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### Studies on the Preparation and Analytical Applications of Various Metal Ion-Selective Membrane Electrodes Based on Polymeric, Inorganic and Composite Materials—A Review

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# Studies on the Preparation and Analytical Applications of Various Metal Ion-Selective Membrane Electrodes Based on Polymeric, Inorganic and Composite Materials—A Review

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Ion-selective membrane electrodes commonly known as electrochemical sensors are important in view of the ability to make direct or indirect measurement of various metal ions. The fact is that the use of ion-selective electrodes for such type of measurements requires relatively inexpensive equipment, which makes ion-selective electrodes attractive to scientists in many disciplines. Thus, potentiometric sensors can offer an inexpensive and convenient method for the analysis of heavy metal ions in solutions providing acceptable sensitivity and selectivity. For this purpose, many organic, inorganic, chelating, intercalating and composite materials were studied as electroactive materials for the preparation of ion-selective membrane electrodes. The present study provides a detailed review of literature for the fabrication, characterization and analytical applications of ion-selective membrane electrode based on different electro active components.

**Keywords:** Ion-selective electrode, membrane, potentiometry, metal ions

## 1. Introduction

A large number of ion-selective electrodes (ISEs) using different types of electroactive compounds have been developed during the past two decades. The literature survey reflected good volume on all topics and it is very difficult, as well as unmanageable, to compile all of them here. The research work on these ion-selective electrodes began in the 1920's, but their systematic studies started after E. Pungor et al. (1,2) in 1961. They studied the behavior of silver iodide precipitates as a model substance. Undoubtedly, the findings of Pungor's group provided an opening for research in this field. These ion-selective electrodes have become an alternate of complicated instruments like visible spectrophotometer, atomic absorption spectrophotometer, inductively coupled plasma instrument and electron spectrophotometer for chemical analysis etc. for the determination of various cations and anions. Research in the field

of ISEs was enormously stimulated by the publication by Frant and Ross (3,4) of their articles on the fluoride and calcium ion-selective electrodes. A number of review articles (5–16) have come across from time to time towards the work done by various eminent persons. These review articles deal with the subject on theoretical, as well as practical fronts. Various applications have also been their interest in analytical, chemical, pharmaceutical and in environmental disciplines.

## 2. Results and discussion

### 2.1. Membrane and selectivity for metal ions

Different kinds of materials (organic, inorganic and organic-inorganic) and their selectivity for some alkali metals, alkaline earth metals, transition metals and rare earth metals were researched from the literature. Materials and their applications as ion-selective electrode are discussed in the following pages and their selectivities for a particular ion are given in Table 1.

An epoxy resin e.g. Araldit type of materials first used by Coetzee et al. proved to be the most suitable and widely used material. They have worked on thallium(I) heteropolyacid salt-epoxy resin membranes in their studies and also determined Cs<sup>+</sup> potentiometrically (14,15).

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**Table 1.** Materials and their selectivities for particular ions

<i>Ions</i>	<i>Materials</i>	<i>References</i>
Cs <sup>+</sup>	Thallium(I) heteropolyacid salt	[14,15]
Cs <sup>+</sup> and Tl <sup>+</sup>	Tungstoarsenate	[16]
Tl <sup>+</sup>	Crown ether	[21–24]
Tl <sup>+</sup>	Dibenzo-20-crown-6 (DB20C6) and dibenzo-22-crown-6 (DB22C6)	[26]
Tl <sup>+</sup>	Calix[6]arene or calix[5]arene derivatives and Calix[4]arene	[27]
Tl <sup>+</sup>	Quinoline-carbonitriles	[28]
Tl <sup>+</sup>	Calix[4]pyrrole	[29]
Tl <sup>+</sup>	Dibenzyl-diaza-18-Crown-6	[30]
Ca <sup>2+</sup>	Didecyl-phosphate in di-n-octyl phosphonate	[4]
Ca <sup>2+</sup>	Ca-bis[2,6-dinitro-4-(1,1,3,3-tetramethylbutyl)] phenoxide	[31]
Ca <sup>2+</sup>	Ca-bis[di{4-(1,1,3,3-tetramethylbutyl) phenyl}]	[32]
Ca <sup>2+</sup>	Calix[6] tetrakisphosphine oxide	[33]
Ca <sup>2+</sup>	Thenoyl trifluoroacetone	[34]
Ca <sup>2+</sup>	Ca(II) rhodizonate	[35]
Mg <sup>2+</sup>	Phenylene bis(ditolylphosphinoxide)	[36]
Mg <sup>2+</sup>	Octamethylene bis(malonic acid diamides) and tris(malonic acid diamides)	[37]
Mg <sup>2+</sup>	Poly(ethylene oxide) units (Brij 35 and Triton X-100)	[40]
Mg <sup>2+</sup>	Strontium complex of polyethylene glycol	[41]
Sr <sup>2+</sup>	Hydrous thorium oxide	[42]
Sr <sup>2+</sup>	Strontium tungstoarsenate	[43]
Sr <sup>2+</sup>	Ester derivative of 4-tert-butylcalix[8] arene	[44]
Sr <sup>2+</sup>	Ethylene glycol-functionalized polystyrene microspheres	[45]
Ba <sup>2+</sup>	Lipophilic electrically neutral carriers	[46]
Ba <sup>2+</sup>	Neutral carboxylic polyether antibiotic	[47,48]
Ba <sup>2+</sup>	Benzo-15-crown-5 and its Ba <sup>2+</sup> -complex	[49]
Ba <sup>2+</sup>	Antarox CO-880 and its Ba-complex	[50]
Ba <sup>2+</sup>	Binaphthyl polyether	[51]
La <sup>3+</sup>	Lanthanum(III)-p-nitrobenzeneazo-chromotrope-213	[57]
Cs <sup>+</sup>	15-crown-5-phosphotungstic acid (PW), 12-crown-4-PW, 1,4-dithia-12-crown-4 and 1,4-dithia-15-crown-5	[59]
La <sup>3+</sup>	Urushiol crown ether rare-earth complexes (Ln = La-Nd)	[60]
Zn <sup>2+</sup>	Zinc salts of bi(4-octylphenyl) hydrogen phosphate	[61]
Zn <sup>2+</sup>	zinc complex of bis(2-ethylhexyl) phosphate	[62]
Zn <sup>2+</sup>	Zn-quinoline-8-carbodithioatein chloroform	[63]
Zn <sup>2+</sup>	Tetrabutylthiuram disulfide Pb <sup>2+</sup> composite cation exchangers	[64]
Zn <sup>2+</sup>	Zinc orthophosphate and zinc mercuric thiocyanate	[65]
Zn <sup>2+</sup>	Salicylaldehyde-formaldehyde resin	[66]
Zn <sup>2+</sup>	Cryptand	[68]
Zn <sup>2+</sup>	Zn-bis(2,4,4-trimethylpentyl) thiophosphinic acid complex	[69]
Zn <sup>2+</sup>	Crown ether	[70]
Zn <sup>2+</sup>	Benzo substituted macrocyclic diaramides	[71]
Zn <sup>2+</sup>	5,6,14, 15-dibenzo-1,4-dioxo-8,12-diazacyclopentadecane-5,14-diene	[72]
Zn <sup>2+</sup>	Porphyrin	[74]
Zn <sup>2+</sup>	Bis(2-nitrophenyl)disulfide carrier	[75]
Zn <sup>2+</sup>	4-tert-butylcalix[4]arene (I)	[76]
Zn <sup>2+</sup>	N,N'-bis(acetylacetone)ethylenediimine (I)	[77]
Zn <sup>2+</sup>	Tetra(2-aminophenyl) porphyrin	[78]
Ni <sup>2+</sup>	Nickel-dimethyl glyoxime complex	[79]
Ni <sup>2+</sup>	Nickel phosphate	[80]
Ni <sup>2+</sup>	Bis-2-(ethylhexyl) phosphate	[81]
Ni <sup>2+</sup>	1-hydroxy-2-naphthaldoxime-formaldehyde polymer	[82]
Ni <sup>2+</sup>	4,4',4'',4'''-21H,23H-porphine-5,10,10,15,20-terayl) tetrakis (benzoic acid) (TBAP) and 2,3,7,8,12,13,17,18-octamethyl-21H, 23H-porphine (OMP)	[83]
Ni <sup>2+</sup>	1,10-dibenzyl-1,10-diaza-18-crown-6 (DBzDA18C6)	[84]

(Continued on next page)

**Table 1.** Materials and their selectivities for particular ions (*Continued*)

<i>Ions</i>	<i>Materials</i>	<i>References</i>
Ni <sup>2+</sup>	Pentacyclooctaaza	[85]
Ni <sup>2+</sup>	Dibenzo[ <i>e,k</i> ]-2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,5,7,9,11-hexaene	[86]
Ni <sup>2+</sup>	Meso-tetrakis-{4-[tris-(4-allyl dimethylsilyl-phenyl)-silyl]-phenyl}porphyrin (I) and (sal)2trien (II)	[87]
Ni <sup>2+</sup>	Dibenzo-18-crown-6	[88]
Ni <sup>2+</sup>	(2 <i>E</i> , 3 <i>E</i> )-2 <i>H</i> -1,4-benzothiazine-2,3(4 <i>H</i> )-dione dioxime	[89]
Ni <sup>2+</sup>	<i>N,N'</i> -bis-(4-dimethylamino-benzylidene)-benzene-1,2-diamine	[90]
Ni <sup>2+</sup>	1,5-diphenylthiocarbazon	[91]
Cu <sup>2+</sup>	Copper sulfide	[103–106]
Cu <sup>2+</sup>	Tungsten oxide	[107]
Cu <sup>2+</sup>	Ion-exchangers	[108,109]
Cu <sup>2+</sup>	Copper(III) complexes	[110–115]
Cu <sup>2+</sup>	Macrocyclic polyethers	[116]
Cu <sup>2+</sup>	polymethylidene	[117]
Cu <sup>2+</sup>	Poly(glycidyl methacrylate- <i>co</i> -ethylene dimethacrylate	[119]
Cu <sup>2+</sup>	Copper(II) salicylaniline	[120]
Cu <sup>2+</sup>	Bis-2-thiophenal propanediamine (TPDA)	[121]
Cu <sup>2+</sup>	3,6,9,14-tetrathiabicyclo [9.2.1] tetradeca-11,13-diene	[122]
Cu <sup>2+</sup>	Polypyrazolymethanes	[123]
Cu <sup>2+</sup>	2,2'-[1,2-ethandiyl-bis(nitrilomethylidene)-bis] <i>meta</i> cresole(I), 2,2'-[1,2-ethandiyl-bis(nitrilomethylidene)-bis] <i>ortho</i> cresole(II), and 2,2'-[1,2-ethandiyl-bis(nitrilomethylidene)-bis] <i>para</i> cresole(III)	[124]
Cu <sup>2+</sup>	1,3,5-Tris(8-quinolinoxymethyl)-2,4,6-trimethylbenzene (MO8HQ)	[125]
Cu <sup>2+</sup>	Bis(acetylaceton)propylenediimine (I)	[126]
Cu <sup>2+</sup>	Chalcogenide glassy-crystalline Cu-As-S alloys	[127]
Cu <sup>2+</sup>	Bis(2-hydroxyacetophenone)butane-2,3-dihydrazone (BHAB)	[128]
Cd <sup>2+</sup>	Cadmium and silver sulfides	[129]
Cd <sup>2+</sup>	CdS-Ag <sub>2</sub> S mixture	[130]
Cd <sup>2+</sup>	CdS-Ag <sub>2</sub> S mixture	[131]
Cd <sup>2+</sup>	CdS-Ag <sub>2</sub> S mixture	[132]
Cd <sup>2+</sup>	Benzo-15-crown-5	[135]
Cd <sup>2+</sup>	2-furoyl-3-benzyl-3-phenylthiourea	[136]
Cd <sup>2+</sup>	Cyanocopolymer matrixes and 8-hydroxyquinoline	[137]
Cd <sup>2+</sup>	1,1'-bicyclohexyl]1,1'2,2'-tetrol	[138]
Cd <sup>2+</sup>	3,4,12,13-dibenzo-2,5,11,14-tetraoxo-1,6,10,15-Tetracyclooctadecane	[139]
Pb <sup>2+</sup>	Lead antimonite	[141]
Pb <sup>2+</sup>	Composite cation exchangers	[142–146]
Pb <sup>2+</sup>	Zr(IV) tungstophosphate	[147]
Pb <sup>2+</sup>	Dibenzo-18-crown-6 and diazadibenzo-18 crown-6	[157]
Pb <sup>2+</sup>	Dibenzo-18-crown-6 and 3,17-diazadibenzo-18-crown-6	[158]
Pb <sup>2+</sup>	15-crown-5	[160]
Pb <sup>2+</sup>	Dibenzopyridino-18-crown-6	[161]
Pb <sup>2+</sup>	Diaza-18-crown-6	[162]
Pb <sup>2+</sup>	Calix[4] arenas	[163]
Pb <sup>2+</sup>	<i>N,N</i> ,-dialkylamide derivatives of the dibenzopolyether dicarboxylic acids	[164]
Pb <sup>2+</sup>	1,10-dibenzyl-1,10-diaza-18-crown-6	[165]
Pb <sup>2+</sup>	<i>Bis</i> (2-ethylhexyl) phosphate and <i>bis</i> (1-butylpentyl) adipate	[166]
Pb <sup>2+</sup>	Dibenzyl phosphate	[167]
Pb <sup>2+</sup>	Tetrabenzyl pyrophosphate and biphenyl phosphinic anhydride	[167]
Pb <sup>2+</sup>	9,10-anthraquinone derivatives	[169]
Pb <sup>2+</sup>	<i>Bis</i> [(1-hydroxy-9,10-anthraquinone)-2-methyl] sulfide	[170]
Pb <sup>2+</sup>	1,4- <i>bis</i> (prop-2'-enyloxy)-9,10-anthraquinone	[171]
Pb <sup>2+</sup>	8-(dodecyloxy-quinoline-2-carboxylic acid)	[172]
Pb <sup>2+</sup>	Capric acid	[173]
Pb <sup>2+</sup>	Tetraphenylporphyrin	[174]

