is 2.1–4.0, and it shows good selectivity for Pb(II) over other mono-, bi-, and trivalent cations that are reported to cause interference in the working of other sensors. Different atropisomers of tetrakis(2-hydroxy-1-naphthyl)porphyrins (THNP) were used by Lee et al. (2004) to develop Pb^{2+}-selective sensors. The sensor based on THNP displayed a good Nernstian response (29.2 mV decadet of activity) to Pb^{2+} over the linear range of 3.2×10^{-5} to 1.0×10^{-1} M. Hassan et al. (2003) developed Pb^{2+}-selective membrane sensors based on chiral 2,6-bis-pyridinecarboximide derivatives. These sensors worked in the concentration range of 4.0×10^{-6} to 1.0×10^{-2} M at pH 4.5–7.0 with a lower detection limit of 0.4–3.7 μg mL^{-1}. Besides this, crown ethers and calixarenes have also been widely investigated as sensing materials to prepare Pb^{2+} sensors. Some of such reported sensors are based on the membranes of 4-tert-butylcalix[6]arene (Bhat et al., 2004) and calixarene carboxyphenyl azo derivative (Lu et al., 2002). Gupta et al. (2006f, 2007b) further reported lead (II)-selective sensors based on *N*,*N*′-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane and N,N′-bis(2-hydroxy-1-napthalene)-2,6-pyridiamine (see Scheme 9) respectively. These sensors work well in the improved concentration range of 1.0×10^{-6} to 1.0×10^{-1} M and 3.2×10^{-6} to 1.0×10^{-1} M respectively for Pb^{2+} with Nernstian slope.

Kim et al. (2007) developed a PVC-based sensor on N,N′-bis-thiophen-2-ylmethylene-pyridine-2,6-diamine. The sensor showed a limit of detection of –log(M) = 5.74 to Pb^{2+} in $Pb(NO_3)_2$ solution at room temperature. Kamel (2007) constructed two PVC matrix chemical sensors for lead. These sensors were based on the use of ion association complexes of trihydroxoplumbate $[Pb(OH)_3]^-$ and tetraiodoplumbate $[PbI_4]^{2-}$ with cetylpyridinium chloride (CP) and iron(II)-4,7-bathophenanthroline $[Fe(bphen)_3]^{2+}$ as novel electroactive materials dispersed in o-nitrophenyloctyl ether (o-NPOE) plasticizer for ionometric sensor controls. The sensing membrane (3 × 5 mm) is immobilized on a wafer polyimide chip (13.5 × 3.5 mm) to offer a planar miniaturized design that could be easily used in a flow injection system. Under static modes of operation, the sensors revealed a near-Nernstian response over a wide Pb^{2+} ion concentration range of 7.9×10^{-7} to 10^{-4} and 3.2×10^{-7} to 10^{-4} mol L^{-1} with detection limits of 100 and 45.5 ng mL^{-1}, respectively. In flow injection potentiometry, excellent reproducibility (RSD% = 0.5%), fast response, high sensitivity, high sampling rate (50 sample h $^{-1}$), and stable baseline was observed in the presence of 5×10^{-2} mol L^{-1} NaOH and 10^{-1} mol L^{-1} KI as a carrier for $[CP][Pb(OH)_3]$ and $[Fe(bphen)_3]$ $[PbI_4]$ membrane-based sensors, respectively. Validation of the assay method according to quality assurance standards revealed good performance characteristics and suggests application for routine determination of lead in industrial wastewater and stack emissions of lead smelters.

A plasticized PVC membrane containing 30% PVC, 53.5% orthonitrophenyloctylether (NPOE), 4.5% sodium tetraphenylborate (NaTPB), and 12% ionophore was directly coated on a graphite rod (Gupta et al., 2002b). This sensor gave a good Nernstian response of 29.7 ± 0.7 mV decade^{-1} over a concentration range of 1×10^{-8}–1×10^{-4} M of lead ions, independent of pH in the range 3–7, with a detection limit of 0.4×10^{-8} M. The dynamic response time of the electrode to achieve a steady potential was very fast and found to be less than 7 s. The electrode exhibited adequate stability with good reproducibility (with a slope of 29.6 ± 1.5 mV for eight weeks). The electrode was successfully used as an indicator electrode for a potentiometric titration of a lead solution using a standard solution of EDTA.

Elmosallamy et al. (2008) developed a potentiometric sensor for lead (II) ions based on the use of 1,4,8,11-tetrathiacyclotetradecane (TTCTD) as a neutral ionophore and potassium tetrakis-(p-chlorophenyl)borate as a lipophilic additive in plasticized PVC membranes. The sensor exhibited linear potentiometric response towards lead (II) ions over the concentration range of 1.0×10^{-5}–1.0×10^{-2} mol L^{-1} with a Nernstian slope of 29.9 mV decade^{-1} and a lower limit of detection of 2.2×10^{-6} mol L^{-1} Pb(II) ions over the pH range of 3–6.5. The sensor showed long life span, high reproducibility, fast response, and long-term stability. Validation of the method by measuring the lower limit of detection, lower limit of linear range, accuracy, precision, and sensitivity revealed good performance characteristics of the proposed sensor. The developed sensor is successfully applied to direct determination of lead (II) in



SCH. 9. N,N′- bis(2-hydroxy-1-napthalene)-2,6-pyridiamine.

real samples. Recently, Lisak et al. (2009) developed a PVC-based sensor for Pb(II) determination on N,N′-diheptyl-N,N′,6,6-tetramethyl-4,8-dioxaundecanediamide. A new PVC membrane electrode was prepared by using polyaminoanthraquinone (PAAQ) microparticles with intrinsic electrical conductivity as a lead (II) ionophore (Li et al., 2009). It was found that the electrode performance was significantly improved by adding 1 wt.% PAAQ microparticles and decreasing the membrane thickness. A 90 μm-thick membrane electrode consisting of PAAQ(salt):poly (vinyl chloride):dioctylphthalate:sodium tetraphenylborate of 1:33:66:1 (wt) but without any traditional lead (II) ionophore achieved optimal performance and exhibited a good Nernstian response for Pb(II) ions over a wide concentration range from 2.5×10^{-6} to 0.1 M with a slope of 28.9 mV/decade and a detection limit down to 776 nM. A reasonably short response time of 12 s was revealed, together with a long lifetime over a period of around four months in a wide pH range between 2.8 and 5.2. A fixed interference method indicated that the electrode had an excellent selectivity for lead (II) ion over alkali, alkaline earth, and other heavy metal ions. The proposed electrode was found to be a powerful indicator electrode for potentiometric titration of Pb(II) ions with EDTA and could be used to accurately monitor the Pb(II) pollution in environmental waters.

Poly(n-butyl acrylate) membranes for potentiometric lead-selective ion-selective electrodes were developed by Michalska et al. (2009). A novel approach resulting in Nernstian responses of the tested sensor was proposed. A series of recently synthesized benzo- and pyridine-substituted macrocyclic diamides were studied to characterize their abilities as lead ion carriers in PVC membrane electrodes (Kazemi et al., 2009). The electrode, based on 3,15,21-triaza-4,5;13,14-dibenzo-6,9,12-trioxabicycloheneicosa-1,17,19-t riene-2,16-dione, exhibited a Nernstian response for Pb^{2+} ions over a wide concentration range (1.3×10^{-2} to 3.6×10^{-6} mol L^{-1}) with a limit of detection of 2.0×10^{-6} mol L^{-1} (0.4 ppm). The response time of the sensor is ~16 s, and the membrane can be used for more than two months without observing any deviation. The electrode revealed comparatively good selectivities with respect to many cations, including alkali earth, transition, and heavy metal ions. The proposed sensor could be used in a pH range of 3.7–6.5. It was used as an indicator electrode in potentiometric titration of chromate ions with a lead ion solution.

A Pt wire coated with phenyl hydrazone derivative-carbon composite in a PVC membrane was used for detection of lead (Abbaspour et al., 2010). The sensor had a Nernstian slope of 29.46 ± 0.41 mV/decade over a wide linear concentration range of 7.7×10^{-7} to 1.0×10^{-1} mol L^{-1} for $Pb(NO_3)_2$. The detection limit was 3.2×10^{-7} mol L^{-1}, and the electrode was applicable in the pH range of 3.7–6.3. It had a short response time of approximately 6 s and was used at least for 70 days. The electrode has exhibited good selectivity for Pb(II) relative to 19 other metal ions. The functionality of the proposed sensor was also investigated in a binary water-alcohol mixture, and it concluded that 23% water-methanol and 20% water-ethanol content could not bring out any changes in its potential. The practical analytical utility of the electrode was demonstrated by measurement of Pb(II) in mineral rock.

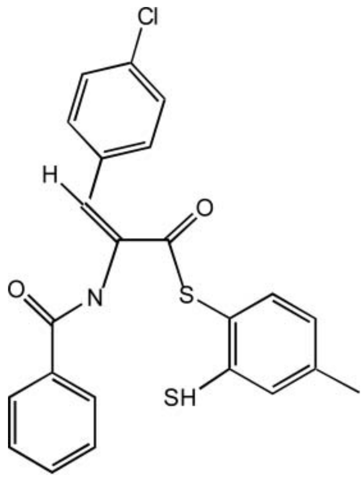
A novel chemical sensor for the highly sensitive and selective determination of Pb^{2+} ions in aqueous solutions was described by Shamsipur et al. (2010) by incorporating L2 as a neutral lead-selective fluoroionophore in the plasticized PVC membrane containing tetrakis(p-chlorophenyl) borate as a liphophilic anionic additive. The response of the sensor is based on the strong selective fluorescence quenching of L2 by Pb^{2+} ions. At pH 5.5, the proposed sensor displays a calibration curve over a wide concentration range of 3.0×10^{-7} to 2.5×10^{-2} M with a relatively fast response time of less than 5 min. In addition to high stability, reversibility, and reproducibility, the sensor shows a unique selectivity towards Pb^{2+} ion with respect to common coexisting cations. The proposed sensor was successfully applied to the determination of lead in plastic toys and tap water sample. Two PVC membrane ion-selective electrodes for Pb(II) ion based on two bis-thioureas, 1,3-bis(N′-benzoylthioureido)benzene and 1,3-bis(N′-furoylthioureido)benzene, as ionophores are reported by Wilson et al. (2010). A first membrane formulated using 1,3-bis(N′-benzoylthioureido)benzene as carrier exhibited a Nernstian response to Pb(II) over a wide concentration range (4.0×10^{-6} to 1.0×10^{-2} M) with a slope of 31.5 ± 1.6 mV/decade. It showed a fast response time ($t_{90\%} = 14$ s) and could be used for 10 weeks without any divergence in potentials. The membrane formulated using 1,3-bis(N′-furoylthioureido)benzene as carrier exhibited a Nernstian response in the concentration range 5.0×10^{-6} to 1.0×10^{-2} M, with a slope of 30.0 ± 1.3 mV/decade. Its response time was $t_{90\%} = 14$ s, and it could be used for 14 weeks without any divergence in potentials. The two proposed potentiometric sensors revealed acceptable selectivities for Pb(II) over a wide variety of other metal ions and could be used in a pH range of 2.2–6.0. Both electrodes were assayed in direct potentiometric determination of lead in soils (10–30 mg/kg range) with very good performance.

Ion et al. (2010) fabricated a Pb^{2+}-selective sensor from PVC matrix membranes containing the ionophore 3,7,11-tris (2-pyridylmethyl)-3,7,11,17-tetraazabicyclo [11.3.1] heptadeca-1(17),13,15-triene (I). The membrane with the composition of I:PVC:o-NPOE:KTpClPB in the percentage ratio (wt.%) of 2:32:60:6 exhibited the best performance, having a slope of 28.5 ± 0.2 mV/decade in the concentration range 10^{-6}–10^{-1} M, a response time of 20 s, and a lifetime longer than four months. The sensor was selective for Pb^{2+} ions over other monovalent, divalent, and trivalent interfering cations and could be used in the pH range of 5–8. The high selectivity in the presence of Cd^{2+} may be important for further studies. The efficiency of the proposed sensor was demonstrated by its application in Pb^{2+} ion determination in water samples. Wardak (2011) prepared a new PVC membrane sensor for Pb^{2+} with solid contact based on an ionic liquid. The electrode shows a Nernstian response for lead ions over a wide concentration range (1×10^{-8} to 1×10^{-1} mol L^{-1}) and a slope of 29.8 mV/decade. The limit of detection is 4.3×10^{-9} mol L^{-1}. It has a fast response time of 5–7 s and can be used for four months without any divergence in potential. The proposed sensor is not pH sensitive in the range 3.5–7.3 and shows a very good discriminating ability towards Pb^{2+} ion in comparison with some alkali, alkaline earth, transition, and heavy metal ions. It was successfully applied as an indicator electrode in potentiometric titration of lead ions with K_2CrO_4 and for direct determination of Pb^{2+} ions in a real sample solution.

Mercury

Mercury is a heavy metal that occurs naturally in the environment. Release of mercury from natural sources has remained fairly stable over the years. Still, mercury concentrations in the environment are increasing; this is ascribed to human activity. Most of the mercury released from human activities is released into air, through mining, solid waste combustion, and industrial wastewater disposal. Mercury has a number of adverse effects on humans, like disruption of the nervous system, damage to brain functions, DNA and chromosomal damage, and negative reproductive effects.

