Highly selective optical-sensing film for lead(II) determination in water samples

Ali A. Ensafi*, A. Katiraei Far, S. Meghdadi

Department of Chemistry, Isfahan Un iversity of Technology, Isfahan, 84156-83111, Iran

ARTICLE INFO

ABSTRACT

An optical sensor is described for a sensitive and selective spectrophotometric determination of Pb(II) ions in aqueous solution. A sensor membrane based on 4-hydroxy salophen has been developed for the determination of Pb(II) ions that displays excellent performance. The membrane responds to lead(II) ions, giving a color change from colorless to yellow in a buffer solution (pH 3.1). The optode has a linear range of 1.0×10^{-3}–1.0×10^{-7} mol L^{-1} Pb(II) ions with a detection limit of 8.6×10^{-8} mol L^{-1} Pb(II). The response time is within 10 min depending on the concentration of Pb(II) ions such that it can quantitatively detect Pb(II) even at concentration levels of 8.6×10^{-8} mol L^{-1} Pb(II) (0.018 ppm). The optode developed here is found to be stable, cost effective, easy to prepare, and efficient for direct determination of Pb(II) in a variety of aqueous samples using spectrophotometry. However, it is for one time use only as the reaction of Pb(II) with 4-hydroxy salophen is irreversible. The optode was successfully used for measuring Pb(II) ions in different water samples and in SRM sample.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The determination of lead is becoming increasingly important. Lead is widely distributed in nature and found in many ores including galena, anglesite, and cerrosite. It has found wide applications in storage batteries, cable sheath, solders, and radiating shielding. The major source of lead in the environment is the use of lead as a petrol additive. Atmospheric pollution by lead has caused considerable concern in the past and many countries have phased-out the use of lead in petrol. However, lead already in the environment is cycled through the biogeochemical cycle, and lead originally released into the atmosphere has ended up in surface and ground waters [1]. Lead can cause damage to the nervous system and the kidneys and is a suspected carcinogen [2]. Lead in the environment is generally present as inorganic Pb(II).

The number of reagents available for the spectrophotometric determination of lead is relatively small. The main reagents are dithizone [3], diethyldithiocarbamate [4], 4-(2-pyridilazo)resorcinol [5], diphenylthiocarbazone [6], and potassium hexacyanoferrate(III)-sodium tetrahydroborate [7]. In addition, several preconcentration methods based on spectrophotometric detection have been reported for lead(II) determination at trace levels [8–17].

Although each chromogenic system has its own advantages and disadvantages with respect to sensitivity, selectivity, and rapidity depending on the chromogenic reagent used, most of them require extraction using an organic solvent, surfactant, or even toxic cyanide as a masking agent to increase the sensitivity or selectivity. Cation detection in chemical, clinical, biological, environmental, and industrial samples is of vital importance. Instrumental methods available for this purpose, including flame photometry, atomic absorption spectrometry, electron microscope analysis, and neutron activation analysis, often suffer from high cost, large sample sizes required, and their inability to be used for continuous monitoring. Thus, over the past two decades, an increasing interest has been focused on the development of sensors which offer distinct advantages in terms of sensitivity, selectivity, response time, and remote sensing. Optical sensors are suited to this type of application as they may easily be incorporated into low-cost, easy-to-use kits while also offering the selectivity and sensitivity necessary for environmental monitoring [1].

Immobilization of dyes into or onto a solid support is a key issue for their application in optical sensing [18]. In general the ideal immobilization techniques should produce a highly stable assembly of molecules that remain strictly accessible to dissolved dye. Covalent attachment to a functionalized support [19] and physical entrapment [20] are two commonly employed techniques. Entrapment is the technically simpler technique, but the response is often relatively long.