*(Continued on next page)*

**Table 1.** Materials and their selectivities for particular ions (*Continued*)

<i>Ions</i>	<i>Materials</i>	<i>References</i>
Pb <sup>2+</sup>	Piroxicam	[175]
Pb <sup>2+</sup>	5,5'-dithiobis-(2-nitrobenzoic acid)	[176]
Pb <sup>2+</sup>	Dimethylbenzotetrathiafulvalene	[177]
Pb <sup>2+</sup>	Tetraphenyl borates of lead(II) complexes of polyhydroxyethylated nonylphenols	[178]
Pb <sup>2+</sup>	1-furoyl-3-(2-hydroxyethyl)thiourea	[179]
Pb <sup>2+</sup>	Dimethylene bis(4-methylpiperidinethiocarbamate)	[180]
Pb <sup>2+</sup>	Cryptland(222)	[181]
Pb <sup>2+</sup>	1-phneyl-2-(2-quinoly)-1,2,-dioxo-2-(4-bromo) phenylhydrazone (PQDBP)	[182]
Pb <sup>2+</sup>	Salicylaldehyde-formaldehyde polymer	[183]
Pb <sup>2+</sup>	Diazacrown ethers	[185]
Pb <sup>2+</sup>	Acyclic amides oxamides	[186,187]
Pb <sup>2+</sup>	Acyclic dithiocarbamates	[188,189]
Pb <sup>2+</sup>	Tetraphenylborate salts of nonionic surfactant polyoxylates	[190]
Pb <sup>2+</sup>	Hexathia-18-crown-6-tetraone (HT-18C6TO)	[191]
Pb <sup>2+</sup>	N,N,- dimethylcyanodiazia-18-crown-6 (DM-CDA18C6)	[192]
Pb <sup>2+</sup>	N,N'-bis(salicylidene)-2,6-pyridinediamine	[193]
Pb <sup>2+</sup>	Porphyrin atropisomers tetrakis(2-hydroxy-1-naphthyl)	[194]
Pb <sup>2+</sup>	2,12-dimethyl-7,17-diphenyltetrapyrazole (I) and 5,11-dibromo-25,27-dipropoxycalix[4]arene (II)	[195]
Pb <sup>2+</sup>	<i>p</i> -tert-butyl calix[4] crown derivatives	[196]
Pb <sup>2+</sup>	Bis[5-((4-nitrophenyl)azo salicylaldehyde)](BNAS)	[198]
Hg <sup>2+</sup>	Diamine donor ligand	[199]
Hg <sup>2+</sup>	2-mercaptobenzimidazole (MBIM) and hexathiacyclooctadecane (HT18C6)	[200]
Hg <sup>2+</sup>	Alicylaldehyde thiosemicarbazone (I)	[201]
Hg <sup>2+</sup>	Thiosemicarbazones	[202]
Hg <sup>2+</sup>	Thiosemicarbazone	[203,204]
Hg <sup>2+</sup>	(1-thiazole) azo-functionalized calix[6]arene	[205]
Hg <sup>2+</sup>	Dithiazone	[206]
Hg <sup>2+</sup>	Dithia crown ethers	[207]
Hg <sup>2+</sup>	Hexathia-18-crown-6-tetraone and 2-mercaptobenzimidazole	[208]
Hg <sup>2+</sup>	1,3-diphenylthiourea	[209]
Hg <sup>2+</sup>	Ethyl-2-benzoyl-2-phenylcarbamoyl acetate (EBPCA)	[210]
Hg <sup>2+</sup>	Triiodomercurate-modified carbon paste electrode	[211]
UO <sub>2</sub> <sup>2+</sup>	Phosphate esters	[212–214]
UO <sub>2</sub> <sup>2+</sup>	Phosphine oxide	[215]
UO <sub>2</sub> <sup>2+</sup>	Diphosphine oxide	[216]
UO <sub>2</sub> <sup>2+</sup>	Phosphate esters	[217]
UO <sub>2</sub> <sup>2+</sup>	Acyclic oligoethers with terminal phosphonate groups	[218]
UO <sub>2</sub> <sup>2+</sup>	Butyl calixarene	[219]
UO <sub>2</sub> <sup>2+</sup>	Macrocyclic	[220]
UO <sub>2</sub> <sup>2+</sup>	O-methyldihexylphosphine oxide O'-hexyl-2-ethyl phosphoric acid	[221]
UO <sub>2</sub> <sup>2+</sup>	Hydroxy-acetophenone oxime-thiourea-trioxane resin	[222]
UO <sub>2</sub> <sup>2+</sup>	Dihydroxy propiophenone oxime formaldehyde resin	[223]
UO <sub>2</sub> <sup>2+</sup>	Ethylviolet-benzoic acid	[224]
UO <sub>2</sub> <sup>2+</sup>	2-thenoyl trifluoroacetone	[225]
UO <sub>2</sub> <sup>2+</sup>	Bis(ethylhexyl) phosphate ester (BEHP)	[226]
UO <sub>2</sub> <sup>2+</sup>	Ionophore	[228]
Al <sup>3+</sup>	7-ethylthio-4-oxa-3-phenyl-2-thioxa-1,2 dihydropyrimido[4,5]pyrimidine	[233]
Al <sup>3+</sup>	Formylsalicylic acid derivatives	[234]
Al <sup>3+</sup>	Tetrachloroferrate(III)-aliquate	[235]
Al <sup>3+</sup>	Stannic arsenate	[236]
Al <sup>3+</sup>	Fe(III) metavanadate	[237]
Al <sup>3+</sup>	Aliquat 336S <sup>+</sup> -Cr(SCN) <sub>4</sub> <sup>-</sup> ion pair	[238]
Cr <sup>6+</sup>	Triheptyldodecylammonium iodide	[239]

*(Continued on next page)*

**Table 1.** Materials and their selectivities for particular ions (*Continued*)

Ions	Materials	References
Cr <sup>6+</sup>	Ethyl violet or victoria blue	[240]
Cr <sup>3+</sup>	8-quinoline-dithiocarboxylate	[241]
Cr <sup>3+</sup>	Chromium dithizonate	[242]
Cr <sup>3+</sup>	Macrocyclic compound	[244]
Cr <sup>3+</sup>	4-dimethylaminoazobenzene	[245]
Cr <sup>3+</sup>	Glyoxal bis(2-hydroxyanil)	[246]
Cr <sup>3+</sup>	Tetraazacyclohexadeca-1,4,9,12-tetraene macrocyclic	[247]
Cr <sup>3+</sup>	Chromium chelates of Schiff bases, <i>N</i> -(acetoacetanilide)-1,2-diaminoethane (L1) and <i>N,N</i> -bis(acetoacetanilide)-triethylenetetraammine (L2),	[248]
Cr <sup>3+</sup>	4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one (AHMTO)	[249]
Cr <sup>3+</sup>	Aurin tricarboxylic acid modified silica	[250]
Cr <sup>3+</sup>	Tri- <i>o</i> -thymotide (I)	[251]
Ce <sup>3+</sup>	1,2,3-trithiane	[252,253]
Ce <sup>3+</sup>	Sulfonamide	[254]
Ce <sup>3+</sup>	Azomethine of pipronylidene-4-[2.2]paracyclophenylamine	[255]
Ce <sup>3+</sup>	Aminobenzothiazol	[256]
Ce <sup>3+</sup>	[4-(4'-nitrobenzyl)-1-phenyl-3,5-pyrazolidinedion)] (NBPP)	[257]
Fe <sup>3+</sup>	Crown ether	[258]

Tungstoarsenate based ion-selective membranes have been developed by Malik et al. (16), and were suitable for the determination of Cs<sup>+</sup> and Tl<sup>+</sup> ions. However, only a few reports exist concerning thallium(I) ion-selective membrane electrodes (17–25). These electrodes need to be improved with regard to their low selectivities against alkali metal ions and linearity. The thallium(I) selective electrodes based on crown ether were described (21–24). These crown ether-based ISEs exhibited good slope of calibration plots and the electrode response was stable over a wide pH range. However, the Tl<sup>+</sup> selectivity against K<sup>+</sup> for one of the bis(15-crown-5)s was fairly poor (21). Yamashoji et al. (26) found that Tl<sup>+</sup>-selective PVC membrane electrodes based on dibenzo-20-crown-6 (DB20C6) and dibenzo-22-crown-6 (DB22C6) showed higher selectivities to Tl<sup>+</sup> than that of symmetrical dibenzo-18-crown-6 (DB18C6). The electrode based on DB18C6, DB20C6 or DB22C6 showed a linear response to the Tl<sup>+</sup> activity over a range of  $3.2 \times 10^{-5}$ – $1.0 \times 10^{-1}$  M TlNO<sub>3</sub> with a slope of 59 mV per decade. Calix[6]arene or calix[5]arene derivatives and Calix[4] and quinoline-carbonitriles have been reported as Tl<sup>+</sup> PVC based ion-selective electrodes (27,28). Park et al. (29) have reported different calix[4] pyrrole for the preparation of Tl<sup>+</sup> ion selective membrane electrodes. Recently, thallium(I)-selective membrane potentiometric sensor based on dibenzylidiazia-18-Crown-6 was reported by Khayatian et al. (30).

There has been widespread interest in developing ion-selective electrodes for determining alkaline earth metals, as they exist in diverse samples. Amongst the alkaline earth metals, most investigated and developed ISEs are Ca<sup>2+</sup>-selective electrodes. The first Ca<sup>2+</sup>-selective electrode was a liquid membrane electrode developed by Ross (4). It was prepared by using a liquid membrane

of didecyl-phosphate in di-*n*-octyl phosphonate. The useful Ca<sup>2+</sup>-selective electrodes were developed by Thomas, Moody and coworkers (31,32) by incorporating Ca-bis[2,6-dinitro-4-(1,1,3,3-tetramethylbutyl)] phenoxide and Ca-bis[di{4-(1,1,3,3-tetramethylbutyl) phenyl}] phosphate in PVC. These electrodes have fast response time, showed good selectivity for Ca<sup>2+</sup> over a large number of cations. McKCervery and coworkers (33) have reported the Ca<sup>2+</sup>-selective electrodes based on Calix[6] arene tetraphosphine oxide with excellent characteristics. The ligand, calix[6]arene bearing phosphine oxide ligand groups on the lower rim is the first report that such ligands can discriminate in favor of calcium ions against magnesium ions and other alkaline metal ions. This calcium selectivity is in complete contrast to the behavior of the known calix[6] arene tetraester derivatives, which are selective for sodium against other alkali metal ions and group II ions. Electrodes based on PVC membrane incorporating ligand display almost Nernstian slopes and excellent selectivity against common interferences, including magnesium. The electrodes demonstrated effective lifetimes of at least 7 weeks and very fast response times.

Didina et al. (34) studied the influence of H<sup>+</sup>, Li<sup>+</sup> and Cs<sup>+</sup> on the potential of the Ca<sup>2+</sup>-selective PVC electrode membrane comprising thenoyl trifluoroacetone, a complexing ion-exchanger and triheptylphosphate, as a plasticizer. The anomalous behavior of these cations was explained by the formation of the association between cations and ion-exchanger. Chattopadhyaya and Misra (35) reported the Ca<sup>2+</sup>-selective heterogeneous precipitate based membrane using Ca(II) rhodizonate as the electroactive material. The electrode was used as an indicator electrode in the precipitation titration of CaCl<sub>2</sub> with Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Little work has been done on the developments of ISEs for two alkaline earth

metal ions,  $\text{Mg}^{2+}$  and  $\text{Sr}^{2+}$ . Only a few such electrodes are reported which showed interference to other alkaline earth metal ions. Recently, an electrode prepared using a membrane of phenylene bis(ditolylphosphinoxide) in PVC was reported as  $\text{Mg}^{2+}$ -sensor (36). The electrode showed good selectivity towards  $\text{Mg}^{2+}$  over  $\text{Ca}^{2+}$  and worked well in the concentration range  $6.0 \times 10^{-5}$ – $1.0 \times 10^{-1}$  M. Another electrode for  $\text{Mg}^{2+}$  has been developed by O'Donnell and coworkers (37) using various octamethylene bis(malonic acid diamides) and tris(malonic acid diamides) in PVC with 2-nitrophenyloctyl ether as solvent mediator. Maj-Zurawska (38) has reviewed the requirements for the magnesium ionophores used in ion-selective electrodes. The search for the best magnesium ionophores, in particular, having good selectivity for magnesium over calcium led to the study of different groups of compounds,  $\beta$ -diketones, monoamides of carboxylic acids, bis- and tris-malondiamides, as well as some of their compounds. As the analytical applications of magnesium ion-selective electrodes are mainly connected with clinical analysis, therefore, the possibility of simple determination of ionized magnesium in blood offers a number of diagnostically important information in medicine.

The characteristics of  $\text{Mg}^{2+}$ -selective electrode with a polymeric membrane and self-made electrode body are presented by Leoca and coworkers (39). Membranes are based on PVC-HMW, with different plasticizers N,N'-diheptyl-N,N'-dimethyl-1,4-butanediamide (ETH 1117) as neutral ligands and a various amounts of lipophilic salt. The electrode exhibited a linear response in the concentration range  $10^{-5}$ – $10^{-1}$  M  $\text{Mg}^{2+}$  ions with a slope of 23.1 mV/decade. The electrode showed good selectivity towards  $\text{Na}^+$  and  $\text{K}^+$  and presented considerable interference from  $\text{Ca}^{2+}$ . The pH of the test solution influences the response which was found to be over pH = 10 and under pH = 5. Meyerhoff et al. (40) described the effect of non-ionic surfactant containing poly(ethylene oxide) units (Brij 35 and Triton X-100) within these structure and alkyl-N-methyl glucamide (MEGA) based surfactants on the potentiometric response of neutral carrier based  $\text{Mg}^{2+}$ -selective electrodes. Results are presented for plasticized PVC membranes doped with Mg carrier ETH 7025 along with the lipophilic anionic additives. Experiments were carried out in model electrolyte solutions and the compositions were found to be similar to that of the blood serum. The ion selectivities of  $\text{Mg}^{2+}$ -selective membrane electrodes can be affected greatly by the presence of Brij 35 or Triton X-100 in the sample.

The first useful  $\text{Sr}^{2+}$ -selective electrode was developed by Baumann (41) using strontium complex of polyethylene glycol as electroactive material. The electrode was selective towards  $\text{Sr}^{2+}$  over  $\text{Ca}^{2+}$  and other bivalent cations with the exception of  $\text{Ba}^{2+}$  and  $\text{Hg}^{2+}$ . Srivastava and Jain (42) have reported a heterogeneous membrane using hydrous thorium oxide embedded in polystyrene, while Jain

et al. (43) have used strontium tungstoarsenate in araldite for  $\text{Sr}^{2+}$ -selective electrodes. The membrane electrode has been used as an end point indicator in the potentiometric titration involving  $\text{Sr}^{2+}$  ions against diammonium hydrogen phosphate. Jain et al. (44) have also reported strontium(II)-selective potentiometric sensor based on ester derivative of 4-tert-butylcalix[8] arene in PVC matrix. The sensor exhibited a good potentiometric response to  $\text{Sr}^{2+}$  over a wide range  $3.2 \times 10^{-5}$ – $1.0 \times 10^{-1}$  M with a Nernstian slope 30 mV per decade change in concentration. The membrane electrode was utilized in the potentiometric titration of  $\text{Sr}^{2+}$  against ethylenediaminetetraacetic acid (EDTA).  $\text{Cs}^+$  ion-selective membrane electrode based on ethylene glycol-functionalized polystyrene microspheres into a plasticized PVC matrix containing sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl] borate as ion-exchanger was developed by Peper et al. (45). The electrodes were evaluated with respect to  $\text{Cs}^+$  in terms of selectivity, sensitivity and dynamic response.