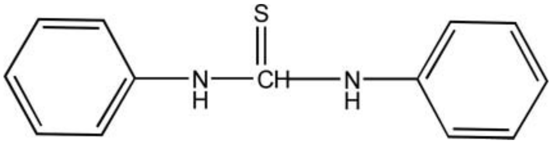
A new ion-selective PVC membrane electrode based on salicyladehyde thiosemicarbazone as an ionophore was developed successfully for mercury (II) ions by Mahajan et al. (2002). The electrode showed excellent potentiometric response characteristics and displayed a linear log [Hg^{2+}] versus EMF response over a wide concentration range of 1.778×10^{-6}–1×10^{-1} M with a Nernstian slope of 29 mV/decade with a detection limit of 1×10^{-6} M. The sensor was also applied as an indicator electrode for potentiometric titration of Hg^{2+} ions with I^- and $Cr_2O_7{}^{2-}$. Another mercury ion–selective electrode was prepared with a polymeric membrane based on a calixarene derivative containing a thiazole azo group as ionophore by Lu et al. (2003). The ISE gave two kinds of response slopes of 61.1 mV/decade in the concentration range of 7.5×10^{-6}–5×10^{-2} M. Another, which has a typical Nernstian response for Hg^{2+}, is obtained at pH 4.0 with a slope of 28.7 mV/decade in the concentration range of 5×10^{-6}–5×10^{-2} M. The construction, performance, and applications of coated-wire mercury (II)-selective electrodes based on 2- mercaptobenzimidazole (MBIM), 2-mercaptobenzothiazole (MBTH), and hexathiacyclooctadecane (HT18C6) carriers in a PVC matrix were described by Mazloum (2000). They were used as indicator electrodes in the potentiometric titration of Hg^{2+} with EDTA and for determination of mercury in wastewater samples. A mercury (II) ion–selective PVC membrane electrode based on Et-2-benzoyl-2-phenylcarbamoyl acetate (EBPCA) as novel nitrogen-containing sensing material was successfully developed by Hassan et al. (2000). The sensor exhibited good linear response of 30 mV/decade within a concentration range of 1×10^{-6}–1×10^{-3} M. The EBPCA-based sensor was suitable for use with aqueous solutions of pH 2.0–4.5 and exhibited minimal interference from Ag(I) and Fe(III), which are known to interfere with other previously suggested sensors.



SCH. 10. 2-benzoylamino-3-(4-chloro-phenyl)-thioacrylic acid *S*-(2-mercapto-4-methyl-phenyl) ester.

A new PVC membrane electrode for Hg(II) ion based on a recently synthesized mercapto compound of 2-benzoylamino-3-(4-chloro-phenyl)-thioacrylic acid *S*-(2-mercapto-4-methyl-phenyl) ester (see Scheme 10) has been reported (Bagheri et al., 2003). The electrode exhibited a Nernstian response for Hg^{2+} ions over a wide concentration range (2.0×10^{-7}–3.0×10^{-2} M) with a slope of 29 (± 1). The limit of detection was 5.0×10^{-8} M. The proposed sensor revealed good selectivities over a wide variety of other cations, including hard and soft metals. This electrode could be used in a pH range of 1.0–4.0. It was used as an indicator electrode in potentiometric titration of mercury (II) ions and can be used in the direct determination of Hg^{2+} in aqueous solutions.

A new liquid membrane, mercury (II) ion–selective electrode based on 1,3-diphenylthiourea (see Scheme 11) as a neutral carrier was developed (Perez-Marin et al., 2000). In solubility tests of 1,3-diphenylthiourea in six different plastizicers, tris(2-ethylhexyl) phosphate (TEHP) showed the best performance and was selected for the membrane. Several ISEs were conditioned and tested for the selection of seven metal ions (Hg^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}, and Ag^{+}). The best Nernstian response was obtained for Hg^{2+} with an experimental slope of 58.6 ± 0.8 mV/decade in the concentration range 6.0×10^{-6}–5.0×10^{-4} mol L^{-1}; the presence of the complex $Hg(OH)^+$ ion explains the slope of the response curve. The ISE showed stable detection



SCH. 11. 1,3-Diphenylthiourea.

reproducibility during six weeks, with a practical detection limit of 10^{-6} mol dm^{-3} and a high selectivity for Cd^{2+}, Pb^{2+}, Co^{2+}, Cu^{2+}, Sr^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, K^{+}, Na^{+}, and $NH_4{}^{+}$ ions. Only Ag^{+} was found to interfere. A second linear response curve for Hg^{2+} was obtained at pH 4 with a slope of 30.8 mV/decade in the concentration range 2.0×10^{-6}–2.1×10^{-4} mol L^{-1}.

Mahajan et al. (2004a) developed a PVC-based sensor with improved working range on *p*-tert-butyl calix [4] crowns with imine units. Gupta et al. (2005c) developed a highly selective mercury electrode based on a diamine donor ligand. Gupta et al. (2007a) further tried to improve the working parameter for a Hg(II) selective sensor; they reported on 2-amino-6-purinethiol (I_1)- and 5-amino-1,3,4-thiadiazole-2-thiol (I_2)-based Hg^{2+} selective sensors, and it was concluded that the performance characteristics of the sensors were improved by using DOP and DOS as plasticizers. The results show that the two plasticizers exhibit wide working concentration ranges of 7.0×10^{-8}–1.0×10^{-1} M and 1.5×10^{-6}–1.0×10^{-1} M with Nernstian slope of 30.0 and 27.7 mV $decade^{-1}$ activity, for (I_1) and (I_2) ionophores, respectively.

Hassan et al. (2006) developed two novel potentiometric sensors that are highly selective to Hg $^{2+}$ ions. These are based on the use of 5,5′-dithio-bis(2-nitrobenzoic acid) (DTNB) and tricyclazole (TCZ) as neutral carriers in plasticized PVC membranes. Fast Nernstian responses are obtained for Hg^{2+} ions over the concentration ranges 7.0×10^{-6}–1.0×10^{-2} and 7.7×10^{-6}–1.0×10^{-2} mol L^{-1} at pH 1.8–3.3 with lower detection limits of 5.0×10^{-6} and 5.6×10^{-6} mol L^{-1} (~ 1 μg mL^{-1}) and calibration slopes of 30.0 and 29.7 mV $decade^{-1}$ with DTNB- and TCZ-based membrane sensors, respectively. Validation of the assay method reveals good performance characteristics, including long life span, good selectivity for Hg^{2+} ions over a wide variety of other metal ions, long-term response stability, and high reproducibility. Applications for direct determination of mercury in hazardous wastes including dental amalgam, mercury bulbs, and fluorescent lamps give results with good correlation with data obtained using cold vapor atomic absorption spectrometry.

Ganjali et al. (2007) prepared a new PVC membrane potentiometric sensor that is highly selective to Hg^{2+} ions, using bis(2-hydroxybenzophenone) butane-2,3-dihydrazone (HBBD) as an excellent hexadendates neutral carrier. The sensor works satisfactorily in the concentration range of 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} (detection limit of 4×10^{-7} mol L^{-1}) with a Nernstian slope of 29.7 mV/decade. This electrode showed a fast response time ($\times 8$ s) and was used for at least 12 weeks without any divergence. The sensor exhibits good Hg^{2+} selectivity for a broad range of common alkali, alkaline earth, transition, and heavy metal ions (lithium, sodium, potassium, magnesium, calcium, copper, nickel, cobalt, zinc, cadmium, lead, and lanthanum). The electrode response is pH independent in the range of 1.5–4.0. Furthermore, the developed sensor was successfully used as an indicator electrode in the potentiometric titration of mercury ions with potassium iodide and the direct determination of mercury in some binary and ternary mixtures.

A new PVC membrane electrode based on 4-(4-N,N-dimethylphenyl)-2,6-diphenylpyrilium tetrafluoroborate as the ionophore was prepared by Yu et al. (2007) that shows good selectivity for mercury (II) ions. The electrode indicates a good linear response for mercury (II) over a wide concentration range from 1.0×10^{-8} to 1.0×10^{-3} M, with a near-Nernstian slope of 34 mV/decade and a detection limit of 1.0×10^{-8} M. This membrane electrode operates well in the pH range of 2.5–7.0 and can be used for at least 30 days without observing any considerable deviation. Selectivity coefficients of some mono-, di-, and trivalent metal ions were also determined. The sensor exhibits high selectivity towards mercury (II) compared with the alkali, alkaline earth, and transition metal ions. The electrode was also applied as an indicator electrode for potentiometric titration of mercury (II) ion with Γ.

Mercury ion-selective electrodes were prepared by Mahajan et al. (2007) with a polymeric membrane based on heterocyclic systems 2-methylsulfanyl-4-(4-nitro-phenyl)-l-p-tolyl-1H-imidazole (I) and 2,4-diphenyl-1-p-tolyl-1H-imidazole (II) as the ionophores. The electrodes based on these ionophores showed a good potentiometric response for Hg^{2+} ions over a wide concentration range of 5.0×10^{-5}–1.0×10^{-1} M with near-Nernstian slopes. Stable potentiometric signals were obtained within a short time period of 20 s. The detection limit and the working pH range of the electrodes were 1.0×10^{-5} M and 1.6–4.4 respectively. The electrodes showed better selectivity for Hg^{2+} ions over many of the alkali, alkaline-earth, and heavy metal ions. Also, sharp end points were obtained when these sensors were used as indicator electrodes for the potentiometric titration of Hg^{2+} ions with iodide ions.

A novel PVC membrane electrode that exhibits high potentiometric response for Hg^{2+} based on bis(amino-triazole sulfurethers) (BATS) as an suitable neutral carrier was developed by Li et al. (2007). The electrode exhibits a wide concentration range of 4.0 mg/L–20 g/L (the limit of detection is 1.7 mg/L) for $Hg(NO_3)_2$ with a Nernstian slope of 33.4 mV/decade at pH 2.0. It has a fast response time of about 10 s and can be used for at least two months. The membrane sensor could be used in pH 1.3–3.3 and revealed good selectivity for Hg^{2+} over a wide variety of other metal ions. The electrode was applied to the determination of mercury in wastewater and different binary mixtures with satisfactory results.

Ensafi et al. (2008) developed a new ion-selective PVC membrane sensor based on bis(benzoyl acetone) diethylene triamine as a potentiometrie sensor for Hg^{2+} ions. The membrane having bis(benzoyl acetone) diethylene triamine as an electroactive material, sodium tetraphenyl phthalate (NaTPB), and dibutyl phthalate (DBP) as an anion excluder in PVC matrix in the percentage ratio of 4.21:2.11:60.25:33.43 (ionophore:NaTPB:DBP:PVC) (w/w) exhibits a linear response to Hg^{+} ions in a concentration range of 1.0×10^{-8} to 1.0×10^{-1} M with a limit of detection of 3.7×10^{-7} M and with a slope of 29.8 ± 1.0 mV/decade over the pH range of 2.0–11.5. Selectivity coefficients for Hg(II) relative to a numbers of potential interfering ions were investigated. The sensor is highly selective for Hg^{2+} ions over a large number of mono-, bi-, and trivalent cations. Normal interferents like Ag^+ and Cd^{2+} do not interfere in the working of the sensor. The sensor has been found to be chemically inert to other ions and shows a fast response time of 1 s; it was used over a period of three months with good reproducibility. The sensor was successfully applied to determine mercury (II) in water samples with satisfactory results.

A mercury (II) ion–selective PVC membrane sensor based on dimethylsulfoxide (DMSO) as a novel oxygen- and sulfur-containing sensing material was successfully developed by Saleh et al. (2008). This reagent has the advantage of low cost and simple chemical material. Dioctylphthalate (DOP) solvent could be selected from different solvents used. DOP was found to play an important role in directing selectivity. Sodium tetraphenylborate (NaTPB) as a lipophilic salt and KC1 solution of 10^{-1} M as an inner solution also have been chosen. The sensor exhibited a good linear response of 30 ± 0.2 mV/decade within the concentration range 10^{-8}–10^{-2} and a detection limit of 0.9 $\times$ 10^{-8}mol L^{-1} Hg(II). Also, it showed good selectivity and fast response for mercury (II) ion with relation to some alkali, alkaline earth, transition, and heavy metal ions. The DMSO-based sensor was suitable for aqueous solutions of pH range 1.5 to 4.0. Moreover, it can be used for three months without any considerable divergence in potential. The formation constant of ionophore complex with Hg(II) ion was calculated by using the segmented sandwich membrane method. The proposed sensor was applied as an indicator electrode for potentiometric titration of Hg(II) ion with EDTA solution, as well as with I^-, OH^-. and $IO3^-$ ions. In addition, the solubility products for the previous ions were determined.

Hosseini et al. (2009) constructed a PVC membrane electrode for Hg(II) ions, based on a new cone-shaped calix[4]arene (L) as a suitable ionophore. The sensor exhibits a linear dynamic in the range of 1.0×10^{-6}–1.0×10^{-1} M, with a Nernstian slope of 29.4 ± 0.4 mV decade^{-1}, and a detection limit of 4.0×10^{-7} M. The response time is quick (less than 10 s), it can be used in the pH range of 1.5–4, and the electrode response and selectivity remained almost unchanged for about two months. The sensor revealed comparatively good selectivity with respect to most alkali, alkaline earth, and some transition and heavy metal ions. It was successfully employed as an indicator electrode in the potentiometric titration of Hg^{2+} ions with potassium iodide and the direct determination of mercury content of amalgam alloy and water samples.

Rofouei et al. (2009) developed a plasticized PVC membrane electrode based on 1,3-bis(2-methoxybenzene)triazene (MBT) for highly selective determination of mercury (II). The electrode showed a good Nernstian response (30.2 ± 0.3 mV decade^{-1}) over a wide concentration range (1.0×10^{-7}–1.0×10^{-2} mol L^{-1}). The limit of detection was 5.0×10^{-8} mol L^{-1}. The electrode has a response time about 15 s and can be used for at least one month without observing any deviation from Nernstian response. The proposed electrode revealed an excellent selectivity toward mercur y(II) ion over a wide variety of alkali, alkaline earth, transition, and heavy metal ions and could be used in the pH range 2.6–4.2. The electrode was used in the determination of Hg^{2+} in aqueous samples and as an indicator electrode in potentiometric titration of Hg(II) ions.

