



A novel PVC-membrane optical sensor for highly sensitive and selective determination of UO_2^{2+} ion based on a recently synthesized benzo-substituted macrocyclic diamide and dibenzoylmethane

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ABSTRACT

A highly sensitive ion-selective bulk optode membrane for sensing UO_2^{2+} ion based on plasticized poly(vinyl chloride) containing 6,7,9,10,12,13,15,16,23,24,25,26-dodecahydrodibenzo[n,v][1,4,7,10,13,17,20]pentaaxa-diazacyclotricosine-22,27-dione as ionophore, dibenzoylmethane as chromoionophore and sodium tetraphenylborate as an ionic additive was prepared. In addition to its high stability, reproducibility and relatively long lifetime, the proposed optical sensor revealed good selectivity for uranyl ion over a large number of alkali, alkaline earth, transition, and heavy metal ions. The proposed sensor displays a calibration response for UO_2^{2+} over a concentration range of 4.3×10^{-6} to 2.5×10^{-8} M with a limit of detection of 8.0×10^{-9} M and a response time of less than 12 min. The proposed optical sensor was applied successfully to the determination of UO_2^{2+} ion in tap water and Khoshumi mine concentrated solution samples.

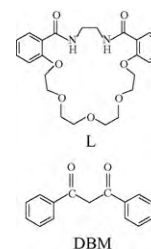
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1. Introduction

The uranyl ion is among those ionic species for which the search for suitable sensors is of increasing interest. This is due to its importance in various physiological, medical, industrial and geochemical processes [1–6]. Uranium as a highly radioactive element is extensively used in the nuclear industry [7–9], and is also well known as a chemical toxin [10]. It exists in low quantities of 10^{-5} to 10^{-3} M in wash streams coming out from nuclear reactors [11]. Moreover, due to relatively high mobility of uranium in surface and near surface environments, its measurements in trace levels in natural waters can be used as a basis for geochemical exploration and some industrial processes. Thus, during the past decade, several ion-selective electrodes based on a variety of suitable ionophores have been developed [12–20]. However, compared with uranyl-selective potentiometric sensors, work on ion-selective bulk optodes for uranyl ion has been quite sparse [21–24].

In the past decade, we have been involved in the design and use of different ion carriers for pre-concentration and selective determination of uranyl ion via solid phase extraction [25–27], supercritical fluid extraction [28] and construction of ion-selective electrodes [14,17,19,20], ion-imprinted polymers

[29] and ion-selective bulk optodes [22]. We have recently synthesized, purified and used 6,7,9,10,12,13,15,16,23,24,25,26-dodecahydrodibenzo[n,v][1,4,7,10,13,17,20]pentaaxa-diazacyclotricosine-22,27-dione (L) as a novel ionophore for the preparation of new plasticized-PVC-membrane-selective electrodes for the determination of uranyl ion by flow injection potentiometry [19]. In this work we used a combination of this ligand, as a selective ionophore, and dibenzoylmethane (DBM), as a suitable lipophilic chromoionophore [26], to prepare a highly sensitive and selective optical sensor for uranyl ion. Although the uranyl ion–DBM complex does not have a high molar absorptivity and its λ_{max} spreads at lower wavelengths of the visible region, its use as a chromoionophore in combination with benzo-substituted macrocyclic diamide L, as a highly selective UO_2^{2+} ionophore [19], for the preparation of an optode membrane for uranyl ion will result in increased selectivity, very low limit of detection, long time stability and good reproducibility of the fabricated optical sensor:



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2. Experimental

2.1. Reagents

Reagent-grade *o*-nitrophenyloctyl ether (NPOE), benzyl acetate (BA), dimethyl sebacate (DMS), dibenzoyl methane (DBM), sodium tetraphenylborate (NaTPB), *trans*-1,2-aminocyclohexane-*N,N,N',N'*-tetraacetic acid (DCTA), tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from Fluka Chemical Company and used as received. The metal salts of all cations used (all from Merck) were of the highest purity available and used without any further purification. Ligand L was synthesized and purified as reported elsewhere [19]. Doubly distilled deionized water was used throughout.

