Monatsh Chem (2010) 141:829–839
DOI 10.1007/s00706-010-0340-2

ORIGINAL PAPER

A novel lariat crown compound as ionophore for construction of a mercury(II)-selective electrode

**Berna Dalkıran · Ayça Demirel Özel ·
Semanur Parlayan · Esin Canel ·
Ümmühan Ocak · Esma Kılıç**

Received: 22 December 2009 / Accepted: 4 June 2010 / Published online: 4 August 2010

Abstract The construction, performance, and application of a new PVC membrane electrode for determination of the mercury(II) ion, based on 8,17-bis(pyren-1-ylmethyl)-6,7,8,9,15,16,17,18-octahydrodibenzo[*f,m*][1,8,4,11]dithiadiazacyclotetradecine as an ionophore, is described. The effects of factors such as membrane composition, the nature and amount of the plasticizers and additives, and pH for the improved sensitivity of the electrode were studied. The electrode had a Nernstian response for mercury(II) ions over the concentration range 1.0×10^{-2}–1.0×10^{-6} mol dm^{-3} with a slope of 27.6 ± 0.6 mV/pHg. The detection limit for mercury(II) was 7.9×10^{-7} mol dm^{-3}. The response time of the electrode was between 5 and 15 s, depending on the concentration of mercury, and it can be used in a pH range 4.0–4.5 for approximately 4 months without any substantial divergence of the response characteristics. It showed higher selectivity for mercury(II) ions than for several common alkali, alkaline earth, and transition metal ions except silver(I). The proposed electrode was successfully applied to direct determination of mercury in a dental filling amalgam alloy as a real sample with a complex matrix and as an indicator electrode in complexation titrations.

Keywords Ion-selective electrode · Poly(vinyl chloride) membrane · Crown compounds · Electrochemistry · Sensors · Dental filling material

B. Dalkıran · A. D. Özel · E. Canel · E. Kılıç (✉)
Department of Chemistry, Faculty of Science,
Ankara University, Ankara, Turkey
e-mail: ekilic@science.ankara.edu.tr

S. Parlayan · Ü. Ocak
Department of Chemistry, Faculty of Arts and Sciences,
Karadeniz Technical University, Trabzon, Turkey

Introduction

The correct and accurate analysis of species in complex matrixes is quite important in analytical chemistry. The instrumentation of most of the methods available for determination of species in trace amounts is quite expensive and complicated [1]. However, potentiometric determinations with ion-selective electrodes have many advantages, for example speed and ease of preparation and procedures, relatively fast response, reasonable selectivity, wide linear dynamic range, and low cost [2, 3]. Therefore, the construction of highly sensitive and selective electrodes for many species, and the development of a method for measurement and detection of the species in various matrixes have become increasingly important [1]. Much work has been done to develop ion-selective electrodes and to apply them in various fields since the 1960s [4]. With the emergence of ion-selective electrodes, potentiometry has begun to be used in different fields, for example elucidation of electrode mechanisms, biochemical and biomedical applications, and clinical and contamination analysis. These electrodes have unique properties in the determination of many ionic, molecular, and gaseous species. Their applications and the number of species determined by use of these electrodes are increasing every day. There are many commercially available ion-selective membrane electrodes in the market (for example electrodes sensitive to copper, cadmium, lead, potassium, sodium, chloride, bromide, sulfate, ammonia, and carbon dioxide). These electrodes can be used for direct determination of the species that they are sensitive to and for the indirect determination of other species. To improve the analytical selectivity of an electrode, it is essential to choose suitable organic or inorganic compounds to be tested as ionophores when developing ion-selective membrane electrodes (ISEs) [5]. ISE membranes containing macrocyclic compounds are classified as ionophore-based liquid-membrane electrodes. Many research institutes throughout the world conduct theoretical and experimental studies to develop this type of ion-selective membrane electrode. Studies performed with natural and synthetic macrocyclic compounds are mainly targeted at the construction of electrodes selective to alkaline, alkaline earth, some transition, and heavy metal ions, and inorganic and organic anions. Among various macrocyclic compounds, for example tetrathiadiazacyclotetradeca-2,9-diene [6], diamine donor ligand [1], hexathia-18-crown-6-tetraone [7], tridodecylmethylammonium iodide [8], ethyl-2-benzoyl-2-phenylcarbamoyl acetate [9], salicylaldehyde thiosemicarbazone [10], palladium dithizonate [11], pentathia-15-crown-5 [12], *N*-(*O*,*O*-diisopropylthiophosphoryl)thiobenzamide [13], tetradecylphosphonium trichloromercurate(II) [14], dithia crown ethers [15], substituted diaza crown ethers [16], thiazole azo group containing calixarene derivatives [17], 1,3-diphenylthiourea [18], mercapto compounds [19, 20], dibenzodiazathia-18-crown-6-dione [21], a Schiff base [22], *N*,*N*-dimethylformamide salicylacylhydrazone [23], and *p*-*tert*-butylcalix[4]crowns [24], in this study a lariat crown compound was used as an ionophore. It is well known that most ligands with an oxygen donor atom form complexes with alkaline and alkaline earth metals whereas ligands containing nitrogen and sulfur atoms form complexes with transition metal ions [25–27]. It has also been shown, by formation of complexes with macrocyclic compounds dissolved in organic solvents, that many metal ions can be extracted from aqueous media [28–32]. Lariat compounds are macrocyclic compounds which are reported to form complexes with some transition and heavy metal ions [32, 33]. The potentially toxic heavy metal ions are generally determined by use of standard methods based on atomic absorption and inductively coupled plasma (ICP) methods. However, these methods are very expensive and require trained operators. Therefore there is still a need for simple, inexpensive, and reproducible chemical sensors sensitive to toxic metal ions such as lead(II), silver(I), and mercury(II). Mercury is of particular interest because of its toxicity, volatility, and the ease with which it is converted to forms that enter the environment and, ultimately, the food chain [34]. Mercury compounds are accumulated by living organisms. Hence, the toxic level of mercury increases with a process called biological magnification from microorganisms to fish, fish eating birds, and mammals. This environmental effect of mercury has led to increasing demands to seek an analytical device to rapidly assess mercury contamination in the field.

As a part of our interest in developing ion-selective electrodes [5, 35–39], in this paper we report the preparation of a mercury(II)-selective electrode based on the lariat crown compound 8,17-bis(pyren-1-ylmethyl)-6,7,8,9,15,16,17,18-octahydrodibenzo[*f*,*m*][1,8,4,11]dithiadiazacyclotetradecine (**1**), which has unique cation-binding capacity because of donor atoms present in its structure (Fig. 1). The purpose was to prepare an electrode with a Nernstian response by changing the amounts of membrane components, the type of the plasticizer and the polymeric compound, the conditioning, the internal filling solution, and the pH of the experimental solutions. Performance characteristics such as optimum working range, slope, response time, and lifetime were investigated and selectivity coefficients for a variety of ions were determined. Furthermore, it was successfully used for determination of mercury(II) present in an amalgam.