Yang et al. (2010) developed a series of calix[4]arene-dithiacrown-5 and -dithiacrown-6 compounds in cone and 1,3-alternate conformations. Responses of these ionophores to Hg^{2+} and competing metal ions were determined in solvent polymeric membrane electrodes. High potentiometric selectivity for Hg^{2+} over Na^+ and a variety of transition and heavy metal ions was obtained. Tyagi et al. (2010a) developed a PVC-based membrane containing p-tert-butylcalix[4]arenethioether derivative as active material along with sodiumtetraphenylborate (NaTPB) as solvent mediator and dibutylphthalate as a plasticizer in the ratio 45:9:460:310 (w/w%) (I:NaTPB:DBP:PVC); it exhibits good properties with a Nernstian response of 29.50 ± 1.0 mV per decade of activity and a working concentration range of 7.2×10^{-8}–1.0×10^{-1} M. The electrode gave stabler potential readings when used around pH 2.5–6.8 and exhibits fast response time of 14 s. The sensors were found to work satisfactorily in partially nonaqueous media up to 40% (v/v) content of acetone, methanol, or ethanol and could be used over a period of seven to nine months. Excellent selectivity for Hg^{2+} ions is indicated by the match potential and fixed interference methods. The sensors could be used successfully in the estimation of mercury in different samples.

Li et al. (2010) developed a novel PVC thin-film light-addressable potentiometric sensor sensitive to mercury (II) ion, tested by gradient concentrations. PVC matrix with 5-amino-1, 3, 4-thiadiazole-2-thiol was prepared and used as target material. The light-addressable potentiometric sensor (LAPS) sensor was chemically modified by silanization. The sensitivities before and after the reaction are 67.299 mV per pH and 4.999 6 mV per pH, and the linear correlations are 0.983 1 and 0.987 7, respectively. Once the PVC membrane was deposited, Hg^{2+}-sensitive LAPS exhibits good stability and repetition. The sensitivity of the potentiometric response shows the slope of 15.381 mV per pHg. The detection limit of the sensor was 1.57 μg/L. The response time maintained 2–4 s, and the application range of pH was located between 3 and 6.

More recently, Khan and Paquiza (2011) synthesized and characterized a cation exchanger polyaniline-zirconium titanium phosphate (PANI-ZTP) nanocomposite for use as electroactive component for the construction of an ion-selective membrane electrode for the detection of mercury (II) ion in aqueous solution.The proposed electrode shows fairly good discrimination of mercury ion over several other inorganic ions. The membrane electrode was mechanically stable, having a wide dynamic range of 10^{-10} to 10^{-1} mol/m^3 of Hg^{2+} ions, with quick response time, and could be operated for at least four months without any considerable divergence in the potential response characteristics. The electrode was successfully applied for direct determination of mercury ions in some real samples with satisfactory results and acts as indicator electrode in complexation titrations.

Zinc

Zinc occurs naturally in air, water, and soil, but zinc concentrations are rising unnaturally due to addition of zinc through human activities. Most zinc is added during industrial activities, such as mining, coal and waste combustion, and steel processing. Although humans can handle proportionally large concentrations of zinc, too much zinc can still cause significant health problems such as stomach cramps, skin irritations, vomiting, nausea, and anemia. Very high level of zinc can damage the pancreas and disturb protein metabolism and cause arteriosclerosis. Extensive exposure to zinc chloride can cause respiratory disorders.

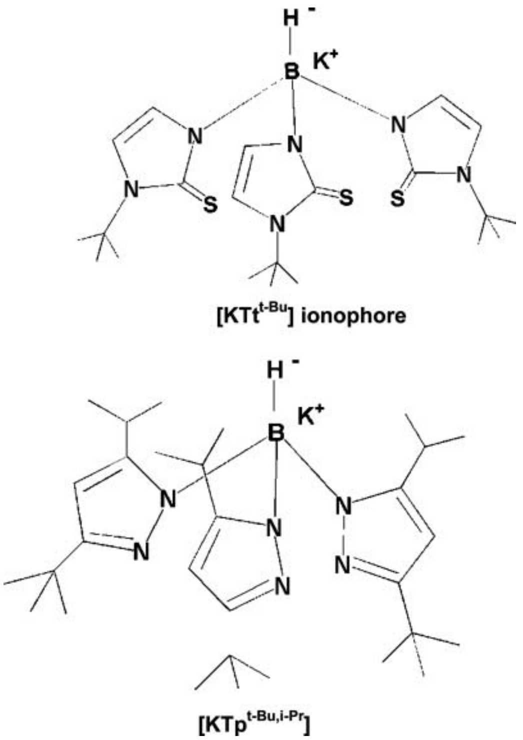
A new PVC membrane electrode for zinc ions based on a recently synthesized benzo-substituted macrocyclic diamide (1,13-diaza-2,3;11,12;15,18-tribenzo-4,7,10-trioxacyclononaoctane-14,19-dione) as membrane carrier was prepared by Shamsipur et al. (1999). The sensor exhibited a Nernstian response for Zn^{2+} over a wide concentration range (1.0×10^{-1}–9.0×10^{-5} M). Gupta et al. (2001) reported a PVC-based membrane incorporating 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine as an electroactive material, sodium tetraphenyl borate (NaTPB) as an additive, and tri-*n*-butyl phosphate (TBP) as solvent mediator, in the ratio 200:5:2:150 (w/w) (PVC:ionophore:NaTPB:TBP) as a Zn^{2+}-selective sensor. The sensor works in a wide concentration range (6.2×10^{-6}–1.0×10^{-1} M) with Nernstian slope (29.0 ± 1.0 mV/decade of activity) and a response time as fast as 12 s. The working pH range of the sensor is 3.8–7.7, and it can tolerate a nonaqueous content up to 25% (v/v) (acetone, methyl alcohol, and ethyl alcohol). A PVC-based membrane of hematoporphyrin IX exhibiting good potentiometric response for Zn^{2+} over a wide concentration range (5×10^{-5}–1×10^{-1} mol dm^{-3}) with a slope of 28.6 mV/decade of Zn^{2+} concentration was reported by Jain et al. (2002). The response time of the sensor is as fast as 30 s, and it has been used for a period of three months. It exhibits selective response towards Zn^{2+} in comparison to alkali, alkaline earth, and heavy metal ions and functions satisfactorily in the pH range 2.0 to 5.5. In another work, an optimal composition for pseudo-liquid membrane chelating potential phase of a zinc function was established by Dumkiewicz et al. (2000). Its basic analytical parameters, such as the slope of characteristics (29 mV $\mathrm{p}a_{\mathrm{Zn}}^{-1}$), the detection limit ($5.6 \times 10^{-6}$ mol dm^{-3}), lifetime (40 days), response time (10 s), and selectivity against nickel, cobalt, cadmium, calcium, magnesium, and sodium ions, as well as the dependence of the electrode potential on pH, were established. The electrode was used to determine the presence of zinc ions in vitamin preparations. The results obtained were compared with the determination made by use of a voltammetric method. Zn^{2+}-selective sensors based on disodium salt of porphyrin 3,7,12,17-tetramethyl-8,13-divinyl 2,18-porphine dipropionic acid have also been reported to exhibit selective response to Zn^{2+} ions (Gupta et al., 2003b). Gupta et al. (2005a) reported a zinc-selective sensor based on dibenzo-24-crown-8 (I) having a working range of 9.2×10^{-5} to 1.0×10^{-1} M, Nernstian slope of 29.0 ± 0.5 mV/decade of activity, fast response time of 12 s, and good selectivity over a number of mono-, bi-, and trivalent cations. The sensor works well in a pH range 4.8–6.2. Zamani et al. (2006) reported a Zn^{2+}-selective sensor based on 5,6-benzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacos-5-ene (BHDE). The proposed sensor exhibits a Nernstian behavior (with slope of 29.1 ± 0.4 mV/decade) over a wide concentration range (1.0×10^{-6}–1.0×10^{-1} mol L^{-1}) with a detection limit of 6.3×10^{-7} mol L^{-1} (41.2 ng mL^{-1}). It can be used for at least 10 weeks in a pH range of 2.8–7.3. Singh et al. (2006d) reported a $[Bzo_2Me_2Ph_2(16)hexaeneN_4]$ (**I**)-based Zn^{2+}-selective sensor. It has shown the concentration range 2.82×10^{-6}–1.0×10^{-1} M with a Nernstian slope of 28.5 ± 0.2 mV/decade of concentration with a detection limit of 2.24×10^{-6} M (0.146 ppm); it should have a response time of less than 10 s and could be used in the pH range 2.5–8.5.

A PVC membrane electrode for Zn^{II} ion based on a heterogeneous chelating inorganic ion exchange resin, i.e., tetracycline hydrochloride sorbed tin (IV) tungstophosphate, was reported by Agarwal and Chandra (2006). The electrode works well over a wide range of concentrations (1.5×10^{5} to 1×10^{-1} M) with a Nernstian slope of 27.3 mV/decade of concentration. The electrode shows a fast response time of 25 s and operates in the pH range 4–6. The sensor can be used for more than three months without any divergence in the potential. The selectivity of the electrode was studied and it was found that the electrode exhibits good selectivity for zinc ions over a wide variety of cations including alkaline earth, transition, and heavy metal ions. The zinc ion selectivity electrode was used an indicator electrode for the potentiometric titration of zinc ions in solution against standard EDTA solution. The sensor had tremendous applicability to zinc (II) ion measurements in high tensile brass.

The potentiometric response characteristics of electrodes based on N,N′-bis(acetylacetone)ethylenediimine (I) in PVC combined with an anion localizing agent (sodium tetraphenyl borate, NaTPB) and solvent mediators o-nitrophenyl octyl ether (NPOE), dibutyl (butyl) phosphonate (DBBP), tri-n-butyl phosphate (TBP), and chloronaphthalene (CN) were investigated by Gupta et al. (2006g). The best result for Zn^{2+} sensing was obtained for the electrode membrane of the composition of I:PVC:NaTPB:NPOE = 5:100:6:200, where the electrode had a Nernstian response (30.0 mV/decade of Zn^{2+} activity) to Zn^{2+} within the concentration range of 1.0×10^{-6} to 1.0×10^{-1} M. The operational pH range of the electrode was 3.2–7.1. Selectivity characteristic of the proposed electrode was also assessed by calculating KA,BPot with a fixed interference method. The sensor has been successfully used in real sample analysis and also in the potentiometric titration of zinc ions with EDTA. The same authors further developed PVC-based membranes containing 4-tert-butylcalix[4]arene (I) as an electroactive material along with anion excluder sodiumtetraphenylborate (NaTPB) and plasticizer tri-butylphosphate (TBP) to fabricate a new zinc-selective sensor (Gupta et al., 2006i). Out of various compositions, the best performance was exhibited by the membrane having I, NaTPB, TBP, and PVC in the ratio 8:5:100:200 (w/w). The sensor works well in the concentration range 9.8 × 10^{-6} to 1.0 × 10^{-1} mol dm^{-3} with a near-Nernstian slope of 28.0 ± 1.0 mV/decade of activity. The detection limit is down to 5.0 × 10^{-7} mol dm^{-3}. The working pH range of this sensor is 2.5–4.3, and it works well in partially nonaqueous medium up to 15% (v/v) (methanol, ethanol, and acetone). It exhibits a fast response time of 30 s and could be used for more than four months without any considerable change in response characteristics. It has excellent selectivity for Zn(II) over other mono-, bi-, and trivalent cations that have been reported to cause interference in the working of other sensors. It has been successfully used as an indicator electrode in the potentiometric titration of Zn(II) against EDTA and also to estimate zinc ions in industrial wastewater. A Zn^{2}-selective sensor has been fabricated by Gupta et al. (2006h) using PVC matrix membranes containing a neutral carrier dithizone (I) as an ionophore. The sensor exhibited the best performance for the following membrane composition: (I):PVC-sodium tetraphenyl borate-1-chloronapthalene (5:150:2:150). This membrane worked well over a wide concentration range of Zn^{2+}, i.e., 5.1 × 10^{-6}–1.0 × 10^{-1} mol L^{-1}, and the corresponding calibration plots exhibited a Nernstian slope of 29.7 ± 0.1 mV/decade of Zn^{2+} activity. The response time of the sensor was shorter than 8 s, and the membrane could be used over a period of six months with good reproducibility. The proposed sensor could be operated over a wide pH range (3.1–6.5) and demonstrated good selectivity towards the analyte in the presence of several mono-, di-, and trivalent cations. It could be also used in partially nonaqueous media containing up to 20% (v/v) of methanol, ethanol, or acetone, and its Nerstian slope in the working concentration range remained almost unchanged. The proposed sensor has been used for determination of Zn^{2+} in human hair samples by direct potentiometry.

Singh et al. (2007d) further worked on zinc selective sensors and reported potassium hydrotris(N-tert-butyl-2-thioimidazolyl) borate [KTt$^{\text{t-Bu}}$]- and potassium hydrotris(3-tert-butyl-5-isopropyl-l-pyrazolyl)borate [KTp$^{\text{t-Bu,i-Pr}}$]-based zinc-selective sensors (see Scheme 12). The best performance was reported with [KTt$^{\text{t-Bu}}$], over a range of 1.4 × 10^{-7} to 1.0 × 10^{-1} mol L^{-1}, with a limit of detection of 9.5 × 10^{-8} mol L^{-1}. It had a relatively fast response time (12 s) and could be used for three months without substantial change of the potential. The membrane sensor had very good selectivity for Zn^{2+} ions over a wide variety of other cations and could be used in a working pH range of 3.5–7.8.