$\text{Ba}^{2+}$ -selective polymeric membrane electrodes have been constructed from lipophilic electrically neutral carriers (46) and neutral carboxylic polyether antibiotic (47,48) and have been found suitable for the titration of  $\text{Ba}^{2+}$  in non-aqueous media, as well as for the determination of  $\text{SO}_4^{2-}$  in the combustion products. The membranes of benzo-15-crown-5 and its  $\text{Ba}^{2+}$ -complex prepared by using an epoxy resin binder were also found suitable as  $\text{Ba}^{2+}$ -sensor (49). These electrodes showed good selectivity for  $\text{Ba}^{2+}$ , and were also used for the titration of  $\text{Ba}^{2+}$  against  $\text{SO}_4^{2-}$ . Thomas and coworkers (50) have prepared two ISEs for  $\text{Ba}^{2+}$  that utilize the membranes of non-ionic, Antarox CO-880 and its Ba-complex in PVC matrix. The electrodes were assessed for measuring  $\text{SO}_4^{2-}$  by analate subtraction. Bouklouze and coworkers (51) have used ethylene/vinylacetate-based membranes of binaphthyl polyether as  $\text{Ba}^{2+}$  sensors. The sensors worked in the concentration range  $3.0 \times 10^{-6}$ – $1.0 \times 10^{-1}$  M  $\text{Ba}^{2+}$  and have been used as indicator electrodes for determining the end point in the potentiometric titration of  $\text{SO}_4^{2-}$  in mineral water.

Yonghua (52) published a micro review on the determination of rare earth with ion selective electrodes. The review reports the construction of rare earth electrodes, the types of electroactive materials including metal oxides, salts and rare earths containing polymers and organic reagents used. W. Jinlan et al. (53) prepared a heavy rare earth ion-selective electrode containing Ag/AgCl as an internal electrode using ytterbium-containing polystyrene as the active material. The electrode is found to be feasible for the determination of heavy rare earths at pH 5.5–6.3 in flow injection system. Solid-state electrodes were prepared in PVC matrix showed the better sensitivity than other electrodes for the rare earth determination (54–56). Chattopadhyaya et al. (57) prepared the coated wire ion selective electrode (CWISE) for La(III) using lanthanum(III)-p-nitrobenzeneazo-chromotrope-213 as an

electroactive material. Agarwal et al. (58) have reported the rare earth hydroxamate complexes as sensor material for the ion-selective electrodes. The use of crown ethers in the determination of rare earth metal ions has also been explored. Shih (59) has reported the Cs<sup>+</sup> selective PVC membrane electrodes based on 15-crown-5-phosphotungstic acid (PW), 12-crown-4-PW, 1,4-dithia-12-crown-4 and 1,4-dithia-15-crown-5 as neutral carriers. These crown ether electrodes exhibited good linear response of 60 mV/decade for cesium. Pan et al. (60) synthesized the saturated urushiol crown ether rare-earth complexes (Ln = La-Nd) by the reaction of lanthanide nitrate and DSU 30C10 in acetonitrile solution. The lanthanum ion-selective electrode exhibited the linear responses in  $1 \times 10^{-2}$ – $1 \times 10^{-6}$  M La(NO<sub>3</sub>)<sub>3</sub>. This electrode showed better selectivity than other La(III) electrodes reported in the literature.

Only few zinc selective electrodes (61–72) are reported in the literature and most of them have poor sensitivity, selectivity, long response time and a short life time (61–68). An electrode was fabricated by incorporating zinc salts of bi(4-octylphenyl) hydrogen phosphate in PVC matrix (61), but the electrode showed serious interference from some metals. Linnarsund and Bhatti (62) tried zinc complex of bis(2-ethylhexyl) phosphate, an extractant, as electroactive material for preparing Zn<sup>2+</sup>-selective electrodes, but it had a very narrow working pH of range 4.5–6.0. Lebedeva and Jansons prepared Zn<sup>2+</sup>-selective electrodes using saturated solutions of Zn-quinoline-8-carbodithioatein chloroform (63). Kojima and Kamata (64) used tetrabutylthiuram disulfide as the carrier in PVC based membrane electrode. Zinc orthophosphate and zinc mercuric thiocyanate (65) were used by Rocheleaw and Purdy as electroactive material on a carbon support for the fabrication of Zn<sup>2+</sup>-selective sensors. The electrode worked well, but suffered interference from Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>. Another electrode, based on salicylaldehyde-formaldehyde resin, for zinc (66) exhibited a working concentration range of 3.0 μM–0.1 M with a near Nernstian slope. A zinc-selective electrode was used by Obmetho et al. (67) for the determination of zinc in zinc alloys. Srivastava et al. (68) used a cryptand for the fabrication of zinc selective sensor but it exhibited a non-Nernstian response. Zn-bis(2,4,4-trimethylpentyl) thiophosphinic acid complex was also used for fabricating Zn<sup>2+</sup>-selective sensor (69) but it suffers interference from copper. Crown ether based electrode has also been reported (70) in the literature for zinc. It exhibited a working concentration range of 70 μM–0.1 M with a Nernstian slope of 29.5 mV/decade of activity. Shamsipur et al. (71) reported a zinc-selective sensor based on benzo substituted macrocyclic diaramides. An electrode based on 5,6,14,15-dibenzo-1,4-dioxo-8,12-diazacyclopentadecane-5,14-diene showed response for zinc (72). It has a working concentration range of 5 μM–100 μM in the pH range of 1.5–7.0. Chelating ion-exchanger resins are found to possess specific selectivity for some metal ions and play an important role in separation processes. Wardak et al. (73) studied the prop-

erties on the ion selective electrode with a chelating pseudo-liquid membrane phase for Zn<sup>2+</sup> determination. A porphyrin based potentiometric sensor for Zn<sup>2+</sup> determinations was prepared by Gupta et al. (74). A PVC membrane electrode based on bis(2-nitrophenyl)disulfide carrier prepared by Gholivand and Mozaffari (75) exhibited a very good response for Zn<sup>2+</sup> in a wide concentration range from  $2.9 \times 10^{-7}$  to  $3.2 \times 10^{-2}$  M with a slope of 29.99 mV per decade of Zn<sup>2+</sup> concentration. The response time of the sensor was found about 10 s and the membrane can be used for more than 3 months without any observed divergence in potentials. The proposed sensor exhibited very good selectivity for Zn<sup>2+</sup> over many cations and can be used in a wide pH range (2–9). Poly(vinyl chloride) (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) have been developed to fabricate a new zinc-selective sensor by Gupta et al. (76). The sensor worked well in the concentration range  $9.8 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M with a near-Nernstian slope of  $28.0 \pm 1.0$  mV/decade of activity. The detection limit is down to  $5.0 \times 10^{-7}$  M. The working pH range of this sensor is 2.5–4.3 and it worked well in a partially non-aqueous medium up to 15% (v/v) (methanol, ethanol and acetone). 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 wastewaters. The potentiometric response characteristics of electrodes based on *N,N'*-bis(acetylaceton)ethylenediimine (I) in poly(vinyl chloride) (PVC) combined with an anion localizing agent (sodium tetraphenyl borate, NaTPB) and solvent mediators, viz. *o*-nitrophenyl octyl ether (NPOE), dibutyl (butyl) phosphonate (DBBP), tri-*n*-butyl phosphate (TBP) and chloronaphthalene (CN) were investigated by Gupta et al. (77), where the electrode had a Nernstian response (30.0 mV/decade of Zn<sup>2+</sup> activity) to Zn<sup>2+</sup> within the concentration range of  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M. The operational pH range of the electrode was 3.2–7.1. A new PVC membrane electrode for Zn<sup>2+</sup> ions based on tetra(2-aminophenyl) porphyrin (TAPP) as membrane carrier is prepared (78). The sensor exhibited a linear stable response over a wide concentration range ( $5.0 \times 10^{-5}$  to  $1.0 \times 10^{-1}$  M) with a slope of 26.5 mV/decade and a limit of detection  $3.0 \times 10^{-5}$  M (1.96 ppm).

A literature survey revealed that the first Ni-ISE was developed by Pungor and coworkers (79) using nickel-dimethyl glyoxime complex. Later on, heterogeneous membranes of nickel phosphate (80) in paraffin and silicone rubber and *bis*-2-(ethylhexyl) phosphate (81) were used for preparing Ni<sup>2+</sup> selective electrodes. Chelating ion-exchange resin (1-hydroxy-2-naphthaldoxime-formaldehyde polymer) containing nitrogen and oxygen donor atoms are prepared and characterized by Srivastava et al. (82). The resin behaved as a selective cheating ion-exchanger for some



metal ions. The PVC based membrane electrodes for the resin showed a Nernstian response for  $\text{Ni}^{2+}$  over a wide concentration range ( $2.94 \times 10^3$ – $5.87 \times 10^3$  M) between pH 3.0 and 7.5. The electrode is found to possess adequate stability and specific selectivity with a response time of 10 s. The sensor can also be used in partially non-aqueous medium having a 35% (v/v) non-aqueous content. Polyvinyl chloride based membrane of 4,4',4'',4'''-21H,23H-porphine-5,10,10,15,20-terayl) tetrakis (benzoic acid) (TBAP) and 2,3,7,8,12,13,17,18-octamethyl-21H, 23H-porphine (OMP) were prepared using dibutylphthalate (DBP), dioctylphthalate (DOP), dibutyl(butyl)phosphonate (DBBP) and 1-chloronaphthalene (CN) as plasticizing solvent mediators and sodium tetraphenylborate as an ion-excluder for  $\text{Ni}^{2+}$  selective sensors (83). A PVC membrane nickel(II) ion-selective electrode was constructed by Mousavi et al. (84) using 1,10-dibenzyl-1,10-diaza-18-crown-6 (DBzDA18C6) as a neutral carrier. The sensor exhibited a Nernstian response for Ni(II) ions over a wide concentration range  $5.5 \times 10^{-2}$ – $2.0 \times 10^{-5}$  M. It has a relatively fast response time and can be used for at least 6 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. Pentacyclooctaaza have been explored as a neutral ionophore for preparing poly(vinyl chloride) (PVC)-based membrane sensors selective to Ni(II) (85). 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 different ratio's was directly coated on the surface of a platinum-wire electrode. The electrode exhibited a near Nernstian response in the concentration range of  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  M Ni(II). The limit of detection, as determined from intersection of the extrapolated linear segments of the calibration graph was  $6 \times 10^{-7}$  M. It has a response time between 5 and 40 s for nickel concentrations ranging from  $1 \times 10^{-1}$  to  $1 \times 10^{-6}$  M. The electrode revealed moderate selectivities over a number of alkali, alkaline earth, 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 EDTA and determination of nickel content of chocolate and milk powder samples. Dibenzo[*e,k*]-2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,5,7,9,11-hexaene has been explored by Singh and Saxena (86), an electroactive material for the fabrication of a poly(vinyl chloride)-based membrane electrode for selective determination of  $\text{Ni}^{2+}$  ions. It worked well in a wide concentration range of  $3.98 \times 10^{-6}$  to  $1.00 \times 10^{-1}$  M with a Nernstian slope of 29.5 mV per decade of activity between pH 2.5 and 7.7. The electrode exhibited a detection limit of  $2.98 \times 10^{-6}$  M and a fast response time of 8s, and was used over a period of 4 months with good reproducibility ( $S=0.2$  mV). PVC-based membranes of meso-tetrakis-{4-[tris-(4-allyl dimethylsilyl-

phenyl)-silyl]-phenyl}porphyrin (I) and (sal)2trien (II) as electroactive material with dioctylphthalate (DOP), tri-*n*-butylphosphate (TBP), chloronaphthalene (CN), dibutylphthalate (DBP) and dibutyl(butyl) phosphonate (DBBP) as plasticizing solvent mediators have been found to act as  $\text{Ni}^{2+}$  selective sensor. The sensor exhibited Nernstian response in the activity range  $2.5 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M over wide pH range (2–5.5) with a fast response time (8 s). The sensor was found to work satisfactorily in partially non-aqueous media up to 20% (v/v) content of methanol or ethanol and acetone and could be used over a period of 4 months (87). Nickel(II)-selective sensors have been fabricated from poly(vinyl chloride) (PVC) matrix membranes containing neutral carrier dibenzo-18-crown-6 as electroactive material, sodium tetraphenylborate (NaTPB) as an anion excluder and tris-(2-ethylhexyl) phosphate (TEHP) as plasticizing solvent mediator (88). The membrane having the composition of crown ether:NaTPB:TEHP:PVC in the ratio 10:1:200:200 (w/w) exhibited best results with linear potential response in the concentration range of  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-1}$  M and a Nernstian slope of 29.5 mV/decade of activity between 2.6 and 6.8. The sensor exhibited a fast response time of <25 s, is inert towards non-aqueous medium up to 15% (v/v) and was used over a period of 4 months with good reproducibility. The suitability of a dioxime derivative, (2*E*, 3*E*)-2*H*-1,4-benzothiazine-2,3(4*H*)-dione dioxime as a neutral ionophore for the preparation of a PVC membrane electrode for Ni(II) ions was investigated by Yari et al. (89). It can be used for at least 4 months without any considerable divergence in potentials and it has a relatively fast response of <10 s. The prepared membrane exhibited a near Nernstian response for  $\text{Ni}^{2+}$  ions over a wide concentration range ( $1.0 \times 10^{-6}$  to 1.0 M) with a detection limit of  $1.6 \times 10^{-6}$  M. At a working pH range of 2.0–6.5, the proposed membrane electrode revealed very good selectivity for  $\text{Ni}^{2+}$  ions over a wide variety of other cations. A new PVC membrane electrode that is highly selective to Ni(II) ions was prepared by using *N,N'*-bis-(4-dimethylamino-benzylidene)-benzene-1,2-diamine as a suitable neutral carrier (90). The sensor exhibited a Nernstian response for nickel ions over a wide concentration range ( $1.0 \times 10^{-2}$  to  $2.0 \times 10^{-7}$  M) with a slope of  $30 \pm 1$  mV per decade. It has a response time of <10 s and can be used for at least 2 months without any measurable divergence in potential. The electrode can be used in the pH range from 4.5 to 9.0. PVC-based membrane of 1,5-diphenylthiocarbazon revealed a Nernstian potentiometric response with the slope of 29.5 mV per decade for Ni over a wide concentration range. The response time of the electrode is quite short and was used for a period of 2 months with a good reproducibility (91). The detection limit of this electrode was  $2.8 \times 10^{-6}$  M. The proposed electrode revealed very high selectivity for  $\text{Ni}^{2+}$  in the presence of a wide variety of metal ions such as  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Tl}^+$ ,  $\text{Hg}^{2+}$ , and  $\text{Fe}^{2+}$  at concentrations  $1 \times 10^{-3}$  M.