2.2. Membrane preparation

The membrane solution was prepared by dissolving 7 mg of L, 2 mg of NaTPB, 7 mg of DBM, 28 mg of powdered PVC and 56 mg of plasticizer NPOE in 1 mL THF by sonication. A volume of 0.1 mL of this solution was pipetted and spread onto a 7 mm × 50 mm dust-free glass plate located in THF saturated desiccator. The membrane film was placed in ambient air for further drying. The thickness of the films was in the order of 3–5 μm (as evaluated from the volume employed for spreading).

2.3. Apparatus and absorbance measurements

All absorbance measurements were carried out on a Scinco UV-Vis 2100 spectrophotometer (UK). A Corning ion analyzer 250-pH/mV meter was used for the pH measurements.

Two identical optode membranes cast similarly on glass plates were placed vertically inside the sample and reference cuvettes containing 3 mL acetate buffer solution of pH 4.0. After 10 min, the sample cell was titrated with microliter amounts of a concentrated uranyl solution, using a pre-calibrated micropipette, and after each addition and waiting for 12 min, the absorbance of the membrane was measured at 406 nm against the blank reference.

The membrane response, α , may be defined as the ratio of the concentration of the uncomplexed chromoionophore [DBM] to the total amount present in membrane [DBM]_t, i.e., $\alpha = [\text{DBM}]/[\text{DBM}]_t$. The α values were then calculated by absorbance measurements at the wavelength of the complexed chromoionophore as $\alpha = (A_1 - A)/(A_1 - A_0)$, where A_1 is the absorbance of the membrane for complete complexation (i.e., at $\alpha = 0$), A_0 is the absorbance value for the free chromoionophore (i.e., at $\alpha = 1$) and A is absorbance measured at any time during the titration procedure.

3. Results and discussion

The design and synthesis of new functionalized macrocyclic ligands for a specific analytical application is a subject of continuous interest [30–32]. The in-built configuration rigidity induced by *N*-substituted amides present in the periphery of benzomacrocyclic invokes preorganization leading to ionophoric selectivity [33–35]. Thus, we have recently reported the successful use of macrocyclic diamides as ionophores in the preparation of PVC-based selective electrodes for Hg²⁺ [36], Sr²⁺ [37], Ca²⁺ [38], Cs⁺ [39], Co²⁺ [40], Ag⁺ [41], Be²⁺ [42], Cu²⁺ [43], and UO₂²⁺ [14,19]. The selection of the L–DBM binary sensing system in this work was based on our previous results on the ability of L for the formation of a selective and stable 1:1 complex with uranyl ion [19] and the very sensitive color formation of DBM in the presence of traces of UO₂²⁺ [26].

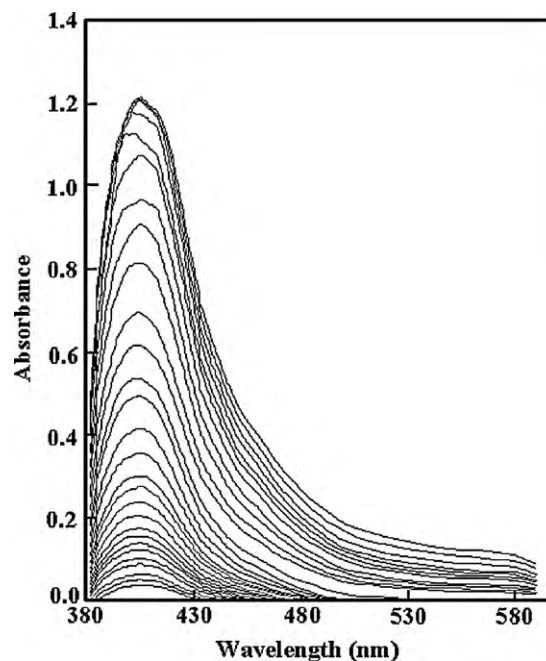
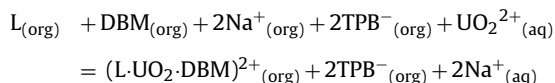


Fig. 1. Absorbance spectra of the proposed optical sensor in the presence of the varying concentrations of UO₂²⁺ ion. The uranyl concentrations are from 1.2×10^{-8} M (bottom) to 1.0×10^{-5} M (top) in an acetate buffer solution of pH 4.0.