A liquid membrane–based Zn^{2+} ion-selective electrode containing N,N′-Bis(2-dimethylaminoethyl)-N,N′-dimethyl-9,10 anthracenedimethanamine (Bis(TMEDA) anthracene) (I) as ionophore has been prepared and characterized by Gupta et al. (2008c). The membrane comprises PVC, ionophore, and plasticizer in the ratio of 33:2:65. It showed the best response in terms of detection limit (1.5 × 10^{-6} M) and working concentration range (1.0 × 10^{-5} M to 1.0 × 10^{-1} M) with Nernstian response towards Zn^{2+} ions. The electrode responds within 15 s of coming in contact with the solution. The potential response remains almost unchanged over a pH range of 3.0–7.5. The electrode can be used for at least three months without any considerable alteration in its response behavior. The proposed electrode detected Zn^{2+} ions from real life samples.



SCH. 12. Zinc-selective sensors.

A potentiometric membrane Zn(II) ion sensor was described based on 3-hydroxy-2-naphthoic hydrazide (HNH) (Gohlivand et al., 2009). The sensor exhibited a Nernstian response over a concentration range of 1.8 × 10^{-7}–3.6 × 10^{-1} mol L^{-1}, with a detection limit of 1.1 × 10^{-7} mol L^{-1}. The best performance was achieved with a membrane composition of 33% PVC, 62% dibutylphethalate (DBP), and 5% HNH. It was found that in the pH range of 2.3–5.4, the potential response of the sensor was not affected by the pH. Furthermore, the electrode presented satisfactory reproducibility, fast response time (<18 s), and relatively good discriminating ability for Zn(II) ions with respect to many common cations and transition metal ions. The sensor was applied to the determination of zinc in seawater, tap water, urine, and human hair.

More recently, a highly selective and sensitive zinc ion-selective membrane electrode based on N,N′-phenylenebis (salicylideaminato) (L) as a new carrier is reported by Hosseini et al.

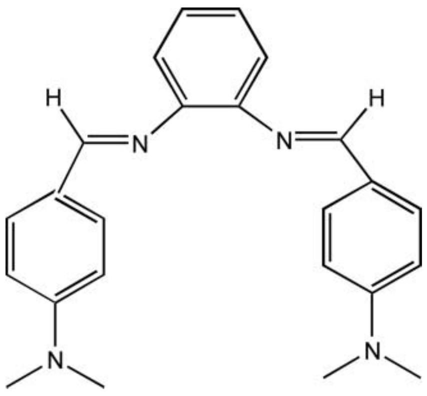
(2011). The membrane is composed of PVC, o-nitrophenyl octyl ether (NPOE) as plasticizer, potassium tetrakis(p-chlorophenyl) borate (KTpClPB), as lipophilic ionic additive, and L as sensing material. The proposed electrode displays a Nernstian response to Zn^{2+} ions over a wide concentration range of 5.0×10^{-7}–1.0×10^{-1} M with a slope of 29.4 ± 0.2 mV/decade and a detection limit of 2.6×10^{-7} M. The sensor has a relatively fast response time of <10 s and it can be used in the pH range of 3.0–7.0 for at least two months without any significant divergence in potential. The selectivity coefficients for mono-, di-, and trivalent cations indicate the good selectivity of the sensor for Zn^{2+} ions over a large number of interfering cations. As a result, the proposed electrode was applied to Zn^{2+} ion determination in mixture solutions and wastewater samples.

Nickel

For many decades, nickel was regarded as a potentially toxic element, since its concentration in various foods was higher than that needed for living organisms. It is now considered as 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 (Pais and Jones, 1997).

A new PVC membrane electrode that is highly selective to Ni(II) ions was prepared by Mashhadizadeh et al. (2003) by using *N*,*N*′-bis-(4-dimethylamino-benzylidene)-benzene-1,2-diamine (NDBBD) as a suitable neutral carrier (see Scheme 13). The sensor exhibits a Nernstian response for nickel ions over a wide concentration range (1.0×10^{-2} to 2.0×10^{-7} M) with a slope of 30 ± 1 mV/decade. It has a response time of <10 s and can be used for at least two months without any measurable divergence in potential. The electrode can be used in the pH range from 4.5 to 9.0.

Mazloum et al. (2002) explored the use of 1,3,7,9,13,15,19,21-octaazapentacyclooctacosane (pentacyclooctaaza) as a neutral ionophore for preparing PVC-based membrane sensors selective to Ni(II). The optimized membrane incorporating pentacyclooctaaza as the active material, dibutyl phthalate as plasticizer, and sodium tetraphenyl borate as an anion excluder and membrane modifier in PVC (in the weight ratio of 5.5:56.5:5.5:32.5, respectively) was directly coated on the surface of a platinum-wire electrode. The electrode exhibited a near-Nernstian response in the concentration range of 1×10^{-6} to 1×10^{-1} M Ni(II). The limit of detection, as determined from intersection of the extrapolated linear segments of the calibration graph, was 6×10^{-7} M. It has a response time between 5 and 40 s for nickel concentrations ranging from 1×10^{-1} to 1×10^{-6} M. The electrode revealed moderate selectivities over a number of alkali, alkaline earth, and several transition and heavy metal ions. The electrode is suitable for use in aqueous solutions in a wide pH range of 3–6. It was applied as an indicator electrode for end point detection in the potentiometric titration of Ni(II) with ethylenediaminetetraacetic acid (EDTA) and determination of nickel content of chocolate and milk powder samples. Another PVC membrane nickel(II) ion-selective electrode was constructed by Mousavi (2000a) using 1,10-dibenzyl-1,10-diaza-18-crown-6 (DBzDA18C6) as a neutral carrier. The sensor exhibits a Nernstian response for Ni(II) ions over a wide concentration range (5.5×10^{-3}–2.0×10^{-5} M). It has a relatively fast response time and can be used for at least six weeks without any considerable divergence in potentials. The proposed sensor revealed relatively good selectivity for Ni(II) over a wide variety of other metal ions and could be used in a pH range of 4.0–8.0. It was used as an indicator electrode in potentiometric titration of nickel ions. A PVC membrane electrode for Ni^{2+} ions based on a recently synthesized mercapto compound as an ionophore was prepared (Mashhadizadeh and Momeni, 2003). The electrode exhibits a Nernstian slope of 28–30 mV per concentration decade at a wide concentration range of 1.0×10^{-2}–1.0×10^{-7} M. It has a fast response time of <15 s and can be used for at least four weeks. The potentiometric response is independent of the pH of the test solution in the pH range 5–8.5. The proposed electrode revealed good selectivity over a wide variety of other cations including alkali, alkaline earth, transition, and heavy metal ions. It was successfully applied to the direct determination and potentiometric titration of nickel ion with EDTA.



SCH. 13. NDBBD.

Another potentiometric sensor based on 5,7,8,14-tetramethyldibenzo[b,i]-1,4,8,11-tetraazacyclotetradecanenickel(II) chloride was fabricated for Ni^{2+} ions (Gupta et al., 2002a). The sensor exhibits a linear response to Ni^{2+} in the concentration range 7.0×10^{-6}–1.0×10^{-1} M with a slope of 29.8 ± 0.2 mV/decade of activity and works well in the pH range 2.0–7.6. The compound 5,7,12,14-tetramethyldibenzotetraazaannulene (Me4Bzo2TAA) was explored by Gupta et al. (2000) as an electroactive material for preparing PVC-based membrane electrodes selective to Ni^{2+}. The membrane having the constituents Me4Bzo2TAA, Na tetra-Ph borate (NaTPB), and PVC in the optimum ratio 2:1:97 (wt./wt.) gave the best working concentration range (7.9×10^{-6}–1.0×10^{-1} M) with a Nernstian slope of 30.0±1.0 mV/decade of activity in the pH range 2.7–7.6. Jain et al. (2005a) reported nickel-selective sensors with comparative analysis based on two nickel chelates of Schiff bases, *N*-(2-hydroxybenzyl)-*N*_-(2-hydroxybenzylidene)ethylenediamine Ni(II) (I) and *N*-(2-hydroxybenzylidene)-*N*_-(2-picolyl)ethylenediamine Ni(II) (II). The best performance was obsereved with the membrane sensor based on chelate (II). The sensor has shown the range 3.2 × 10^{-6} to 5.0 × 10^{-2} M Ni(II) and performs satisfactorily over wide pH range of (2.2–5.9) with a fast response time (∼10 s). The sensor was also found to work satisfactorily in partially nonaqueous media up to 25% (v/v) content of acetone, methanol, or ethanol and could be used over a period of four months.

Yari et al. (2006) reported that a dioxime derivative, (2E, 3E)-2H-1,4-benzothiazine-2,3(4H)-dione dioxime ionophore, for the preparation of a PVC membrane electrode for Ni(II) ions was investigated. The proposed sensor worked over a wide concentration range (1.0 × 10^{-6} to 1.0 M) with a detection limit of 1.6 × 10^{-6} M at a working pH range of 2.0–6.5. A new PVC membrane ion-selective electrode that is highly selective towards Ni(II) ions was constructed using a Schiff base containing a binaphthyl moiety as the ionophore (Kumar et al., 2006b). The sensor exhibited good Nernstian response for nickel ions over the concentration range 1.0 × 10^{-1}–5.0 × 10^{-6} M with a lower limit of detection of 1.3 × 10^{-6} M. It has a fast response time and can be used for a period of four months with a good reproducibility. The sensor is suitable for use in aqueous solutions in a wide pH range of 3.6–7.4 and works satisfactorily in the presence of 25% (v/v) methanol or ethanol. The sensor shows high selectivity to nickel ions over a wide variety of cations. It has been successfully used as an indicator electrode in the potentiometric titration of nickel ions against EDTA and also for the direct determination of nickel content in real samples: effluent samples, chocolates, and hydrogenated oils. The suitability of a dioxime derivative, (2E, 3E)-2H-1,4-benzothiazine-2,3(4H)-dione dioxime, as a neutral ionophore for the preparation of a PVC membrane electrode for Ni(II) ions was investigated by Gupta et al. (1997). It can be used for at least four months without any considerable divergence in potentials and it has a relatively fast response of <10 s. The prepared membrane exhibits a near-Nernstian response for Ni^{2+} ions over a wide concentration range (1.0 × 10^{-6} to 1.0 M) with a detection limit of 1.6 × 10^{-6} M. At a working pH range of 2.0–6.5 the proposed membrane electrode revealed very good selectivity for Ni^{2+} ions over a wide variety of other cations. It was applied successfully as an indicator electrode in potentiometric titration of nickel ions with EDTA and in the determination of Ni^{2+} in some water samples. Kumar et al. (2006a) reported a nickel (II) selective sensor based on thiophene-derivative Schiff base. The sensor worked over the concentration range of 1.0 × 10^{-1}–5.0 × 10^{-6} M (limit of detection of 1.8 ×10^{-6} M) with a slope of 29.5 ± 1.0 mV per decade of activity. It has a fast response time of < 20 s and can be used for a period of four months with good reproducibility. The sensor is suitable for use in aqueous solutions of a wide pH range of 3.2–7.9.

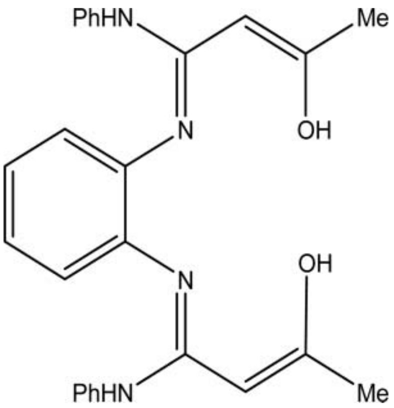
Gupta et al. (2007d) reported a Ni^{2+}-selective sensor based on dibenzo-18-crown-6. The sensor worked well over a working range of 1.0 × 10^{-5} to 1.0 × 10^{-1} M and a Nernstian slope of 29.5 mV/decade of activity with a pH range of 2.6–6.8.

PVC-based membranes of meso-tetrakis-{4-[tris-(4-allyl dimethylsilyl-phenyl)-silyl]-phenyl}porphyrin (I) and $(sal)_2$trien (II) as electroactive material with dioctylphthalate (DOP), tri-n-butylphosphate (TBP), chloronapthalene (CN), dibutylphthalate (DBP) and dibutyl(butyl) phosphonate (DBBP) as plasticizing solvent mediators have been found to act as Ni^{2+}-selective sensors by Gupta et al. (2007e). The best performance was obtained with the sensor having a membrane of composition of I:sodium tetraphenyl borate:PVC in the ratio 5:5:150. The sensor exhibits Nernstian response in the activity range 2.5 × 10^{-6} to 1.0 × 10^{-1} M and performs satisfactorily over wide pH range (2–5.5) with a fast response time (∼8 s). The sensor was found to work satisfactorily in partially nonaqueous media up to 20% (v/v) content of methanol or ethanol and acetone and could be used over a period of four months. Potentiometric selectivity coefficients determined by the matched potential method (MPM) indicate excellent selectivity for Ni^{2+} ions. The sensors could be used successfully in the estimation of nickel in different brands of chocolate and also as an indicator electrode in potentiometric titration.

