

Full Paper

Benzo15-crown-5 as Sensory Molecule for Fabrication of a Lead(II) Ion-selective Potentiometric Sensor

Parisa Heidari¹, Abbasali Zamani², Mahdieh Koorepazan Moftakhar¹ and Mohammad Reza Yaftian^{1,*}

¹*Phase Equilibria Research Laboratory, Department of Chemistry, Faculty of Science, University of Zanjan, 45371-38791, Zanjan, Iran*

²*Environmental Science Research Laboratory, Department of Environmental Science, Faculty of Science, University of Zanjan, 45371-38791, Zanjan, Iran*

* Corresponding Author, Tel.: +98 24 3305 2581; Fax: +98 24 3228 3203

E-Mail: yaftian@znu.ac.ir (M. R. Yaftian)

Received: 25 July 2014 / Received in Revised form: 6 December 2014 /

Accepted: 7 December 2014 / Published online: 31 December 2014

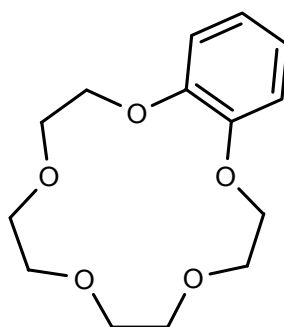
Abstract- Benzo15-crown-5 (B15C5) has been examined as an ion sensing material for fabricating a PVC membrane lead ion-selective potentiometric sensor. The best performance of the electrode was observed with a membrane composition formed by 29% PVC, 60% dibutylphthalate (DBP) as plasticizing solvent mediator, 2% sodium tetraphenylborate (NaTPB) as ion excluder and 9% of B15C5 as ionophore. The electrode presents a nearly Nernstian response (a slope of 29.7 ± 0.5 mV/decade) over a concentration range 1×10^{-5} - 1×10^{-3} M of lead ions, with a limit of detection 8.4×10^{-6} M. Its potential response was independent on pH variation in the range 2.8-4.5. The dynamic response time of the electrode to achieve a steady potential was found to be about 25 seconds. The selectivity of the prepared electrode relative to some mono-, di-, tri- and tetra-valent metal ions was examined. This electrode can be used for 2 months without considerable divergences in the potential response. It was successfully used as an indicator electrode for the complex formation titration of lead in water samples by EDTA.

Keywords- Benzo15-crown-5, Lead selective electrode, Potentiometry, PVC membrane

1. INTRODUCTION

PVC-membrane ion selective electrodes are included four constituents: PVC powder, ionophore, plasticizer and anion excluder. The sensing surfaces of ion selective electrodes are comprised of a homogeneous polymer matrix containing organic compound as ionophore for the target ion. The binding characteristics of the selected ionophore towards desired ions are important for achieving to efficient and suitable potentiometric ion selective sensors [1-3].

Due to importance of determination of lead ions as a toxic chemical species in environment samples [4] on the one hand, and good advantages of ion selective electrodes as analytical tools in clinical, industrial and environmental analysis [5,6] on the other hand, a great number of Pb^{2+} potentiometric sensors have been constructed and used [7-10]. In such investigations both acyclic and cyclic ionophores have been used [11]. Derivative of oxadiazamides [12], Schiff base ligands [13], thioamides [14], derivatives of quinaldic acid [15], benzyl disulphide [16] and piroxicom [17] are among the acyclic compounds used for constructing lead ion-selective electrodes. The size selective properties of macrocyclic compounds have attracted the attention of many research groups to utilize these ionophores for lead potentiometric sensors. To this end the application of dibenzopyridine-18-crown-6 [18], diazacrown ether derivatives [19], thiocrown ethers [20], functionalized calixarenes [21-25] and porphyrins [26] have been investigated.



