

Potentiometric Sensors for Heavy Metals – An Overview

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Abstract: An overview of potentiometric sensors that are capable of detecting heavy metal ions is presented. Notwithstanding the tremendous work performed so far, it is obvious that severe limitations still exist in terms of selectivity, limits of detection, dynamic ranges, applicability to specific problems, and reversibility. A survey of important advances in potentiometric sensors with regard to high selectivity, lower detection limit, fast response time and on-line environmental analysis is given.

Keywords: Chemical sensors · Heavy metals · Potentiometric sensors · Sensors

1. Introduction

Electroanalytical chemistry can play a very important role in the protection of our environment, in particular, with the use of 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 to the nature of the electrical signal): amperometric or potentiometric. In contrast to the 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) to obtain 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 [1] has, in part, inspired work to develop compounds that selectively respond to specific heavy metal ions for use as ion sensors [2]. Potentiometric sensors based on plasticized PVC membranes doped with neutral carriers have been extensively developed for many ions [3][4]. 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 derivatised 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, 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, fast response time towards specific heavy metals. For an overview, see the Table.

2. 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 with the 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 [5]. Heavy metals, by definition, are metals with a density $>5 \text{ g cm}^{-3}$. Heavy metals are prevalent in municipal and industrial effluents; they modify the structure and productivity of ecosystems [6].

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.

Over 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.

2.1. Cobalt

A cobalt selective solid contact electrode was prepared on the basis of titanium ditelluride and reported by Velikanova *et al.* [7]. The electrode exhibits the slope of the electrode function $-(29 \pm 1) \text{ mV/pC}$ and provides the determination of 1×10^{-5} – $1 \times 10^{-1} \text{ M}$ 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 $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$. The intercalant concentration range providing optimal ion-selective properties was deter-

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Table. Summary of the discussed potentiometric sensors

S.No	Ionophore	Concentration Range (M)	Slope mV/ decade	pH Range	Ref. No.
Co²⁺					
1.	Titanium ditelluride	1×10^{-5} – 1×10^{-1}	29	4.5–6.5	[7]
2.	(2-Mercapto-4-methylphenyl)-2-benzamido-3-phenyl-thioproüenoate	4×10^{-7} – 1×10^{-2}	30	5.0–8.0	[8]
3.	5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrinato-cobalt	1.9×10^{-5} – 1×10^{-1}	30.5	1.9–5.8	[9]
4.	Oxime of 1-(2-oxocyclohexanediol	1×10^{-6} – 1×10^{-1}	29.8	3.5–8.0	[10]
Cr³⁺					
5.	4-Dimethylaminoazobenzene	1.6×10^{-6} – 1.0×10^{-2}	19.5	3.0–5.5	[11]
6.	2,3,8,9-Tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene	1×10^{-6} – 1×10^{-1}	19.5	3–5.5	[12]
7.	2-Hydroxybenzaldehyde-O,O'-(1,2-dioxetane-1,2-diyl)oxime	1.5×10^{-6} – 8.0×10^{-3} (PME) 4.0×10^{-7} – 3.0×10^{-3} (CGCE)	Nernstian		[13]
8.	3,10-c-meso-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecanediperchlorate	1.77×10^{-6} – 10^{-1}	20	3.0–6.5	[14]
9.	Oxalic acid bis (cyclohexylidene hydrazide)	1.0×10^{-7} – 1.0×10^{-2}	19.8	1.7–6.5	[15]
Cd²⁺					
10.	Tetrathia-12-crown-4	4×10^{-7} – 1×10^{-1}	29.0	2.5–8.5	[16]
11.	N,N,N',N'-tetradodcecyl-3,6-dioxaoctane dithioamide	Detection limit 10^{-10} M			[17]
12.	[1,1'-Bicyclohexyl]-1,1',2,2'-tetrol	1×10^{-5} – 1×10^{-1}	27.8	4.0–7.0	[18]
13.	Dicyclohexano-18-crown-6	2.1×10^{-5} – 1.0×10^{-1}	29.0	1.9–7.0	[19]
14.	8-Hydroxyquinoline	4.46×10^{-4} – 1.0×10^{-1}	29.0	3.2–6.8	[20]
Pb²⁺					
15.	1,10-Dibenzyl-1,10-diaza-18-crown-6	5×10^{-5} – 1×10^{-2}	Nernstian		[21]
16.	1,8-Dihydroxy-2,7-bis(prop-2'-enyl)-9,10-anthraquinone	2×10^{-6} – 2×10^{-3}	Nernstian		[22]
17.	2,2'-Dithiodibenzoic acid	5×10^{-6} – 1×10^{-2}	29.9	4.0–6.5	[23]
18.	N,N'-Dimethylcyanodiaza-18-crown-6	1×10^{-7} – 1×10^{-2}	Nernstian		[24]
19.	Piroxicam	1×10^{-5} – 1×10^{-1}	30	4.0–8.0	[25]
20.	Calixarene derivative containing carboxyphenyl azo groups	10^{-6} – 10^{-2}	29.4		[26]
21.	Capric acid	1×10^{-5} – 1×10^{-2}	29.0		[27]
22.	4-tert-Butylcalix[4]arene	1.1×10^{-5} – 1×10^{-1}	30.0	2.1–4.0	[28]
Hg²⁺					
23.	Salicyladehyde thiosemicarbazone	1.778×10^{-6} – 1×10^{-1}	29.0		[29]
24.	Calixarene derivative containing a thiazole azo group	7.5×10^{-6} – 5×10^{-2} 5×10^{-6} – 5×10^{-2}	61.1 28.7	4.0	[30]
25.	2-mercaptobenzimidazole, 2-mercaptobenzothiazole and hexathiacyclooctadecane	Detection limit 6×10^{-7}	Near Nernstian		[31]
26.	Et-2-benzoyl-2-phenylcarbamoyl acetate	10^{-6} – 10^{-3}	30.0	2.0–4.5	[32]
27.	2-Benzoylamino-3-(4-chloro-phenyl)-thioacrylic acid S-(2-mercapto-4-methyl-phenyl) ester	2.0×10^{-7} – 3.0×10^{-2}	29.0	1.0–4.0	[33]
28.	1,3-Diphenylthiourea	6.0×10^{-6} – 5.0×10^{-4} 2.0×10^{-6} – 2.1×10^{-4}	58.6 30.8	4.0	[34]