Zamani et al. (2008a) developed a PVC membrane containing 5-methoxy-5,6-diphenyl-4,5 dihydro-3(2H)-pyridazinethione (LH_2) as a suitable ionophore, which exhibits a Nernstian response for Ni^{2+} ions over a wide concentration range between 1.0 × 10^{-2} and 1 × 10^{-6} M, with a limit of detection of 6.7 × 10^{-7} M. It has a fast response time (<15 s), operates well in the pH range of 4.0–6.0, and can be used for at least 45 days without observing any considerable deviation. This sensor presented very good selectivity and sensitivity towards the Ni^{2+} ions over a wide variety of cations, including alkali, alkaline earth, transition, and heavy metal ions. The practical utility of the proposed chemical sensor has been observed by using it as an indicator electrode in the titration of Ni^{2+} ions with EDTA. The electrode was also used for nickel ion detection in the sample wastewater of industrial nickel electroplating.

Gupta et al. (2008b) further worked on a Ni^{2+}-selective sensor to improve the working parameters and reported a comparative analysis based on Schiff bases, 3-hydroxy-N-{2-[(3-hydroxy-N-phenylbutyrimidoyl)-amino]-phenyl}-N′-phenylbutyramidine (M_1) (see Scheme 14) and bis-4-(ethyliminomethyl)naphthalene-1-ol (M_2) (see Scheme 15). The sensor based on M_1 showed the best performancic characteristics over a wide concentration range of 1.6 × 10^{-7} to 1.0 × 10^{-2} M with Nernstian compliance (30.0 ± 0.2 mV/decade of activity) within a pH range of 2.5–9.5 and a fast response time of 10 s.

A novel polymeric membrane electrode (PME) and a coated graphite electrode (CGE) for nickel ion were prepared based

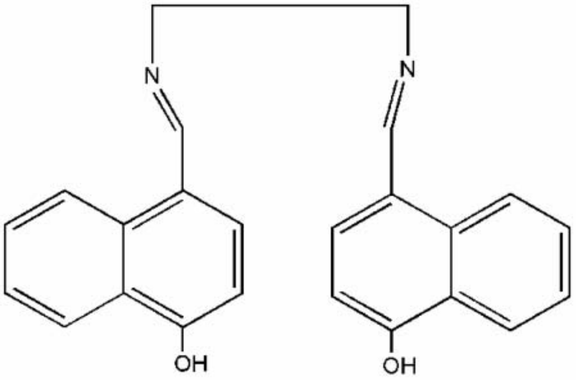


SCH. 14. 3-Hydroxy-N-{2-[(3-hydroxy-N-phenylbutyrimidoyl)amino]phenyl}-N′-phenylbutyramidine (M_1).

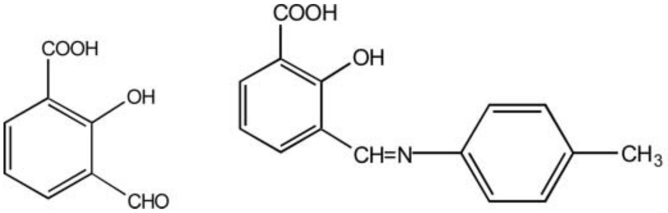
on 2,9-(2-methoxyaniline) $_2$-4,11-Me_2-[14]-1,4,8,11-tetraene-1,5,8,12-N_4 as a suitable neutral ionophore by Singh et al. (2009a). The best performance was obtained for the membrane sensor having a composition of I:NaTPB:TBP:PVC in the ratio 6:4:100:90 (w/w; mg). The electrodes exhibit Nernstian slopes for Ni^{2+} ions over wide concentration ranges of 4.6×10^{-7}–1.0×10^{-1} M for PME and 7.7×10^{-8}–1.0×10^{-1} M for CGE with limits of detection of 2.7×10^{-7} M for PME and 3.7×10^{-8} M for CGE. The response times for PME and CGE was found to be 10 and 8 s respectively. The potentiometric responses are independent of the pH of the test solution in the pH range 3.0–8.0. The proposed electrodes revealed good selectivities over a wide variety of other cations including alkali, alkaline earth, transition, and heavy metal ions. The coated graphite electrode was used in direct determination in different fruit juices and wine samples.

Iron

Iron is an essential metal and is used for the treatment of anemia, but excessive intake or overdosing requires a selective analytical method and medication. Iron is the principal alloying element in steel manufacture. During the welding process, iron oxide fumes arise from both the base metal and the electrode. The primary acute effect of this exposure is irritation of nasal passages, throat, and lungs.



SCH. 15. 4-(E)-2-(E)-(4-Hydroxynaphthalen-1yl) methyleneamino ethylimino methyl naphthalene-1-ol (M_2).

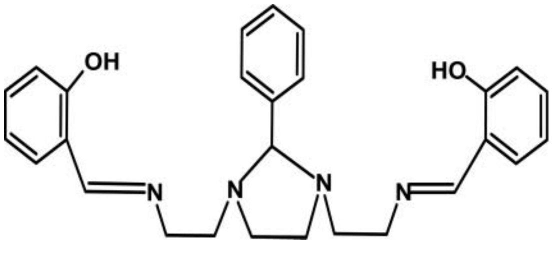


SCH. 16. Formylsalicylic acid derivatives.

Novel iron (III)-selective PVC membrane electrodes based on formylsalicylic acid derivatives (see Scheme 16) were studied by Saleh (2000). The electrode based on *p*-chloroaniline-3-formylsalicylic acid as a sensor, containing potassium tetrakis(4-chlorophenyl)borate as a lipophilic salt and *o*-nitrophenyl octyl ether as a plasticizer, gave the best performance. The electrode exhibits good Nernstian response for 10^{-1}–5.0×10^{-5} mol L^{-1} $FeCl_3$ with a slope of 20 mV/decade. It shows a high selectivity for iron (III) in comparison with alkali, alkaline earth, and heavy metal ions. The electrode response and selectivity remained almost unchanged for at least one month. The effects of plasticizers, membrane supports, lipophilic salts, and pH on the potential response of the electrode were also studied. The electrode was successfully applied to the determination of iron (III) contents in some rocks.

The work described by Gupta et al. (2011b) comprises the determination of Fe(III) by ion-selective potentiometry using a coated-wire ion-selective electrode (CWISE) based on iron-cyclam complex. Linear Nernstian response for this electrode was obtained over the total Fe(III) concentration range of 1×10^{-2} to 1×10^{-6} M in 0.05 M HNO_3, H_2SO_4, $HClO_4$, HCl, KNO_3, and KCl media, with a slope of 60 ± 5 mV/decade change. Working pH range of the electrode was found to be 1.3–3.5. Selectivity coefficients of some mono- and divalent metal ions were determined. Analysis of alloys, electroplating bath solutions, and pharmaceutical samples has been carried out using this CWISE, and the results are found to be comparable with those obtained by using conventional methods. A PVC membrane potentiometric sensor that is highly selective to Fe(III) ions was prepared (Mashhadizadeh et al., 2004) by using 2-[(2-hydroxy-1-propenyl-buta-1,3-dienylimino)-methyl]-4-*p*-tolylazo-phenol [HPDTP] as a suitable carrier. The electrode exhibits a linear response for iron (III) ions over a wide concentration range (3.5×10^{-6} to 4.0×10^{-2}) with a super Nernstian slope of 28.5 (± 0.5) per decade. The electrode can be used in the pH range from 4.5 to 6.5. The proposed sensor shows fairly a good discriminating ability towards Fe^{3+} ion in comparison to some hard and soft metals such as Fe^{2+}, Cd^{2+}, Cu^{2+}, Al^{3+}, and Ca^{2+}. It has a response time of <15 s and can be used for at least two months without any measurable divergence in response characteristics. The electrode was used in the direct determination of Fe^{3+} in aqueous samples and as an indicator electrode in potentiometric titration of Fe(III) ions.

Mahmoud (2001) described the composition and general performance characteristics of four PVC membrane sensors respective to iron. Three of these sensors are based on the ion association complexes of iron (II) 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ) with tetraphenylborate (TPB) or phosphotungstic acid (PTA) as novel electroactive materials dispersed in dibutyl sebacate plasticizer on glass assemblies and solid-state graphite support. The fourth sensor is based on a plasticized carboxylated PVC matrix membrane. The developed sensors were used for the assay of iron in some pharmaceutical preparations. The sensors displayed a rapid and linear response for doubly charged iron over the concentration range from 5×10^{-7} to 10^{-2} M. The pH does not affect the sensor performance within the pH range 3.2–7.1. Acceptable selectivity was obtained for iron against many inorganic cations, sugar, and amino acids. The constructed sensors were used as indicator electrodes in potentiometic titration of $[Fe(TPTZ)_2]^{2+}$ with tetraphenylborate solution in standard and various pharmaceutical forms. The sensors can be used for more than three months without observing any deviations. Sil et al. (2005) reported a coated-wire ion-selective electrode (CWISE) based on iron-cyclam complex. The sensor has shown a concentration range of 1×10^{-2} to 1×10^{-6} M with a slope of 60 ± 5 mV/decade change. The working pH range of the electrode was found to be 1.3–3.5. Ekmekci et al. (2007) reported a *trans*-dinitro-dibenzo-18-6 crown–based iron (III)–selective sensor. The sensor worked over a potential range of 1×10^{-6} to 1×10^{-1} M with a slope of 57 ± 1 mV/10-fold concentration changes in iron (III). Gupta et al. (1999b) reported bis-bidentate Schiff base (BBS)–based iron (III)–selective sensor with a working range of 1.0×10^{-7}–1.0×10^{-2} M and a low detection limit (7.49×10^{-8} M). The potentiometric response of the sensor is independent of pH of the solution in the pH range 1.9–5.1. Gupta et al. (2007f) reported a 2-phenyl-1,3-bis[3′-aza-4′-(2′-hydroxyphenyl)-prop-4-en-1′-yl]-1,3-imidazolidine (I)–based iron (III)–selective sensor (see Scheme 17) that worked over a improved concentration range of 6.3×10^{-6} to 1.0×10^{-1} M (detection limit 5.0×10^{-6} M) with Nernstian slope of 20.0 mV/decade of activity between pH 3.5 and 5.5 with a quick response time of 15 s.



SCH. 17. 2-phenyl-1,3-bis[3′aza-4′-(2′-hydroxyphenyl)-prop-4-en-1′-yl]-1,3-imidazolidine (V).

A Fe^{3+} ion-selective membrane sensor was fabricated from PVC matrix membrane containing bis-bidentate Schiff base (BBS) as a neutral carrier, sodium tetraphenyl borate (NaTPB) as anionic excluder, and o-nitrophenyloctyl ether (NPOE) as a plasticizing solvent mediator (Zamani et al., 2008b). The effects of the membrane composition, pH, and additive anionic influence on the response properties were investigated. The best performance was obtained with a membrane containing 32% PVC, 62.5% NPOE, 3% BBS, and 2.5% NaTPB. The electrode shows a Nernstian behavior (slope of 19.3 ± 0.6) over a very wide iron ion concentration range (1.0×10^{-7}–1.0×10^{-2} M) and has a low detection limit (7.4×10^{-8} M). The potentiometric response of the sensor is independent of pH of the solution in the pH range 1.9–5.1. The proposed sensor has a very low response time ($<$15 s) and a good selectivity relative to a wide variety of other metal ions including common alkali, alkaline earth, heavy, and transition metal ions. The electrode can be used for at least 60 days without any considerable divergence in potentials. The proposed sensor was successfully applied as an indicator electrode for the potentiometric titration of 1.0×10^{-2} M Fe^{3+} ions with 1.0×10^{-4} M EDTA and the direct determination of Fe^{3+} in mineral water and wastewater samples.

An inorganic cation exchanger, aluminum tungstate (AT), has been synthesized by adding 0.1 M sodium tungstate gradually into 0.1 M aluminium nitrate at pH 1.2 with continuous stirring (Naushad, 2008). A Fe(III) ion-selective membrane electrode was prepared by using this cation exchange material as an electroactive material. It was observed that the membrane containing the composition AT:PVC:DBP in the ratio 2:20:15 displayed a useful analytical response with excellent reproducibility, low detection limit, wide working pH range (1–3.5), quick response time (15 s), and applicability over a wide concentration range of Fe(III) ions from 1×10^{-7} to 1×10^{-1} M with a slope of 20 ± 1 mV/decade. The selectivity coefficients were determined by the mixed solution method and revealed that the electrode was selective for Fe(III) ions in the presence of interfering ions. The electrode was used for at least five months without any considerable divergence in response characteristics. The constructed sensor was used as indicator electrode in the potentiometric titration of Fe(III) ions against EDTA and Fe(III) determination in a rock sample, a pharmaceutical sample, and a water sample. The results are found to be in good agreement with those obtained by using conventional methods.

Zamani et al. (2008c) developed a a unique ionophore for the selective determination of Fe(III) ions. This ionophore was N-(2-hydroxyethyl)ethylenediamine-N,N′,N″-triacetic acid (NTA), presenting a high affinity towards trivalent iron cations. The designed sensor exhibited a wide linear response with a slope of 19.5 ± 0.4 mV/decade over the concentration range of 1.0×10^{-9}–1.0×10^{-2} mol L^{-1}, while the illustrated detection limit was 3.0×10^{-10} mol L^{-1} of the Fe(III) ion concentration. It was concluded that the sensor response was pH independent in the range of 1.8–4.5. The sensor possessed the advantages of short conditioning time, fast response time (10 s), and, especially, good selectivity towards the transition and heavy metal ions as well as some mono-, di-, and trivalent cations. Concerning the electrode lifetime, no considerable potential divergence was noticed for at least 10 weeks. Sensor accuracy was investigated in the potentiometric titration of a Fe(III) solution with EDTA.