Results and discussion

It is known that sulfur-containing ligands form stable complexes with mercury(II) and silver(I) ions, which have high affinity for soft coordination sites such as sulfur. That is why use of these compounds as ionophores in ISEs is expected to increase selectivity towards mercury and silver ions over other metal ions. The compound given in Fig. 1 would therefore be a suitable ionophore for PVC membrane ion-selective electrodes responding to transition and heavy metal ions with suitable dimensions and charges. For this purpose, 17 ion-selective electrodes were prepared and their responses to various cations were examined. The sensitivity of the prepared electrodes towards lithium(I), silver(I), ammonium(I), cesium(I), cobalt(II), copper(II), nickel(II), cadmium(II), calcium(II), zinc(II), potassium(I), strontium(II), magnesium(II), mercury(II), and lead(II) ions was determined. The calibration results obtained for electrode 1, given in Table 1, are plotted in Fig. 2. The results showed that the electrode was not sensitive to other metal ions and that for the cations investigated the most sensitive response was obtained for mercury(II) ions. These results

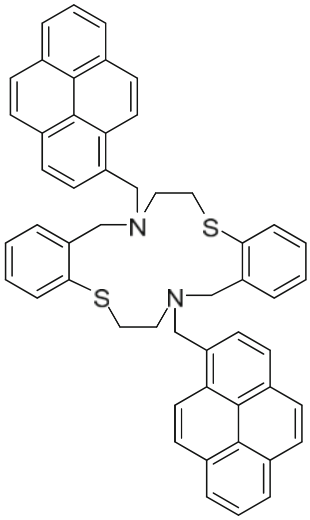

Fig. 1 The structure of compound **1**

Table 1 Membrane compositions and effect of plasticizers on the response of the mercury(II)-selective PVC membrane electrodes based on compound **1**

Electrode no.	Ionophore (mg)	PVC (mg)	KTpClPB (mg)	Plasticizer (mg)	Slope (mV/pHg) $\pm ts\sqrt{N}$	Working range (mol dm^{-3})
1	4.3	140.4	2.3	280.7 TEHP	27.6 ± 0.6	1.0×10^{-6}–1.0×10^{-2}
2	8.5	140.4	2.3	280.7 TEHP	17.0 ± 0.7	1.0×10^{-6}–1.0×10^{-2}
3	4.3	140.4	2.3	280.7 *o*-NPOE	23.6 ± 0.6	1.0×10^{-6}–1.0×10^{-2}
4	8.5	140.4	2.3	280.7 *o*-NPOE	19.5 ± 0.4	1.0×10^{-5}–1.0×10^{-2}
5	4.3	140.4	–	280.7 TEHP	–	–
6	4.3	136.1	2.3	285.0 *o*-NPOE	20.3 ± 0.4	1.0×10^{-6}–1.0×10^{-2}
7	8.5	136.1	2.3	285.0 *o*-NPOE	16.3 ± 0.5	1.0×10^{-6}–1.0×10^{-2}
8	8.5	136.1	2.3	285.0 TEHP	21.7 ± 0.7	1.0×10^{-6}–1.0×10^{-2}
9	4.3	136.1	2.3	285.0 TEHP	21.1 ± 0.3	1.0×10^{-6}–1.0×10^{-2}
10	4.3	131.9	2.3	289.3 *o*-NPOE	20.3 ± 0.8	1.0×10^{-5}–1.0×10^{-2}
11	4.3	144.6	2.3	276.5 *o*-NPOE	20.1 ± 0.9	1.0×10^{-5}–1.0×10^{-2}
12	4.3	140.4	2.3	280.7 DBP	18.4 ± 0.9	1.0×10^{-5}–1.0×10^{-2}
13	4.3	140.4	2.3	280.7 DOS	25.0 ± 0.8	1.0×10^{-4}–1.0×10^{-2}
14	4.3	140.4	2.3	280.7 DOA	30.5 ± 0.5	1.0×10^{-5}–1.0×10^{-2}
15	4.3	140.4	2.3	280.7 DBS	26.5 ± 0.9	–
16	4.3	140.4	2.3	280.7 DOP	24.6 ± 0.2	1.0×10^{-5}–1.0×10^{-2}
17	4.3	140.4	2.3	280.7 BBPA	39.5 ± 0.7	1.0×10^{-5}–1.0×10^{-2}

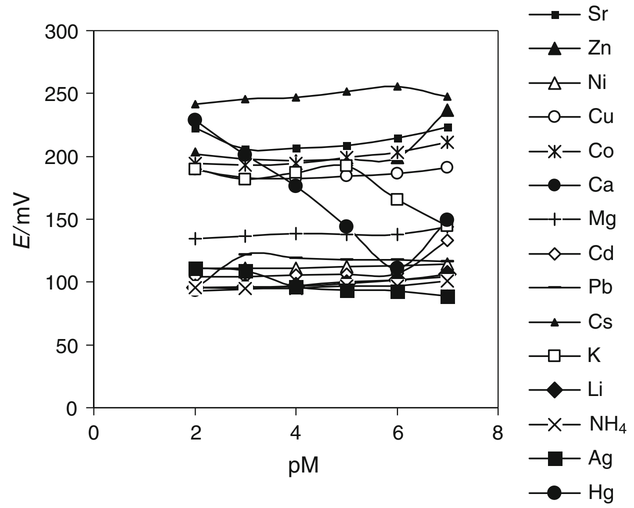

Fig. 2 Potential response to a variety metal ions of PVC membrane ion-selective electrode based on compound **1**

indicate that mercury(II) ions are easily attracted to the PVC-lariat crown compound membrane, resulting in a Nernstian potential response when the metal ion concentrations were changed between 1.0×10^{-2} and 1.0×10^{-7} mol dm^{-3}.

Effect of membrane composition on the response of the electrode

The selectivity and the accuracy of the ion-selective electrodes are dependent not only on the nature of the carrier used, but also on the membrane composition and properties of the additives employed. A literature survey showed that the most commonly used composition in the preparation of PVC membranes was 1–7% macrocyclic compound (ionophore), 28–33% PVC (internal matrix), 60–69% plasticizer (solvent), and 0.03–2% lipophilic additive. The optimum membrane composition was determined by changing the amounts of components within these ranges. Concerning the effect of concentration of the ionophore upon the performance characteristics of the electrode, the literature reveals that the stoichiometry of the complex formed between the ionophore and the species to be determined has a notable effect on these feature [40]. Thus, in preliminary experiments, two different membranes were prepared containing 1% (4.3 mg) and 2% (8.5 mg) ionophore. The calibration curves of mercury(II)-selective electrodes 1 and 2 are plotted in Fig. 3. Comparison of electrode 1 with electrode 2; electrode 3 with electrode 4; electrode 6 with electrode 7, and electrode 8 with electrode 9 in Table 1 showed that electrodes prepared by use of membranes containing approximately 1% ionophore (4.3 mg ionophore/425 mg membrane) have generally higher slopes and wider linear working ranges. It is difficult to account the decrease of the performance of the electrode with increasing amount of ionophore according to the data presented in Table 1 and Fig. 3. This was explained by the observations we made during the experiments. It was seen that membranes prepared by increasing the amount of ionophore clearly indicated that the ionophore was not fully soluble in these