S.No	Ionophore	Concentration Range (M)	Slope mV/ decade	pH Range	Ref. No.
Zn²⁺					
29.	1,13-Diaza-2,3;11,12;15,18-tribenzo-4,7,10-trioxa-cyclononaoctane-14,19-dione	9.0×10^{-5} – 1.0×10^{-1}	Nernstian		[35]
30.	5,10,15,20-Tetraphenyl-21 <i>H</i> ,23 <i>H</i> -porphine	6.2×10^{-6} – 1.0×10^{-1}	29.0	3.8–7.7	[36]
31.	Hematoporphyrin IX	5×10^{-5} – 1×10^{-1}	28.6	2.0–5.5	[37]
32.	2-(Hydroxy-1 naphthylazo)-1,3,4,-thiadiazole	Detection limit 5.6×10^{-6}	29.0		[38]
33.	Disodium salt of porphyrin 3,7,12,17-tetramethyl-8,13-divinyl 2,18-porphine dipropionic acid	1.3×10^{-5} – 1×10^{-1}	30.0	3.0–7.4	[39]
Ni²⁺					
34.	N,N'-bis-(4-dimethylamino-benzylidene)-benzene-1,2-diamine	1.0×10^{-2} – 2.0×10^{-7}	30.0	4.5–9.0	[41]
35.	1,3,7,9,13,15,19,21-Octaazapentacyclooctacosane (pentacyclooctaaza)	1×10^{-6} – 1×10^{-1}	Near-Nernstian	3.0–6.0	[42]
36.	1,10-Dibenzyl-1,10-diaza-18-crown-6	2.0×10^{-5} – 5.5×10^{-3}	Nernstian	4.0–8.0	[43]
37.	Mercapto compound	1.0×10^{-7} – 1.0×10^{-2}	28–30	5–8.5	[44]
38.	5,7,8,14-tetramethyldibenzo[b,i]-1,4,8,11-tetraaza-cyclo tetradecanenickel(II) chloride	7.0×10^{-6} – 1×10^{-1}	29.8	2.0–7.6	[45]
39.	5,7,12,14-tetramethyl dibenzotetraazaannulene	7.9×10^{-6} – 1×10^{-1}	30	2.1–7.6	[46]
Fe³⁺					
40.	<i>p</i> -Chloroaniline-3-formylsalicylic acid	5.0×10^{-5} – 10^{-1}	20		[47]
41.	Iron–cyclam complex	1×10^{-6} – 1×10^{-2}	60	1.3–3.5	[48]
42.	2-[(2-Hydroxy-1-propenyl-but-1,3-dienylimino)-methyl]-4- <i>p</i> -tolylazo-phenol	3.5×10^{-6} – 4.0×10^{-2}	28.5	4.5–6.5	[49]
43.	Complexes of iron (II) 2,4,6-tri(2-pyridyl)-1,3,5-triazine	5×10^{-7} – 10^{-2}		3.2–7.1	[50]
Cu²⁺					
44.	Schiff Base complexes: diaminopyridine{vallin H} and diaminopyridine-{vallin H} ₂	5.0×10^{-6} – 1.0×10^{-1}	29.6	1.9–5.2	[51]
45.	1,3-Dithiane,2-(4-methoxy phenyl)	3.0×10^{-6} – 5.0×10^{-2}	29.5	4.0–7.0	[52]
46.	Copper(II)-salicylaniline Schiff's base complex	2.5×10^{-7} – 1.0×10^{-2}	27.59		[53]
47.	Polypyrazolylmethanes	10^{-6} – 5×10^{-3}			[54]
48.	Dithiosalicylic (DTS) and thiosalicylic acids (TS)	Detection limit $10^{-7.9}$ (DTS) and $10^{-6.3}$ M (TS)	27.7(DTS) Super Nernstian (TS)		[55]
49.	Copper(II) complex of ethambutol	7.9×10^{-6} – 1×10^{-1}	29.9	2.1–6.3	[56]