B15C5

Fig. 1. Chemical structure of benzo-15-crown-5

Benzo-15-crown-5 (Fig. 1) is used for preparation of ion-selective electrodes of cadmium [27] uranium [28], potassium [29,30], lanthanum [31,32] and sodium ions [33]. Besides, the applicability of benzo-15-crown-5 as sensing molecule in lead ion-selective polypyrrole solid-contact electrode [34] and the potential of 15-crown-5 derivatives for complexation of lead ions [35] has been demonstrated. These applicability and our interests on the application of macrocyclic compounds as ion sensing agents for preparing metal ion-selective potentiometric sensors [36-40], motivate us to study the properties of benzo-15-crown-5 as a sensory molecule for preparation of a PVC-based lead ion-selective electrode. To the best of

our knowledge such application for the examined crown ethers has not been previously reported. The optimum composition of the membrane were investigated, and its characteristics with respect to linear concentration range, working pH range, detection limit, response time, selectivity and their applicability were evaluated and discussed.

2. EXPERIMENTAL

2.1. Reagents

Benzo-15-crown-5 (Alfa, Karlsruhe, Germany), sodium tetraphenylborate (NaTPB, Merck, Munchen, Germany), tetrahydrofuran (THF, Dae Jung, Gyonggi-do, Korea), *O*-nitrophenyloctyl ether (*O*-NPOE, Fluka, Buchs, Switzerland), dioctylphthalate (DOP, Fluka, Buchs, Switzerland), dibutylphthalate (DBP, Hohenbrunn, Germany), oleic acid (OA, Merck, Munchen, Germany) high relative molecular weight polyvinyl chloride (PVC, Fluka, Buchs, Switzerland) hydrochloric acid, sodium hydroxide and disodium salt of EDTA and the nitrate salts (Merck, Darmstadt, Germany) were analytical reagent grade and were used as received.

2.2. Electrode preparation and potential measurements

The general procedure for preparing the membranes involved mixing the optimized quantity of membrane constituents, including PVC powder, ionophore, plasticizer and anion excluder in 5 mL of THF. This mixture was mixed well and it was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily mixture was obtained. A Pyrex tube (5 mm o.d.) was dipped into the mixture for about 5 seconds. A transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 10 h. It was then filled with the internal solution (lead nitrate, 1×10^{-2} M). The prepared membrane was finally conditioned for 48 h by soaking in a 1×10^{-2} M solution of $\text{Pb}(\text{NO}_3)_2$. A pH-meter Metrohm (model 780) was used for potential and pH measurements. All pH adjustments were made with nitric acid and sodium hydroxide solutions. A silver/silver chloride reference electrode (Azar Electrode, Iran) was used for potential measurements at $25.0 \pm 0.1^\circ\text{C}$. All potential measurements were performed using the following assembly;

Ag, AgCl (sat'd)/internal solution ($\text{Pb}(\text{NO}_3)_2$, 1×10^{-2} M)/PVC membrane/test solution/Ag, AgCl (sat'd.)

3. RESULTS AND DISCUSSION

3.1. Membrane composition

Thirteen electrodes were prepared by using various amounts of PVC, plasticizer (DBP, DOP and NPOE), B15C5 as ionophore and additive (NaTPB). The potential variation as a

function of the logarithm of the lead concentration between 1×10^{-6} and 1×10^{-2} M was investigated. The studied compositions with the corresponding slopes, found for the linear part of the curves, are given in Table 1. The response presented by the electrodes with compositions 1 and 2 is far from Nernstian response, confirming the crucial role of both ionophore and anion excluder in the membrane's composition. Besides, the response of the electrodes bearing compositions 4, 5 and 6 shows the crucial dependency of the electrodes to the amount of ionophore B15C5. The comparison of slopes of potential versus lead concentration curves presented by the electrodes with composition 6, 7 and 8 shows clearly the role of the plasticizer on the electrode characteristics. Among the studied plasticizer (DBP, *O*-NPOE and DOP) the electrode constructed by DBP presents a near Nernstian slope with respect to the other plasticizers. The electrodes prepared by the compositions 6 and 9 reveals the importance of ionophore additive on the response of the electrodes. It is seen that sodium tetraphenylborate salt plays its role as an anion excluder better than oleic acid.