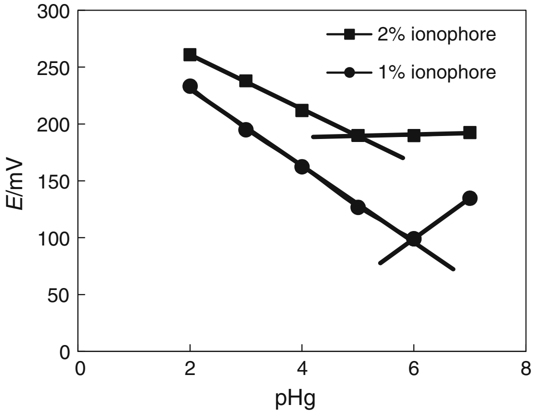

Fig. 3 Effect of amount of compound **1** on the response of the PVC membrane mercury(II)-selective electrode

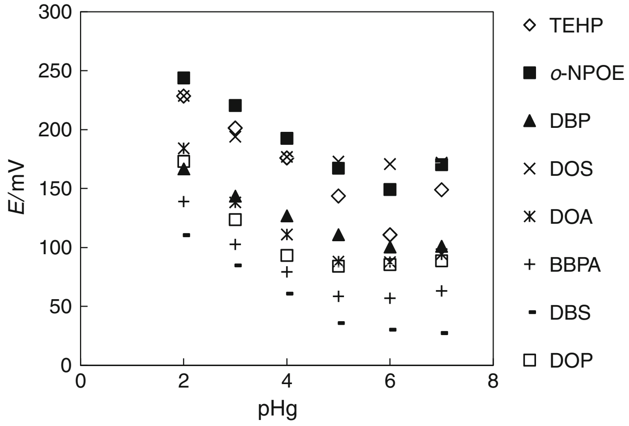

Fig. 4 Effect of plasticizer on the response of the PVC membrane mercury(II)-selective electrode based on compound **1**

media. Therefore, the decrease in the performance of the electrode was attributed to the decrease in the solubility of the ionophore.

It is known that the type of plasticizer has an important role in the selectivity, accuracy, and detection limits of ion-selective electrodes [41–44]. It is also stated in the literature that the dielectric constant of the plasticizer has an important effect on selectivity and the response times of the electrodes. In order to investigate the effect of the type of the plasticizer [40], PVC membrane mercury(II)-selective electrodes were prepared by use of the different plasticizers *o*-NPOE, TEHP, DBP, DOS, DOA, DBS, DOP, and BBPA (electrodes 1, 3, 12–17; see "Experimental"). Comparison of the slopes, linear working ranges, and the detection limits of the electrodes prepared showed that the best plasticizers were TEHP and *o*-NPOE (Fig. 4).

In our study, the effect of the plasticizer-to-PVC ratio upon the response of the electrode was also examined. For this purpose, four different ratios were investigated by use of KTpClPB as lipophilic additive and *o*-NPOE (electrode 3, 6, 10, 11) and TEHP (electrodes 1 and 9) as plasticizers with 1% ionophore. Comparison of the potentiometric responses of the electrodes revealed that the best performance was observed for electrodes 1 and 3, according to the slopes and the working ranges. The plasticizer-to-PVC ratio of these electrodes was approximately 2. This was in good agreement with the literature [45].

It is reported that addition of a lipophilic anion to the membrane improves the performance of the electrode. However, addition of such anions is known to change the selectivity of the electrode toward other cations. This was explained by the increase in the activity of the charged particles in the membrane phase and the decrease in the activity of the free macrocyclic compound [46]. As is apparent for electrodes 1 and 5 in Table 1, investigation of the effect of the lipophilic additive showed that addition of KTpClPB to the membrane changed the response and the selectivity of the membrane by quite an extent and that electrodes without the lipophilic additive gave no response.

The data obtained so far showed that the best membrane for a mercury(II) ion-selective PVC membrane electrode was that containing 4.3 mg ionophore, 140.4 mg PVC, 280.7 mg TEHP, and 2.3 mg KTpClPB (electrode 1). Subsequent studies were carried out with electrode 1 prepared by the use of this membrane.

The effect of conditioning solutions on the response of mercury(II)-selective electrodes

It is reported that the concentration and the composition of the internal filling solution has a quite significant effect upon the response of the PVC membrane electrodes. The change of the internal filling solution alters the selectivity and the working range of the electrode by quite a large extent. Because of ion-transporting features of the membrane, it is generally recommended that one should use a lower amount of internal filling solution in order to improve the working range of the electrode [47]. There are also studies using internal filling solutions containing inert ions rather than the analyte ion. In some cases, inert electrolytes ($CaCl_2$, NaCl) are used as internal filling solutions in order to prevent leakage of the analyte ion from the internal filling solution to the experimental solution, to increase the detection limit [48]. That was why the internal filling solution used for the mercury(II) ion-selective PVC membrane electrodes was 1.0×10^{-3} mol dm^{-3} $CaCl_2$ and the effect of different solutions was not investigated. Two electrodes (electrode 1) prepared in the same way were conditioned in 1.0×10^{-3} mol dm^{-3} $Hg(NO_3)_2$ and 1.0×10^{-5} mol dm^{-3} $Hg(NO_3)_2$ solutions and then, to determine the slopes and working ranges their calibration curves were plotted. The best slopes were obtained with the electrode conditioned in 1.0×10^{-3} mol dm^{-3} $Hg(NO_3)_2$

solution. The other electrodes in Table 1 were investigated by conditioning with this solution.

Effect of pH on the response of the electrode

At the beginning of these studies, the sensitivity of the electrodes towards pH was determined and it was found that the electrodes were sensitive to changes in pH. Therefore the experiments were carried out at fixed pH. The effect of pH on the response of mercury(II)-selective electrodes was studied over the pH range 2.0–8.0 for 1.0×10^{-3}, 1.0×10^{-4}, and 1.0×10^{-5} mol dm^{-3} mercury(II) containing solutions. Because of the formation of a hydroxy complex of the mercury ion at high pH, all measurements were made at pH within the range 4.0–4.5.