mined. A PVC membrane electrode for Co²⁺ ions based on (2-mercapto-4-methylphenyl)-2-benzamido-3-phenyl-thioproenoate as an excellent neutral carrier was prepared and reported by Mashhadizadeh *et al.* [8]. The electrode exhibits a Nernstian response for Co²⁺ ions over a wide concentration range (1×10^{-2} – 4×10^{-7} M) with a slope of 30 ± 1 mV per decade. 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 5.0–8.0. Gupta *et al.* [9] reported PVC based membranes of 5,10,15,20-tetrakis(4-methoxyphenyl) porphyrinatocobalt (TMOPP-Co) as electroac-

tive material with sodium tetraphenyl 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} – 1.0×10^{-1} M) with a slope of 30.5 mV/decade over the pH range 1.9–5.8. Ganjali *et al.* [10] 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 Co²⁺. The electrode displayed a Nernstian slope of 29.8 mV per decade in the pH range 3.5–8.0.

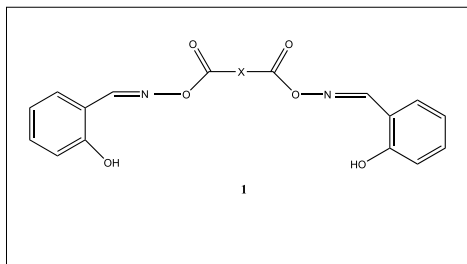
2.2. Chromium

Chromium (III) is an essential nutrient for humans and its shortages 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 the steel, leather and textile manufacturing industries.

A literature survey revealed that among the reported ISEs, very limited studies have been carried out for Cr³⁺ ions.

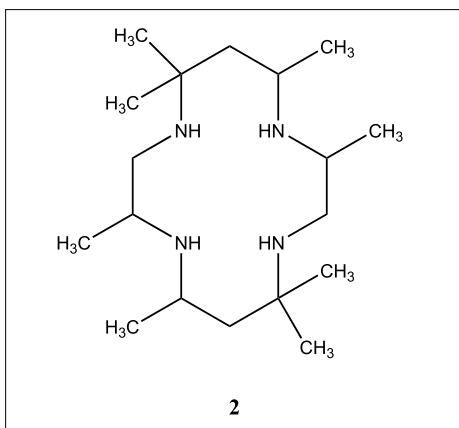
A PVC-based membrane of 4-dimethylaminoazobenzene with a Nernstian potentiometric response (with slope of $19.5 \pm$

0.6 mV per decade) for Cr(III) over a wide concentration range (1.66×10^{-6} – 1.0×10^{-2} M) was reported by Abbaspour and Izadyar [11]. The potential of the reported electrode was independent of pH in the range 3.0–5.5. A plasticized Cr(III) ion sensor made by incorporating the 2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene (TTCT) ionophore was reported by Ganjali *et al.* [12] which exhibited a good response over a wide concentration range 1×10^{-1} – 1×10^{-6} M with a slope of 19.5 mV per 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.* [13] synthesized Schiff's bases and studied their ability as Cr³⁺ 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 (**1**) exhibited Nernstian response for Cr³⁺ ion over 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).

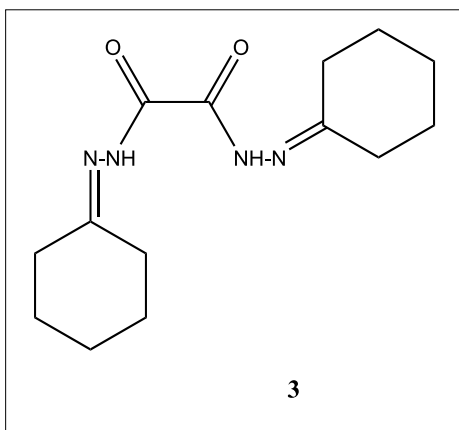


Singh *et al.* [14] reported a poly(vinyl chloride)-based membrane of 3,10-*c-meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane diperchlorate (**2**) with sodium tetraphenyl borate (STB) as an anion excluder and dibutyl phthalate (DBP), dibutyl butylphosphonate (DBBP), tris(2-ethylhexyl) phosphate (TEP) and tributyl phosphate (TBP) as plasticizing solvent mediators which was 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 per 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 4 months with good reproducibility ($s = 0.4 \text{ mV}$). The selectivity coefficients for mono-, di- and trivalent cations indicate excellent selectivity for Cr(III) ions over a large number of cations. Anions such as Cl[−] and SO₄^{2−} do not interfere and the electrode also works satisfactorily in a partially non-aqueous medium. The sensor has been used as an indicator electrode in the

potentiometric titration of Cr(III) with EDTA. 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 analyse some food materials for the determination of Cr(III) ion.