The construction, performance characteristics, and application of a novel iron (III) membrane sensor based on a new bis-benzilthiocarbohydrazide (BBTC) are reported by the same authors (Zamani et al., 2009c). The sensor is prepared by incorporating BBTC, nitrobenzene (NB), and sodium tetraphenyl borate (NaTPB) into a plasticized PVC membrane. The electrode reveals Nernstian behavior over a wide iron ion concentration range (1.0×10^{-2}–1.0×10^{-7} mol L^{-1}) and relatively low detection limit (8.6×10^{-8} mol L^{-1}). The potentiometric response is independent of the pH of the solution in the range of 1.6–4.3. The electrode shows a very short response time (<10 s). The proposed electrode can be used for at least nine weeks without any considerable divergence in potentials. It exhibits very good selectivity relative to a wide variety of alkali, alkaline earth, transition, and heavy metal ions. In fact, the selectivity of the proposed sensor shows great improvement compared to the previously reported electrodes for the iron ion.

A new PVC membrane electrode that is highly selective to Fe(II) ions was prepared using N-phenylaza-15-crown-5 (NPA15C5) as a suitable neutral carrier by Aghaie et al. (2009a). The sensor shows a Nernstian response for Fe(II) ions over a wide concentration range (1.0×10^{-2} to 1.0×10^{-6} M) with a slope of 29.2 ± 0.6 mV/decade. It has a response time of <15 s and can be used for at least two months without any measureable divergence in potential. The electrode was used for direct determination of Fe^{2+} in ferrous sulfate syrup.

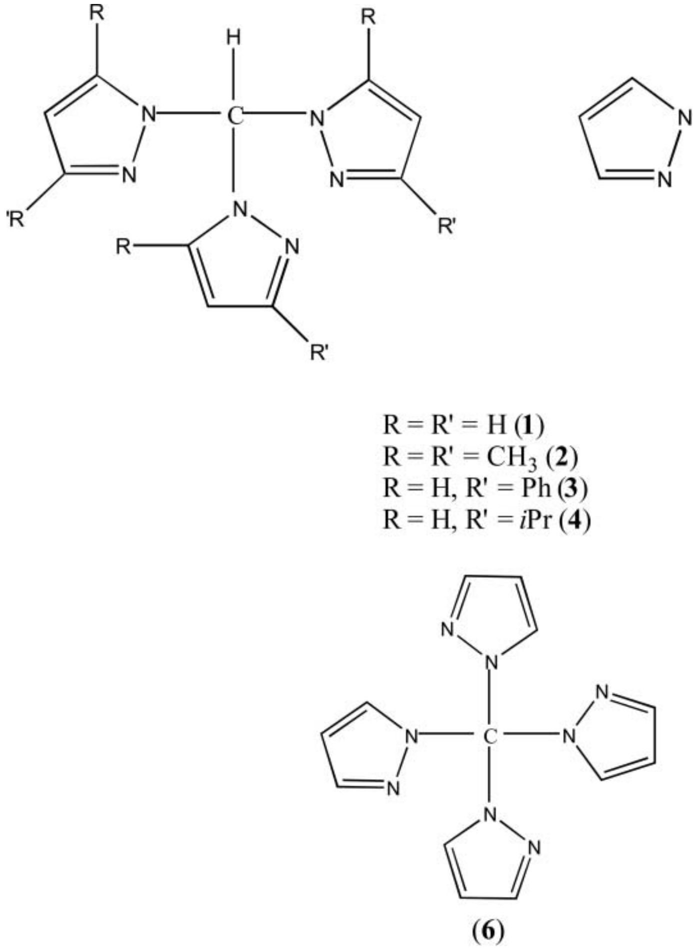
Zamani et al. (2009a) prepared a new PVC membrane electrode that is highly selective to Fe^{3+} ions by using 4,4′-dimethoxybenzil bisthiosemicarbazone (DBTS) as a suitable neutral carrier. The membrane incorporating 4,4′-dimethoxybenzil bisthiosemicarbazone (DBTS) as ionophore with composition DBTS:NaTPB:NB:PVC in the ratio 2:2:64:32 (w/w) exhibits the best result for potentiometric sensing of Fe^{3+} ions. The electrode exhibited a near-Nernstian response to Fe^{3+} in the concentration range of 1.0×10^{-6} to 1.0×10^{-2} M with a slope of 19.4 ± 0.5 mV/decade. The proposed sensor can be used over a period of two months. The lower limit of detection was 3.6×10^{-7} M. This electrode showed high selectivity with respect to alkaline, alkaline earth, and heavy metal ions and could be used over a pH range of 1.8–5.0. It has been successfully used as an indicator electrode in potentiometric titration of Fe^{3+} against EDTA as well as for the determination of Fe^{3+} in water sample solutions (tap and mineral water samples).

Babakhanian et al. (2010) developed a iron (III)-PVC membrane sensor based on a new 1,1′-(iminobis(methan-1-yl-1-ylidene))dinaphthalen-2-ol (IBMYD) synthetic ionophore as a suitable carrier. The best performance was observed for the membrane composition including 33.0% PVC, 65.0% TEHP, 1.0% NaTPB, and 1.0% ionophore. The electrode displayed a linear potential response over a wide concentration range from 1.0×10^{-7} to 1.0×10^{-1} mol L^{-1}, with a detection limit of 5.0×10^{-8} mol L^{-1} and a good Nernstian slope of 19.9 ± 0.3 mVdecade^{-1}. The sensor possessed some advantages such as short conditioning time, very fast response time (<12 s), and, especially, good discriminating ability towards Fe(III) ions over a wide variety of alkali, alkaline earth, transition, and heavy metal ions. The potential response of the proposed sensor was independent of the pH of the test solution in the pH working range from 3.0 to 6.3. The fabricated electrode was applied for at least two months without any measurable divergence in the potential characteristics. The optimized sensor was used successfully for direct and indirect determination of free iron species in some different synthetic and real samples with satisfactory results.

Copper

Copper is a very common substance that occurs naturally in the environment and spreads through the environment through natural phenomena. Humans widely use copper. For instance, it is applied in industry and in agriculture. The production of copper has increased over recent decades, and due to this, copper quantities in the environment have expanded. Copper can be found in many kinds of food, in drinking water, and in air. Because of that we absorb significant quantities of copper each day by eating, drinking, and breathing. The absorption of copper is necessary, because copper is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of copper, too much copper can still cause health problems. Long-term exposure to copper can cause irritation of the nose, mouth, and eyes, and it causes headaches, stomachaches, dizziness, vomiting, and diarrhea. Intentionally high uptake of copper may cause liver and kidney damage and even death.

Recently, plasticized membranes using Schiff base complexes, derived from 2,3-diaminopyridine and *o*-vanilin, have been prepared and explored as Cu^{2+}-selective sensors (Singh and Bhatnagar, 2004). The sensor works satisfactorily in the concentration range 5.0×10^{-6} to 1.0×10^{-1} M (detection limit 0.3 ppm) with a Nernstian slope of 29.6 mV per decade of activity. Wide pH range (1.9–5.2), fast response time (<30 s), high nonaqueous tolerance (up to 20%), and adequate shelf life (>4 months) indicate the vital utility of the proposed sensor. The tolerance level of Hg^{2+}, which causes serious interference in the determination of Cu^{2+} ions ($K_{Cu}{}^{2+}{}_{Hg}{}^{2+Pot}$(MPM): 0.45), was determined as a function of Cu^{2+} concentration in simulated mixtures. Abbaspour and Kamyabi (2002) demonstrated a PVC membrane electrode for copper ion based on 1,3-dithiane,2-(4-methoxy phenyl) as ionophore and *o*-nitrophenyl octyl ether as a plasticizer. The electrode exhibits a Nernstian slope of 29.5 ± 1 mV/decade in a linear range of 3.0×10^{-6} to 5.0×10^{-2} M



(5)

R = R' = H (**1**)
R = R' = CH_3 (**2**)
R = H, R' = Ph (**3**)
R = H, R' = *i*Pr (**4**)

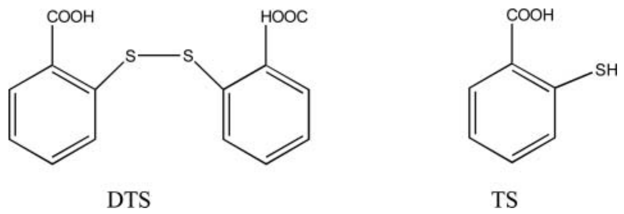
(6)

SCH. 18. Polypyrazolylmethanes.

for Cu^{2+} ion. The detection limit of this electrode is 1.0×10^{-6} mol/L. This sensor has a very short response time of about 5 s and could be used in a pH range of 4.0–7.0.

The potential response of cyanocopolymer-based Cu^{2+} ion-selective electrodes has been studied (Gupta and D'Arc, 2001) as a function of concentration of ionophore (Schiff's base complex), plasticizer (dioctylphthalate), and molecular weight of the cyanocopolymers. The concentration variation in electrode constituents has shown significant effect on the sensitivity, selectivity, detection limits, response, time and extent of interference from foreign ions during potentiometric measurements of electroactive ions. The hydrophobic nature and high dipole moment of the employed cyanocopolymers enhanced the average lifetime of the electrode and shows the least interference from solution anions. Electrodes prepared with an optimum amount of the ionophore (2.7×10^{-2} mol kg^{-1}), plasticizer (2.1×10^{-3} mol kg^{-1}), and cyanocopolymers (2.0 g) of molecular weight 59.565 kg mol^{-1} have shown a Nernstian slope of 27.59 ± 0.053 mV per decade activity of the Cu^{2+} ions with a response time of 13.00 ± 0.002 s. These electrodes with an optimized amount of constituents have shown a working range of 2.5×10^{-7} to 1.0×10^{-2} mol dm^{-3} activities of the Cu^{2+} ions. The electrode response as a function of concentration variation of ionophore, plasticizer, and molecular weights of cyanocopolymers has been explained in terms of ionophore interaction energy and plasticization of the polymer matrix.

Yoshimoto et al. (2003) developed novel ion-selective membrane electrodes based on polypyrazolylmethanes, represented by the general formula $H_{4-n}C(pz)_n$ (pz: 1-pyrazolyl) (see Scheme 18). $HC(pz)_3$ (**1**), $HC(3,5\text{-}Me_2pz)_3$ (**2**), $HC(3\text{-}Phpz)_3$ (**3**), $HC(3\text{-}i\text{Prpz})_3$ (**4**), $HOCH_2C(pz)_3$ (**5**), and $C(pz)_4$ (**6**) were prepared and incorporated as an ionophore in a PVC membrane. The selectivity of the electrodes changed with the substituents of polypyrazolylmethanes. The electrodes of **3**, **4**, and **6** were selective for Cu^{2+} at pH 5.5. The electrode of **5** was selective for Pb^{2+} and Cu^{2+} at pH 5.5. Since the selectivity coefficient log $K_{Cu,M}^{pot}$ of electrode **4** was less than −6.4 for the divalent cations, it was the most selective for Cu^{2+} among all Cu^{2+} selective electrodes ever reported. The detection limit and dynamic range for Cu^{2+} were 2×10^{-6} and 10^{-6} to 5×10^{-3} M,



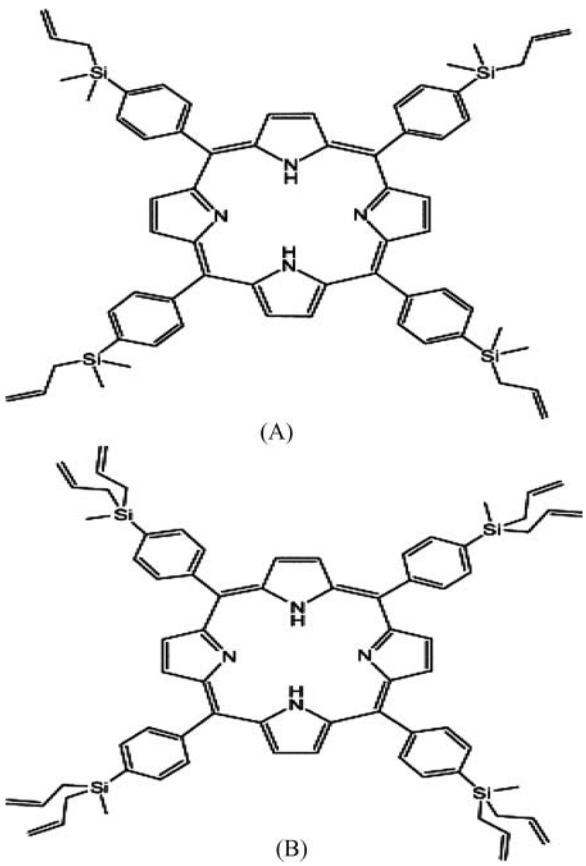
SCH. 19. Dithiosalicylic acid and thiosalicylic acid.

respectively. Electrode **4** showed rapid response time (∼10 s) and reproducible results for more than four months and was successfully applied to potentiometric titration of Cu^{2+} with EDTA.

Potentiometric carbon paste electrodes for copper (II) based on dithiosalicylic and thiosalicylic acids are described by Gismera et al. (2003). The sensor based on dithiosalicylic acid (DTS) exhibits a linear response with a nearly Nernstian slope of 27.7 mV/decade, whereas the electrode based on thiosalicylic acid (TS) shows a super-Nernstian slope (see Scheme 19). The limits of detection for the DTS sensor and the TS sensor are $10^{-7.9}$and $10^{-6.3}$ M for copper (II) activity, respectively. The DTS electrode is successfully used for potentiometric titration of humic acids with copper in order to get more information about complexing properties of these acids.

Copper (II) complex of ethambutol was prepared by Gupta et al. (2003a) and used in the fabrication of a Cu^{2+-}selective ISE membrane. The membrane having Cu(II)-ethambutol complex (I) as electroactive material, along with sodium tetraphenylborate (NaTPB) as anion discriminator, and dioctylphthalate (DOP) as plasticizer in a PVC matrix in the percentage ratio 6:2:190:200 (I:NaTPB:DOP:PVC) (wt./wt.) gave a linear response in the concentration range 7.94×10^{-6} to 1.0×10^{-1} M of Cu^{2+} with a slope of 29.9 ± 0.2 mV per decade of activity and a fast response time of 11 ± 2 s.