Working range and slope of the electrode

In order to determine the linear working ranges and slopes of the electrodes prepared with the optimum membrane composition, the electrochemical cell mentioned below was used. Potentials of a series of solutions with mercury(II) concentrations ranging between 1.0×10^{-7} and 1.0×10^{-2} mol dm^{-3} with a pH of 4.0 were measured. The potential values measured for each calibration solution were plotted against pHg values to obtain the calibration graphs. From these calibration curves the linear working ranges and slopes of the electrodes were determined; they are given in Table 1. As is apparent from Table 1, the electrodes prepared by the use of TEHP and *o*-NPOE as plasticizers and KTpClPB as the lipophilic additive (electrodes 1 and 3) gave approximately Nernstian slopes within a mercury(II) concentration range of 1.0×10^{-6}–1.0×10^{-2} mol dm^{-3} with detection limits of 1.4×10^{-6} and 7.9×10^{-7} mol dm^{-3}, respectively. The calibration graphs for the electrodes are given in Fig. 5. Table 1 reveals that the working range of the electrode prepared by using TEHP as plasticizer (electrode 1) has a superior working range compared with the electrodes prepared by use of other plasticizers. Therefore, all performance studies and analytical applications were carried out using electrode 1. Under the optimum experimental conditions and membrane compositions, the optimum electrode gave a linear response of 27.6 ± 0.6 mV/pHg within the mercury(II) concentration range 1.0×10^{-6}–1.0×10^{-2} mol dm^{-3} with a detection limit of 7.9×10^{-6} mol dm^{-3}.

The response time and lifetime of the electrode

An electrode should have a very short response time to be used in analytical applications. The response time was determined as the time taken for the potential to reach a stable value after the ion-selective and the reference electrode were immersed in calibration solution within the range 1.0×10^{-7}–1.0×10^{-2} mol dm^{-3} mercury(II) concentration. The response time which was observed to be 10–15 s in dilute solutions decreased to 5–10 s in concentrated solutions. These results indicate that the response time of the electrode prepared was comparable with or even shorter than most of the mercury(II)-selective electrodes reported in the literature. This mercury(II)-selective electrode can, therefore, easily compete with the electrodes reported in literature [7, 9, 12, 14, 16–18, 20]. The lifetime of the mercury(II)-selective electrode was determined by plotting the calibration curves every day for four months (Fig. 6). It was observed that the slope of the electrode decreased gradually during this time. It can easily be said that the lifetime of the mercury(II)-selective PVC membrane electrode described here is at least 100 days. This indicated that the lifetime of the electrode proposed was comparable with or even better than some similar mercury(II)-selective electrodes reported in the literature [16, 17, 20].

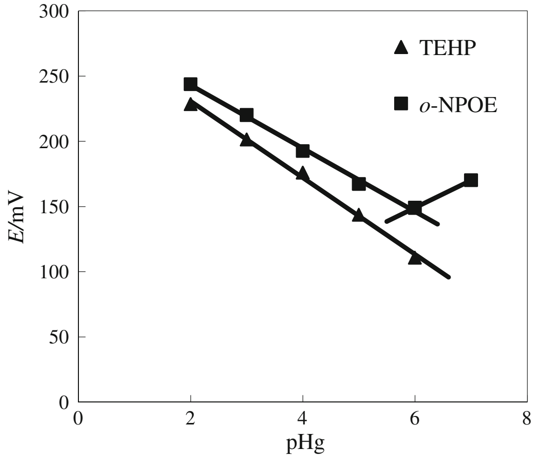

Fig. 5 Effect of plasticizer on the response of the PVC membrane mercury(II)-selective electrode based on compound **1**: *triangles*, TEHP; *squares*, *o*-NPOE

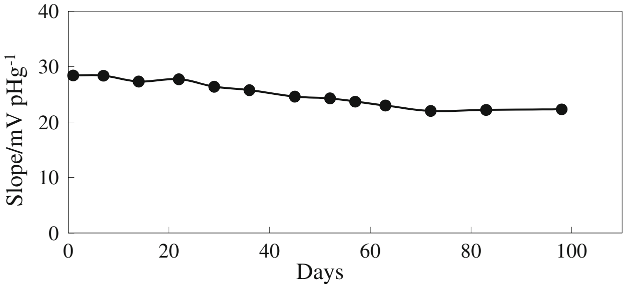

Fig. 6 The lifetime of the proposed electrode based on compound **1**

The selectivity of the electrodes

The selectivity of the prepared electrode towards lithium(I), silver(I), ammonium(I), cesium(I), cobalt(II), copper(II), nickel(II), cadmium(II), calcium(II), zinc(II), potassium(I), strontium(II), magnesium(II), and lead(II) cations was determined by the fixed interference method. For this purpose, mercury(II) ion was varied in the concentration range 1.0×10^{-7}–1.0×10^{-2} mol dm^{-3} while that of the interfering ion was 1.0×10^{-1}, 1.0×10^{-2}, and 1.0×10^{-3} mol dm^{-3}. The potentials of the calibration solutions containing these ions were measured and related calibration curves for each ion were plotted (Figs. 7, 8, 9). It was observed that the interference effect increased as the concentrations of the related interfering ions were increased. When we examined the calibration curves plotted in Figs. 7, 8, 9, among the cations investigated except Ag(I), none of the cations had an interfering effect upon the response of the electrode when their concentrations were changed from 1.0×10^{-3} to 1.0×10^{-2} mol dm^{-3}. Additionally, Sr(II) started to show interference when its concentration became 1.0×10^{-1} mol dm^{-3}. This clearly shows that the electrode prepared is selective towards mercury(II) among many cations. The selectivity coefficients for some common ions interfering with the proposed electrode based on the lariat crown compound are in accordance with the corresponding values previously reported for PVC-membrane mercury(II)-selective electrodes based on different neutral ion carriers [12, 49].

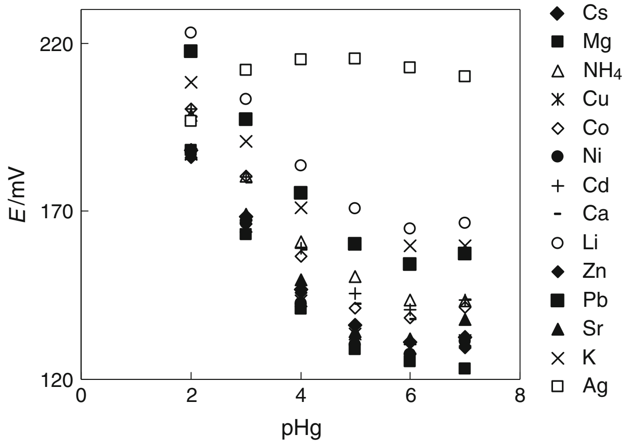

Fig. 7 The response of the mercury(II)-selective electrode based on compound **1** in the presence of interfering ions (conditions: electrode 1 in Table 1 and concentration of interfering ion was 1.0×10^{-3} mol dm^{-3})