Gohlivand and Raheedayat [15] reported a poly(vinyl chloride) membrane sensor based on oxalic acid bis (cyclohexylidene hydrazide) (OABCH) (**3**) as membrane carrier Cr(III)-selective electrode. The electrode reveals a Nernstian behaviour (slope $19.8 \pm 0.4 \text{ mV decade}^{-1}$) over a wide Cr(III) ion concentration range 1.0×10^{-7} – $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ with a very low limit of detection (*i.e.* down to $6.3 \times 10^{-8} \text{ mol dm}^{-3}$). 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 the advantages of very fast response, relatively long lifetime and especially good selectivity to 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 waste water and alloy samples.



2.3. Cadmium

In industry cadmium is a by-product of zinc, lead, and copper extraction. It then enters the environment mainly through the

ground and is found in manures and pesticides. Health effects that can be caused by cadmium are diarrhoea, stomach pains, reproductive failure, damage to CNS, 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 [16] reported a Cd²⁺ selective PVC based membrane electrode exhibiting a wide concentration range (1×10^{-1} – 4×10^{-7} M) with a slope of 29 mV per decade. The limit of detection was 0.01 ppm and can be used in the pH range 2.5–8.5. Pretsch and coworkers [17] determined selectivity behaviour for two membranes based on the ionophore, N,N,N',N'-tetradodecyl-3,6-dioxaoctanedithioamide (ETH 5435) and the best lower detection limit of 10^{-10} M or 11 ppt Cd²⁺ was achieved at pH 7 with an ionic background of 10^{-4} M NaNO₃. A new PVC membrane electrode for Cd²⁺ ions based on [1,1'-bicyclohexyl]-1,1',2,2'-tetrol as membrane carrier was prepared by Shamsipur and coworkers [18]. 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 per decade. The limit of detection was 9×10^{-6} M and it can be used in the pH range 4.0–7.0. Gupta and coworkers [19] reported PVC based membrane containing dicyclohexano-18-crown-6 as the active material along with sodium tetraphenyl borate (NaTPB) as an anion excluder and dibutyl phthalate as solvent mediator in the ratio (dicyclohexano-18-crown-6/NaTPB/DBP/PVC) 20:4:150:150 (w/w). This membrane exhibits good properties with a Nernstian response of $29.0 \pm 1.0 \text{ mV per decade}$ 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) non-aqueous 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 Cd²⁺ against EDTA as well as for Cd²⁺ determination in wastewaters. Another Cd²⁺ ion-selective electrode based on poly(styrene-*co*-acrylonitrile) copolymer (SAN) has been prepared by Gupta and D'Arc [20] using 8-hydroxyquinoline as an electroactive ionophore and dibutylphthalate as a plasticizing agent. The Cd²⁺ ion-selective electrode in the presence of sodium tetraphenyl borate (NaTPB) as an anion excluder exhibited a linear response within 4.46×10^{-4} – $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ activities of Cd²⁺ 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 Cd²⁺ ions over a period of six months. The selectivity of the prepared electrode for Cd²⁺ ions in presence of a number of interfering cations is found to be high within the working range of the electrode. However, Pb²⁺, Cu²⁺ and Mg²⁺ ions have shown interference when the activities of the Cd²⁺ ions in the solution were less than 1 × 10⁻⁶ mol dm⁻³.

2.4. Lead

Lead is ubiquitous in the environment and is hazardous to health. 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.* [21] constructed PVC membrane Pb(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 the potentiometric titration of EDTA with lead ions and used for direct determination of lead in wastewater. Shamsipur and coworkers [22] studied four different 9,10-anthraquinone derivatives and characterised 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 Pb²⁺ ions over a wide concentration range (2 × 10⁻³–2 × 10⁻⁶ M). It was used as an indicator electrode in potentiometric titration of sulphate 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 Gholivand and Abdorrezas [23]. The electrode exhibited a Nernstian response for Pb(II) cations over a wide concentration range (5 × 10⁻⁶–1 × 10⁻² M) with a slope of 29.9 mV per decade. Its selectivity to Pb²⁺ 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'-dimethylcyanodiaz-18-crown-6 (DMCDA18C6) for determination of ultra trace amounts of lead was prepared by Ganjali and coworkers [24]. The electrode exhibited a Nernstian response for Pb(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 H₂O samples. An ion selective electrode for lead based on piroxicam as a suitable ionophore is described by Sadeghi *et al.* [25]. The electrode responds to Pb²⁺ in a linear range from 1 × 10⁻⁵–1 × 10⁻¹ M with a slope of 30 mV per 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 and coworkers [26] with polymeric membranes based on a calixarene derivative containing carboxyphenyl azo groups. The electrode gave good Nernstian responses of 29.4 mV per 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 Pb(II) ion carrier in PVC membrane electrodes by Mousavi *et al.* [27]. The electrodes based on capric acid [CH₃(CH₂)₈COOH] showed good Nernstian response for Pb²⁺ ions. The optimum composition of the membrane was 30 wt.% PVC, 60wt.% 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 per decade of Pb²⁺ over a concentration range 1 × 10⁻⁵–1 × 10⁻² M. Recently membranes of 4-*tert*-butylcalix[4]arene (**1**) as an electroactive material, sodium tetra-Ph borate (NaTPB) as an anion excluder, and di-Bu phthalate (DBP) as solvent mediator in poly(vinyl chloride) (PVC) matrix were tried by Gupta *et al.* [28] for developing lead-selective sensors. 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 which are reported to cause interference in the working of other sensors.