Jain et al. (2005c), incorporating bis[acetylacetonato] Cu(II), bis[ethylacetoacetate] Cu(II), and bis[salicyldehyde] Cu(II) chelates, developed Cu(II)-selective sensors. The best responsive sensor worked well in the concentration range of 1.0×10^{-5} to 1.0×10^{-1} for Cu^{2+} with Nernstian slope. Zamani et al. (2005) reported a zinc selective sensor based on 6-methyl-4-(1-phenylmethylidene)amino-3-thioxo-1,2,4-triazin-5-one (MATTO) as an excellent sensing material. The electrode exhibits a Nernstian slope of 29.2 ± 0.4 mV/decade over a very wide concentration range between 1.0×10^{-1} and 1.0×10^{-6} M, with a detection limit of 4.8×10^{-7} M (30.5 ng/mL). The sensor has the working pH range of 3.0–6.8. In 2006 a great deal of work was been done on Cu^{2+}-selective sensors: Ardakani et al. (2006), based on 1,8bis(2-hydroxynaphthaldiminato)3, 6-dioxaoctane; Singh et al. (2006a), with comparative analysis based on 3-(2-pyridinyl)-2H-pyrido[1,2,-a]-1,3,5-triazine-2,4(3H)-dithione (L_1) and acetoacetanilide (L_2); and Gupta et al. (2006c), based on porphyrins meso-tetrakis-[4-(allyl dimethyl silyl)phenyl] porphyrin (**A**) and meso-tetrakis-[4-(diallyl methyl silyl)phenyl] porphyrin (**B**) (see Scheme 20). Mahajan et al. (2007) reported a copper (II)-selective sensor based on 2,2′:5′,2″-terthiophene. The sensor worked over a concentration range of 5.0×10^{-6}–1.0×10^{-1} M.



SCH. 20. Meso-tetrakis-[4-(allyl dimethyl silyl)phenyl] porphyrin (A) and meso-tetrakis-[4-(diallyl methyl silyl)phenyl] porphyrin (B).

Copper (II) complex of 2,4-dimethyl-1,5,9,12-tetraazacyclopentadeca-1,4-diene, $[Me_2(15)dieneN_4]$ was synthesized by Singh et al. (2006b) and used in the fabrication of a Cu^{2+}-selective ISE membrane in a PVC matrix. The membrane has Cu(II) macrocyclic complex as electroactive material along with sodium tetraphenyl borate (NaTPB) as anion discriminator. Dibutyl phthalate (DBP) as plasticizer in a PVC matrix was prepared for the determination of Cu^{2+}. The best performance was observed by the membrane having Cu(II) complex PVC-NaTPB-DBP with composition 1:5:1:3. The sensor worked well over the concentration range of 1.12×10^{-6}–1.0×10^{-1} M between pH 2.1 and 6.2, with a fast response time of 10 ± 2 s and a lifetime of six months. Electrodes exhibited excellent selectivity for Cu^{2+} ion over other mono-, di-, and trivalent cations. In the same year, Norouzi et al. (2006) developed a Cu^{2+} ion-selective membrane microelectrode from a PVC matrix membrane containing a new symmetrical hexadentate Schiff base 2-{1-(E)-2-((Z)-2-{(E)-2-[(Z)-1-(2-hydroxyphenyl) ethylidene] hydrazono}-1-methylpropylidene)hydrazono]ethyl}phenol (HDNOS) as a neutral carrier, potassium tetrakis(4-chlorophenyl) borate (KTpClPB) as an anionic excluder, and o-nitrophenyloctyl ether (NPOE) as a plasticizing solvent mediator. The microelectrode displays linear potential response in the concentration range of 1.0×10^{-5}–1.0×10^{-11} M of Cu^{2+}. The microelectrode exhibits a nice Nernstian slope of 25.9 ± 0.3 mV decade^{-1} in the pH range of 3.1–8.1. The sensor has a relatively short response time in whole concentration ranges (∼5 s). The detection limit of the proposed sensor is 5.0×10^{-12} M (320 pg/L), and it can be used over a period of eight weeks. The proposed membrane electrode was used for the direct determining of Cu^{2+} content in black and red pepper and in a wastewater sample.

Shamsipur et al. (2007) fabricated a novel PVC membrane (PME) and coated graphite (CGE) Cu^{2+}-selective electrodes based on 5,6,7,8,9,10-hexahydro-2H-1,13,4,7,10-benzodioxatriazacyclopentadecine-3,11(4H,12H)-dione [161]. The electrodes reveal a Nernstian behavior over wide Cu^{2+} ion concentration ranges (1.0×10^{-7}–1.0×10^{-1} M for PME and 1.0×10^{-8}–1.0×10^{-1} M for CGE) with very low limits of detection (7.8×10^{-8} M for PME and 9.1×10^{-9} M for CGE). The potentiometric responses are independent of the pH of the test solutions in the pH range 2.7–6.2. The proposed electrodes possess very good selectivities for Cu^{2+} over a wide variety of the cations including alkali, alkaline earth, transition, and heavy metal ions. The practical utility of the proposed electrodes has been demonstrated by their use in the study of interactions between copper ions and human growth hormone (hGH) in biological systems, potentiometric titration of copper with EDTA, and determination of copper content of a sheep blood serum sample and some other real samples. Gohlivand et al. (2007) used bis(2-hydroxyacetophenone)butane-2,3-dihydrazone (BHAB) as a new N-N Schiff base in the construction of a Cu(II) membrane sensor. The best performance was obtained with a membrane composition of 30% PVC, 55% o-nitrophenyloctyl ether (NPOE), 7% BHAB, and 8% oleic acid (OA). This sensor shows very good selectivity and sensitivity towards copper ion over a wide variety of cations, including alkali, alkaline earth, transition, and heavy metal ions. The electrode exhibits Nernstian behavior (with a slope of 29.6 mV/decade) over a very wide concentration range (5.0×10^{-8} to 1.0×10^{-2} mol L^{-1}) with a detection limit of 3.0×10^{-8} mol L^{-1} (2.56 ng mL^{-1}). It shows relatively fast response time, in the whole concentration range (<15 s), and can be used for at least 12 weeks in the pH range of 2.8–5.8.

Aksuner et al. (2009) developed a highly sensitive and selective optical sensor for the determination of trace amounts of Cu^{2+}. The sensing membrane was prepared by immobilization of a novel fluorescent Schiff base ligand, 4-(1-phenyl-1-methylcyclobutane-3-yl)-2-(2-hydroxy-5-romobenzylidene)aminothiazole, on PVC. The novel sensor, which has a linear range of 1.0×10^{-8}–5.7×10^{-4} mol L^{-1} for Cu^{2+} ions with a detection limit of 8.8×10^{-9} mol L^{-1} (0.56 μg L^{-1}), is fully reversible and the response time (τ_{90}) was approximately 2.5 min. The optode was highly selective and can readily be regenerated by treatment with 10^{-2} mol L^{-1} HCl. The accuracy of the proposed sensor was confirmed by analyzing standard reference materials of natural water and peach leaves. The sensor was successfully applied for the determination of copper in tap water and tea samples.

Plasticized membranes using 2-[{(2-hydroxyphenyl)imino}methyl]-phenol (L_1) and 2-[{(3-hydroxyphenyl)imino}methyl]-phenol (L_2) have been prepared and investigated as Cu^{2+} ion-selective sensors by Singh et al. (2009b). Optimum performance was observed with membranes of (L_1) having composition L_1:DBS:OA:PVC in the ratio of 6:54:10:30(w/w%). The sensor works satisfactorily in the concentration range 3.2×10^{-8}–1.0×10^{-1} mol L^{-1} with a Nernstian slope of 29.5 ± 0.5 mV decade $^{-1}$ of $a_{cu}2+$. The detection limit of the proposed sensor is 2.0×10^{-8} mol L^{-1} (1.27 ng mL^{-1}). A wide pH range (3.0–8.5), fast response time (7 s), sufficient (up to 25% v/v) no-aqueous tolerance, and adequate shelf life (three months) indicate the utility of the proposed sensor. The potentiometric selectivity coefficients as determined by the matched potential method indicate selective response for Cu^{2+} ions over various interfering ions, and it therefore could be successfully used for the determination of copper in edible oils, tomato plant material, and river water.

Jeong et al. (2010) synthesized a Schiff base 1,2-bis(E-2-hydroxy benzylidene amino)anthracene-9,10-dione and explored it as an ionophore for preparing PVC-based membrane sensors selective to copper ion. The best performance was shown by the membrane of composition (w/w) of ionophore of 1 mg, PVC: 33 mg, DOP: 66 mg, and KT_pClPB as additive was added at 50 mol% relative to the ionophore in 1 mL THF. The proposed sensor's detection limit is 2.8×10^{-7} M over pH 5 at room temperature (Nernstian slope of 31.76 mV/decade) with a response time of 15 s, and it and showed good selectivity to copper ion over a number of interfering cations. Lee et al. (2010) synthesized a new lipophilic bis(salphenH_2) derivative, N, N, N′N″-tetrakis-(3, 5-di-tert-butylsalicylidene)-3, 3′, 4, 4′- biphenylene tetramine, L_1, and tested it as an ionophore for copper (II) ion in (PVC membrane electrodes. The combination of this ditopic receptor, L_1, with dioctylsebacate (DOS) as a plasticizer shows a super-Nernstian slope of 36.1 mV/decade of Cu(II), and a detection limit of 2.0×10^{-6} M is well observed in the pH range from 2.6 to 4.2 with a response time less than 30 s. The proposed electrode in practice offered good end points when the sensor was used as an indicator electrode in the potentiometric titration of copper ions with EDTA. The simple PVC-based membrane containing N,N′,N″,N‴-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (TPMC) as an ionophore and dibutyl phthalate as a plasticizer, directly coated on a glassy carbon electrode, was examined as a new sensor for Cu^{2+} ions by Petković et al. (2010). The potential response was linear within the concentration range of 1.0×10^{-1}–1.0v × v10^{-6} M with a

Nernstian slope of 28.8 mV/decade and detection limit of 7.0 × 10^{-7} M. The electrode was used in aqueous solutions over a wide pH range (1.3–6). The sensor exhibited excellent selectivity for Cu^{2+} ion over a number of cations and was successfully used in its determination in real samples. Kamel et al. (2010) similarly examined a novel macrocyclic calix[4]arene derivative as an ionophore for an ion-selective polymeric membrane electrode toward Cu^{+2} ions. The sensor showed a near-Nernstian response for Cu(II) ions over a concentration range from 8.1 × 10^{-6} to 1.0 × 10^{-2} mol L^{-1} with a slope of 34.2 ± 0.4 mV per concentration decade in an acidic solution (pH 5). The limit of detection was 0.47 μ gmL^{-1}. It had a response time of <20 s and can be used for at least three months without any divergence in potentials. It was shown that membrane electrodes formulated with the ionophore and appropriate anionic additive exhibited enhanced potentiometric response toward Cu^{2+} over all other cations tested. The sensors were used for direct measurement of copper content in different rocks collected from different geological zones. The results agreed fairly well with data obtained using atomic absorption spectrometry.

Kopylovich et al. (2011) used 1-phenyl-2-(2-hydroxyphenylhydrazo)butane-1,3-dione (H_2L) as an effective ionophore for copper-selective PVC membrane electrodes. Optimization of the composition of the membrane and of the conditions of the analysis was performed, and under the optimized conditions the electrode has a detection limit of 6.30 × 10^{-7} M Cu(II) at pH 4.0 with response time 10 s and displays a linear EMF versus log[Cu^{2+}] response over the concentration range 2.0 × 10^{-6} to 5.0 × 10^{-3} M Cu(II) with a Nernstian slope of 28.80 ± 0.11 mV/decade over the pH range of 3.0–8.0. The sensor is stable for nine weeks and exhibits good selectivity with respect to alkali, alkali earth, and transition metal ions (e.g., Na^+, K^+, Ba^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Fe^{2+}, Al^{3+}) in the 3.0–8.0 pH range. It was successfully applied for the direct determination of copper (II) in zinc, aluminum, and nickel-based alloys, in soils polluted by oil, and as an indicator electrode for potentiometric titration of copper ions with EDTA.