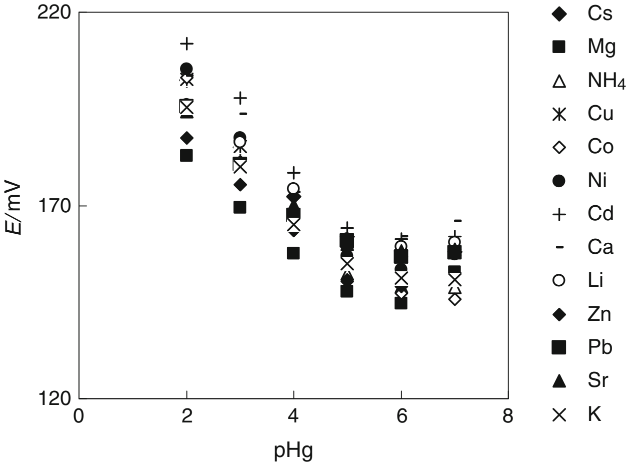

Fig. 8 The response of the mercury(II)-selective electrode based on compound **1** in the presence of interfering ions (conditions: electrode 1 in Table 1 and concentration of interfering ion was 1.0×10^{-2} mol dm^{-3})

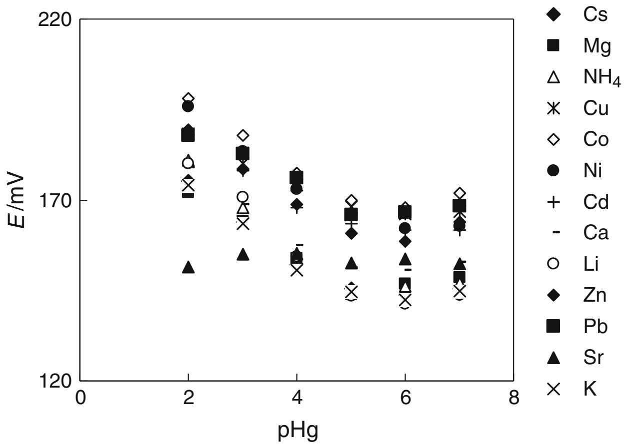

Fig. 9 The response of the mercury(II)-selective electrode based on compound **1** in the presence of interfering ions (conditions: electrode 1 in Table 1 and concentration of interfering ion was 1.0×10^{-1} mol dm^{-3})

Analytical applications of the electrode

The optimized mercury(II)-selective electrode was found to work well for the typical titration of 1.0×10^{-3} mol dm^{-3} mercury(II) nitrate solution with approximately 0.020 mol dm^{-3} EDTA (Fig. 10). The results indicated that it could be conveniently used as an indicator electrode in the potentiometric titration of mercury(II) with EDTA for some analytical purposes. In order to investigate whether the electrode prepared could be used for real samples, the amount of mercury in a dental filling amalgam was determined. For this purpose silver–mercury amalgam, a dental filling material, was used. The amalgam was prepared with the procedure described in the Experimental section and titrated with EDTA solution by use of mercury(II)-selective PVC membrane electrode. Figure 11 is an example of the curves for this titration with a good inflection point. There were no statistically significant differences between the

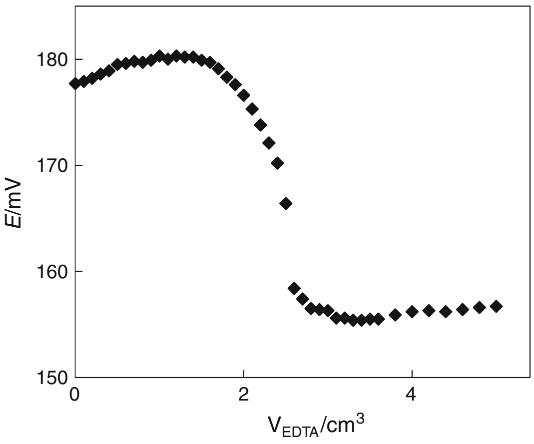

Fig. 10 Potentiometric titration curve of Hg(II) solution with EDTA solution, using the PVC membrane mercury(II)-selective electrode based on compound **1**

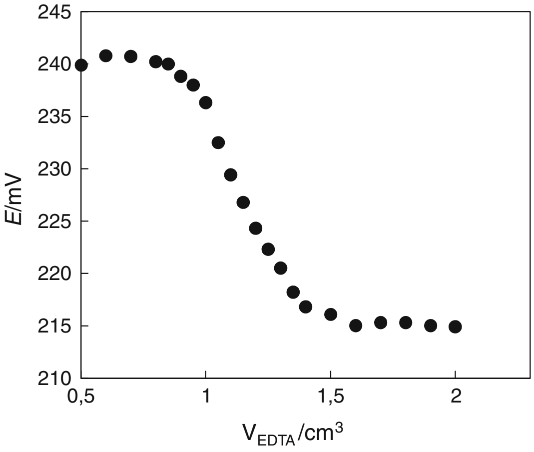

Fig. 11 Potentiometric titration curve of the determination of mercury in amalgam sample solution, using the PVC membrane mercury(II)-selective electrode based on compound **1**

results obtained with the proposed mercury(II)-selective electrode and the nominal value at a confidence level of 95%. The selectivity studies showed that Ag(I) ions have a deteriorating effect. But silver in amalgam precipitates during the preparation of the sample and mercury could be accurately determined with the mercury(II)-selective PVC membrane electrode proposed. In order to prove whether the mercury(II)-selective PVC membrane electrode could be conveniently used in the determination of mercury in amalgam samples, recovery studies were also carried out. Therefore, certain amounts were taken from the sample solution. Specific amounts of standard mercury(II) solution was added to them and the total amounts of mercury were determined. Recovery was found to be 101 ± 2.4% at the confidence level of 95%. These values indicate that species such as copper(II) and zinc(II) present in the amalgam samples have no interfering effect. It was concluded that the mercury(II)-selective PVC membrane electrode prepared could be successfully employed in the determination of mercury in amalgams.

Conclusion

On the basis of the results obtained in this study, the lariat crown compound can be successfully used as an ionophore for construction of mercury(II)-selective PVC membrane electrodes. The proposed electrode was shown to have good operating characteristics, for example sensitivity, detection limit, wide working range, response time, lifetime, stability, and reproducibility. As can be seen in Table 2, it was comparable with or even better than most similar electrodes reported in the literature [1, 5–24, 26, 50–65]. Moreover, the electrode was successfully used as an indicator electrode in the titration of mercury(II) solutions with EDTA and for determination of mercury in water and amalgam samples.

Experimental

Reagents

Compound **1** was synthesized at the Department of Chemistry of Karadeniz Technical University by using procedures developed in Ref. [51]. High-molecular-weight poly(vinyl chloride) (PVC), tris(2-ethylhexyl) phosphate (TEHP), *o*-nitrophenyl octyl ether (*o*-NPOE), dibutyl phthalate (DBP), bis(2-ethylhexyl) sebacate (DOS), bis(2-ethyhexyl) adipate (DOA), dibutyl sebacate (DBS), bis(2-ethylhexyl) phthalate (DOP), bis(1-butylpentyl) adipate (BBPA), and tetrahydrofuran (THF) in selectophores were obtained from Fluka and the lipophilic anionic additive potassium tetrakis(4-chlorophenyl)borate (KTpClPB) was obtained from Aldrich. Calcium chloride (Riedel–de Haën), nitrate salts of the metal ions (Fluka), and all of the chemical substances were of reagent grade, and were used without further purification. Stock solutions of mercury(II) nitrate (Fluka) were prepared using deionized water, and working solutions were obtained by dilution of the stock solutions with deionized water. The studies were carried out using deionized water obtained from an ELGA Purelab Option ultrapure water system. For analytical application of the proposed electrode, an amalgam sample used as dental filling (46% Hg, 56% Ag, 27.9% Sn, 15.4% Cu, 5% In, and 2% Zn) was supplied by Southern Dental Industries, Australia.