Due to the vital importance of copper in many biological systems (92,93) and industry (94), the urgent need for a copper-selective electrode for potentiometric monitoring of  $\text{Cu}^{2+}$  in different industrial, medicinal and environmental samples, a variety of ion carriers have been used in the construction of copper(II) selective electrodes. These copper ion carriers include small size thiocrown ethers (95,96), non-cyclic neutral ionophores containing dithiocarbamate groups (97) and nitrogen atom (98), calix (99), arenes (100), Schiff's bases (99–101) and macrocycles diamides (102) various species. However, all of these copper sensors have one, two, or in some cases, all of the following problems: (1) high detection limit, (2) narrow working concentration range and (3) serious interfering effect of cations such as  $\text{Fe}^{3+}$ ,  $\text{Na}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cs}^+$ ,  $\text{K}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ . Potentiometric measurements with a  $\text{Cu}^{2+}$  ion-selective electrode allow determining free ion concentration in water samples directly. For copper determination, solid membrane electrodes based on copper sulfide (103–106), tungsten oxide (107), ion-exchangers (108,109) and copper(III) complexes (110–115) as electroactive material have also been tried as copper potentiometric sensors. Macrocyclic polyethers (116) and polymethylidene (117) based sensors have been developed for the potentiometric determination of  $\text{Cu}^{2+}$ . Talantsev and Syroratskaya (118) determined  $\text{Cu}^{2+}$  potentiometrically by using ISEs with a crystal membrane, which is found to be more sensitive than the photometric method using diethylthiocarbamate. Comparative analyses were made with river water and the method has better characteristics than the photometric method and can be used for the analysis of natural and wastewater. Banes et al. (119) have synthesized a novel highly copper(II) selective chelating ion-exchanger electrode based on poly(glycidyl methacrylate-co-ethylene dimethacrylate) beads modified with aspartic acid derivatives. A copper(II) ion-selective electrode based on copper(II) salicylaniline Schiff's base complex in styrene-co-acrylonitrile copolymer (SAN) has been developed by Gupta et al. (120). SAN-based membrane electrode containing copper(II)–Schiff's base complex, dioctylphthalate as plasticizer and sodium tetraphenylborate as an anion excluder exhibited a linear response with a Nernstian slope of 30 mV/decade within the concentration range of  $1 \times 10^{-6}$  –  $1 \times 10^{-2}$  M of  $\text{Cu}^{2+}$  ions. The selectivity of electrode for  $\text{Cu}^{2+}$  ion has been found to be better in comparison to other various interfering ions. The prepared electrode can be used successfully as an indicator electrode for the potentiometric titration of the  $\text{Cu}^{2+}$  ion using EDTA. Ganjali et al. (121) have also reported a novel copper selective electrode by using a new Schiff's base bis-2-thiophenal propanediamine (TPDA) as an excellent neutral carrier for the potentiometric monitoring of ultra trace amount of  $\text{Cu}^{2+}$  ions. The membrane electrode was successfully used for the direct determination of copper in black tea and as an indicator electrode in potentiometric titration of copper ion. Mashhadizadeh et al. (122) prepared a new PVC mem-

brane electrode that was highly selective for Cu(II) ions. The electrode was prepared by using 3,6,9,14-tetrathiaibicyclo [9.2.1] tetradeca-11,13-diene as a neutral carrier. The electrode exhibited a Nernstian slope of 28 mV per decade change in concentration over a wide range i.e.,  $10^{-7}$  M  $\text{Cu}^{2+}$ . Polypyrazolymethanes, represented by the general formula  $\text{H}_m\text{C}(\text{pz})_n(\text{pz}:1\text{-pyrazolyl})$ , form a six-membered  $\text{MN}_4\text{C}$  chelate ring of a shallow boat configuration, acting as tridentate or bidentate ligands. Yoshimoto et al. (123) developed novel ion-selective membrane electrodes based on polypyrazolymethanes and reported the first results of their use.  $\text{HC}(\text{pz})_3$  (1),  $\text{HC}(3,5 \text{ Me}_2\text{pz})_3$  (2),  $\text{HC}(3\text{-Phpz})_3$  (3),  $\text{HC}(3\text{-}i\text{Prpz})_3$  (4),  $\text{HOCH}_2\text{C}(\text{pz})_3$  (5), and  $\text{C}(\text{pz})_4$  (6) were prepared as described in the literature and incorporated as an ionophore in PVC membrane. The selectivity of the electrodes changed with the substituents of polypyrazolymethanes. The electrodes of 3,4 and 6 were selective for  $\text{Cu}^{2+}$  at pH 5.5. The electrode 4 showed rapid response time ( $\sim 10$  s) and reproducible results for more than 4 months, and successfully applied to potentiometric titration of  $\text{Cu}^{2+}$  with EDTA.

Recently, Fakhari et al. (124) reported a Cu(II) ion-selective membrane electrode based on 2,2'-(1,2-ethandiyl-bis(nitrilomethylidene)-bis) *meta* cresole(I), 2,2'-(1,2-ethandiyl-bis(nitrilomethylidene)-bis) *ortho* cresole(II), and 2,2'-(1,2-ethandiyl-bis(nitrilomethylidene)-bis) *para* cresole(III) as excellent neutral ion carriers. New PVC membrane ion selective electrode based on 1,3,5-Tris(8-quinolinoxymethyl)-2,4,6-trimethylbenzene (MO8HQ) was reported by Mittal et al. (125). The electrode exhibited a good Nernstian response to Cu (II) ions in the range of  $1.0 \times 10^{-6}$  to  $1 \times 10^{-1}$  M with a reasonably fast response time of 15 s. The effect of pH and electrode response is also reported. It showed good selectivity for Cu(II) ions in comparison to heavy metal ions, transition metal ions and for alkali and alkaline earth metal ions. The electrode response and selectivity remains unchanged for at least 5 months. The potentiometric response characteristics of  $\text{Cu}^{2+}$ -selective electrode based on bis(acetylaceton)propylenediimine (I) combined with anion localizing agent (sodium tetraphenyl borate (NaTPB)) and solvent mediator (dibutyl butyl phosphonate (DBBP), tri-*n*-butyl phosphate (TBP) and chloronaphthalene (CN)) was investigated (126). The electrode had a Nernstian response (30.0 mV/decade) to  $\text{Cu}^{2+}$  within the concentration range  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-1}$  M and detection limit of 0.5 ppm. The operational pH range of the electrode was 3.3–7.0. The response of copper (II) ion-selective electrode based on chalcogenide glassy-crystalline Cu–As–S alloys was described by Cali et al. (127). The potentiometric measurements showed a Nernstian behavior in a large range of copper (II) concentration with short response time and a detection limit close to  $1 \times 10^{-6}$  M. The selectivity and the effect of the pH on the response have been determined. Bis(2-hydroxyacetophenone) butane-2,3-dihydrazone (BHAB) was used as new N-N Schiff's base

which plays the role of an excellent ion carrier in the construction of a Cu(II) membrane sensor (128). The electrode exhibited a Nernstian behavior (with slope of 29.6 mV per decade) over a very wide concentration range ( $5.0 \times 10^{-8}$  to  $1.0 \times 10^{-2}$  M) with a detection limit of  $3.0 \times 10^{-8}$  M. It showed relatively fast response time, in whole concentration range (<15 s), and can be used for at least 12 weeks in the pH range of 2.8–5.8.

In measuring the heavy metal ions like  $\text{Cd}^{2+}$  in the industrial wastewater, the ion-selective electrodes are very convenient because of simplicity and selectivity. Ross et al. (129,130) have reported the precipitate based solid state CdS- $\text{Ag}_2\text{S}$  mixture membrane by stoichiometric reaction. Hirata et al. (131) have also developed the ceramic solid-state CdS- $\text{Ag}_2\text{S}$  mixture membrane by baking the CdS- $\text{Ag}_2\text{S}$  mixed powder or its pressed membrane at  $700^\circ\text{C}$ . Hopertenam and Cosma (132) have reported some preparation methods for mixtures of cadmium and silver sulfides with  $\text{Cd}^{2+}$ -selective electrode properties. Sodium sulfide, thioacetamide and sodium thiosulfate were used for simultaneous precipitation of CdS and  $\text{Ag}_2\text{S}$ . The selectivity of the  $\text{Cd}^{2+}$  ion-selective electrode is affected by  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Fe}^{3+}$  ions co-existed in industrial wastewater. Also, it interfered by an oxidizer such as chlorine or hypochlorite ion. The detection limit and the calibration curve were slightly changed by pH of samples as in basic solutions  $\text{Cd}^{2+}$  ion becomes cadmium hydroxide  $\text{Cd}(\text{OH})_2$ . In the acidic solution, the detection limit becomes inferior owing to the increasing of solubility of CdS. All sample measurements should be performed in the best pH region. Therefore, the buffer solution for  $\text{Cd}^{2+}$  ion measurement such as Orion TISAB (total ion strength adjustment buffer) (133) for the fluoride ion measurement, which could mask the interfering substances, was developed for the practical use. Loginova and Chernysheva (134) have also reported the  $\text{Cd}^{2+}$ -buffer for potentiometry with ion-selective electrodes in micellar media. Srivastava et al. (135) have reported a plasticized PVC based membrane of benzo-15-crown-5, which exhibited a good response for  $\text{Cd}^{2+}$  in a wide concentration range ( $3.16 \times 10^{-5}$ – $1.00 \times 10^{-1}$  M) with a slope of 20 mV/decade of ( $\text{Cd}^{2+}$ ). The electrode was used at one stretch, for a period of 2 months and is played good selectivity for  $\text{Cd}^{2+}$  over alkali, alkaline earth and transition metal ions. The membrane sensor was also used as an indicator electrode in potentiometric titration involving Cd(II) ions. Parez-Marín and coworkers (136) have used 2-furoyl-3-benzyl-3-phenylthiourea, which was deposited on an epoxy resin and employed as neutral barrier for the ion detection of cadmium. The sensor exhibited a Nernstian slope of 29.8 mV/decade. Potential response of Cd(II) ion-selective electrode based on cyanocopolymer matrixes and 8-hydroxyquinoline as ionophore was evaluated by Gupta and D'Arc (137). The cyano groups of the copolymers contributed significantly to enhance the selectivity of the electrode. The electrode showed an appreciable average life of 6 months without any significant

drift in the electrode potential, which is explained considering phase boundary model based on thermodynamics considerations. Shamsipur and coworkers (138) have developed a cadmium(II) ion-selective membrane electrode based on newly synthesized 1,1'-bicyclohexyl]1,1',2,2'-tetrol as membrane carrier. The proposed membrane sensor showed excellent discrimination ability towards  $\text{Cd}^{2+}$  ion with regard to several alkali, alkaline earth, transition and heavy metal ions. It was successfully applied for the direct determination of  $\text{Cd}^{2+}$  in solution and as an indicator electrode in potentiometric titration of cadmium ions. Singh et al. (139) have reported a polystyrene based membrane of 3,4,12,13-dibenzo-2,5,11,14-tetraoxo-1,6,10,15-tetracyclooctadecane as a membrane carrier for  $\text{Cd}^{2+}$  ions. It was found that some amounts of surfactants do not disturb the functioning of the sensor and also used to estimate  $\text{Cd}^{2+}$  ions in real samples. Because of the increased industrial use of lead on one hand, and its serious hazardous effect to human health, on the other (140), the electrochemical properties and preparation of the Pb(II) ion-selective membrane electrodes have been extensively studied by using different active materials. Thind et al. (141) have developed a  $\text{Pb}^{2+}$  ion-selective membrane using lead antimonate as an electroactive phase and araldite as a polymer binder. Khan et al. (142–146) have published their finding for the determination of Hg(II), Cd(II), Pb(II), by potentiometric titration using polypyrrole/polyantimonic, polyaniline Sn(IV) tungstoarsenate, polyaniline Sn(IV) arsenophosphate, polypyrrole Th(IV) phosphate, polyaniline Sn(IV) phosphate and poly-o-toluidine Zr(IV) phosphate electrically conducting organic-inorganic composite based ion-selective membrane electrodes.

Gupta et al. (147) have published their results on the studies of araldite based Zr(IV) tungstophosphate (ZWP) cation-exchanger membrane as Pb(II) ion-selective electrode. Besides the solid-state membranes (148–153) and liquid ion-exchange membranes (154,155), there has been increasing interest in the use of ionophore ligands as sensing materials for neutral carrier type Pb(II) ion-selective electrodes, mainly due to the unique selectivities of these compounds. Very few of the  $\text{Pb}^{2+}$ -selective ionophores described so far have been characterized as ISEs (156). In 1986 Shpigun et al. (157) used five macrocyclic ligands as Pb carriers in PVC membranes plasticized with 66% dioctylphthalate or o-nitrophenyl octyl ether. Dibenzo-18-crown-6 and diazadibenzo-18 crown-6 were found to be good carriers for  $\text{Pb}^{2+}$ -selective electrodes for potentiometry in solutions containing  $2 \times 10^{-6}$ – $1 \times 10^{-2}$  M Pb(II) ions. In 1987, Navikov et al. (158) used dibenzo-18-crown-6 and 3,17-diazadibenzo-18-crown-6 as carriers for lead selective electrodes. Lead in environmental samples was determined using an ISE by Li and Liu (159). In 1995, a PVC-based membrane of 15-crown-5 was used by Srivastava et al. (160) for a lead selective electrode. Tavakkoli and Shamsipur (161) had reported a Pb-ISE based on dibenzopyridino-18-crown-6 as membrane carrier. This

lead selective electrode exhibited comparatively good selectivities with respect to alkali, alkaline earth and some transition and heavy metal ions. Malinowska et al. (162) have reported a lead selective membrane electrode containing ionophores based on diaza-18-crown-6 units possessing amide and sulfonamide functions. Malinowska et al. have also reported polymeric membrane ion-selective membrane electrodes based on thioamide functionalized calix[4]arenes for which the selectivity coefficients for  $\text{Pb}^{2+}$  relative to  $\text{Cu}^{2+}$  were  $10^{-3}$ – $10^{-4}$  (163). While Ohki et al. (164) have made solvent polymeric membrane ISEs by using twelve kinds of N,N-dialkylamide derivatives of the dibenzopolyether dicarboxylic acids as  $\text{Pb}^{2+}$ -selective neutral carriers. Potentiometric selectivities of the ISEs for the  $\text{Pb}^{2+}$  over other heavy metal cations, alkali metal cations and alkaline earth metal cations have been assessed. Another  $\text{Pb}^{2+}$ -selective membrane electrode based diaza-18-crown-6 was reported by Mousavi et al. (165). They constructed a PVC membrane lead(II) ion selective electrode using 1,10-dibenzyl-1,10-diaza-18-crown-6 as membrane carrier. This electrode was employed as an indicator electrode in potentiometric titration of EDTA with lead ions and used for direct determination of lead in wastewater. Bis(2-ethylhexyl) phosphate is quite suitable for making a  $\text{Pb}^{2+}$  selective electrode. Thus, an electrode constructed using bis(2-ethylhexyl) phosphate and bis(1-butylpentyl) adipate as a solvent mediator in a PVC membrane matrix showed high selectivity and sensitivity (166). When (2-ethylhexyl) group was replaced by benzyl group, the sensitivity and selectivity to  $\text{Pb}^{2+}$  were considerably improved. Thus, Xu and Katsu (167) employed dibenzyl phosphate and bis(1-butylpentyl) adipate as a solvent mediator in a PVC membrane matrix and exhibited a near-Nernstian response to  $\text{Pb}^{2+}$  in the concentration range from  $3 \times 10^{-6}$  to  $1 \times 10^{-2}$  M with a slope of 30.1 mV per concentration decade. They have also employed tetrabenzyl pyrophosphate and biphenyl phosphinic anhydride with two phosphoryl groups as liganding sites, which can be used as novel ionophores to make  $\text{Pb}^{2+}$ -selective membrane electrodes. A good result was obtained with tetrabenzylpyrophosphate and the electrode based on this ionophore and the electrode membrane matrix with PVC exhibited a near-Nernstian response to  $\text{Pb}^{2+}$  in the concentration range of  $1 \times 10^{-5}$ – $1 \times 10^{-2}$  M with a slope of 28.7 mV/concentration decade in a solution containing 0.1 M  $\text{Mg}(\text{NO}_3)_2$ . The addition of potassium tetrakis(*p*-chlorophenyl) borate (40% mol relative to tetrabenzyl-pyrophosphate) caused a drastic change in the response slope (53.3 mV/concentration decade), probably due to the formation of  $\text{PbA}^+$ , where A stands for anions present in the sample solution, and significantly decreased the electrode selectivity to other metal cations (167). 9,10-Anthraquinones are the largest group of natural quinines and have significant chemical importance. In addition to a wide variety of chemical and industrial applications (168), recently synthetic derivatives of anthraquinones have employed as a lead carrier in PVC