3.1. Principle of operation

The optical sensor proposed responds to UO₂²⁺ ion on the basis of a cation-exchange mechanism, as described elsewhere [13,44]. The organic membrane contains L as UO₂²⁺ ion-selective ionophore, DBM as chromoionophore and NaTPB as a lipophilic salt. The lipophilic anion sites (TPB[−]) provide the optode membrane with the necessary ion-exchange properties, because both the ionophore L and chromoionophore DBM are neutral and, therefore, cannot function as ion exchangers. Under the experimental conditions used, the response of this optical system can be described by the following ion-exchange mechanism:



The UV–vis spectra of the proposed bulk optode membrane in an acetate buffer solution of pH 4.0 and in the presence of increasing concentration of UO₂²⁺ are shown in Fig. 1. As is obvious, upon selective extraction of UO₂²⁺ ion by the organic membrane, its color turns from colorless to yellow; the absorbance (at $\lambda_{\text{max}} = 406$ nm) increases with increasing concentration of uranyl ions in aqueous solution.

3.2. Effect of membrane composition

The membrane composition is well known to largely influence the response characteristics and working concentration ranges of both potentiometric [12–20,36–45] and optical sensors [21,22,44,46]. Thus, the composition of membrane was optimized by studying the influences of plasticizer/PVC ratio, the nature of plasticizer, the amounts of ionophore and chromoionophore and addition of NaTPB on the response behavior of the membrane sensor, and the results are summarized in Table 1.

The effect of plasticizer/PVC ratio was changed between 1.9 and 2.5, and the absorbance response was measured. The best response characteristics for the proposed membrane sensor were obtained

Table 1
Optimization of the membrane composition.

No.	Composition (%)					Working concentration range (M)
	PVC	Plasticizer	NaTPB	L	DBM	
1	28	56, NPOE	2	4	10	6.4×10^{-5} to 2.2×10^{-7}
2	28	54, NPOE	2	12	4	7.1×10^{-5} to 9.8×10^{-7}
3	30	56, NPOE	2	2	7	1.3×10^{-5} to 1.7×10^{-6}
4	30	56, NPOE	2	10	2	8.2×10^{-5} to 1.3×10^{-7}
5	30	56, NPOE	2	7	5	8.1×10^{-6} to 6.7×10^{-8}
6	24	60, NPOE	2	7	7	4.3×10^{-6} to 6.2×10^{-8}
7	28	58, NPOE	0	7	7	1.4×10^{-5} to 1.1×10^{-7}
8	28	56, NPOE	2	7	7	4.3×10^{-6} to 2.5×10^{-8}
9	28	58, BA	0	7	7	2.8×10^{-5} to 7.8×10^{-7}
10	28	56, BA	2	7	7	1.5×10^{-5} to 2.1×10^{-7}
11	28	58, DMS	0	7	7	1.3×10^{-3} to 2.1×10^{-5}
12	28	56, DMS	2	7	7	9.8×10^{-4} to 8.5×10^{-6}

at a plasticizer/PVC ratio of 2, as it has also been reported in the literature [44].

In bulk liquid membrane optodes, the mass transfer of analyte from the sample solution into the membrane phase is required, in order to facilitate the establishment of a thermodynamic equilibrium between the membrane and the sample [47]. Thus, in the proposed uranyl optical sensor the presence of 2% of NaTPB as a lipophilic anionic additive was necessary to facilitate the ion-exchange equilibrium. The absence of additive not only affected the working concentration range of the sensor (Table 1, membrane nos. 7, 9 and 11 compared with no. 8, 10 and 12, respectively), but also caused its prolonged response time and reduced selectivity [48].