2.5. Mercury

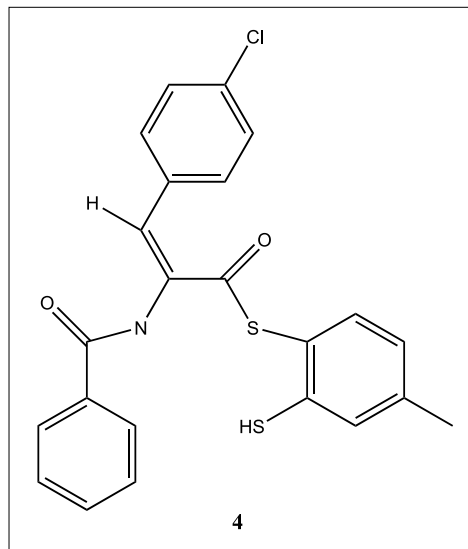
Mercury is a heavy metal that occurs naturally in the environment. Release of mercury from natural sources has remained approximately the same over the years. However mercury concentrations in the environment are increasing; this is ascribed to human activity. Most of the mercury released from human activities is released into air, through mining, solid waste combustion and industrial wastewater disposal. Mercury has a number of adverse effects on

human, like disruption of the nervous system, damage to brain functions, DNA and chromosomal damage, negative reproductive effects *etc.*

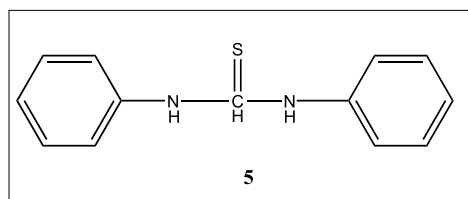
A new ion selective PVC membrane electrode based on salicylaldehyde thiosemicarbazone as an ionophore was developed successfully for mercury (II) ions by Mahajan and coworkers [29]. The electrode showed excellent potentiometric response characteristics and displayed a linear log [Hg²⁺] versus EMF response over a wide concentration range of 1.778 × 10⁻⁶–1 × 10⁻¹ M with a Nernstian slope of 29 mV per decade with the detection limit of 1 × 10⁻⁶ M. The sensor was also applied as an indicator electrode for potentiometric titration of Hg²⁺ ions with I⁻ and Cr₂O₇²⁻. 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.* [30]. The ISE gave two kinds of response slope of 61.1 mV per decade in the concentration range of 7.5 × 10⁻⁶–5 × 10⁻² M and another, which has a typical Nernstian response, for Hg²⁺, is obtained at pH 4.0 with a slope of 28.7 mV per 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 PVC matrix were described by Mazloum *et al.* [31]. They were used as indicator electrodes in the potentiometric titration of Hg²⁺ with EDTA and for determination of mercury in wastewater samples. 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 Saad *et al.* [32]. The sensor exhibited good linear response of 30 mV per decade within concentration range 10⁻⁶–10⁻³ 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.

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 (**4**) has been reported [33]. The electrode exhibited a Nernstian response for Hg²⁺ ions over a wide concentration range (2.0 × 10⁻⁷–3.0 × 10⁻² M) with a slope of 29 (±1) mV. 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 poten-

tiometric 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 (ISE) based on 1,3-diphenylthiourea (**5**) as a neutral carrier was developed [34]. In solubility tests of 1,3-diphenylthiourea in six different plasticizers, 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 per decade in the concentration range 6.0×10^{-6} – 5.0×10^{-4} mol l^{-1} ; the presence of the complex $\text{Hg}(\text{OH})^+$ ion explains the slope of the response curve. The ISE showed stable detection 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 per decade in the concentration range 2.0×10^{-6} – 2.1×10^{-4} mol l^{-1} .



2.6. 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 emitted during industrial activities, such as mining, coal, and waste combustion and steel process-