A few papers have been published on optical sensors for lead(II) determination using hexamethine–hemicyanine dyes [21] and 3,3′,5,5′-tetramethyl-*N*-(9-anthrylmethyl)benzidine [22] as a fluorescence sensor, xylenol orange [23], dithizone [24], nile blue [25], gallocyanine [26], and oxodiamide derivative [27] as an absorbance/reflectance sensor, and quinolinesulphonic acid

* Corresponding author. Tel.: +98 311 3912351; fax: +98 311 3912350.
E-mail address: Ensafi@cc.iut.ac.ir (A.A. Ensafi).

derivatives as a phosphorescence sensor [28]. The enzyme is also used as a biosensor [29]. The reported methods suffer from low sensitivity and/or poor selectivity. The bio-detection system needs expensive materials and/or complicated instrumentation [29]. Many of the reported optical sensors named above [21–27] are based on blending of the ligand with a plasticizer and fixing them in a holder such as polyvinyl chloride. A common weak point of many of these optical sensors is the leakage of the reagent into aqueous solutions on contact with them. Recently, He et al. [30], Chen et al. [31] and Rivera et al. [21] have introduced a new type of fluorescent probes for lead(II) ions determination using dicarboxylate pseudocrown receptor [28], and DNA probe [30]. These probes can be limited by interfering background fluorescence or non-specific quenching from competing metal ions [30,31] and/or has not enough sensitivity [21]. However, a main shortcoming of most of the reported lead ion optical sensors is their long response time. Thus, sensitive and simple lead optode with relatively short response times are still being sought for.

In this work, a simple method is developed for detecting trace levels of lead(II). Spectrophotometric reagent, 4-hydroxy salophen, has been immobilized on triacetyl cellulose as the solid and transparent phase. 4-Hydroxy salophen is covalently bonded to a transparent triacetyl cellulose film. The sensitivity of the membrane in contact with lead(II) ions in a solution with pH 3.1 and its absorbance depend on Pb(II) concentration. Generally speaking, the optical sensing system developed provides a sensitive and selective method for lead(II) ion determination.

2. Experimental

2.1. Chemicals and reagents

All chemicals were of analytical-reagent grade and were purchased from Merck (Darmstadt, Germany) unless otherwise stated, and were used directly without further purification. Triply distilled water was used to prepare buffer and reagent solutions.

Stock solutions of Pb(II), 1.0×10^{-2} mol L^{-1}, was prepared by dissolving Pb(NO$_3$)$_2$ in 100 mL of distilled water. Working standard solutions of Pb(II) were prepared by appropriate dilution of the stock solution before used.

4-Hydroxy salophen was synthesized as reported elsewhere [32]. Solution of 5.7×10^{-4} mol L^{-1} 4-hydroxy salophen (0.020% w/v) was prepared daily by dissolving 0.020 g of the reagent in distilled water in a 100 mL standard flask.

Polyvinyl alcohol solution was prepared by dissolving 0.500 g of the reagent in 100 mL of water.

Thiourea solution was prepared by dissolving 0.600 g of the reagent in 100 mL water.

A buffer solution (containing boric acid, citric acid, acetic acid and sodium hydroxide, 0.1 mol L^{-1}) with different pH values were used for the study of the influence of pH.

2.2. Apparatus

A homemade cell holder [33] was used with a special frame with a size of 8.5 mm × 35 mm (Fig. 1).

UV–vis spectra were obtained with a UV/Vis/NIR Jasco spectrophotometer, Model V-570 (Tokyo, Japan), connected to a Pentium IV computer was used for getting the absorption spectra and absorbance measurements. The control sample was stretched in the same way inside the cuvette using a frame of the same size. The reference cell contained a membrane without any 4-hydroxy salophen reagent.

A Shimadzu, Model AA-680G (Kyoto, Japan), furnace atomic absorption spectrometer furnished with a Pb-hollow cathode lamp

was used. The instrument was set at a wavelength of 283.3 nm operated at 20 mA and all of other parameters were adjusted according to the standard recommendation.

A Corning pH-meter, Model 140 (New York, USA) with a double junction glass electrode was used to check the pH of the solutions.