Table 1. Examined composition for optimization the membrane ingredients^a

No.	PVC	Plasticizer	B15C5	NaTPB	Slope/mV decade ^{-1 b}
1	30	65 (DBP)	5	0	8.3 (± 1.0)
2	30	65 (DBP)	0	5	9.5 (± 1.2)
3	30	62 (DBP)	8	0	15.5 (± 0.7)
4	30	63 (DBP)	5	2	14.3 (± 0.7)
5	30	60 (DBP)	8	2	20.1 (± 0.6)
6	29	60 (DBP)	9	2	29.7 (± 0.5)
7	29	60 (<i>O</i> -NPOE)	9	2	24.8 (± 0.6)
8	29	60 (DOP)	9	2	13.4 (± 0.9)
9	29	60 (DBP)	9	2 (OA)	21.1 (± 1.3)
10	29	61 (DBP)	9	1	15.7 (± 1.1)
11	29	61 (DBP)	8	2	24.4 (± 1.1)
12	29	60.5 (DBP)	9	1.5	26.5 (± 0.9)
13	29	63 (DBP)	6	2	12.4 (± 1.2)

^aValues in %w/w, ^bStandard deviations determined for three independent electrodes

As an example, Fig. 2 shows the potential response of the membrane (composition 6) at varying concentration of Pb^{2+} ions. The prepared membrane with the composition 29% PVC, 60% DBP, 2% NaTPB and 9% of B15C5 indicates a rectilinear range in 1×10^{-5} to 1×10^{-3} M.

The slope of the calibration curves were 29.7 ± 0.5 mV per decade of lead ion concentration (for four independent prepared electrodes with the same composition). This composition was used throughout the work. The detection limit as determined from the intersection of the two extrapolated segments of the calibration graph [41] was found to be 8.4×10^{-6} M.

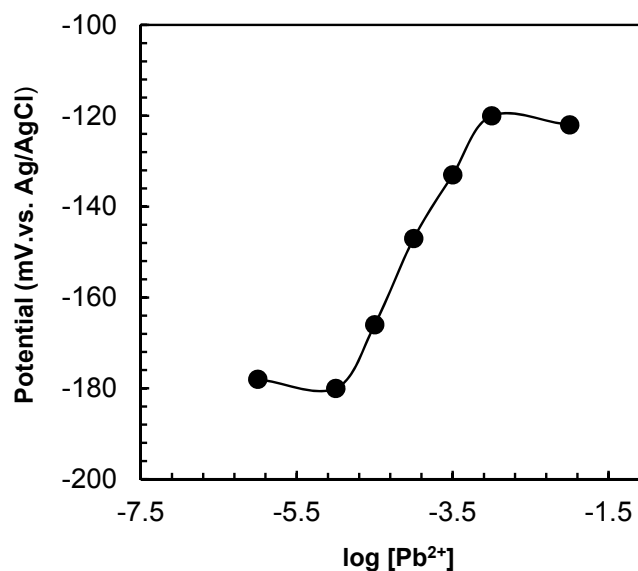


Fig. 2. Potential response of the electrode prepared with composition 29% PVC, 60% DBP, 2% NaTPB and 9% of B15C5 (composition 6 in Table 1).

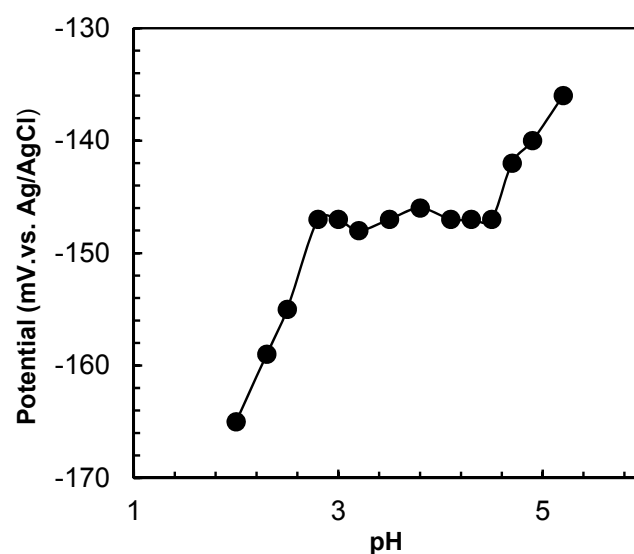


Fig. 3. Effect of the pH of the test solution (1×10^{-4} M of Pb^{2+}) on the potential response of the prepared lead ion-selective electrode with composition 6 in Table 1