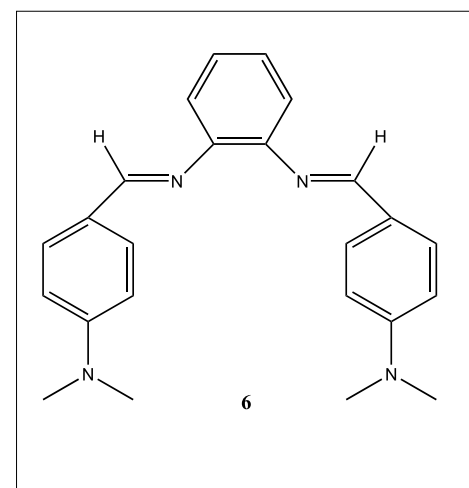
ing. Although humans can handle proportionally large concentrations of zinc, too much zinc can still cause health problems such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. 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.* [35]. The sensor exhibited a Nernstian response for Zn^{2+} over a wide concentration range (1.0×10^{-1} – 9.0×10^{-5} M). Gupta and coworkers [36] reported 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 (PVC/ionophore/NaTPB/TBP) 200:5:2:150; (w/w) 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 non-aqueous content up to 25% (v/v) (acetone, methyl alcohol and ethyl alcohol). A poly(vinyl chloride) 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 per decade of Zn^{2+} concentration was reported by Jain *et al.* [37]. 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.* [38]. Its basic analytical parameters, such as the slope of characteristics (29 mV $\text{pa}_{\text{Zn}^{2+}}^{-1}$), the detection limit (5.6×10^{-6} mol dm^{-3}), lifetime (40 d), response time (10 s), 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 using a voltammetric method. Zn^{2+} based 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 [39].

2.7. 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. More recently, it is now considered as 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 [40].

A new PVC membrane electrode that is highly selective to Ni(II) ions was prepared by Mashhadizadeh and coworkers [41] by using *N,N*-bis-(4-dimethylamino-benzylidene)-benzene-1,2-diamine (NDBBD) (**6**) as a suitable neutral carrier. 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 per 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.* [42] explored the use of 1,3,7,9,13,15,19,21-octaazapentacyclooctacosane (pentacyclooctaaza) as a neutral ionophore for preparing poly(vinyl chloride) (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,

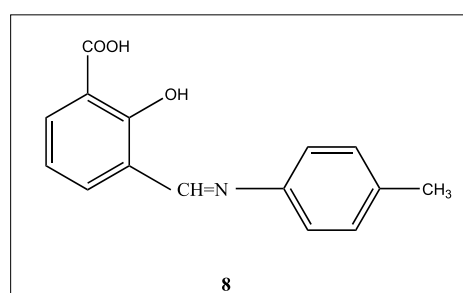
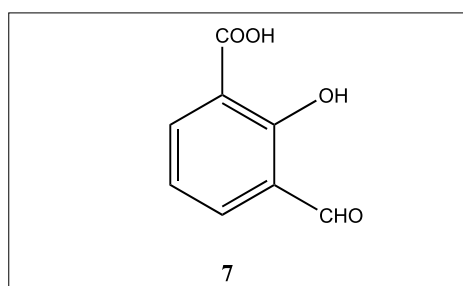
alkaline earth and several transition and heavy metal ions. The electrode is suitable for use in aqueous solutions in a wide pH range of 3–6. It was applied as an indicator electrode for the end point detection in the potentiometric titration of Ni(II) with ethylenediaminetetraacetic acid (EDTA) and determination of nickel content of chocolate and milk powder samples. Another PVC membrane nickel(II) ion-selective electrode was constructed by Mousavi *et al.* [43] 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 new PVC membrane electrode for Ni²⁺ ions based on a recently synthesized mercapto compound as an ionophore was prepared [44]. The electrode exhibits a Nernstian slope of 28–30 mV per concentration decade at 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. Another potentiometric sensor based on 5,7,8,14-tetramethyldibenzo[b,i]-1,4,8,11-tetraazacyclotetradecanenickel(II) chloride was fabricated for Ni²⁺ ions [45]. The sensor exhibits a linear response to Ni²⁺ 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. 5,7,12,14-tetramethyldibenzotetraazaannulene (Me4Bzo2TAA) was explored by Gupta and coworkers [46] as an electroactive material for preparing poly(vinyl chloride) (PVC)-based membrane electrodes selective to Ni²⁺. 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 (30.0 ± 1.0 mV/decade of activity) in the pH range 2.7–7.6.

2.8. Iron

Iron is an essential metal and is used for the treatment of anaemia, but excessive intake or overdosing requires detection by

selective analytical methods 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.

Novel iron(III)-selective PVC membrane electrodes based on formylsalicylic acid derivatives **7** and **8** were studied by Saleh [47]. 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 a good Nernstian response for 10^{-1} – 5.0×10^{-5} mol l⁻¹ FeCl₃ with a slope of 20 mV per 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 Sil *et al.* [48] comprises the determination of Fe(III) by ion selective potentiometry using a coated-wire ion-selective electrode (CWISE) based on an 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 HNO₃, H₂SO₄, HClO₄, HCl, KNO₃ and KCl media, with a slope of 60 ± 5 mV per 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 pharma-

ceutical samples have been carried out using this CWISE and the results are found to be comparable with those obtained by using conventional methods. A new PVC membrane potentiometric sensor that is highly selective to Fe(III) ions was prepared [49] 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 Fe(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 Fe³⁺ ion in comparison to some hard and soft metals such as Fe²⁺, Cd²⁺, Cu²⁺, Al³⁺ and Ca²⁺. 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 Fe³⁺ in aqueous samples and as an indicator electrode in potentiometric titration of Fe(III) ions. Mahmoud [50] described the compositions 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 plasticized carboxylated poly(vinyl chloride) (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 the doubly charged iron over the concentration range from 5×10^{-7} to 10^{-2} M. The pH does not affect the sensor performances 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 potentiometric 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.