Silver (I)

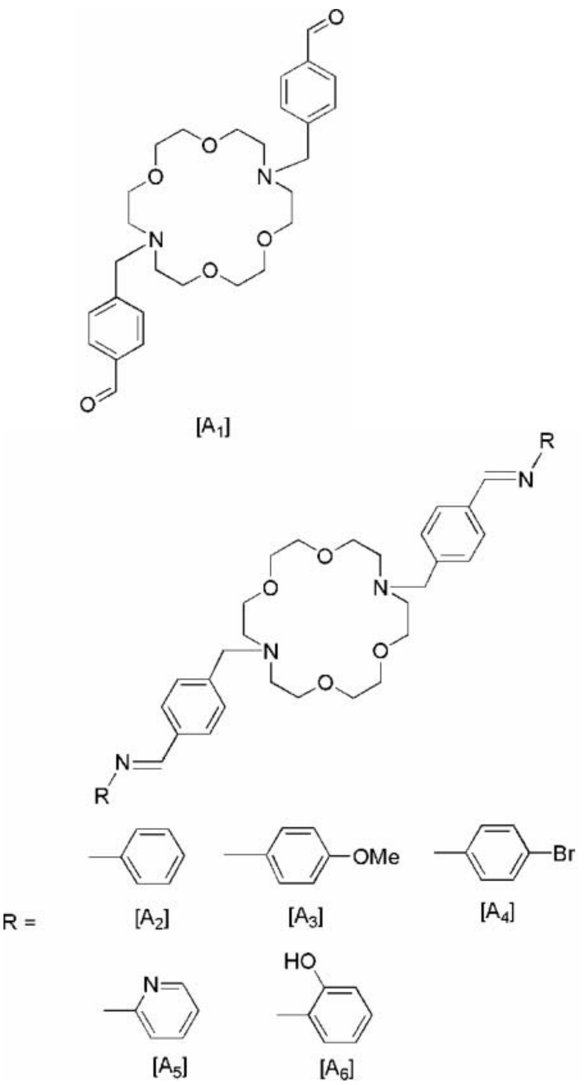
Silver is used widely in the production of coins, jewellery, tableware, and alloys and in the manufacture of electrical apparatus, mirrors, and chemicals for photographic processes. Additionally, it is used in the production of dental amalgams and burn creams as silver sulfadiazine cream (SSD), due to its antibacterial properties (Jain et al., 1995a; Cao et al., 2009; Russell and Hugo, 1994). Silver metal is practically nontoxic; acute toxicity by ingestion is low. However, chronic absorbtion may cause argyria, a blue/grey discoloration of various tissues, ocular injury, and leukopenia, and toxicity in kidney, liver, and neurologic tissues (Wan et al., 1991). Silver concentrations in the blood, urine, liver, and kidneys of subjects without industrial or medical exposure are <2.3 μg/L, 2 μg/day, 0.05 μg/g wet tissues, and 0.05 μg/g wet tissues respectively. In keeping with increased awareness of the environmental and human health issues associated with silver (I), a diverse range of molecular architectures have been used as ionophores to design neutral Ag(I) selective electrodes.

Lai and Shis (1986) developed mercury (Hg^{2+}) and silver (Ag^+) ion-selective PVC membrane electrodes based on 1,4-dithia-12-crown-4 and 1,4-dithia-15-crown-5. Both electrodes exhibited poor concentration ranges of 10^{-2}–10^{-6} M $Hg(NO_3)_2$ and 10^{-1}–0^{-6} M $AgNO_3$. Malinowska et al. (1994) and Casabo et al. (1994) separately reported silver (I)-selective electrodes based on thioether functionalized calix [4] arenes and 1,3-bis [(ethylthio) methyl] benzene, 1,3-bis-[(pentylthio)methyl] benzene, 1,3-bis [(octylthio) methyl] benzene, and 1,3-bis [(dodecylthio) methyl] benzene respectively, but there was still not much improvement in the working range beyond 1.0 × 10^{-6}–1.0 × 10^{-2}. A sulfur-containing podand-based silver-selective membrane electrode was developed by Chung et al. (1997). Shamsipur et al. (2002) developed a silver-selective sensor based on two azathioether crown ethers that exhibited a good detection limit of 1.0 × 10^{-8} M. Singh et al. (2003) developed silver-selective PVC-based membrane sensor based on diazatetrathia (N_2S_4) macrocyclic ligand with a poor working range of 3.98 × 10^{-6}–1.0 × 10^{-1} M. In 2004, Mahajan et al. (2004b) reported a silver-selective sensor based on 2,6-bis-methylsulfanyl-[1,3,5]thiadiazine-4-thione that exhibited a near-Nernstian response of 52 mV/decade with a poor concentration range of 1.0 × 10^{-5}–1.0 × 10^{-1} M. Badr (2005) reported a Ag(I)-selective sensor based on 2,20-dithiobis(benzothiazole), DTBBT, as a neutral carrier and analytically utilized it by measuring the silver concentrations in natural water spiked with silver nitrate and by analyzing the silver in electroplating wastewater samples. Zhang et al. (2006) developed a silver-selective sensor based on 5,10,15-tris(pentafluorophenyl)corrole that exhibited a working range of 5.1 × 10^{-6} to 1.0 × 10^{-1} M but shows interference of Hg^{2+} and Cd^{2+}.

A new PVC membrane potentiometric sensor for Ag(I) ion based on a recently synthesized calix[4]arene compound of 5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-calix[4]arene-thiacrown-4 was developed (Demirel et al., 2006). The electrode exhibits a Nernstian response for Ag(I) ions over a wide concentration range (1.0 × 10^{-2}–1.0 × 10^{-6} M) with a slope of 53.8 ± 1.6 mV/decade. It has a relatively fast response time (5–10 s) and can be used for at least two months without any considerable divergence in potentials. The proposed electrode can be used in a pH range of 2–6. It was successfully used as an indicator electrode in potentiometric titration of a mixture of chloride, bromide, and iodide ions. A polystyrene-based membrane of 7,8:16,17-dibenzo-6,9,15,18-tetraoxo-1,5,10,14-tetrathiacyclooctadeca-7,16-diene [Bz_2Oxo_4(18) dieneS_4] was fabricated using sodium tetraphenylborate (NaTPB) and dioctyl phthalate (DOP) as anion excluder and plasticizing agent by Singh and Saxena (2006). The best performance was obtained from the membrane with the composition ionophore [Bz_2Oxo_4(18)dieneS_4]:polystyrene:DOP:NaTPB, 5:100:150:10 (w/w). The response of the electrode was linear over a wide range of concentrations, 1.26×10^{-6}–1.00×10^{-1} mol L^{-1} for silver ion with a Nernstian slope of 58.4 ± 0.1 mV/decade and a detection limit of 1.0×10^{-6} mol L^{-1}. The electrode was found to be chemically inert and of adequate stability with a response time of 10 s and could be used for a period of three months without change of potential. It worked satisfactorily in mixtures containing up to 35% (v/v) nonaqueous content. The proposed membrane sensor had good selectivity for Ag^+ over a wide variety of metal ions in the pH range 2.2–8.5. It was successfully used as an indicator electrode in potentiometric titration of silver ions. The electrode was also useful for determination of Ag^+ in waste from photographic films.

Mittal et al. (2007) used a new sensing material for fabricating a liquid membrane electrode for silver determination. The electrode was systematically characterized by the electrode response, measuring range (1×10^{-4} to 1×10^{-1} M), detection limit (6×10^{-5} M), pH range (3.3–8.0), and selectivity coefficients for the closely related metal ions. The electrode shows a good response to silver ions in the presence of mercury ions. The electrode works well in mixed solvent media also. The electrode is used extensively as an indicator electrode for the determination of Ag^+ in various synthetic samples and also used for the determination of SCN^-, CN^-, S^{2-}, and I^-. Silver ion-selective electrodes were prepared by Yan et al. (2007) by incorporating six new bis(dialkyldithiocarbamates) as the neutral ionophores into plasticized PVC membranes. Better results have been obtained with membranes containing ligands L3-L6 with dibutyl phthalate (DBP) as a plasticizer. These electrodes work well over a wide range of concentrations (1.0×10^{-6} to 1.0×10^{-3} M) with Nernstian slopes. The present silver ISEs display very good selectivity for Ag^+ ions against an interferent, Hg^{2+} ion, and the values are around −3.0. The silver ISEs have been used as indicator electrodes for potentiometric titration of Cl^- ions in vitamin B_1 tablets using a standard solution of $AgNO_3$. The proposed electrodes have also been used for the direct determination of silver ions in water samples.

Aghaie et al. (2009b) reported two new PVC-based membrane electrodes that were highly selective to Ag(I) ions prepared by using calyx[4]arenes as suitable neutral carriers. The silver (I) ion-selective electrodes exhibited a good response for silver ion over a wide concentration range of 1.0×10^{-1} to 4.2×10^{-6} M and 1.0×10^{-1} to 6.5×10^{-6} M with a Nernstian slope of 60 mV/decade and 58 mV/decade respectively at 25°C and were found to be very selective, precise, and usable within the pH range 4.0–8.0. In the same year, Gupta et al. (2009d) developed silver selective sensors as a comparative analysis with improved sensor characteristics based on six Schiff base lariat ether chelates (A_1 to A_6) of 4,13-diaza-18-crown ether (see Scheme 21). The addition of potassium tetrakis(4-chlorophenyl) borate and various plasticizers, *o*-NPOE, DBP, DBBP, DOP, and CN, has been found to substantially improve the performance of the sensors. The best performance was obtained with the sensor having a membrane of chelate (A_6) with composition (w/w) chelate (2.8%):PVC (45.7%):*o*-NPOE (48.6%):KT-pClPB (2.8%). This sensor exhibits Nernstian response with a slope of 59.3 mV/decade of activity in the concentration range 5.6×10^{-8}–1.0×10^{-1} M Ag(I) and performs satisfactorily over wide pH range of 3.0–8.0 with a fast response time (12 s). The sensor was also found to work satisfactorily in partially nonaqueous media up to 25% (v/v) content of acetonitrile, methanol, or ethanol and can tolerate a concentration of 1.0×10^{-2} M of ionic (SDS, TBC) and nonionic (Triton X-100) surfactants. The proposed sensor can be used over a period of four months without significant drift in potentials. The response of the sensor was highly selective to Ag^+ over a large number of cations, and it could therefore be used for Ag^+ estimation in blood of occupationally exposed persons.



SCH. 21. Schiff base lariat ether chelates (A_1 to A_6) of 4,13-diaza-18-crown ether.

Mohammadi et al. (2010) reported a new silver (I) ion-selective electrode based on 1, 3-bis(2-ethoxyphenyl)triazene as a neutral carrier for detection and determination of trace amounts of silver (I) in aqueous solutions. Nernstian electrode response (59.8 ± 0.7 mV decade^{-1}) for silver ion was observed over a wide concentration range (3.2×10^{-7}–1.0×10^{-1} M) with a low detection limit (8.5×10^{-8} M). The electrode revealed good selectivity toward Ag(I) ion over a wide variety of alkali, alkaline earth, transition, and heavy metal ions. The proposed silver (I) ion-selective electrode was used for the determination of Ag(I) in aqueous samples and as an indicator electrode in potentiometric titration of Ag(I) ions. Hassouna et al. (2010) prepared highly selective silver (I) electrodes by incorporating N,N′-bis(3-methyl-1-phenyl-4-benzylidine-5-pyrazolone)propylenedia mine (I2) as a neutral ionophore into plasticized PVC membranes. The best response characteristics were obtained using the composition I2:KTpClPB:PVC:DBP in the percentage ratio of 4:1.5:60:120 (w:w). The electrodes exhibit a linear response with a near Nernstian slope of 59.3 mV/decade within the silver ion concentration range of 10^{-6}–0.1 mol L^{-1}, with a working pH range of 4–10. The electrodes possessed a fast response time of 30 s for low concentration (10^{-6} mol L^{-1}) and 5 s for higher concentration (10^{-5}–0.1 mol L^{-1}). The electrodes displayed a very good selectivity for silver ion against the serious interferents Hg^{2+} and Cu^{2+} ions, which is a valuable property of these electrodes. These electrodes were successfully used in the potentiometric titration of halides with silver ions and in the determination of silver in radiology films. The Schiff base N,N′-bis(pyridin-2-ylmethylene)benzene-1,2-diamine [BPBD] has been synthesized and explored as ionophore for preparing PVC-based membrane sensors selective to the silver (Ag^+) ion by Seo et al. (2010). Potentiometric investigations indicate high affinity of this receptor for silver ions. The best performance was shown by the membrane of composition (w/w) of ionophore of 1 mg, PVC: 33 mg, o-NPOE: 66 mg, and additive was added at 50 mol% relative to the ionophore in 1 mL THF. The sensor works well over a wide concentration range of 1×10^{-3} to 1.0×10^{-7} M by pH 6 at room temperature (slope of 58.6 mV/decade) with a response time of 10 s and showed good selectivity to silver ions over a number of cations. It could be used successfully for the determination of silver ion content in environmental and wastewater samples.

More recently, a solid-state silver-selective PVC membrane electrode was developed by Topcu et al. (2011) by using recently synthesized [N, N′-ethylenebis-(3-methoxy salicylaldimine)] as an active component of the membrane. The best sensitivity and selectivity for Ag^+ ions were obtained for the electrode membrane containing ionophore-NPOE-PVC and KTpClTB in the composition of 4:62:33:1 (w/w). The proposed electrode had a Nernstian response (56.0 mV/decade) to Ag^+ within the concentration range of 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} and with a detection limit of 8.3×10^{-7} mol L^{-1}. The electrode worked well between pH 3.0 and 8.0 and had a fast response time of 15 s. The electrode was used for three months without any significant change in its sensitivity. The electrode was successfully used in the potentiometric titration of silver ions with standard solution of potassium iodide and in the direct determination of silver ions in spiked wastewater and photographic film developing solutions.

CONCLUSION

This work describes the characteristic of some selected ion-selective electrodes for heavy metals and dug molecules. The selective parameters such as working range, pH range, and slope are also described for heavy metals in Table 1 so as to make easy recognition of a particular reference on the basis of its working parameters (please see the supplementary table file on the journal's website). In addition to these, several other electrodes are reported for miscellaneous species (Gupta and Ali, 2008; Gupta et al., 1999a, c, 2005b, 2006b, e, j, 2009b, c, e, f, g, h, 2010a, b, c, d, e, f; Norouzi et al., 2011; Khani et al., 2010; Ali and Gupta, 2007; Jain et al., 1995c, 1997b, c, 1998, 2005b, 2006; Prasad et al., 2004; Srivastava et al., 1995a; Gupta and Agarwal, 2005). Although a great deal of work has been done on ion-selective electrodes, particularly for heavy metal ion, a continuous approach is essentially needed to increase the working parameters of ion-selective electrodes, as can be clearly concluded from Table 1.

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