2.3. Membrane preparation

In order to increase the porosity of the membrane, the triacetyl cellulose film was hydrolyzed to de-esterify the acetyl groups. This was accomplished by treating the membrane with 0.1 mol L^{-1} KOH solution for 24 h. The film was then washed with distilled water. It was found that further activation processes were not necessary [19,33]. The cellulose membrane was immediately treated with a mixture of 0.60% (w/v) thiourea and 0.50% (w/v) polyvinyl alcohol solution for 24 h at 25 °C. Then, the cellulose membranes were treated with a 5.7×10^{-4} mol L^{-1} 4-hydroxy salophen solution at 25 °C and in the buffer solution (pH 6.2) for 5 h. The activated membranes were washed with distilled water and dried at room temperature.

2.4. Recommended procedure

The membranes with the immobilized indicator were placed vertically inside the cuvette using a specially designed frame with an opening size of 8.5 × 35 mm (Fig. 1). The control sample against which the measurement was performed consisted of a triacetyl cellulose film treated in the same way but without an indicator. It was also placed vertically inside the cuvette using a frame of the same size. The membrane was immersed into a Pb(II) solution in a buffer solution (pH 3.1) for 10 min, and subsequently washed with distilled water and dried. The absorbance of the membrane was measured spectrophotometrically at 434 nm. The Pb(II) con-
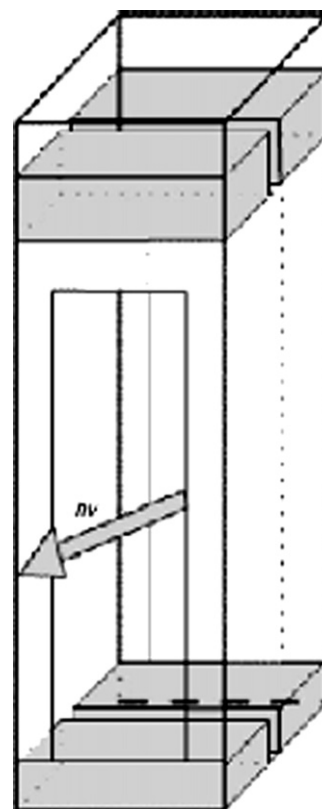

Fig. 1. Schematic diagram of the homemade cell.

tent was measured according to the calibration graph, produced by the same procedure for different concentrations of Pb(II) ions.

2.5. Sample collection

Water samples were collected in prewashed (with detergent, doubly deionized distilled water, dilute HNO_3 and doubly deionized distilled water, respectively) polyethylene bottles. Tap water was sampled from our laboratory in the Department of Chemistry at the Isfahan University of Technology, Isfahan. River water was obtained from Zayandeh Roud river in Isfahan, Iran. Industrial wastewater was obtained from wastewater of Mobarke Steel Complex (Isfahan, Iran). The samples were stored in 1 L polyethylene bottles and acidified to 1% with nitric acid and were analyzed before 4 h of the sampling. In addition, a standard reference material (SRM 1640, natural water sample) containing a known amount of lead(II) was purchased to further test the accuracy of the method. To apply the presented method, 10 mL of water sample was taken in a beaker, and then the pH of the sample was adjusted to pH 3.1 with the buffer solution. Then the Pb(II) contents was measured according to the recommended procedure, using standard addition method.

3. Results and discussion

4-Hydroxy salophen is a four dentate ligand without any amino group in the ring. Dye molecules can be linked to the cellulose acetate film by special treatment. Kostov et al. [34] showed that only the dye with amino groups could be linked to cellulose acetate. We found that using thiourea, dyes with or without amino groups, could be linked to the cellulose acetate film [35]. Considering the structure of 4-hydroxy salophen (Fig. 2) and the fact that only the reagent with amino groups could be linked chemically to tri-acetyl cellulose, we used thiourea plus polyvinyl alcohol as a bridge between 4-hydroxy salophen and the triacetyl cellulose film. The condensation between the hydroxyl methyl groups of the carrier
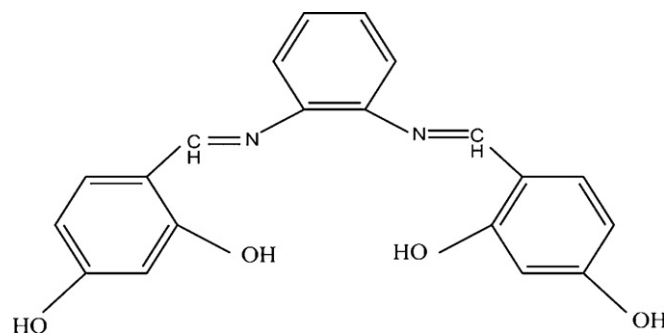