Table 2 Comparison of the proposed mercury(II)-selective PVC membrane electrode based on compound **1** with electrodes reported in the literature

Ref.	Slope (mV/pHg)	Ionophore	Membrane composition	Working range (mol dm^{-3})	Lifetime (month)	Applications
[50]	31.0	Chelate of diketohydrindylidene-diketohydrindamine (DYDA)	Liquid membrane	1.0×10^{-5}–1.0×10^{-1}	1.25	Potentiometric titration with I^{-}, Cl^{-}, Br^{-}, and SCN^{-}
[11]	30.0	Palladium dithizonate Pd(HDz)$_2$	Graphite membrane	1.0×10^{-6}–1.0×10^{-1}	–	Titration of halides alone and in mixtures
[14]	58.0	Tetradecylphosphonium trichloromercurate(II) ion-pair complex	PVC	1.0×10^{-6}–1.0×10^{-5}	–	Determination of mercury(II) in hydrochloric acid solutions
[13]	29.0	*N*-(*O*,*O*-diisopropylthiophosphoryl) thiobenzamide	Liquid membrane	5.0×10^{-5}–1.0×10^{-2}	–	End-point indicator in the titration of Hg(II) ions with EDTA
[15]	30.0 ± 1	1,4-Dithia-12-crown-4	PVC	1.0×10^{-6}–1.0×10^{-3}	–	Potentiometric titration with I^{-} and $Cr_2O_7^{2-}$
[16]	41.0	*N*,*N*′-substituted 4,13-diaza-18-crown-6 ethers	PVC	1.0×10^{-5}–1.0×10^{-3}	1.33	–
[16]	38.0	*N*,*N*′-substituted 4,13-diaza-18-crown-6 ethers	PVC	1.0×10^{-5}–1.0×10^{-3}	1.33	–
[12]	32.1	Pentathia-15-crown-5	PVC	2.5×10^{-5}–1.0×10^{-1}	1.50	–
[7]	29.0	Hexathia-18-crown-6-tetraone	PVC	4.0×10^{-6}–1.0×10^{-3}	3	Potentiometric titration of mercury ions
[21]	29.0 ± 0.5	Dibenzodiazathia-18-crown-6-dione	PVC	8.0×10^{-6}–1.0×10^{-2}	3	Potentiometric titration of mercury ions
[52]	28.4	4,7,13,16-Tetrathenoyl-1,10-dioxa-4,7,13,16-tetraazacyclodecane	PVC	3.2×10^{-6}–1.0×10^{-3}	–	Determination of mercury(II) in water samples
[9]	30.0	Ethyl-2-benzoyl-2-phenylcarbamoyl acetate (EBPCA)	PVC	1.0×10^{-6}–1.0×10^{-3}	3	Determination of mercury(II) in amalgam samples
[18]	30.8 (pH 4)	1,3-Diphenylthiourea	Liquid membrane	6.0×10^{-6}–5.0×10^{-4}	1.5	–
[18]	58.6 ± 0.8 (pH 6–7)	1,3-Diphenylthiourea	Liquid membrane	2.0×10^{-6}–2.0×10^{-4}	1.5	–
[20]	29.6	2-Mercaptobenzothiazole (MBTH)	PVC	1.0×10^{-5}–1.0×10^{-1}	2	Potentiometric determination of mercury in waste water samples
[20]	28.6	Hexathiacyclooctadecane (HT18C6)	PVC	1.0×10^{-6}–1.0×10^{-1}	2	Potentiometric determination of mercury in waste water samples
[20]	28.5	2-Mercaptobenzimidazole (MBIM)	PVC	1.0×10^{-5}–1.0×10^{-1}	2	Potentiometric determination of mercury in waste water samples
[8]	30.0-32.0 (pH 2–4)	Tridodecylmethylammonium iodide (TDMAI)	PVC	1.0×10^{-5}–1.0×10^{-1}	4	Direct determination of iodide in edible salt and titrimetric determination of mercury in a coal sample
[8]	48.0 (pH 6–8)	Tridodecylmethylammonium iodide (TDMAI)	PVC	1.0×10^{-5}–1.0×10^{-1}	4	Direct determination of iodide in edible salt and titrimetric determination of mercury in a coal sample
[22]	30.0 ± 1.0	Bis[5-((4-nitrophenyl)azosalicylaldehyde)] (BNAS)	PVC	7.0×10^{-7}–5.0×10^{-2}	3	Potentiometric determination of mercury in water samples
[10]	29.0	Salicylaldehyde thiosemicarbazone	PVC	1.8×10^{-5}–1.0×10^{-1}	2	Potentiometric titration with I^{-} and $Cr_2O_7^{2-}$
[17]	28.7 (pH 4)	5,11,17,23,29,35-Hexakis[(1-thiazolyl)azo]-37,38,39,40,41,42-hexahydroxycalix[6]arene	PVC	5.0×10^{-6}–1.0×10^{-2}	1	Determination of mercury in synthetic solutions
[17]	61.1 (pH 6.5)	5,11,17,23,29,35-Hexakis[(1-thiazolyl)azo]-37,38,39,40,41,42-hexahydroxycalix[6]arene	PVC	7.5×10^{-6}–5.0×10^{-2}	1	Determination of mercury in synthetic solutions
[19]	29.5 ± 0.8	2-Benzoylamino-3-(4-chloro-phenyl)thioacrylic acid S-(2-mercapto-4-methylphenyl)ester	PVC	2.0×10^{-7}–3.0×10^{-2}	3	Determination of mercury in water and amalgam samples
[6]	30.0	2,3,4,9,10,11-Dipyridine-3,10-diaza-1,5,8,12-tetrathiacyclotetradeca-2,9-diene	Polystyrene	1.4×10^{-6}–1.0×10^{-1}	4	End-point indicator in the titration of Hg(II) ions with EDTA
[24]	27.3	*p*-*tert*-Butylcalix[4]crown	PVC	5.0×10^{-5}–1.0×10^{-1}	3	Potentiometric titration with I^{-} and $Cr_2O_7^{2-}$