The influence of the amounts of ionophore L and chromoionophore DBM on the uranyl optode was also investigated (Table 1, membrane nos. 1–8). As seen, the response signal of the uranyl optode found to increase with increasing amounts of both components in the membrane until a value of approximately 7% was reached. The best working concentration range together with the highest uranyl ion selectivity was reached with membranes containing 7% of ionophore L and chromoionophore DBM (membrane nos. 6 and 8). It is interesting to note that a further change in relative amount of L and DBM from the optimum value of 7%-to-7% resulted in decreased performance characteristics of the optode membrane (membrane nos. 1–5). Thus 7% of each reagent was used for the preparation of the optode membrane for UO_2^{2+} ion.

For the preparation of a homogeneous membrane phase, the plasticizer should be physically compatible with the polymer [44]. In addition, the nature of plasticizer is also known to influence largely the measuring concentration range and selectivity of the membrane sensors [36,44]. Thus, in this work, we studied the effect of three different plasticizers (i.e., NPOE, BA and DMS) on the response of the uranyl-selective membrane optode and the results are given in Table 1 (membrane nos. 8–12). As is obvious, among the three different plasticizers used, NPOE was found to be the most effective solvent mediator in preparing the uranyl-selective optode, as it was previously reported for most membrane sensors for uranyl ion [14,19,20,22].

On the basis of the results thus obtained a PVC/NPOE/L/DBM/NaTPB percentage ratio of 28:56:7:7:2 (membrane no. 8) resulted in the lowest detection limit and shortest response time.

3.3. Effect of pH of test solution

Fig. 2 shows the influence of pH of test solution on the absorbance response of the proposed uranyl-selective optical sensor. The absorbance measurements were made in the presence of a 4.4×10^{-7} M UO_2^{2+} solution of different pH values. The pH

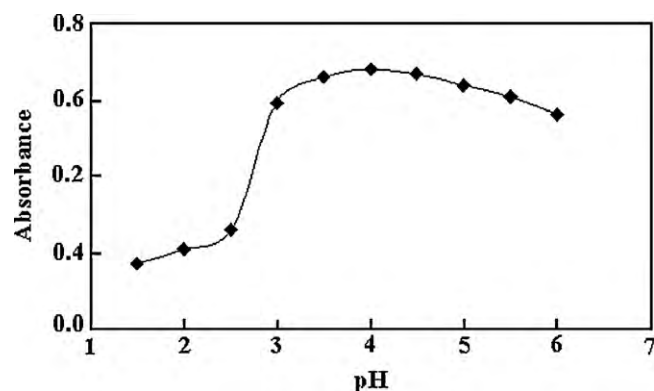


Fig. 2. Effect of pH of the test solution on the optical response of the uranyl ion-selective sensor in the presence of 4.4×10^{-7} M UO_2^{2+} .

of the solutions was adjusted by either HCl or NaOH. As seen, the response of the sensor passes through a more or less plateau between pH 3.6 and 4.5. While, beyond this pH range, the optical response is decreased. The diminished signals at $\text{pH} < 3.6$ could be due to the extraction of H^+ from the aqueous solution into the PVC-membrane via protonation of the ionophoric ligand. On the other hand, the reduced absorbance of the sensor at $\text{pH} > 4.5$ is most possibly because of the formation of hydroxyl complexes of the UO_2^{2+} ion. Thus, in the subsequent experiments, solutions of pH 4.0 adjusted by the use of an acetate buffer were used.

3.4. Calibration plot and dynamic response time

Fig. 3 shows the optical response of the proposed uranyl-selective bulk optode at different uranyl ion concentrations, obtained under optimal membrane ingredients at pH 4.0. The plot of absorbance (or α) against $\log[\text{UO}_2^{2+}]$ can be used as a calibration plot for determination of uranyl ions over the concentration range

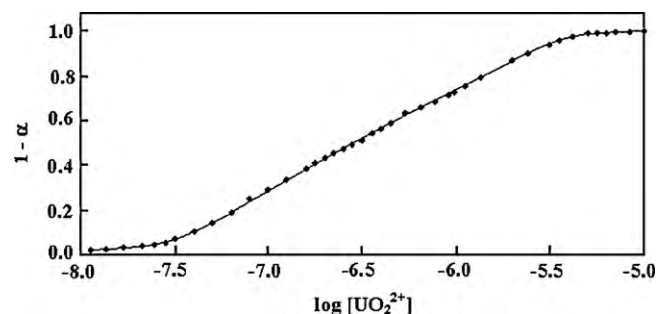


Fig. 3. Calibration plot of $1 - \alpha$ against $\log[\text{UO}_2^{2+}]$ for the proposed optical sensor.