3.2. Working pH range of the electrode

Potential response dependency of the sensor on the pH of a solution containing 1×10^{-4} M of Pb^{2+} ion in the range of 2.0-5.2 was investigated (Fig. 3). The potential is independent on pH in the range 2.8-4.5. The increase of potentials out of this range can be attributed to the competition between hydrogen ions and lead ions at pH region lower than 2.8 and an increase in sodium ion concentration due to the increase in amount of sodium hydroxide at higher pH values than 4.5.

3.3. Dynamic response time

Dynamic response time is one of the important factors revealing the performance of a potentiometric sensor. For evaluating the response time of the prepared electrode, it was alternatively immersing in stirred lead solutions of 1×10^{-4} and 1×10^{-3} M (Fig. 4). The response time of the steps varies between 20-30 s, depending on the concentration of the test solution.

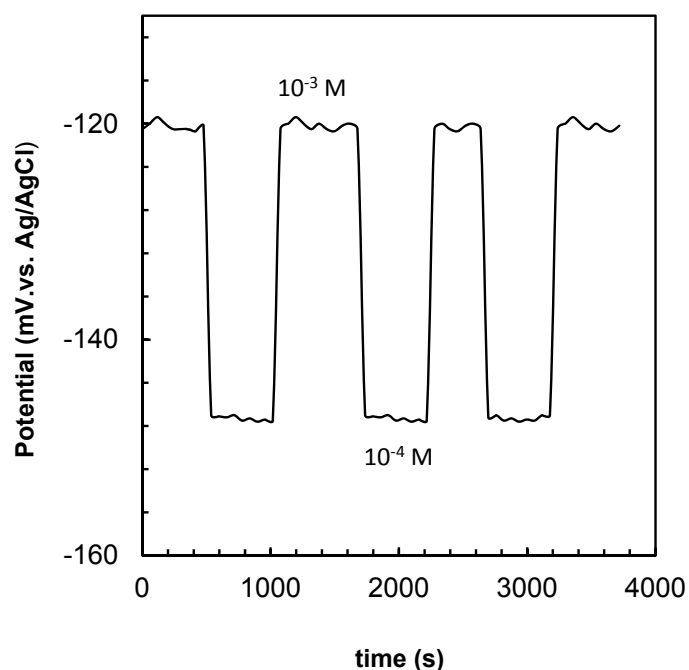


Fig. 4. Dynamic response time of the prepared lead ion-selective electrode (with composition 6 in Table 1) by stepwise addition of the lead ion concentration

3.4. Lifetime of the electrode

The electrode lifetime was studied by periodically recalibrating the electrode response versus $\log[\text{Pb}^{2+}]$ over the concentration range of 1×10^{-5} - 1×10^{-3} M of Pb^{2+} each week over a

period of 2 months. The electrode was stored in air and reconditioned with 1×10^{-2} M lead nitrate solution about 48 h before use. The slope remained nearly constant (29.0 ± 1.0 mV decade $^{-1}$) and presents an adequate stability.

3.5. Selectivity of the electrode

Undoubtedly selectivity presented by an ISE is the most important characteristics of this type of sensors; especially this is a critical parameter for direct potentiometric measurements. Selectivity of the electrode towards lead ions over some mono-, di- and trivalent ions was tested using the match potential method [42]. In this method, a specified amount of the analyte (here Pb^{2+}) is added to a reference solution with a given concentration (here 1×10^{-5} M) and the potential change is measured (30 mV). In other experiments, a quantity of the interfering ion (M^{n+}) is gradually introduced to an identical reference solution of Pb^{2+} , as before, until the potential is equal to the potential of the preceding solution. The selectivity coefficient ($K_{\text{Pb},\text{M}}^{\text{MPM}}$) can be obtained as the added Pb^{2+} over added M^{n+} concentrations to the reference solution by using $K_{\text{Pb},\text{M}}^{\text{MPM}} = [\text{Pb}^{2+}]/[\text{M}^{n+}]$. Monovalent (Li^+ , Na^+ , K^+ , Ag^+ , and NH_4^+), divalent (Ca^{2+} , Mg^{2+} , Sr^{2+} , Mn^{2+} , Cu^{2+} , Co^{2+} , Cd^{2+} , Ni^{2+} , Hg^{2+} and Zn^{2+}), and trivalent (Fe^{3+} , Al^{3+} and Sm^{3+}) ions were tested as interfering ions. The resulting selectivity coefficients are presented in Table 2. It is seen that the selectivity presented by the prepared electrode is suitable for the majority of the tested ions and it shows lower selectivity towards K^+ , Li^+ , Na^+ and Sr^{2+} ions.