membrane. Shamsipur et al. (169) used four different 9,10-anthraquinone derivatives to characterize their abilities as lead(II)-ion selective electrodes in PVC matrix membrane. The electrode based on 1,8-dihydroxy-2,7-bis(prop-2'-enyl)-9,10-anthraquinone exhibited a Nernstian response for  $\text{Pb}^{2+}$  ions over a wide concentration range ( $2.0 \times 10^{-3}$ – $2.0 \times 10^{-6}$  M). Another 9,10-anthraquinone derivatives e.g., bis[(1-hydroxy-9,10-anthraquinone)-2-methyl] sulfide (170) and 1,4-bis(prop-2'-enyloxy)-9,10-anthraquinone (171) have also been used as a lead(II) membrane carrier. The derivative of quinaldic acid, 8-(dodecyloxy-quinoline-2-carboxylic acid), was used as an ionophores in the development of a Pb(II) selective electrode by Casado et al. (172). Solvent extraction studies showed that this compound is selective for Pb(II) and Cu(II) over a variety of divalent and monovalent metals. The electrode is selective for  $\text{Pb}^{2+}$  over  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  with  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$ , the most interfering metal ions. Mousvi et al. (173) studied a PVC-based capric acid membrane potentiometric sensor for lead(II) ions. The optimum composition of the membrane was 30 wt% PVC, 60 wt% NPOE as plasticizers, 5 wt% ionophore and 5 wt% potassium tetrakis(*p*-chlorophenyl)borate as lipophilic salt. The electrode was used for the potentiometric titration of chromate ions with  $\text{Pb}^{2+}$  ions. Sadeghi and Shamsipur (174) has reported a PVC membrane electrode for  $\text{Pb}^{2+}$  ions based on tetraphenylporphyrin. The sensor exhibited a Nernstian response for  $\text{Pb}^{2+}$  ions over a wide concentration range ( $1 \times 10^{-5}$ – $1 \times 10^{-2}$  M). The proposed electrode showed a fairly good discriminating ability towards  $\text{Pb}^{2+}$  ions in comparison to some alkali, alkaline earth, transition and heavy metals ions and was used as an indicator electrode in potentiometric titration of  $\text{Pb}^{2+}$  ions. They have also reported an ion-selective membrane electrode for the determination of  $\text{Pb}^{2+}$  ions based on a non cyclic ion-carrier, piroxicam (175). In competition with PbS-based Pb(II) electrodes, the piroxicam-lead(II) ISEs demonstrated the advantage of virtually no interference from some common transition metal ions such as  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$  and only slight interference from alkaline earth metal ions is observed. Ganjali et al. (176) have employed 5,5'-dithiobis-(2-nitrobenzoic acid) as a suitable ion carrier to construct a lead selective PVC based membrane electrode which exhibited significantly high selectivity to lead ion over alkali, alkaline earth and several transition metal ions. Ganjali et al. (177) have also reported a PVC membrane electrode for  $\text{Pb}^{2+}$  ion based on recently synthesized dimethylbenzotetrahydrofulvalene as membrane carrier. The electrode exhibited a very low limit of detection of  $8 \times 10^{-6}$  M and can be used as an indicator electrode in potentiometric titrations of  $\text{Pb}^{2+}$  ions in both  $\text{H}_2\text{O}$  and 90% MeOH solutions. Kulapina et al. (178) proposed lead selective electrode from tetraphenyl borates of lead(II) complexes of polyhydroxyethylated nonylphenols with various number of hydroxyethyl groups. Perez-Marin et al. (179) studied the 1-furoyl-3-(2-hydroxyethyl)thiourea as

ionophores for lead(II) in an electrode of liquid membrane of neutral carrier. This PVC polymeric membrane was deposited dropwise directly into a composite graphite-epoxy support. The sensor exhibited a Nernstian slope at 29.17 mV/decade and a linear response range between  $4 \times 10^{-5}$ – $6.9 \times 10^{-3}$  M. Isidak (180) has reported the solid state lead(II) ion selective PVC membrane electrode using dimethylene *bis*(4-methylpiperidinthiocarbamate) as a neutral ionophore and nitrophenyloctyl ether or dioctylsebacate as plasticizers. They found that the response properties of solid state contact PVC membrane electrode prepared with nitrophenyloctyl ether was better than that those of the membrane electrode prepared with dioctylsebacate.

Ensaf et al. (181) have developed the lead(II)-selective membrane electrode by incorporating cryptand(222) as the neutral carrier into a plasticized PVC membrane. The electrode was used as an indicator electrode in the potentiometric titration of  $Pb^{2+}$  with EDTA. In this connection, more recently they have also reported the use of 1-phenyl-2-(2-quinolyl)-1,2-dioxo-2-(4-bromo) phenylhydrazone (PQDBP) as an excellent neutral carrier in construction of a lead-PVC membrane electrode (182). The membrane electrode was also applied to the titration of  $Pb^{2+}$  solution with potassium chromate as well as determination of lead in mineral samples. Vardhan and Singh (183) have reported a lead(II)-selective electrode having a chelating ion-exchange resin (salicylaldehyde formaldehyde polymer) containing nitrogen and oxygen donor atoms, as electroactive material. The characteristics of two ion-selective electrodes based on PVC and polystyrene membrane in the presence of interfering ions has been studied. The ion-exchange coefficients and diffusion of Pb(II) in Nafion-modified electrodes were determined by Liu et al. (184) in the process of ion-exchange. Yang et al. (185) have reported the use of diazacrown ethers bearing double armed thenoyl and thiphenacetyl groups as potential selective agents for  $Pb^{2+}$  ion-selective membranes. Acyclic amides oxamides have also been investigated as potential ionophores for lead (186,187). Kamata and Onoyama (188,189) used acyclic dithiocarbamates as ionophore for  $Pb^{2+}$  ion-selective electrodes. Jabar et al. (190) introduced liquid ion-exchange membranes incorporating the tetraphenylborate salts of nonionic surfactant polyoxylates for the preparation of lead selective sensor. Shamsipur et al. (191) reported the use of hexathia-18-crown-6-tetraone (HT-18C6TO) as an excellent neutral carrier in construction of lead PVC membrane electrode. Ganjali et al. (192) introduced a high selective and sensitive lead ion selective membrane coated on a graphite (CGISE) for potentiometric monitoring of ultra trace amount of  $Pb^{2+}$  in environment samples by using N,N'-dimethylcyanodiaz-18-crown-6 (DM-CDA18C6) as an excellent ionophore. Jeong et al. (193) described the fabrication and characterization of new lead ion-selective electrode based on N,N'-bis(salicylidene)-2,6-pyridinediamine as an ionophore. The coordinating effect for the selective re-

sponse of lead ion was also investigated by using PVC membrane. The lead(II)-selective electrodes based on porphyrin atropisomers tetrakis(2-hydroxy-1-naphthyl) was reported by Lee et al. (194). The membrane electrode displayed a good Nernstian response (29.2 mV/decade) to  $Pb^{2+}$  over the linear range of  $3.2 \times 10^{-5}$  to  $1 \times 10^{-1}$  M. Most of the metal ions would not affect the selectivity of the lead electrode seriously. Jain et al. (195) studied in detail a comparative study of  $Pb^{2+}$ -selective sensors based on the membrane of 2,12-dimethyl-7,17-diphenyltetrapyrzole (I) and 5,11-dibromo-25,27-dipropoxycalix[4]arene (II).

Mahajan et al. (196) reported a mercury ion selective electrode based on the p-tert-butyl calix[4] crown derivatives with imine units as an ionophore. The electrode exhibited a good response for mercury(II) ions over a concentration range of  $5.0 \times 10^{-5}$ – $1.0 \times 10^{-1}$  M with a near Nernstian slope of 27.3 mV per decade. The electrode showed high selectivity for Hg(II) ions over most of the alkali, alkaline earth and transition metal ions.  $Fe^{3+}$  and  $Ag^{+}$  ions were found to be the interfering ions. Mashhadizadeh et al. (197) reported the use of Schiff base ligand recently synthesized in his laboratory (198) of bis[5-((4-nitrophenyl)azo salicylaldehyde)](BNAS) as an excellent neutral carrier in construction of mercury(II)-PVC membrane electrode. The electrode was utilized as a potentiometric sensor for the titration of mercury(II) solution with EDTA. Gupta et al. (199) reported the electroanalytical applicability of a diamine donor ligand as mercury ion sensor. The results showed that the sensor developed for Hg(II) ion using the above system as an electroactive phase in a PVC matrix has a wide working concentration range and a fast response time with reproducible results. The construction, performance, and applications of coated-wire mercury(II) selective electrodes based on 2-mercaptobenzimidazole (MBIM) and hexathiacyclooctadecane (HT18C6) carriers, in plasticized PVC matrix, were described by Mazloum et al. (200). The influences of membrane composition and pH on the potentiometric response of the electrodes were investigated. The electrodes exhibited near Nernstian responses for  $Hg^{2+}$  ions over a wide concentration range (4 to 5 decades of the concentration), and a detection limit of about  $6 \times 10^{-7}$  M. The response time of the electrodes is in between 20–100 s, depending on the concentration of mercury, and can be used for about 2 months without any considerable divergence in potential. The proposed sensors revealed good selectivity for  $Hg^{2+}$  in the presence of several metal ions. The best selectivity was observed for the electrode based on MBIM carrier. These electrodes were also used as indicator electrodes in the potentiometric titration of  $Hg^{2+}$  with EDTA and for the determination of mercury in wastewater samples. Mahajan et al. (201) reported mercury(II) ion-selective electrode based on alicylaldehyde thiosemicarbazone (I) as an ionophore. Thiosemicarbazones are an important class of ligands with enormous biochemical applications (202). The electrode exhibited high selectivity for mercury(II)

ions over alkali, alkaline earth and some transition metals ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ag}^+$ ). This is the first report on the use of a thiosemicarbazone as ionophore for metal ions (203,204). The membrane electrode was also applied in the titration of  $\text{Hg}^{2+}$  with iodide ion. Lu et al. (205) reported the hitherto unknown selective complexation of the (1-thiazole) azo-functionalized calix[6]arene derivative as a novel ionophore used in a mercury ion-selective PVC membrane electrode. In this work, the effect on the response of changing the acidity and the anionic site and the response characteristics of the electrode produced were investigated. The results showed that the proposed electrode could be applied in real samples. Dithiazone (206), dithia crown ethers (207), hexathia-18-crown-6-tetraone (208) and 2-mercaptobenzimidazole were also used as potential selective agents for  $\text{Hg}^{2+}$  PVC membrane electrodes having a good Nernstian response and high ion selectivity. Recently, 1,3-diphenylthiourea (209) has been reported as a very selective ionophore for the  $\text{Hg}^{2+}$  ISE, but the applicability has not been described. Mercury (II) ion-selective PVC membrane sensor based on ethyl-2-benzoyl-2-phenylcarbamoyl acetate (EBPCA) as novel nitrogen containing sensing material was developed by Hassan et al. (210). The sensor exhibited good linear response of 30 mV per decade within the concentration range  $1 \times 10^{-6}$ – $1 \times 10^{-3}$  M  $\text{Hg}(\text{II})$ . The sensor showed good selectivity for mercury(II) ion in comparison with alkali, alkaline earth, transition and heavy metal ions. The proposed sensor was also applied as a sensor for the determination of  $\text{Hg}(\text{II})$  content in some amalgam alloys. Jain et al. and Srivastava et al. have also fabricated polystyrene supported heterogeneous ion-exchange membrane electrode of heteropolyacid salts (e.g.,  $\text{Ce}(\text{IV})$  selenite), which were found to be selective for  $\text{Hg}^{2+}$ . Recently, Abbas et al. (211) have reported a new triiodomercurate-modified carbon paste electrode for the potentiometric determination of  $\text{Hg}(\text{II})$  ions.

Potentiometric membrane sensors for uranium(IV) were commonly prepared using phosphate esters (212–214), phosphites (215), phosphine oxides (216), diphosphine oxide (217), acyclic oligoethers with terminal phosphonate groups (218), butyl calixarene (219) and macrocyclic (220) ionophores. Bifunctional chelating agent O-methyldihexylphosphine oxide O'-hexyl-2-ethyl phosphoric acid has also been proposed as a single molecular unit which combines the overall synergetic properties of phosphine oxide and ester of phosphoric acid (221) and has been used as an electroactive material in a membrane sensor. Hydroxy-acetophenone oxime-thiourea-trioxane resin (222), dihydroxy propiophenone oxime formaldehyde resin (223), tertiary ion association complexes of uranyl ion with ethylviolet-benzoic acid (224) and binary complexes with 2-thenoyl trifluoroacetone (225) have also been used in polymeric membrane based uranyl sensors. However, many of these sensors suffer from the disadvantages of a narrow range of response (226), interfer-

ence from associated anions (227,228) and some common cations (229,230) and the need for several time consuming steps for ionophore preparation (222,223,226). Although bis(ethylhexyl) phosphate ester (BEHP) has been used in PVC membrane sensors responding to uranyl ions (226), the more lipophilic derivative tris(ethylhexyl)phosphate (TEHP) has never been examined. On the other hand, a literature survey showed that O-(1,2-dihydro-2-oxo-1-pyridyl)-*N,N,N',N'* bis(tetramethyl)uranium hexafluorophosphate (TPTU) has no analytical applications despite the presence of four active chelating centers in its structure (227). Both reagents are commercially available and are used either as a solvent or as a peptide-coupling agent. Therefore, DTP A and TPTU reagents were examined by Hassan et al. (228) as novel ionophores in PVC based membrane sensors for uranyl ions. Sensors with optimized membrane composition displayed enhanced selectivity, stability, fast and linear response for a wide concentration range of uranyl ion. Characterization and applications of these sensors for quantification of uranium in certified and naturally occurring ores are also described.

Less attention has been given for determining tripositive metal ions. Very few potentiometric devices have been designed for aluminum (229–232). Saleh et al. (233) developed a novel potentiometric membrane sensor for selective determination of  $\text{Al}(\text{III})$  ions. In this PVC matrix membrane sensor incorporating 7-ethylthio-4-oxa-3-phenyl-2-thioxa-1,2 dihydropyrimido[4,5]pyrimidine ionophore has been used as a membrane carrier for  $\text{Al}^{3+}$  ions. This electrode has a minimum interference of  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ions and successfully applied for the potentiometric titration of  $\text{HPO}_4^{2-}$  with  $\text{Al}^{3+}$  and for direct potentiometry of  $\text{Al}^{3+}$  content of some rock samples. A novel  $\text{Fe}(\text{III})$ -selective PVC membrane electrodes based on formylsalicylic acid derivatives were also reported by Saleh (234). A  $\text{Fe}^{3+}$  ion-selective membranes sensor based on the use of coated wire anionic membrane incorporating tetrachloroferrate(III)-aliquate suffered from significant interference from many cations such as  $\text{Sn}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$  (235). These difficulties also arise on using a heterogeneous solid-state cation-exchanger membrane with stannic arsenate dispersed in epoxy resin (236). Volkov et al. (237) have developed a  $\text{Fe}(\text{III})$  selective solid phase electrode with an ion-sensitive material  $\text{Fe}(\text{III})$  metavanadate.