4.3×10^{-6} to 2.5×10^{-8} M. The limit of detection (LOD) based on 3σ of the blank was 8.0×10^{-9} M.

The dynamic response time of the proposed membrane optode was studied by plotting α as a function of time upon step changing of the uranyl ion concentration in solution, over a concentration range of 8×10^{-8} to 4.0×10^{-6} M. It was found that, over the entire concentration range of uranyl ion tested, the optical sensor response reaches its equilibrium value in less than 12 min.

3.5. Regeneration, reproducibility, short-term stability and lifetime

The absorbance signal of the proposed optode membrane was not recovered completely when the solution was switched from high to low uranyl ion concentrations. However, after immersion of a used optode membrane for 12–15 min in a 1.0×10^{-3} M solution of EDTA, the absorbance was found to be fully recovered. By re-immersion of the recovered membrane in the same uranyl solution the absorbance was reached to its former value. After 4 times repeating of this process, the final absorbance of the recovered membrane reached a value of about 85% of the absorbance of the original membrane.

The reproducibility was examined by preparing 8 different membranes from the same mixture and measuring the absorbance of each membrane in a 4.4×10^{-7} M UO_2^{2+} (three repeated determinations) in acetate buffer solutions of pH 4. The resulting coefficient of variation was found to be $\pm 2.4\%$.

The short-term stability of the optical sensor was studied by its absorbance measurements in contact with a 4.4×10^{-7} M uranyl solution at pH 4.0 over a period of 8 h. From the absorbance measurements after every 30 min ($n=16$), it was found that the response is almost complete with only 3.0% increase in absorbance after 8 h monitoring.

In addition, it was found that the membrane sensor could be stored in wet conditions without any measurable changes in its absorbance for at least 5 weeks, which implies that the ionophore and chromoionophore are quite stable in a membrane contacting with water. Thus, the membrane sensor was immersed in an acetate buffer solution of pH 4.0 when not in use.

3.6. Selectivity

For the selectivity investigation, the interference of different inorganic cations on the response of the proposed optical sensor was examined using a 4.4×10^{-7} M solution of uranyl ion and variable concentrations of the interfering cations in an acetate buffer

Table 3
Results of three replicate determinations of uranyl in different samples.

Sample	Amount of UO_2^{2+} (M)		
	Added	Found by sensor	Found by ICP
Spiked tap water (1)	3.0×10^{-7}	$3.21(\pm 0.14) \times 10^{-7}$	$3.32(\pm 0.19) \times 10^{-7}$
Spiked tap water (2)	5.0×10^{-7}	$4.45(\pm 0.21) \times 10^{-7}$	$5.12(\pm 0.08) \times 10^{-7}$
Spiked tap water (3)	7.0×10^{-7}	$6.81(\pm 0.31) \times 10^{-7}$	$6.91(\pm 0.17) \times 10^{-7}$
Spiked tap water (4)	9.0×10^{-7}	$9.30(\pm 0.08) \times 10^{-7}$	$9.43(\pm 0.22) \times 10^{-7}$
Khoshumi real sample	–	$3.63(\pm 0.12) \times 10^{-7}$	$3.71(\pm 0.17) \times 10^{-7}$

Table 4
Performance characteristics of some uranyl optodes based on various ionophores.