2.9. 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 used in industry and in agriculture. The production of copper has increased over the last decades and due to this copper quantities in the environment have risen. Copper can be found in many kinds of food, in drinking water and in air. Because of that we absorb consider-

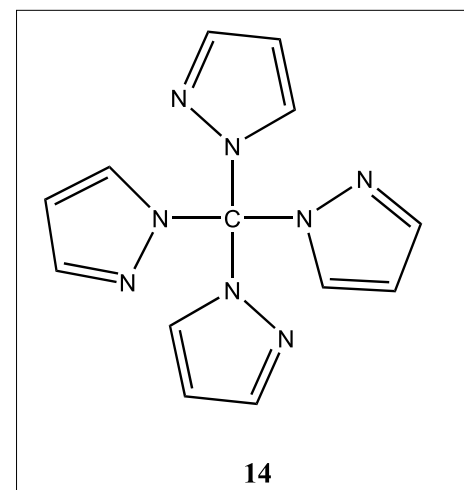
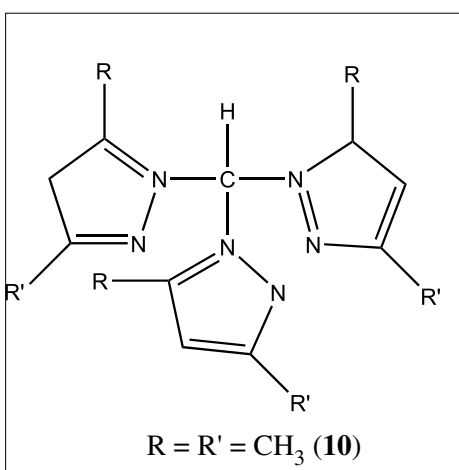
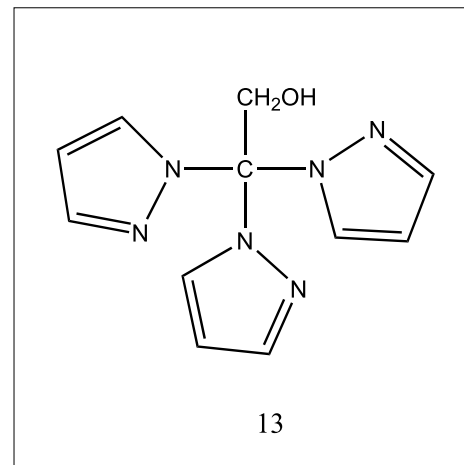
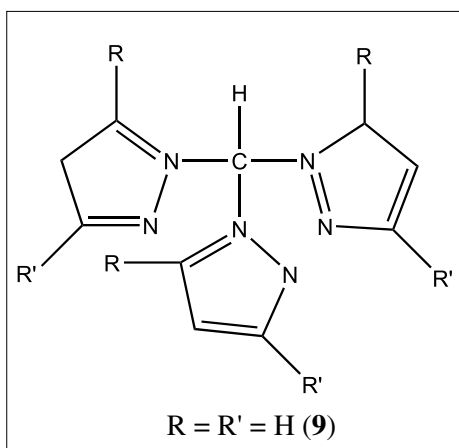
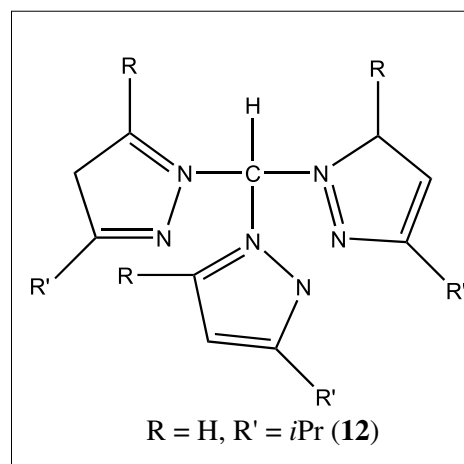
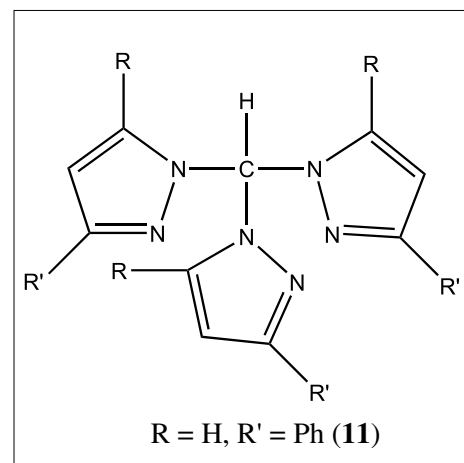
able quantities of copper each day by eating, drinking and breathing. The absorption of copper is necessary, because copper is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of copper, too much copper can still cause health problems. Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomach aches, dizziness, vomiting and diarrhoea. Intentionally high uptakes 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 Cu²⁺-selective sensors [51]. 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 non-aqueous tolerance (up to 20%) and adequate shelf life (>4 months) indicate the vital utility of the proposed sensor. The tolerance level of Hg²⁺, which causes serious interference in the determination of Cu²⁺ ions ($K^{\text{Pot}}_{\text{Cu}^{2+}\text{Hg}^{2+}}(\text{MPPM}): 0.45$), was determined as a function of Cu²⁺ concentration in simulated mixtures. Abbaspour and Kamyabi [52] 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 per decade in a linear range of 3.0×10^{-6} to 5.0×10^{-2} M for Cu²⁺ 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.