Table 2 continued

Ref.	Slope (mV/pHg)	Ionophore	Membrane composition	Working range (mol dm^{-3})	Lifetime (month)	Applications
[27]	79.4	Tetraethyl thiuramdisulfide (TETDS)	Carbon paste electrode	$1.0 \times 10^{-7.18}$–$1.0 \times 10^{-3.22}$	–	Potentiometric titration of humic acids
[1]	25.0 ± 0.1	$(H_2NCHMeCH_2NH_2)(H_2O)_2HgCl_2$	PVC	1.3×10^{-5}–1.0×10^{-1}	4	Determination of mercury in binary mixtures
[53]	28.0–30.0	Hg[dimethylglyoxime(phene)]$^{2+}$	Organic PVC membrane	1.0×10^{-6}–1.0×10^{-1}	–	–
[54]	30.0 ± 0.4	Ethylenediamine bis(thiophenecarboxaldehyde)	PVC	1.0×10^{-7}–1.0×10^{-2}	3	Determination of mercury in amalgam samples
[23]	29.6	*N*,*N*-dimethylformamide salicylacylhydrazone (DMFAS)	PVC	6.2×10^{-7}–8.0×10^{-2}	2	Determination of mercury(II) ion in vegetables and in *Azolla filiculoides*
[55]	69.0 ± 0.5 (mV/pHgBr^{3-})	Tribromomercurate–Rhodamine B (TBM-RB)	PVC	1.0×10^{-5}–1.0×10^{-2}	2	Determination of mercury(II) ion in wastewater and microbial media
[56]	30.0	Polyaniline Sn(IV) phosphate composite	Polyaniline	1.0×10^{-6}–1.0×10^{-1}	3	End-point indicator in the titration of Hg(II) ions with EDTA
[57]	34.0	4-(4-*N*,*N*-Dimethylphenyl)-2,6-diphenylpyrilium tetrafluoroborate	PVC	1.0×10^{-8}–1.0×10^{-3}		Potentiometric titration of Hg(II) ions with I$^-$
[58]	–	Trityl-picolinamide (T-Pico)	PVC	–	–	Potentiometric determination of mercury in water samples
[59]	30.0	2-Amino-6-purinethiol	PVC	7.0×10^{-8}–1.0×10^{-1}	2	Determination of mercury in synthetic solutions and water samples
[60]	29.8 ± 0.75	Bis(benzoylacetone) diethylenetriamine ($H_2(BA)_2PD$)	PVC	1.0×10^{-6}–1.0×10^{-1}	3	Determination of mercury(II) in water samples
[61]	32.25	2-Methylsulfanyl-4-(4-nitrophenyl)-1-(*p*-tolyl)-1*H*-imidazole	PVC	5.0×10^{-5}–1.0×10^{-1}	4	Potentiometric titration of Hg(II) ions with KI
[61]	27.61	2,4-Diphenyl-1-(*p*-tolyl)-1*H*-imidazole	PVC	5.0×10^{-5}–1.0×10^{-1}	4	Potentiometric titration of Hg(II) ions with KI
[5]	59.3 ± 0.6	Cryptand derivative (I)	PVC	1.0×10^{-5}–1.0×10^{-2}	1	End-point indicator in the titration of Hg(II) ions with EDTA
[5]	61.3 ± 0.7	Cryptand derivative (II)	PVC	1.0×10^{-5}–1.0×10^{-2}	1	End-point indicator in the titration of Hg(II) ions with EDTA
[62]	31.9	Calix[4]arene derivatives	PVC	5.0×10^{-5}–1.0×10^{-1}	6	Potentiometric titration with I$^-$ and $Cr_2O_7^{2-}$
[63]	–	2-Mercapto-2-thiazoline (MTZ)	PVC	2.0×10^{-10}–1.5×10^{-5}	1	Potentiometric determination of mercury in water samples
[64]	29.6	1,4,8,11-tetrathiacyclotetradecane	PVC	1.0×10^{-7}–1.0×10^{-1}	1	Potentiometric determination of mercury in urine samples
[65]	30.71	Mercury(II) complex of poly(4-vinylpyridine)	Poly(Hg(II)-4-vinylpyridine)	1.0×10^{-7}–1.0×10^{-2}	4	Potentiometric determination of mercury in water samples
[61]	29.8 ± 0.5	Bis(benzoylacetone) diethylenetriamine	PVC	1.0×10^{-6}–1.0×10^{-1}	3	Potentiometric determination of mercury in water samples
This work	27.6 ± 0.6	**1**	PVC	1.0×10^{-6}–1.0×10^{-2}	≈4	Determination of mercury in a dental filling amalgam alloy as a real sample with complicated matrix

Preparation of the electrode

The procedure used to prepare the membrane of the mercury(II)-selective potentiometric sensor was as follows: 4.3 mg lariat crown compound, 280.7 mg TEHP, and 2.3 mg KTpClPB were dissolved in 5 cm^3 tetrahydrofuran. PVC (140.4 mg) was slowly added to this mixture. The homogenous mixture formed was poured on to a glass disc with a diameter of 3.5 cm attached to a glass plate and was kept at room temperature for 24 h for evaporation of the tetrahydrofuran. A 0.7 cm diameter disk of the polymer membrane was cut and fixed to the end of a glass tube with a diameter of

0.5 cm and a length of 10 cm. An internal filling solution containing 1.0×10^{-3} mol dm^{-3} $CaCl_2$ was put into this glass tube and an AgCl-coated silver wire was placed into it. The prepared PVC membrane electrode was conditioned in 1.0×10^{-3} mol dm^{-3} mercury(II) nitrate solution for 24 h.

Potential measurements

Using the double-junction Ag/AgCl reference and the mercury(II)-selective electrodes, the following electrochemical cell was prepared:

$$\text{Reference electrode/analyte solution/membrane/}\\ \text{internal filling solution/AgCl/Ag}$$

All emf measurements were carried out in this cell by using an Orion model 720A pH ion meter. The reference electrode was an Orion 9002 double-junction Ag/AgCl electrode containing a 17% KNO_3 and 5% KCl mixture saturated with AgCl (cat. no. 900002) as the inner chamber filling solution; the outer chamber filling solution consisted of 10% KNO_3 (cat. no. 900003). The pH measurements were done with an Ingold (10.402.3311) combined glass pH electrode. The combined glass electrode was kept in water when not in use. The experimental solution was stirred with a magnetic stirrer and the potentials were recorded after the equilibrium potentials had been reached. All experimental work was carried out at 20 ± 1 °C.

Amalgam sample preparation

The sample was dissolved in 60% nitric acid with intense heating to near dryness. Acid treatment and evaporation were repeated twice, then the residue was dissolved in the smallest volume of water. Potassium permanganate was then added as an oxidizing agent to form mercury(II) ions from possible mercury(I) ions formed in small amounts of acidic solutions. Afterwards, hydrogen peroxide was added until the color of potassium permanganate disappeared. Silver(I) ions were precipitated as AgCl in order to prevent the interfering effect of silver in the amalgam sample. The clear solution was quantitatively transferred into a volumetric flask and the pH of the solution was adjusted to 4.0. The prepared solution was used for determination of mercury by use of the proposed electrode.

Acknowledgments We gratefully acknowledge the financial support of Ankara University Research Fund Project No 2002-07-05-068.