Table 2. Selectivity coefficient of the prepared sensor with composition 6 in Table 1, measured using match potential method

M^{n+}	$K_{\text{Pb},\text{M}}^{\text{MPM}}$	M^{n+}	$K_{\text{Pb},\text{M}}^{\text{MPM}}$
Li^+	1.3×10^{-2}	Co^{2+}	3.1×10^{-3}
Na^+	6.1×10^{-2}	Ni^{2+}	9×10^{-4}
K^+	2×10^{-2}	Zn^{2+}	9×10^{-4}
NH_4^+	3.6×10^{-4}	Cd^{2+}	9.6×10^{-3}
Ag^+	4.7×10^{-4}	Hg^{2+}	4.1×10^{-4}
Ca^{2+}	8.9×10^{-4}	Mn^{2+}	2.5×10^{-4}
Sr^{2+}	3.7×10^{-2}	Fe^{3+}	3.7×10^{-3}
Mg^{2+}	1.5×10^{-3}	Al^{3+}	7.3×10^{-3}
Cu^{2+}	4.4×10^{-3}	Sm^{3+}	5.1×10^{-3}

3.6. Application of the electrode

The prepared sensor was used as indicator electrode for potentiometric titration of lead solutions (20 mL of 5×10^{-3} M) by standard solution of EDTA (1×10^{-2} M). The potentiometric curves are presented in Fig. 5. The curves show that the electrodes can be used successfully for determination of lead ions in such experiments. In addition, the applicability of the prepared sensor has been also tested by titration of lead ions injected in three water samples (tap water of the University of Zanjan campus, Zanjan city center and a type of mineral water purchased from the market). The results shown in Table 3 show the potential of the prepared electrode as an indicator for the titration of lead ions in such water samples. It is noteworthy that the determined amount of lead ions in these samples by flame atomic absorption spectrometry reveals no detectable amount of lead in the tested samples.

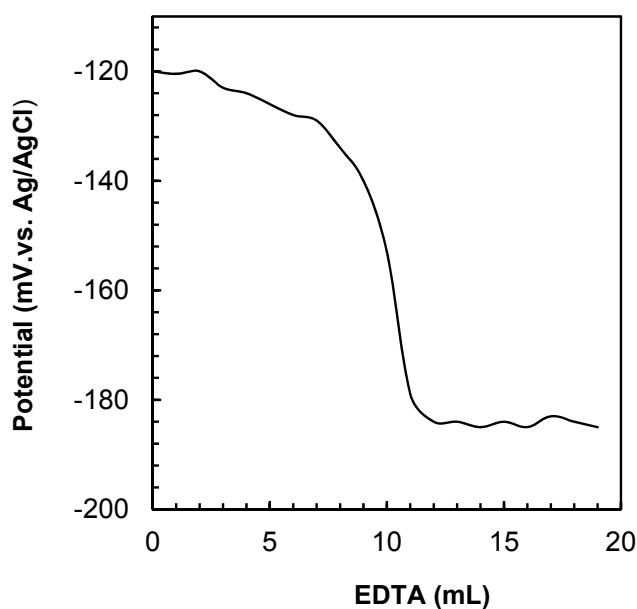


Fig. 5. Potential titration curve of 20 mL solution of lead ions (5×10^{-3} M), adjusted at pH 4 by a solution of EDTA (1×10^{-2} M), using the prepared electrode with composition 6 in Table 1