A literature survey revealed that very little work has been done on the development of ISEs for  $\text{Cr}(\text{III})$  ion, the first report on  $\text{Cr}(\text{III})$  was in 1980 (238). In this study, a PVC based chromium(III)-wire electrode was made by incorporating ( $\text{Aliquat } 336\text{S}^+ - \text{Cr}(\text{SCN})_4^-$ ) ion pair, and the electrode gave a fully linear response in the  $\text{Cr}(\text{SCN})_4^-$  concentration range of  $10^{-5}$ – $10^{-2}$  M and has the Nernstian slope of 58 mV per decade of  $\text{Cr}(\text{III})$  concentrations. In 1983 (239), a  $\text{Cr}(\text{VI})$  selective electrode with PVC membrane based on triheptyldodecylammonium iodide was described. The response of the electrode was Nernstian for  $\text{Cr}(\text{VI})$  concentration down to  $2 \times 10^{-6}$  M in 0.03–0.13 M hydrogen fluoride solution with

limit of detection of  $5 \times 10^{-7}$  M. In 1984 (240), PVC matrix membrane Cr(VI) selective electrodes based on ethyl violet or victoria blue were prepared at pH 3.5 and in a concentration range of  $2.5 \times 10^{-5}$ – $1 \times 10^{-1}$  M of Cr(VI). The detection limit of this electrode was  $1.1 \times 10^{-5}$  M. In 1987, an ion selective electrode for determination of chromium(III) was reported. In this electrode, 8-quinoline-dithiocarboxylate was used as a membrane-active substance (241). In 1989, an ion-selective electrode based on chromium dithizonate was built that was a precipitate based selective electrode (242). During the past decades, numerous ISEs based on PVC membrane were reported, but very little was published on PVC-based trivalent ions (243). A PVC-based Cr(III) ion selective electrode which was recently been prepared is based on a macrocyclic compound with a concentration range of  $1.77 \times 10^{-6}$ – $0.1$  M and a Nernstian slope of 20 mV per decade (244). Abbaspour and Izadyar (245) reported a PVC matrix ion selective electrode for chromium(III), which is based on 4-dimethylaminoazobenzene with a concentration range of  $1.66 \times 10^{-6}$ – $1 \times 10^{-2}$  and limited detection of  $8.0 \times 10^{-7}$  M, and also possessed the advantages of design simplicity in membrane preparation. A poly(vinyl chloride) membrane based on glyoxal bis(2-hydroxyanil) as membrane carrier was prepared by Gholivand et al. (246) and investigated as a Cr(III)-selective electrode. The electrode has a linear dynamic range of  $3.0 \times 10^{-6}$ – $1.0 \times 10^{-2}$  M with a Nernstian slope of 19.89 mV per decade and a detection limit of  $6.3 \times 10^{-7}$  M. It has a fast response time of 20 s and can be used for at least 3 months without any considerable divergence in potential. The membrane sensor has been used very successfully for the analysis of some food materials and alloys for the determination of Cr(III) ion. A polystyrene based membrane of tetraazacyclohexadeca-1,4,9,12-tetraene macrocyclic ionophore was used as Cr(III) ion-selective electrode by Singh et al. (247). The electrode has been found to be chemically inert and of adequate stability with good reproducibility over a period of 100 days. The membrane electrode worked satisfactorily in a partially non-aqueous medium up to a maximum 30% (v/v) content of methanol and ethanol. The selectivity coefficient values indicated that the membrane electrode is highly selective for Cr(III) ions over a number of monovalent, divalent and trivalent cations. Chromium chelates of Schiff bases, *N*-(acetoacetanilide)-1,2-diaminoethane (L1) and *N,N*-bis(acetoacetanilide)-triethylenetetraammine (L2), were synthesized by Singh et al. (248) and explored as neutral ionophores for preparing poly(vinylchloride) (PVC) based membrane sensors selective to Cr(III). The addition of lipophilic anion excluder (NaTPB) and various plasticizers viz. *o*-Nitrophenyloctyl ether (*o*-NPOE), dioctylphthalate (DOP), dibutylphthalate (DBP), tris(2-ethylhexyl)phosphate (TEHP), and benzyl acetate (BA) have found to improve the performance of the sensors. Nernstian response in the concentration range  $8.9 \times 10^{-8}$  to  $1.0 \times 10^{-1}$  M  $\text{Cr}^{3+}$  with a limited detection of

$5.6 \times 10^{-8}$  M. The proposed sensor manifest 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 sensor was found to work satisfactorily in partially non-aqueous media up to 20% (v/v) content of methanol, ethanol and acetonitrile and could be used for a period of 3 months. The proposed electrode was also used as an indicator electrode in potentiometric titration of chromium ion with EDTA and in direct determination in different water and food samples. H.A. Zamani et al. (249) prepared a poly vinyl chloride membrane sensor for chromium(III) ions based on 4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one (AHMTO) as a membrane carrier. The sensor has a linear dynamic range of  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M, with a Nernstian slope of  $19.7 \pm 0.3$  mV per decade, and a detection limit of  $5.8 \times 10^{-7}$  M. It has a fast response time of <10 s and can be used for at least 3 months without any considerable divergences in its potential. The practical utility was demonstrated as an indicator electrode in potentiometric titration of Cr(III) with EDTA and also to the determination of Cr(III) in wastewater of chromium electroplating industries.

A new chelating resin, Aurin tricarboxylic acid modified silica, was synthesized by Sharma and Goel (250). The resin behaved as a selective chelating ion exchanger for Cr(III) at a pH 3.8–5.5. A polyvinyl chloride-based membrane electrode of the modified silica has been fabricated and explored as sensor for Cr(III) ions. The membrane works well over the concentration range  $7.0 \times 10^{-6}$  to  $1 \times 10^{-1}$  M of Cr(III) with a Nernstian slope of 19.0mV per decade of concentration. The response time of the sensor is 10 s and it can be used for a period of 5 months. The performance of the sensor is best in the pH range 3.5–6.5 and it also works well in partially non-aqueous medium. Tri-*o*-thymotide (I) has been used as an electroactive material in PVC matrix for fabrication of chromium(III)-selective Sensor by Gupta et al. (251). 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) exhibited a working concentration range of  $4.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M with a Nernstian slope of  $20.0 \pm 0.1$  mV per decade of activity in the pH range of 2.8–5.1. The detection limit of this sensor is  $2.0 \times 10^{-7}$  M. The electrode exhibited a fast response time of 15 s, showed good selectivity towards  $\text{Cr}^{3+}$  over a number of mono-, bi- and trivalent cations and can also be used in partially non-aqueous medium (up to 15%, v/v).

Few reports on Ce(III)-selective electrodes based on 1,2,3-trithiane (252,253) sulfonamide (254), azomethine of pipronylidene-4-[2.2]paracyclophenylamine (255) and aminobenzothiazol (256) as ionophores were developed as sensors for Ce(III) ions. The selectivity coefficients recorded by these electrodes showed interferences of some

cations such as Hg(II) and Fe(III). A novel ion-selective PVC membrane sensor for cerium(III) ions based on [4-(4'-nitrobenzyl)-1-phenyl-3,5-pyrazolidinedion] (NBPP) as a new ionophore has been prepared and studied by Saleh et al. (257). This electrode has a wide linear dynamic range from  $10^{-1}$  to  $2.5 \times 10^{-6}$  M with a Nernstian slope of 29.5 mV per decade and low detection limit of  $1.6 \times 10^{-6}$  M. It has a fast response time ( $<10$  s) and good selectivity with respect to different metal ions. The proposed electrode has also been used successfully as an indicator electrode in potentiometric titration of phosphate and oxalate in aqueous media and carbonate, fluoride and acetylsalicylate in some drugs. A new membrane electrode selective to iron(III) (in  $\text{FeCl}_4^-$  structure) has been developed based on crown ether (258). The electrode consisted of *trans*-dinitro-dibenzo-18-6 crown ether as a neutral carrier, 2-nitrophenyl pentyl ether as plasticizer and tetrabutylammonium tetraphenylborate as a conductivity increaser. An analytically useful potential change occurs in the  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  M concentration range. The slope of linear portion ( $1 \times 10^{-4}$  to  $10^{-1}$  M) is  $57 \pm 1$  mV/10-fold concentration changes in iron(III).

### 3. Conclusion

Materials discussed were found selective for various metal ions like as  $\text{Ti}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{UO}_2^+$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Ce}^{3+}$ , and  $\text{Fe}^{3+}$ . These materials are either organic or inorganic or organic-inorganic in nature. In most of the cases, binders are also used in preparation of membrane. A maximum number of materials were found selective for  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{UO}_2^+$ , very few materials were found selective for Fe and  $\text{Cr}^{6+}$ . Although a great deal of research work has already been done in this area, still it requires improvement because it is one of the simplest method for detection and determination of an ion in a complex mixture of ions.

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### References

- Pungor, E. and Hollos-Rokosinyi, E. (1961) *Acta Chim. Acad. Sci. Hung.*, 27, 63–68.
- Pungor, E. (1976) *Anal. Chem.*, 39, 28–36.
- Frant, M.S. and Ross, J.W. (1966) *Science*, 154(3756), 1553–1555.
- Ross, J.W. (1967) *Science*, 156(3780), 1378–1379.
- Koryta, J. (1977) *Anal. Chim. Acta*, 91(1), 1–85.
- Koryta, J. (1979) *Anal. Chim. Acta*, 111, 1–65.
- Buck, R.P. (1976) *Anal. Chem.*, 48(5), 23–39.
- Fricke, G.H. (1980) *Anal. Chem.*, 52(5), 259–275.
- Arnold, M.A. and Meyerhoff, M.E. (1984) *Anal. Chem.*, 56(5), 20–48.
- Arnold, M.K. and Solsky, R.L. (1986) *Anal. Chem.*, 58, 19R.
- Solsky, R.L. (1988) *Anal. Chem.*, 60, 106R.
- Janata, J., Josowicz, Z.M. and Devaney, D.M. (1994) *Anal. Chem.*, 66, 207R.
- Janata, J. and Josowicz, Z.M. (1998) *Anal. Chem.*, 70, 179R.
- Coetzee, C.J. and Besson, A.J. (1971) *Anal. Chim. Acta*, 56(2), 321–324.
- Coetzee C.J. and Besson, A. J. (1971) *J. Anal. Chim. Acta*, 57(2), 478–480.
- Malik, W.U., Srivatava, S.K., Razdan, P.N. and Kumar, S. (1976) *J. Electroanal. Chem.*, 72(1), 111–116.
- Coetzee, C.J. and Basson, A.J. (1973) *Anal. Chim. Acta*, 64(2), 300–304.
- Szczepaniak, W. and Ren, K. (1976) *Anal. Chim. Acta*, 82(1), 37–44.
- Coetzee C.J. and Basson, A.J. (1977) *Anal. Chim. Acta*, 92(2), 399–403.
- Coetzee, C.J. (1985) *Talanta*, 32(8), 821–823.
- Tamura, H., Kimura K. and Shono, T. (1980) *J. Electroanal. Chem.*, 115(1), 115–121.
- Masuda, Y., Yakabe, K., Shibutani, Y. and Shono, T. (1994) *Anal. Sci.*, 10(3), 491–496.
- Kim, S.M., Jung, S.O., Kim, J., Lee, S.S. and Kim, J.S. (1993) *J. Korean Chem. Soc.*, 37(8), 773–778.
- Ouchi, M., Shibutani, Y., Yakabe, K., Shono, T., Shintani, H., Yoneda, Y., Hakushi, T. and Weber, E. (1999) *Bioorg. Med. Chem.*, 7(6), 1123–1126.
- Kimura, K., Tatsumi, K., Yokoyama, M., Ouchi, M. and Mocerino, M. (1999) *Anal. Commun.*, 36, 229–230.
- Yamashoji, Y., Tanaka, M., Nagamune, S., Ouchi, M., Hakushi, T. and Shono, T. (1991) *Anal. Sci.*, 7(3), 485–486.
- Katsu, T., Ido, K., Takaiishi, K. and Yokosu, H. (2002) *Sens. Actuat. B: Chem.*, 87(2), 331–335.
- Saleh, M.B. (1998) *J. Electroanal. Chem.*, 448(1), 33–39.
- Park, K.S., Jung, S.O., Lee, S.S. and Kim, J.S. (2000) *Bull. Korean Chem. Soc.*, 21(9), 909–912.
- Khayatian, G., Shariati, S. and Salimi, A. (2003) *Bull. Korean Chem. Soc.*, 24(4), 421.
- Kamata, S., Moody, G.J., Thomas, J.D.R. (1979) *Anal. Chim. Acta*, 108, 385–388.
- Khalil, S.A.H., Moody, G.J., Thomas, J.D.R. and Lima, J.L.F.C. (1986) *Analyst*, 111, 611–617.
- McKittrick, T., Diamond, D., Marrs, D.J., O'Hagan, P. and McKervey, M.A. (1996) *Talanta*, 43(7), 1145–1148.
- Didina, S.E., Shilin, A.G., Grekovich, A.L., Veshev, S.A., Materova, E.A. and Mikhel'son, K.N. (1987) *Electrochimica*, 23, 588–601.
- Misra, R.C. and Chattopadhyaya, M.C. (1997) *J. Indian Chem. Soc.*, 74, 516–519.
- Saleh, M.B. (1994) *J. Electroanal. Chem.*, 373(1–2), 89–95.
- O'Donnell, J., Rusterholz, B., Aebersold, B., Ruegg, D., Simon, W. and Pretsch, E. (1994) *Mikrochim. Acta*, 113(1–2), 45–52.
- Maj-Zurawska, M. (1997) *Chem. Anal. (Warsaw)*, 42, 187–190.
- Leoca, I., Pogaceanu, O., Stefan, I. C. and Cordos, E. (1996) *Stud. Univ. Babeş-Bolyai. Chem.*, 41(2), 235–238.
- Milnowska, E., Mannoni, A. and Meyerhoff, M.E. (1999) *Anal. Chim. Acta*, 382(3), 265–275.
- Baumann, E.W. (1975) *Anal. Chem.*, 47(6), 959–961.
- Srivastava, S.K. and Jain, A.K. (1984) *Bunseki Kagaku*, 33, 525–529.
- Jain, A.K., Srivastava, S.K., Singh, R.P. and Agarwal, S. (1977) *J. Appl. Chem. Biotechnol.*, 27(6), 680–684.