References

1. Gupta VK, Chandra S, Lang H (2005) Talanta 66:575
2. Shahrokhian S, Taghani A, Moattar F (2002) Electroanalysis 14:1621
3. Antonisse MMG, Reinhoudt DN (1999) Electroanalysis 11:1035
4. Pungor E, Toth K (1987) Anal Sci 3:387
5. Acar P, Demirel Özel A, Canel E, Ocak Ü, Şentürk HB, Gök Y, Kılıç E (2007) Main Group Met Chem 30:117
6. Singh AK, Bhattacharjee G, Singh R (2004) Sens Actuators B 99:36
7. Fakhari AR, Ganjali MR, Shamsipur M (1997) Anal Chem 69:3693
8. Somer G, Kalaycı Ş, Ekmekci G (2001) Sens Actuators B 81:122
9. Hassan SSM, Saleh MB, Gaber AAA, Mekheimer RAH, Kream NAA (2000) Talanta 53:285
10. Mahajan RK, Kaur I, Lobana TS (2003) Talanta 59:101
11. Baiulescu GE, Ciocan N (1977) Talanta 24:37
12. Gupta VK, Jain S, Khurana U (1997) Electroanalysis 9:478
13. Szczepaniak W, Oleksy J (1986) Anal Chim Acta 189:237
14. Kopytin AV, Gabor-Klatsmanyi P, Izvekov VP, Pungor E (1983) Anal Chim Acta 148:35
15. Lai MT, Shih JS (1986) Analyst 111:891
16. Brzozka Z, Pietraszkiewicz M (1991) Electroanalysis 3:855
17. Lu J, Tong X, He X (2003) J Electroanal Chem 540:111
18. Perez-Marin L, Macedo-Miranda G, Avila-Perez P, Lopez-Valdivia H, Otazo-Sanchez E, Chamaro JA (2000) Analyst 125:1787
19. Bagheri M, Mashhadizadeh MH, Razee S, Momeni A (2003) Electroanalysis 15:1824
20. Mazloum M, Amini MK, Mohammadpoor-Baltork I (2000) Sens Actuators B 63:80
21. Javanbakht M, Ganjali MR, Eshghi H, Sharghi H, Shamsipur M (1999) Electroanalysis 11:81
22. Mashhadizadeh MH, Sheikhshoaie I (2003) Talanta 60:73
23. Ye G, Chai Y, Yuan R, Dai J (2006) Anal Sci 22:579
24. Mahajan RK, Kaur R, Kaur I, Sharma V, Kumar M (2004) Anal Sci 20:811
25. Fabre B, Marrec P, Simonet J (2000) J Electroanal Chem 485:94
26. Gismera MJ, Hueso D, Procopio JR, Sevilla MT (2004) Anal Chim Acta 524:347
27. Su CC (2008) J Mol Struct 888:33
28. Yaftian MR, Zamani AA, Parinejad M, Shams E (2005) Sep Purif Technol 42:175
29. Yoshio M, Noguchi H (1982) Anal Lett 15:1197
30. Szczepaniak W, Juskowiak B, Ciszewska W (1984) Anal Chim Acta 156:235
31. Zolotov YA, Kuzmin NM, Petrukhin OM, Spivakov BY (1986) Anal Chim Acta 180:137
32. Ocak Ü, Gök Y, Şentürk HB (2009) Sep Sci Technol 44:1240
33. Bagatur'yants AA, Freidzon AY, Alfimov MV, Baerends EJ, Howard JAK, Kuz'mina LG (2002) J Mol Struct Theochem 588:55
34. Russell DD (2002) Patent US 6436259 B1
35. Erden S, Demirel A, Memon S, Yılmaz M, Canel E, Kılıç E (2006) Sens Actuators B 113:290
36. Demirel A, Doğan A, Akkuş G, Yılmaz M, Kılıç E (2006) Electroanalysis 18:1019
37. Erol S, Demirel Özel A, Yılmaz M, Kılıç E (2009) Rev Anal Chem 28:27
38. Taştekin M, Doğan A, Demirel Özel A, Kılıç E (2009) Rev Anal Chem 28:51
39. Canel E, Erden S, Demirel Özel A, Memon S, Yılmaz M, Kılıç E (2008) Turk J Chem 32:323
40. Zolotov YA (1997) Macrocyclic compounds in analytical chemistry, vol 143. Wiley, New York, p 285
41. Morf WE (1981) The principles of ion-selective electrodes and of membrane transport. Elsevier, Amsterdam, p 223
42. Mala Z, Senkyr J (1988) Talanta 35:591
43. Armstrong RD, Horvai G (1990) Electrochim Acta 35:1

44. Bakker E, Xu A, Pretsch E (1994) Anal Chim Acta 295:253
45. Bakker E, Meyerhoff ME (2000) Anal Chim Acta 416:121
46. Chen L, Zhang J, Zhao W, He X, Liu Y (2006) J Electroanal Chem 589:106
47. Bobacka J, Vaananen V, Lewenstam A, Ivaska A (2004) Talanta 63:135
48. Bakker E, Bühlmann P, Pretsch E (1999) Electroanalysis 11:915
49. Singh LP, Bhatnagar JM (2004) J Appl Electrochem 34:391
50. Baiulescu GE, Coşofret VV (1976) Talanta 23:677
51. Ocak Ü, Ocak M, Başoğlu A, Parlayan S, Alp H, Kantekin H (2009) J Incl Phenom Macrocycl Chem 67:19
52. Yang X, Hibbert DB, Alexander PW (1998) Anal Chim Acta 372:387
53. Arida HA, Kloock JP, Schoning MJ (2006) Sensors 6:435
54. Saleh MB, Soliman EM, Gaber AAA, Ahmed SA (2006) Anal Lett 39:659
55. Othman AM (2006) Intern J Environ Anal Chem 86:367
56. Khan AA, Inamuddin (2006) Sens Actuators B 120:10
57. Yu X, Zhou Z, Wang Y, Liu Y, Xie Q, Xiao D (2007) Sens Actuators B 123:352
58. Kuswandi B, Nuriman, Dam HH, Reinhoudt DN, Verboom W (2007) Anal Chim Acta 591:208
59. Gupta VK, Singh AK, Khayat MA, Gupta B (2007) Anal Chim Acta 590:81
60. Ensafi AA, Meghdadi S, Allafchian AR (2008) IEEE Sens J 8:248
61. Mahajan RK, Sood P, Mahajan MP, Marwaha A (2007) Ann Chim 97:959
62. Mahajan RK, Kaur R, Bhalla V, Kumar M, Hattori T, Miyano S (2008) Sens Actuators B 130:290
63. Amini MK, Khezri B, Firooz AR (2008) Sens Actuators B 131:470
64. Ion AC, Ion I, Stefan DN, Barbu L (2008) Mater Sci Eng C 29:1
65. Bakhtiarzadeh F, Ghani SA (2008) J Electroanal Chem 624:139