Active reagents	t_R (min)	LOD (M)	Interferences	Ref.
Arsenazo III	20	5.2×10^{-9}	Th^{4+} , Ca^{2+}	[21]
TOPO-DBM	8	2.5×10^{-6}	–	[22]
Piroxicam-Alizarin	<5	6.0×10^{-9}	Th^{4+} , Cd^{2+} , Cu^{2+} , Ce^{3+} , Zn^{2+} , Ni^{2+}	[23]
TOPO-PAN	8	8.2×10^{-7}	Hg^{2+} , Pb^{2+} , Fe^{3+} , Cr^{3+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Ag^+ , Cd^{2+}	[24]
L-DBM	<12	8.0×10^{-9}	–	This work

Table 2

Tolerance ratio (TR) for different interfering ions in the determination of 4.4×10^{-7} M UO_2^{2+} .

Ion	TR	Ion	TR	Ion	TR
Na^+	521	Sr^{2+}	147	Fe^{3+}	47 ^a
Cs^+	474	Mn^{2+}	156	Al^{3+}	53
Li^+	598	Cu^{2+}	125	Ce^{3+}	41
K^+	403	Zn^{2+}	118	Cr^{3+}	46
NH_4^+	261	Co^{2+}	173	La^{3+}	31 ^a
Tl^+	360	ZrO^{2+}	64	Th^{4+}	21 ^a
Rb^+	271	Ni^{2+}	98		
VO^+	84	Pb^{2+}	88		
Mg^{2+}	280	Cd^{2+}	74		
Ca^{2+}	175	Fe^{2+}	63		

^a After addition of 5.0×10^{-4} M of DCTA.

of pH 4.0. The tolerance ratio was defined as the ratio of the concentration of interfering ion over the concentration of uranyl ion that caused a relative error of 5%. The resulting tolerance ratios of $\text{TR} = [\text{M}^{n+}]/[\text{UO}_2^{2+}]$ for the interfering ions M^{n+} are summarized in Table 2. It should be noted that some observed interfering effects of Th^{4+} , La^{3+} and Fe^{3+} ions were considerably diminished in the presence of 5.0×10^{-4} M of DCTA as a proper masking agent [47].

As is obvious from Table 2, the uranyl ion content of solutions can be selectively determined using the proposed optical sensor in the presence of excess amounts of the potential interferences examined. The above results indicated that the proposed uranyl optical sensor can be applied to the determination of traces of UO_2^{2+} ion in real samples, in the presence of excess of several other co-existing cationic species. Such high level of selectivity is critical for the determination of UO_2^{2+} in the presence of comparable amounts of Fe^{3+} ion in the groundwater and subsurface samples such as uranium mine [9,48], where the interference from Fe^{3+} ion limits the application of the organophosphorus compound-based ISEs.

3.7. Analytical applications

The proposed UO_2^{2+} -selective optode was found to work well under laboratory conditions. It was successfully applied to the direct determination of uranyl content of the Khoshumi uranium mine (Yazd, Iran) diluted solution and spiked tap water samples. The Khoshumi mine concentrated solution was diluted with HCl and the pH of the final solution was adjusted to pH 4 using an appropriate acetate buffer. The results were compared with the data obtained from inductively coupled plasma (ICP) spectrometric measurements (Table 3). From the data, taken from three replicate measurements, it is immediately obvious that there is a satisfactory

agreement between the results obtained by the proposed UO_2^{2+} ion-selective optode and those by ICP.

4. Conclusion

The results presented in this paper demonstrated that the entrapment of DBM, as a suitable lipophilic chromoionophore, and the benzo-substituted macrocyclic diamide L, as a highly selective uranyl ionophore, in a plasticized-PVC-membrane could result in a stable, selective and sensitive optical sensor for UO_2^{2+} ion. A comparison of the performance characteristics of the developed uranyl optode with those of the previously reported ones [21–24] (Table 4) revealed that the proposed sensor possesses some improvements over the existing bulk optodes for uranyl ion with respect to response time, limit of detection and, especially, selectivity. Satisfactory results were obtained from the application of the proposed sensor to the direct determination of uranyl content of the Khoshumi uranium mine (Yazd, Iran) diluted solution and spiked tap water samples.