3.7. Comparison of the prepared electrode with some related studies

Table 4 contains characteristics of some lead ion-selective electrodes prepared based on some crown ether macrocyclic compounds bearing 18-crown-6 units i.e. nitrobenzo-18-crown-6 (NB18C6), dicyclohexyl-18-crown-6 (DC18C6), dibenzo-18-crown-6 (DB18C6), dibenyl-diaza-18-crown-6 (DBzDA18C6), hexathia-18-crown-6-tetraone (HT18C6-TO), N,N'-dimethylcyanodiaza-18-crown-6 (DMCN18C6) and 1-pyrrolidine dicarbodithioicte/18-crown-6 (PDCT18C6). Although more suitable adaptation is between the lead ions and the

18-crown-6 cavity [43], the selectivity presented by the prepared electrode in the present work is comparable with the examined electrodes. It is important to note that except for the electrode reported in this report and that fabricated by N,N'-dimethylcyanodiaza-18C6, all other electrodes suffers from interference of Hg^{2+} and/or Fe^{3+} ions. The detection limit of the prepared electrode is comparable with the lead ion-selective electrodes based on NB18C6, DC18C6 and DB18C6. The electrode based on B15C5 shows a comparable rapid response time with respect to the mentioned electrodes, although its lower lifetime can be considered as its disadvantage.

Table 3. Results of the determination of lead ions injected in water samples by their potentiometric titration by EDTA using the prepared electrode as indicator

Sample	Added Pb^{2+} (M)	Recovery
Distilled water	5×10^{-3}	99.4 (± 0.7)
Tab Water (University of Zanjan)	5×10^{-4}	101.6 (± 1.0)
	1×10^{-3}	100.7 (± 0.8)
Tab water (Zanjan City)	5×10^{-4}	101.2 (± 0.8)
	1×10^{-3}	100.9 (± 1.1)
Mineral water	5×10^{-4}	101.3 (± 1.4)
	1×10^{-3}	100.8 (± 1.1)

Table 4. Comparison of the characteristics of the lead selective sensors based on some crown ethers as ionophore

Ionophore	Characteristics						
	L. R. ^a	Slope ^b	Resp. Time ^c	D. L. ^d	Working pH	Interference	Lifetime ^e
B15C5 (This work)	1×10^{-5} - 1×10^{-3}	29.7 \pm 0.5	25	8.4×10^{-6}	2.8-4.5	Li^+ , Na^+ , K^+ , Sr^{2+}	2
DC18C6 [38]	1×10^{-5} - 1×10^{-2}	30.0 \pm 1.0	12	6.3×10^{-6}	5.2-4.6	Ag^+ , Hg^{2+} , Cu^{2+}	8
DB18C6 [38]	1×10^{-5} - 1×10^{-2}	28.0 \pm 1.0	6	7.1×10^{-6}	3.1-4.9	Na^+ , K^+ , Ag^+ , Hg^{2+} , NH_4^+	8
NB18C6 [40]	1×10^{-5} - 1×10^{-2}	30.5 \pm 0.5	6	8.9×10^{-6}	2.2-4.1	K^+ , Ag^+ , Hg^{2+} , Cu^{2+}	9
DBzDA18C6 [44]	5×10^{-5} - 1×10^{-2}	29.3	10	2.8×10^{-5}	^f	Li^+ , K^+ , Ag^+ , Hg^{2+} , NH_4^+	10
HT18C6-TO [45]	1×10^{-6} - 8×10^{-3}	29.0	40	8.0×10^{-7}	3.0-6.0	Hg^{2+}	10
DMCN18C6 [46]	1×10^{-7} - 8×10^{-2}	29.5 \pm 0.3	10	7.0×10^{-7}	3.5-7.0	No interference	10
PDCT18C6 [47]	5×10^{-5} - 1×10^{-1}	29.5 \pm 0.5	-	1.0×10^{-7}	7.0-10.0	Na^+ , Ag^+ , Fe^{3+}	10

^aLinear concentration range in M; ^bIn mV decade⁻¹; ^cResponse time in seconds; ^dDetection limit in M;