44. Jain, A.K., Gupta, V.K. and Raisoni, J.R. (2004) *Sensors*, 4, 115–124.
45. Peper, S., Gonczy, C. and Runde, W. (2005) *Talanta*, 67(4), 713–717.
46. Laeubli, M.W., Dinten, O., Pretsch, E. and Simon, W. (1985) *Anal. Chem.*, 57(14), 2756–2758.
47. Suzuki, K., Tohda, K., Aruga, H., Matsuzoe, M., Inoue, H. and Shirai, T. (1988) *Anal. Chem.*, 60(17) 1714–1721.
48. Suzuki, K., Tohda, T., Sasakura, H. and Shirai, T. (1987) *Anal. Lett.*, 20(1) 39–45.
49. Lal, U.S., Chattopadhyaya, M.C. and Dey, A.K. (1982) *J. Indian Chem. Soc.*, 59, 493–496.
50. Moody, G.J., Thomas, J.D.R., Lima, J.L.F.C. and Machado, A.A.S.C. (1988) *Analyst*, 113, 1023–1027.
51. Bouklouze, A.A., Vire, J.C. and Cool, V. (1993) *Anal. Chim. Acta*, 273(1–2) 153–163.
52. Yonghua, Z. (1987), 15, 88–92.
53. Jinlan, W. and Yonghua, Z. (1992) *Zhongguo Xitu Xuebao*, 10, 180–183.
54. Yonghua, Z., Jinlan, W. and Wang, E. (1993) *Electroanalysis*, 5(9–10), 863–867.
55. Yonghua, Z. and Jinlan, W. (1993) *Zhongguo Xitu Xuebao*, 11, 135–139.
56. Jaber, M.Y. (1989) *Anal. Chim. Acta*, 223, 449–459.
57. Chattopadhyaya, M.C., Kar, R. and Azam, N. (1992) *Bull. Chem. Soc. Ethiop.*, 6(1), 109–112.
58. Agarwal, Y.K., Menon, S.K. and Amarchand, S. (2000) *Electroanalysis*, 12(7), 522–526.
59. Shih, J.S. (1987) *Chieh Mein K'o Hsueh Hui Chih*, 10, 11–14.
60. Pan, E., Xuemei, X. and Huang, Z. (1994) *Yingyong Huaxue*, 11, 20–5.
61. Gorton, L. and Fiedler, U. (1977) *Anal. Chim. Acta*, 90, 233–236.
62. Linnarsund, U.F. and Bhatti, K.M. (1979) *Anal. Chim. Acta*, 111, 57–70.
63. Lebedeva, O.A. and Jansons, E. (1987) *Latv. PSR Zinat. Akad. Vestis. Kim. Ser.*, 4, 483–485
64. Kojima, R. and Kamata, S. (1994) *Anal. Sci.*, 10(3), 409–412.
65. Rojchleaw, M.J. and Purdy, W.C. (1990) *Talanta*, 37(3), 307–311.
66. Srivastava, S.K., Vardhan, H., Singh, M., Rao, G.N. and Srivastava, S.A. (1995) *Anal. Proc.*, 32, 173–174.
67. Obmetho, A.A., Rakhmanko, E.M., Lomako, V.L. and Starvobinets, G.L. (1988) *Zh. Anal. Khim.*, 43, 444–452.
68. Srivastava, S.K., Gupta V.K. and Jain, S. (1996) *Anal. Chem.*, 68(7), 1272–1275.
69. Gupta, V.K., Jain, A.K., Singh, L.P. and Khurana, U. (1998) *Electrochim. Acta.*, 43(14–15), 2047–2052.
70. Gupta, V.K. (1999) *Sens. Actuat. B. Chem.*, 55(2–3) 195–200.
71. Shamsipur, M., Rouhani, S., Ganjali, M.R., Sharghi, H. and Eshghi, H. (1999) *Sens. Actuat. B: Chem.*, 59(1), 30–34.
72. Fakhari, A.R., Alaghemand, M. and Shamsipur, M. (2000) *Anal. Lett.*, 33(11), 2169–2181.
73. Dumkiewicz, R., Wardak, C. and Zareba, S. (2000) *Analyst*, 125, 527–530.
74. Gupta, V.K., Saini, D.K., Agarwal, S., Antonijevec, M.M. and Lang, H. (2003) *Sensors*, 3, 223–225.
75. Gholivand, M.B. and Mozaffari, Y. (2003) *Talanta*, 59(2) 399–407.
76. Gupta, V.K., Goyal, R.N., Khayat, M.A., Kumar, P. and Bachheti, N. (2006) *Talanta*, 69(5), 1149–1155.
77. Gupta, V.K., Agarwal, S., Jakob, A. and Lang, H. (2006) *Sens. Actuat. B: Chem.*, 114(2), 812–818.
78. Fakhari, A.R., Shamsipur, M. and Ghanbari, K. (2002) *Anal. Chim. Acta*, 460(2), 177–183.
79. Pungor, E., Toth, K. and Havas, J. (1966) *Acta Chim. Acad. Sci. Hung.*, 48, 17–24.
80. Buchanon, E.B. and Seago, J.L. (1968) *Anal. Chem.*, 40(3), 517–521.
81. Awasthi, S.P., Kulkarni, V.T. and Sudarsan, M. (1988) *J. Electrochem. Soc. India*, 37, 309–313.
82. Rao, G.N., Srivastava, S., Srivastava, S.K. and Singh, M. (1996) *Talanta*, 43(10), 1821–1825.
83. Singh, L.P. and Bhatnagar, J.M. (2003) *Sensors*, 3, 393–403.
84. Mousavi, M.F., Alizadeh, N., Shamsipur, M. and Zohari, N. (2000) *Sens. Actuat. B: Chem.*, 66(1–3), 98–100.
85. Mazloum, M., Niassary, M.S. and Amini, M.K. (2002) *Sens. Actuat. B: Chem.*, 82(2–3), 259–264.
86. Singh, A.K. and Saxena, P. (2007) *Sens. Actuat. B: Chem.*, 121(2), 349–355.
87. Gupta, V.K., Jain, A.K., Ishtaiwi, Z., Langb, H. and Maheshwari, G. (2007) *Talanta*, 73(5), 803–811.
88. Gupta, V.K., Goyal, R.N., Agarwal, S., Kumar, P. and Bachheti, N. (2007) *Talanta*, 71(2), 795–800.
89. Yari, A., Azizi, S. and Kakanejadifard, A. (2006) *Sens. Actuat. B: Chem.*, 119(1), 167–173.
90. Mashhadizadeh, M.H., Sheikhshoae, I. and Saeid-Nia, S. (2003) *Sens. Actuat. B: Chem.*, 94(3), 241–246.
91. Abbaspour, A. and Izadyar, A. (2001) *Microchem. J.*, 69(1), 7–11.
92. Dadfarnia, S. and Shamsipur, M. (1992) *J. Membr. Sci.*, 75(1–2), 61–68.
93. Marston, H.R. (1952) *Physiol. Rev.*, 32, 66–121.
94. Greenwood, N.N. and Earnshaw, A. Chemistry of Elements, Pergamon Press: New York, 1984.
95. Kamata, S., Yamasaki, Y., Higo, M., Bhale, A. and Fukanaga, Y. (1988) *Analyst*, 113, 45–47.
96. Casabo, J., Mestres, L., Escriche, L., Texidor, F. and Perez-Jimenez, C. (1991) *J. Chem. Soc., Dalton. Trans.*, 1969–1971.
97. Kamata, S., Bahale, A., Funkanaga, Y. and Murata, H. (1988) *Anal. Chem.*, 60(22), 2464–2467.
98. Brzozka, Z. (1988) *Analyst*, 113, 1803–1805.
99. Cobben, P.L.H.M., Eggerink, R.J.M., Bomer, J.B., Bergveld, P., Verboom, W. and Reinhoudt, D.N. (1992) *J. Am. Chem. Soc.*, 114(26), 10573–10582.
100. Ren, K. (1989) *Talanta*, 36(7), 739–742,
101. Alizadeh, N., Ershard, S., Naeimi, H., Sharghi, H. and Shamsipur, M. (1999) *Fresenius J. Anal. Chem.*, 365(6), 511–515.
102. Shamsipur, M., Ronhani, S., Ganjali, M.R., Eshghi, H. and Sharghi, H. (1999) *Microchem. J.*, 63(2), 202–210.
103. Kouljenovic, J., Martinac, V. and Radic, N. (1990) *Anal. Chim. Acta*, 231, 137–141.
104. Stankovic, S.M., Javanovic, V.M. and Javanovic, M.S. (1990) *J. Serb. Chem. Soc.*, 55, 125–1230.
105. Neshkova, M. (1993) *Anal. Chim. Acta*, 273(1–2), 255–265.
106. Marco, R.D., Mackey, D.J. and Zirino, A. (1997) *Electroanalysis*, 9(4), 330–334.
107. Chen, Z. and Alexander, P.W. (1997) *Electroanalysis*, 9(2), 141–144.
108. Awasthai, S.P., Thambi, T.C. and Sunderesan, M. (1990) *J. Electrochem. Soc.*, 39, 34–41.
109. Jain, A.K., Singh, P. and Singh, L.P. (1994) *Indian J. Chem.*, 33A, 272–275.
110. Ren, K. (1989) *Talanta*, 36(7) 767–771.
111. Kamata, S., Murata, H., Kubo, Y. and Bhale, A. (1989) *Analyst*, 114, 1029–1031.
112. Askerov, G.A., Chyragov, F.M., Gambarov, D.G. and Ayubova, A.M. (1992) *Zh. Anal. Khim.*, 47, 337–348.
113. Nagashima, K., Guo, J. and Hobo, T. (1992) *Bunseki Kagaku*, 41, 153–157.
114. Sun, C.Q., Sun, Y.P., Zhang, Y., Xu, H.D. and Shen, J.C. (1995) *Anal. Chim. Acta*, 312(2), 207–212.
115. Pleniceanu, M., Preda, M., Huresam, N. and Simoiu, L. (1996) *Anal. Lett.*, 29(9), 1485–1496.
116. Brzozka, Z. (1990) *Chem. Anal. (Warsaw)*, 35, 415–422.
117. Jain, A.K., Guptak, V.K., Sahoo, B.B. and Singh, L.P. (1995) *Anal. Proc.*, 32, 99–106.
118. Talantsev, V.I. and Syroratskaya, G.V. (1994) *Fiz. Khim. Metody Anal. Veshchestva*, 44, CA:125:157150w:1996.

119. Horak, D., Banes, M.J., Gumargaljena, K. and Zaikov, G. (2001) *J. Appl. Polym. Sci.*, 80(7), 913–916.
120. Gupta, K.C. and D'Arc, M.J. (2000) *Sens. Actuat. B: Chem.*, 62(3), 171–176.
121. Ganjali, M.R., Poursaberi, T., Haji-Agha Babaei, L., Rouhani, S., Yousefi, M., Kargar-Razi, M., Moghimid, A., Aghabozorg, H. and Shamsipur, M. (2001) *Anal. Chim. Acta*, 440(2), 81–87.
122. Mashhadizadeh, M.H., Mostafavi, A., Razavi, R. and Shamsipur, M. (2002) *Sens. Actuat. B: Chem.*, 86(2–3), 222–228.
123. Yoshimoto, S., Mukai, H., Kitano, T. and Sohrin, Y. (2003) *Anal. Chim. Acta*, 494(1–2), 207–13.
124. Fakhari, A.R., Raji, T.A. and Naeimi, H. (2005) *Sens. Actuat. B: Chem.*, 104(2), 317–323.
125. Mittal, S.K., Kumar, A.S.K., Gupta, N., Kaur, S. and Kumar, S. (2007) *Anal. Chim. Acta*, 585(1), 161–170.
126. Gupta, V.K., Goyal, R.N., Bachheti, N., Singh, L.P. and Agarwal, S. (2005) *Talanta*, 68(2), 193–197.
127. Cali, C., Foix, D., Taillades, G., Siebert, E., Gonbeau, D., Pradel, A. and Ribes, M. (2002) *Mater. Sci. Engg.: C*, 21(1–2), 3–8.
128. Gholivand, M.B., Rahimi-Nasrabadi, M., Ganjali, M.R. and Salavati-Niasari, M. (2007) *Talanta*, 73(3), 553–560.
129. Ross, J.W. in *Ion Selective Electrodes*, R.A. Durst, (Ed.), NBS special publication No. 314, Government Printing Office, Washington, 1969.
130. Frant, S. and Ross, J.W. U.S. Patent No. 3591464, 6, July, 1971.
131. Hirata, H., Higashiyama, K. and Date, K. (1970) *Anal. Chim. Acta*, 51(2), 209–212.
132. Hopertenam, E. and Cosma, V. (1994) *Stud. Univ. Babeş Bolyai Chem.*, 39, 178–180.
133. Orion Research Inc., Application Bull. No. 5A, 1969.
134. Loginova, L.P. and Chernyseva, O.S. *Visn. Khark. Univ. (Ukraine)*, 2 (Chem.) (1998) 258. CA: 132:199655q; 2000.
135. Srivastava, S.K., Gupta, V.K. and Jain, S. (1996) *Electroanalysis*, 8(10), 938–940.
136. Parez-Marin, L., Miranda-Macedo, G., Avila-Perez, P., Otazo-Sanchez, E., Carrasco-Abrego, H., Lapez-Valdivia, H., Alonso-Chamarro, J. and Esterez-Hernandez, O. (1999) *Afinidad*, 56, 397.
137. Gupta, K.G. and D'Arc, M.J. (2000) *Talanta*, 52(6), 1087–1103.
138. Javanbakht, M., Shabani-Kia, A., Darvich, M.R., Ganjali, M.R. and Shamsipur, M. (2000) *Anal. Chim. Acta*, 408(1–2), 75–81.
139. Panwar, A., Baniwal, S., Sharma, C.L. and Singh, A.K. (2000) *J. Anal. Chem.*, 368(8), 768–772.
140. Lynarn, D.R., Plantanida, L.G. and Cole, J.F. *Environmental Lead*, Academic Press, New York, 1975.
141. Thind, P.S., Singh, H. and Bindal, T.K. (1982) *Indian J. Chem.*, 21A, 295–299.
142. Khan, A.A. and Alam, M.M. (2004) *Anal. Chim. Acta*, 504(2), 253–264.
143. Khan, A.A. and Alam, M.M. (2003) *React. Funct. Polym.*, 55(3), 277–290.
144. Khan, A.A. Inamuddin, and Alam, M.M. (2005) *React. Funct. Polym.*, 63(2), 119–133.
145. Khan, A.A. and Inamuddin (2006) *Sens. Actuat. B: Chem.*, 120(1), 10–18.
146. Khan, A.A., Inamuddin and Akhtar, T. (2008) *Anal. Sci.*, 24(7), 881–887.
147. Gupta, A.P. and Renuka, *Indian J. Chem.*, 36A(12), (1997) 1073–1074.
148. Kivalo, P., Virtanen, R., Wickstrom, K., Wilson, M., Pungor, E., Horval, G. and Toth, K. (1976) *Anal. Chim. Acta*, 87(2), 401–409.
149. Hansen, E.H. and Ruzicka, J. (1974) *Anal. Chim. Acta*, 72(2), 365–373.
150. Pungor, E., Toth, K., Nagy, G., Polos, L., Ebel, M.F. and Wernisch, I. (1983) *Anal. Chim. Acta*, 147, 23–32.
151. Vlasov, Y.G., Byakov, E.A. and Legin, A.V. (1987) *Sovl. Electrochem.*, 22, 1379–1384.
152. Van Staden, J.F. (1989) *Fresenius Z. Anal. Chem.*, 335(2), 226–35.
153. Mittal, S.K. (1991) *Indian J. Chem. Tech.*, 29, 283–286.
154. Ruzicka, J. and Tjell, J.C. (1970) *Anal. Chim. Acta*, 49(2), 346–348.
155. Jaber, A.M.Y., Moodym, G.J. and Thomas, J.D.R. (1988) *Analyst*, 113(9) 1409–1413.
156. Buhlmann, P., Pretsch, E. and Bakker, E. (1998) *Chem. Rev.*, 98(4), 1593–1688.
157. Shpigun, L.K., Novikov, E.A. and Zolotov, Y.A. (1986) *Zh. Anal. Khim.*, 41, 617–623.
158. Novikov, E.A., Shigun, L.K. and Zolotov, Y.A. (1987) *Zh. Anal. Khim.*, 41, 885–889.
159. Li, Z. and Liu, J. (1993) *Fenxi Huaxue*, 21, 122–126.
160. Srivastava, S.K., Gupta, V.K. and Jain, S. *Analyst*, 120(2), (1995) 495–498.
161. Tavakkoli, N. and Shamsipur, M. (1996) *Anal. Lett.*, 29(13), 2269–2279.
162. Malinowska, E., Wroblewski, W., Ostoszewski, R. and Jurczak, J. (2000) *Pol. J. Chem.*, 74(5), 701–706.
163. Malinowska, E., Brzózka, Z., Kasiura, K., Richard, Egberink, J.M. and Reinhoudt, D.N. (1994) *Anal. Chim. Acta*, 298(2), 253–258.
164. Ohki, A., Kim, J.S., Suzuki, Y., Hayashita, T. and Maeda, S. (1997) *Talanta*, 44(6), 1131–1135.
165. Mousavi, M.F., Sahari, S., Alizadeh, N. and Shamsipur, M. (2000) *Anal. Chim. Acta*, 414(1–2) 189–194.
166. Xu, D. and Katsu, T. (1999) *Anal. Chim. Acta*, 401(1–2), 111–115.
167. Xu, D. and Katsu, T. (2000) *Talanta*, 51(2), 365–371.
168. Thomson, R.H. *Naturally Metabolism in Microorganisms, Plants and Animals*, Springer-Verlag, Berlin, 1984.
169. Tavakkoli, N., Khojasteh, Z., Sharghi, H. and Shamsipur, M. (1998) *Anal. Chim. Acta*, 360(1–3), 203–208.
170. Pouretedal, H.R., Forghaniha, A., Sharghi, H. and Shamsipur, M. (1998) *Anal. Lett.*, 31(15), 2591–2605.
171. Rahmani, A., Barzegar, M., Shamsipur, M., Sharghi, H. and Mousavi, M.F. (2000) *Anal. Lett.*, 33(13), 2611–2629.
172. Casado, M., Daunert, S. and Valiente, M. (2001) *Electroanalysis*, 13(1), 54–60.
173. Mousavi, M.F., Barzegar, M.B. and Sahari, S. (2001) *Sens. Actuat. B: Chem.*, 73(2–3), 199–204.
174. Sadeghi, S. and Shamsipur, M. (2000) *Anal. Lett.*, 33(1), 17–28.
175. Sadeghi, S., Dashti, G.R. and Shamsipur, M. (2002) *Sens. Actuat. B: Chem.*, 81(2–3), 223–228.
176. Rouhollahi, A., Ganjali, M.R. and Shamsipur, M. (1998) *Talanta*, 46(6), 1341–1346.
177. Fathi, M.R., Darviche, F. and Ganjali, M.R. (2000) *Anal. Lett.*, 33(6), 1025–1035.
178. Kulapina, E.G., Koroleva, S.A. and Apukhtina, L.V. (2000) *J. Anal. Chem.*, 55(2): 165–168.
179. Parez-Marin, L., Miranda-Macedo, G., Avila-Perez, P., Otazo-Sanchez, E., Carrasco-Abrego, H., Lapez-Valdivia, H., Alonso-Chamarro, J. and Esterez-Hernandez, O. (1999) *Afinidad*, 56, 295–300.
180. Isildak, I. (2000) *Turk. J. Chem.*, 24(4), 389–394.
181. Amini, M.K., Mazloun, M. and Ensafi, A.A. (1999) *Fresenius J. Anal. Chem.*, 364(8), 690–693.
182. Zare, H.R., Ardakani, M.M., Nasirizadeh, N. and Safari (2005) *J. Bull. Korean Chem. Soc.*, 26(1): 51–56.
183. Vardhan, H. and Singh (1997) *Spec. Publ. R. Soc., Chem.*, 196 (Progress in Ion Exchange), 104.
184. Liu, B., Sun, X., Xu, J. and Tomoo, J.J.M. (1996) *Huaquao Daxue Xuebao, Ziran Kexueban*, 17, 14–19.
185. Yang, X., Kumar, N., Chi, H., Hibbert, D.B. and Alexander, P.W. (1997) *Electroanalysis*, 9(7), 549–553.
186. Linden, E., Toth, L., Behm, F., Oggenfuss, O., Welti, D.H., Ammann, D., Morf, W.E., Pretsch, E. and Simon, W. (1984) *Anal. Chem.*, 56(7), 1127–1131.
187. Malinowska, E. (1990) *Analyst*, 115(8), 1085–1087.