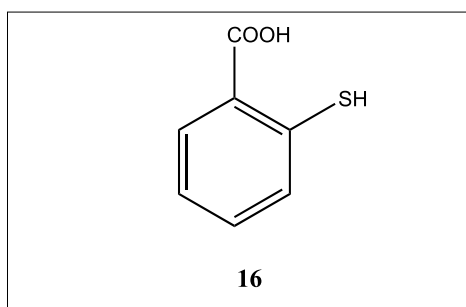
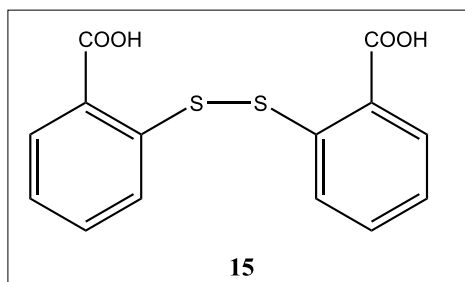
The potential response of cyanocopolymer based Cu²⁺ ion selective electrodes has been studied [53] as a function of concentration of ionophore (Schiff's base complex), plasticizer (dioctylphthalate) and molecular weight of the cyanocopolymers. The concentration variation in electrode constituents has shown significant effect on the sensitivity, selectivity, detection limits, response time and extent of interference from foreign ions during potentiometric measurements of electroactive ions. Hydrophobic nature and high dipole moment of the employed cyanocopolymers have enhanced the average lifetime of the electrode and shown least interference from solution anions. Electrodes prepared with 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 Cu²⁺ ions with a response time of 13.00 ± 0.002 s. These electrodes with 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 Cu²⁺ ions. The electrodes' 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.* [54] developed novel ion-selective membrane electrodes based on polypyrazolymethanes, represented by the general formula H_{4-n}C(pz)_n (pz: 1-pyrazolyl). HC(pz)₃ (9), HC(3,5-Me₂pz)₃ (10), HC(3-Phpz)₃ (11), HC(3-*i*Prpz)₃ (12), HOCH₂C(pz)₃ (13), and C(pz)₄ (14) were prepared and incorporated as an ionophore in PVC membrane. The selectivity of the electrodes changed with the substituents of polypyrazolymethanes. The electrodes of 11, 12, and 14, were selective for Cu²⁺ at pH 5.5. The electrode of 13 was selective for Pb²⁺ and Cu²⁺ at pH 5.5. Since the selectivity coefficient $\log K_{\text{Cu},\text{M}}^{\text{pot}}$ of electrode 12 was less than -6.4 for the divalent cations, it was most selective for Cu²⁺ among all Cu²⁺ selective electrodes ever reported. The detection limit and dynamic range for Cu²⁺ were 2×10^{-6} and 10^{-6} to 5×10^{-3} M, respectively. The electrode 12 showed rapid response time (~10 s) and reproducible results for more than four months, and successfully applied to potentiometric titration of Cu²⁺ with EDTA.



Potentiometric carbon paste electrodes for copper (II) based on dithiosalicylic and thiosalicylic acids are described by Procopio *et al.* [55]. The sensor based on dithiosalicylic acid (DTS) (**15**) exhibits a linear response with a nearly Nernstian slope of 27.7 mV per decade, whereas the electrode based on thiosalicylic acid (TS) (**16**) shows a super-Nernstian slope. 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.* [56] and used in the fabrication of Cu^{2+} selective ISE membrane. The membrane having Cu(II) -ethambutol complex as electroactive material, along with sodium tetraphenylborate (NaTPB) as anion discriminator, dioctylphthalate (DOP) as plasticizer in poly(vinyl chloride) (PVC) matrix in the percentage ratio (Cu(II) -ethambutol/NaTPB/DOP/PVC) 6:2:190:200 (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.

3. Conclusions

A review of some recent development of potentiometric sensors for heavy metals as an important kind of chemical sensors is given. The design and synthesis of new systems that can be switched between different states have been used satisfactorily for the development of new chemical sensors. A large number of novel and analytically useful ionophores have been discovered only in the past few years, indicating

that this field is steadily moving forward. The advantages of ISEs over many other methods for cation detections are their easy handling, non-destructive analysis and inexpensive sample preparation. Traditional ISE detection limits have been reasonably improved and measurement down to picomolar range is now possible.

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