^fUnbuffered solution; ^eIn months

4. CONCLUSIONS

The prepared lead ion-selective potentiometric sensor based on the crown ether benzo-15-crown-5 can be used for determination of lead ions in the concentration range 1×10^{-5} - 1×10^{-3} M. Its detection limit was calculated to be 8.6×10^{-6} M. The Pb^{2+} ion-selective electrode shows an acceptable response time. It shows suitable selectivity towards mono- di- and tri-valent cations NH_4^+ , Ag^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Mn^{2+} , Fe^{3+} , Al^{3+} and Sm^{3+} , and lower selectivity with respect to Li^+ , Na^+ , K^+ and Sr^{2+} ions. The working pH of the electrode lies in 2.8-4.5. It is an advantages because is close to the pH of solutions in many industrial water samples. The prepared sensor can be successfully used for complexometric titration of lead ions by EDTA as potentiometric indicator.

REFERENCES

- [1] E. Bakker, E. Pretsch, and P. Bühlmann, *Anal. Chem.* 72 (2000) 1127.
- [2] E. Bakker, *Anal. Chem.* 76 (2004) 3285.
- [3] E. Bakker, and Y. Qin, *Anal. Chem.* 78 (2006) 3965.
- [4] L. Patrick, *Altern. Med. Rev.* 11 (2006) 2.
- [5] Y. Tani, and Y. Umezawa, *Sensor Lett.* 3 (2005) 99.
- [6] M. R. Ganjali, P. Norouzi, F. Faridbod, M. Rezapour, and M. R. Pourjavid, *J. Iran. Chem. Soc.* 4 (2007) 1.
- [7] L. Chen, J. Zhang, W. Zhao, X. He, and Y. Liu, *J. Electroanal. Chem.* 589 (2006) 106.
- [8] D. Wilson, M. de la Ángeles Arada, S. Alegret, and M. del Valle, *J. Hazard. Mater.* 181 (2010) 140.
- [9] M. R. Huang, X. W. Rao, X. G. Li, and Y. B. Ding, *Talanta* 85 (2011) 1575.
- [10] V. K. Gupta, M. R. Ganjali, P. Norouzi, H. Khani, A. Nayak, and S. Agarwal, *Crit. Rev. Anal. Chem.* 41 (2011) 282.
- [11] M. Guziński, G. Lisak, J. Kupis, A. Jasiński, and M. Bocheńska, *Anal. Chim. Acta* 791 (2013) 1.
- [12] E. Lindner, K. Toth, E. Pungor, F. Behm, P. Oggenfuss, D. H. Welti, D. Ammann, W. E. Morf, E. Pretsch, and W. Simon, *Anal. Chem.* 56 (1984) 1127.
- [13] T. Jeong, H. K. Lee, D. C. Jeong, and S. Jeon, *Talanta* 65 (2005) 543.
- [14] S. Kamata, and K. Onoyama, *Anal. Chem.* 63 (1991) 1295.
- [15] M. Casado, S. Daunert, and M. Valiente, *Electroanalysis* 13 (2001) 54.
- [16] A. Abbaspour, and F. Tavakol, *Anal. Chim. Acta* 378 (1999) 145.
- [17] S. Sadeghi, G. R. Dashti, and M. Shamsipur, *Sensor. Actuat. B: Chem.* 81 (2002) 223.
- [18] N. Tavakkoli, and M. Shamsipur, *Anal. Lett.* 29 (1996) 2269.
- [19] M. F. Mousavi, S. Sahari, N. Alizadeh, and M. Shamsipur, *Anal. Chim. Acta* 414 (2000) 189.