188. Kamata, S. and Onoyama, K. (1991) *Anal. Chem.*, 63(13), 1295–1298.
189. Kamata, S. and Onoyama, K. (1991) *Chem. Lett.*, 20(4), 653–656.
190. Jabar, A.M.Y., Moody, G.T. and Thomas, J.D.R. (1998) *Analyst*, 123(6), 1409.
191. Shamsipur, M., Ganjali, M.R. and Rouhollahi, A. (2001) *Anal. Sci.*, 17(8), 935–938.
192. Ganjali, M.R., Hosseini, M., Basiripour, F., Javanbakht, M., Hashemi, O.R., Rastegar, M.F., Shamsipur, M. and Buchanen, G.W. (2002) *Anal. Chim. Acta*, 464(2), 181–186.
193. Jeong, T., Lee, H.K., Jeong, D.C. and Jeon, S. (2005) *Talanta*, 65(2), 543–548.
194. Lee, H.K., Song, K., Seo, H.R., Choi, Y.K. and Jeon, S. (2004) *Sens. Actuat. B: Chem.*, 99(2–3): 323–329.
195. Jain, A.K., Gupta, V.K., Singh, L.P. and Raisoni, J.R. (2006) *Electrochim Acta*, 51(12): 2547–2553.
196. Mahajan, R.K., Kaur, R., Kaur, I. and Sharma, V. (2004) *Anal. Sci.*, 20(5), 811–814.
197. Mashhadizadeh, M.H. and Sheikhsaie, I. (2003) *Talanta*, 60(1), 73–80.
198. Heravi, M.J., Khandar, A.A. and Sheikhsaie, I. (1999) *Spectrochim Acta A*, 55(12): 2537–2544.
199. Gupta, V.K., Chandra, S. and Lang, H. (2005) *Talanta*, 66(3), 575–580.
200. Mazloum, M., Amini, M.K. and Baltork, I.M. (2000) *Sens. Actuat. B: Chem.*, 63(1–2), 80–85.
201. Mahajan, R.K., Kaur, I. and Lobana, T.S. (2003) *Talanta*, 59(1), 101–105.
202. Lobana, T.S., Sanchez, A., Casas, J.S., Castineiras, A., Sordo, J., Garcia-Tasende, M.S. and Vazquez-Lopez, E.M. (1997) *J. Chem. Soc. Dalton Trans.*, 22, 4289–4299.
203. Lobana, T.S., Sanchez, A., Casas, J.S., Castineiras, A., Sordo, J. and Garcia-Tasende, M.S. (1998) *Polyhedron*, 17(21), 3701–3709.
204. Lobana, T.S., Sanchez, A., Casas, J.S., Castineiras, A., Sordo, J. and Garcia-Tasende, M.S. (2001) *Main Group Metal Chem.*, 24, 61.
205. Lu, J., Tong, X. and He, X. (2003) *J. Electroanal. Chem.*, 540(2), 111–117.
206. Ruzicka, J. and Tjell, J.C. (1970) *Anal. Chim. Acta*, 51(1), 1–19.
207. Lai, M.T. and Shih, J.S. (1986) *Analyst*, 111(8), 891–895.
208. Fakhari, A.R., Ganjali, M.R. and Shamsipur, M. (1997) *Anal. Chem.*, 69(18): 3693–3696.
209. Pérez-Marín, L., Macedo-Miranda, G., Avila-Pérez, P., López-Valdivia, H., Otazo-Sánchez, E. and Alonso Chamero, J. (2000) *Analyst*, 125(10), 1787–1790.
210. Hassan, S.S.M., Saleh, M.B., Abdel Gaber, A.A., Mekheimer, R.A.H. and Abdel Kream, N.A. (2000) *Talanta*, 53(2), 285–293.
211. Abbas, M.N. and Mostafa, G.A.E. (2003) *Anal. Chim. Acta*, 478(2), 329–335.
212. Manning, D.L., Stokely, J.R. and Magouyrk, D.W. (1974) *Anal. Chem.*, 46(8): 1116–1119.
213. Serebrennikova, N.V., Kukushkina, I.I. and Plotnikova, N.V. (1982) *Zh. Anal. Khim.*, 37: 645–649.
214. Moody, G.J., Slater, J.M. and Thomas, J.D.R. (1988) *Analyst*, 113(5): 699–703.
215. Goldberg, I. and Meyerstein, D. (1980) *Anal. Chem.*, 52(13), 2105–2108.
216. Luo, C.S., Chang, F.C. and Yeh, Y.C. (1982) *Anal. Chem.*, 54(13), 2333–2336.
217. Petrukhin, O.M., Avdeeva, E.N., Zhukov, A.F., Polosuchina, I.B., Krylova, S.A., Rogatinskaya, S.L., Bodrin, G.V., Nesterova, N.P., Polikarpov, Y.M. and Kabachnik, M.I. (1991) *Analyst*, 116(7), 715–719.
218. Khramov, A.N., Garifzyanov, A.R. and Toropova, V.F. (1994) *Zh. Anal. Khim.*, 49(10): 1124–1126.
219. Gupta, V.K., Mangla, R., Khurana, U. and Kumar, P. (1999) *Electroanalysis*, 11(8), 573–576.
220. Johnson, S., Moody, G.J., Thomas, J.D.R., Kohnke, F.H. and Stoddart, J.F. (1989) *Analyst*, 114(9), 1025–1028.
221. Florido, A., Casas, I., Garcia-Raurich, J., Arad-Yellin, R. and Warshawsky, A. (2000) *Anal. Chem.*, 72(7), 1604–1610.
222. Jain, A.K., Gupta, V.K., Khurana, U. and Singh, L.P. (1997) *Electroanalysis*, 9(11), 857–860.
223. Jain, A.K., Gupta, V.K. and Singh, L.P. (1995) *Anal. Proc.*, (London), 32, 263–266.
224. Feng, D. (1984) *Huaxue Tongbao*, 3, 15.
225. Materova, E.A. and Lebedeva, N.S. (1982) *Ionnyi. Obmenlonomel-riya*, 3, 152.
226. Saleh, M.B. (1992) *Indian J. Chem.*, 31A, 12.
227. Aldrich Catalog Handbook of Fine Chemicals, Milwaukee, USA, 1995, p. 521.
228. Hassan, S.S.M., Ali, M.M. and Attawiya, A.M.Y. (2001) *Talanta*, 54(6), 1153–1161.
229. Pedrena, C.S., Ortuno, J.A. and Torreillas, M.C. (1986) *Analyst*, 11(12): 1359–1361.
230. Dan, D. and Dong, Y. (1988) *Talanta*, 35(7), 589–590.
231. Jaber, A.M.Y. (1989) *Anal. Chim. Acta*, 223, 449–459.
232. Chowdhury, D.A., Ogata, T., Kamata, S. and Ohashi, K. (1996) *Anal. Chem.*, 68(2): 366–370.
233. Saleh, M.B. (2000) *Analyst*, 125(1), 179–183.
234. Saleh, M.B., Hassan, S.S.M., Gaber, A.A.A. and Kream, N.A.A. (2001) *Anal. Chim. Acta*, 434(2), 247–253.
235. Cattrall, R.W. and Chin-Poth, P. (1975) *Anal. Chem.*, 47(1), 93–95.
236. Thind, P.S. and Mittal, S.K. (1988) *Bull. Electrochem.*, 4, 431.
237. Volkov, V.L. and Kruchnina, M.V. (1996) *Izobretenya (Russ.)*, 17, 232.
238. Masuda, Y., Ishida, E. and Hiraga, K. (1980) *Nippon Kagaku Kaishi*, 1453.
239. Dammig, F. and Chengzhi, C. (1983) *Huaxue Huebao*, 41, 371.
240. Lizhen, C., Xuelmig, D., Suying, H. and Xuebao, S.D. (1984) *Ziran Kexueban*, 24, 43.
241. Lebedeva, O.A. and Yanson, E.Y. (1987) *Fromotkriya Izobret*, 39, 195.
242. Chattopadhyaya, M.C. (1989) *J. Indian Chem. Soc.*, 66(1), 54.
243. Frant, M.S. (1994) *Analyst*, 119(11), 2293–2301.
244. Ashok, K.S., Panwar, A., Shallendra, K. and Seema, B. (1999) *Analyst*, 124(4): 521–525.
245. Abbaspour, A. and Izadyar, A. (2001) *Talanta*, 53(5), 1009–1013.
246. Gholivand, M.B. and Sharifpour, F. (2003) *Talanta*, 60(4), 707–713.
247. Singh, A.K., Singh, R. and Saxena, P. (2004) *Sensors*, 4(12), 187–195.
248. Singh, A.K., Gupta, V.K. and Gupta, B. (2007) *Anal. Chim. Acta*, 585(1) 171–178.
249. Zamani, H.A., Rajabzadeh, G. and Ganjali, M.R. (2006) *Sens. Actuat. B: Chem.*, 119(1), 41–46.
250. Sharma, R.K. and Goel, A. (2005) *Anal. Chim. Acta*, 534(1), 137–142.
251. Gupta, V.K., Jain, A.K., Kumar, P., Agarwal, S., Maheshwari, G. (2006) *Sens. Actuat. B: Chem.*, 113(1), 182–186.
252. Shamsipur, M., Yousefi, M. and Ganjali, M.R. (2000) *Anal. Chem.*, 72(11), 2391–2394.
253. Shamsipur, M., Yousefi, M., Hosseini, M. and Ganjali, M.R. (2001) *Anal. Lett.*, 34(13), 2249–2261.
254. Karami, H., Mousavi, M.F., Shamsipur, M., Yavari, I. and Alizadeh, A.A. (2003) *Anal. Lett.*, 36(6), 1065–1078.
255. AbdelGaber, A.A. (2003) *Anal. Lett.*, 36(12), 2585–2596.
256. Akhnod, M., Najafi, M.B. and Tashkourian, J. (2004) *Sens. Actuat. B: Chem.*, 99(2–3), 410–415.
257. Saleh, M.B., AbdelGaber, A.A., Khalafi, M.M.R. and Tawfeek, A.M. (2006) *Sens. Actuat. B: Chem.*, 119(1), 275–281.
258. Ekmekci, G., Uzunb, D., Somerb, G. and Kalayci, S. (2007) *J. Memb. Sci.*, 288(1–2), 36–40.