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References

- [1] S.R. Qiu, H.F. Lai, M.J. Roberson, M.L. Hunt, C. Amrhein, L.C. Giancarlo, G.W. Flynn, J.A. Yarmoff, *Langmuir* 16 (2000) 2230–2236.
- [2] M. Yazzie, S.L. Gamble, E.R. Civitello, D.M. Stearns, *Chem. Res. Toxicol.* 16 (2003) 524–530.
- [3] M.C. Duff, D.B. Hunter, D.T. Hobbs, S.D. Fink, Z. Dai, J.P. Bradley, *Environ. Sci. Technol.* 38 (2004) 5201–5207.
- [4] A.J. Francis, C.J. Dodge, J.A. McDonald, G.P. Halada, *Environ. Sci. Technol.* 39 (2005) 5015–5021.
- [5] L. Wang, Z. Yang, J. Gao, K. Xu, H. Gu, B. Zhang, X. Zhang, B. Xu, *J. Am. Chem. Soc.* 128 (2006) 13358–13359.
- [6] C.R. Preetha, J.M. Gladis, T.P. Rao, *Environ. Sci. Technol.* 40 (2006) 3070–3074.
- [7] W. Miller, R. Alexander, N. Chapman, L. McKinley, J. Smeli, *Natural Analogue Studies in Geological Disposal of Radioactive Waste*, Elsevier, Amsterdam, 1994.
- [8] T. Sato, T. Murakami, N. Yanase, H. Isobe, T.E. Payne, P.L. Airey, *Environ. Sci. Technol.* 31 (1997) 2854–2858.
- [9] R.J. Reeder, M. Nugent, G.M. Lamb, C.D. Tait, D.E. Morris, *Environ. Sci. Technol.* 34 (2000) 638–644.
- [10] R.J. Lewis, *Sax's Dangerous Properties of Industrial Materials*, Van Nostrand Reinhold, New York, 1996.
- [11] S.Y. Bae, G.L. Sothard, G.M. Murray, *Anal. Chim. Acta* 397 (1999) 173–181.
- [12] V.K. Gupta, R. Mangla, U. Khurana, P. Kumar, *Electroanalysis* 11 (1999) 573–575.
- [13] A. Florido, I. Casas, J. Garcia-Raurich, R. Arad-Yellin, A. Warshawsky, *Anal. Chem.* 72 (2000) 1604–1610.
- [14] M. Shamsipur, A. Soleymanpour, M. Akhond, H. Sharghi, A.R. Massah, *Talanta* 58 (2002) 237–246.
- [15] M.B. Saleh, S.S.M. Hassan, A.A. Abdel Gaber, N.A. Abdel Kream, *Sens. Actuators B* 94 (2003) 140–144.
- [16] J. Ramkumar, B. Maiti, *Sens. Actuators B* 96 (2003) 527–532.
- [17] M. Shamsipur, M. Saeidi, A. Yari, A. Yaganeh-Faal, G. Azimi, M.H. Mashhadizadeh, H. Naeimi, H. Sharghi, *Bull. Korean Chem. Soc.* 25 (2004) 629–633.
- [18] M.S. Saleh, E.M. Soliman, A.A. Abdel Gaber, S.A. Ahmed, *Actuators B* 114 (2006) 199–205.
- [19] M. Shamsipur, F. Mizani, M.F. Mousavi, N. Alizadeh, K. Alizadeh, H. Eshghi, H. Karami, *Anal. Chim. Acta* 589 (2007) 22–32.
- [20] M. Shamsipur, F. Mizani, K. Alizadeh, M.F. Mousavi, V. Lippolis, A. Garau, C. Caltagirone, *Sens. Actuators B* 130 (2008) 300–309.
- [21] G.E. Collins, Q. Lu, S. Abubeker, E. Vajs, *Appl. Spectrosc.* 56 (2002) 464.
- [22] M. Shamsipur, J. Tashkhourian, H. Sharghi, *Anal. Bioanal. Chem.* 382 (2005) 1159–1162.
- [23] S. Sadeghi, S. Doosti, *Sens. Actuators B* 135 (2008) 139–144.