- [20] M. Shamsipur, M. R. Ganjali, and A. Rouhollahi, *Anal. Sci.* 17 (2001) 935.
- [21] L. X. Chen, J. Zhang, W. F. Zhao, X. W. He, and Y. Liu, *J. Electroanal. Chem.* 589 (2006) 106.
- [22] M. Bochenska, P. J. Cragg, M. Guzinski, A. Jasinski, J. Kulesza, P. M. Marcos, and R. Pomecko, *Supramol. Chem.* 21 (2009) 732.
- [23] E. Malinowska, Z. Brzozka, K. Kasiura, R. J. M. Egberink, and D. N. Reinhoudt, *Anal. Chim. Acta* 298 (1994) 253.
- [24] M. Bochenska, M. Guzinski, and J. Kulesza, *Electroanalysis* 21 (2009) 2054.
- [25] J. Kulesza, M. Guzinski, V. Hubscher-Bruder, F. Arnaud-Neu, and M. Bochenska, *Polyhedron* 30 (2011) 98.
- [26] H. K. Lee, K. Song, H. R. Seo, Y. K. Choi, and S. Jeon, *Sensor. Actuat. B: Chem.* 99 (2004) 323.
- [27] S. K. S. K. Srivastava, V. K. Gupta, and S. Jain, *Electroanalysis* 8 (1996) 938.
- [28] S. K. Agrahari, S. D. Kumar, and A. K. Srivastava, *J. Anal. Chem.* 69 (2014) 36.
- [29] R. Raghunathan, P. Neelamegam, and M. Murugantham, *Res. J. Pharm. Biol. Chem. Sci.* 5 (2014) 11.
- [30] O. Şendil, E. Peçenek, G. Ekmekçi, and G. Somer, *Curr. Anal. Chem.* 5 (2009) 53.
- [31] M. H. Arab Zavar, S. Heidari, G. H. Rounaghi, and N. Ahtari, *J. Electrochem. Soc.* 158 (2011) F142.
- [32] M. H. Arab Zavar, S. Heidari, and G. H. Rounaghi, *Arab. J. Chem.* (in press, 2014).
- [33] A. Kenar, D. Yüzer, H. Nazir, and B. Çiçek, *Rev. Anal. Chem.* 26 (2007) 219.
- [34] J. Shim, E. J. Jang, and K. C. Chung, *Anal. Lett.* 40 (2007) 3038.
- [35] J. Zolgharnein, G. Shahmoradi, and S. Amani, *J. Incl. Phenom. Macrocycl. Chem.* 60 (2008) 163.
- [36] M. Parsa, M. R. Yaftian, and D. Matt, *J. Chin. Chem. Soc.* 54 (2007) 1529.
- [37] M. R. Yaftian, M. Parinejad, and D. Matt, *J. Chin. Chem. Soc.* 54 (2007) 1535.
- [38] A. A. Zamani, N. Khorsihdi, Z. Mofidi, and M. R. Yaftian, *J. Chin. Chem. Soc.* 58 (2011) 673.
- [39] A. A. Zamani, M. Parinejad, F. Jamali, M. R. Yaftian, and D. Matt, *Turk. J. Chem.* 36 (2012) 907.
- [40] P. Heidari, Sh. Jalali, Z. Mofidi, A. A. Zamani, and M. R. Yaftian, *Anal. Bioanal. Electrochem.* 3 (2013) 305.
- [41] M. R. Ganjali, M. Rezapour, A. Rasoolipour, P. Norouzi, and M. Adib, *J. Braz. Chem. Soc.* 18 (2007) 352.
- [42] Y. Umezawa, K. Umezawa, and H. Sato, *Pure Appl. Chem.* 67 (1995) 67.
- [43] A. A. Zamani, A. S. Zarabadi, and M. R. Yaftian, *J. Incl. Phenom.* 63 (2009) 327.
- [44] M. F. Mousavi, S. Sahari, N. Alizadeh, and M. Shamsipur, *Anal. Chim. Acta* 414 (2000) 189.

- [45] M. Shamsipur, M. R. Ganjali, and A. Rouhollahi, *Anal. Chem.* 17 (2001) 935.
- [46] M. R. Ganjali, M. Hosseini, F. Basiripour, M. Javanbakht, O. R. Hashemi, M. Faal Rastegar, M. Shamsipur, and G. W. Buchanen, *Anal. Chim. Acta* 454 (2002) 181.
- [47] M. M. Zareh, A. K. Choneim, and M. H. Abd El-Aziz, *Talanta* 54 (2001) 1049.