- [24] V. Zare-Shahabadi, M. Akhond, J. Tashkhourian, F. Abbasitabar, *Sens. Actuators B* 141B (2009) 34–39.
- [25] Y. Yamini, P. Ashtari, A.R. Khanchi, M. Ghannadi-Maragheh, M. Shamsipur, *J. Radioanal. Nucl. Chem.* 242 (1999) 783–786.
- [26] M. Shamsipur, A.R. Ghiasvand, Y. Yamini, *Anal. Chem.* 71 (1999) 4892–4895.
- [27] M. Shamsipur, Y. Yamini, P. Ashtari, A.R. Khanchi, M. Ghannadi-Maragheh, *Sep. Sci. Technol.* 35 (2000) 1011–1019.
- [28] M. Shamsipur, A.R. Ghiasvand, Y. Yamini, *J. Supercrit. Fluids* 20 (2001) 163–169.
- [29] M. Shamsipur, J. Fasihi, K. Ashtari, *Anal. Chem.* 79 (2007) 7116–7123.
- [30] H. An, J.S. Bradshaw, R.M. Izatt, Z. Yan, *Chem. Rev.* 94 (1994) 939–991.
- [31] H.W. Gibson, D.S. Nagvekar, *Can. J. Chem.* 75 (1997) 1375–1384.
- [32] K. Kimura, T. Shono, in: Y. Inoue, G.W. Gokel (Eds.), *Cation Binding by Macrocycles*, Marcel Dekker, New York, 1999.
- [33] Y.A. Ibrahim, A.H.M. Wlwahy, *Synthesis* 1993 (1993) 503–508.
- [34] X. Wang, T. Wei, J. Chen, J. Li, *Synth. Commun.* 26 (1996) 2567–2765.
- [35] N. Fukada, T. Ohtsu, M. Miwa, M. Mashino, Y. Takeda, *Bull. Chem. Soc. Jpn.* 69 (1996) 1397–1401.
- [36] M. Javanbakht, M.R. Ganjali, H. Eshghi, H. Sharghi, M. Shamsipur, *Electroanalysis* 11 (1999) 81–84.
- [37] M. Shamsipur, S. Rouhani, H. Sharghi, M.R. Ganjali, H. Eshghi, *Anal. Chem.* 71 (1999) 4938–4943.
- [38] M. Shamsipur, G. Khayatian, S.Y. Kazemi, K. Niknam, H. Sharghi, *J. Incl. Phenom.* 40 (2001) 303–307.
- [39] M. Shamsipur, S.Y. Kazemi, H. Sharghi, K. Niknam, *Fresenius J. Anal. Chem.* 371 (2001) 1104–1108.
- [40] M. Shamsipur, S. Rouhani, T. Poursaberi, M.R. Ganjali, H. Sharghi, K. Niknam, *Electroanalysis* 14 (2002) 729–735.
- [41] M. Shamsipur, S.Y. Kazemi, K. Niknam, H. Sharghi, *Bull. Korean Chem. Soc.* 23 (2002) 53–58.
- [42] M. Shamsipur, A. Soleymanpour, M. Akhond, H. Sharghi, *Electroanalysis* 16 (2004) 282–288.
- [43] M. Shamsipur, F. Mizani, A.A. Saboury, H. Sharghi, R. Khalifeh, *Electroanalysis* 19 (2007) 587–596.
- [44] E. Bakker, P. Buhlmann, E. Pretsch, *Chem. Rev.* 97 (1997) 3083–3132.
- [45] M.R. Ganjali, A. Rouhollahi, A.R. Mardan, M. Hamzelo, A. Moghimi, M. Shamsipur, *Microchem. J.* 60 (1998) 122–133.
- [46] A.P. De Silva, N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, *Chem. Rev.* 97 (1997) 1515–1566.
- [47] W.E. Morf, K. Seiler, P. Sorensen, E. Pungor (Eds.), *Ion-Selective Electrodes*, vol. 5, *Academiai Kiado*, Budapest, 1989, p. 141.
- [48] T. Rosatzin, E. Baaker, K. Suzuki, W. Simon, *Anal. Chim. Acta* 280 (1993) 197–203.