Fig. 2. Structure of 4-hydroxy salophen.

and the protein is accomplished through the transformation of the hydroxyl groups in the alkaline pH region and the amino group in the acidic pH region. In addition, the reactivity of the activated carrier is so high that it was considered that interaction was possible with low molecular weight compounds that have a free *ortho* position in the molecule. For this reason, indicators having amino groups or free *ortho* positions in their structure could be used. Along these lines, we used thiourea as a bridge to connect the dye molecules (with or without amino groups) to the membrane cellulose acetate film. A possible scheme for the reaction of 4-hydroxy salophen with the activated cellulose acetate film is shown in Fig. 3.

The optical properties of 4-hydroxy salophen as immobilized on the hydrolyzed cellulose acetate film, both in the absence and in the presence of Pb(II) ions, showed that the maximum absorption wavelength of the Pb(II)-4-hydroxy salophen in the membrane was 434 nm, whereas that for the complex in solution was 423 nm (Fig. 4). It is evident that the immobilized and solution forms of Pb(II)-4-hydroxy salophen complex exhibit marked differences in optical properties due to the covalent binding of 4-hydroxy salophen to the activated matrix. The fact that the immobilization changes the heights and positions of the absorption maxima of the
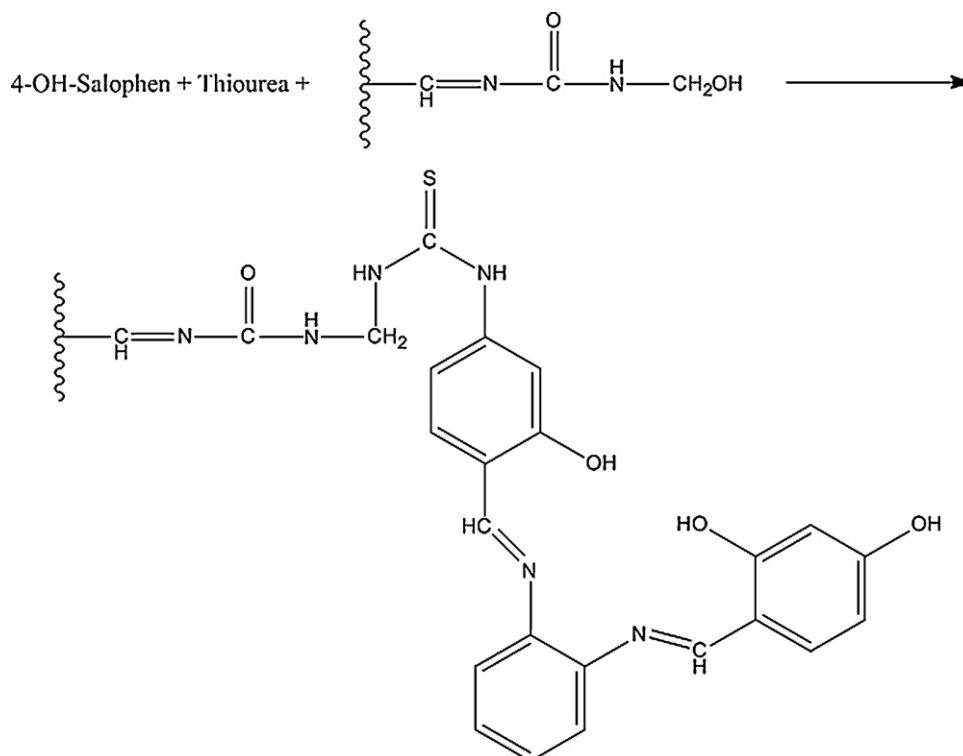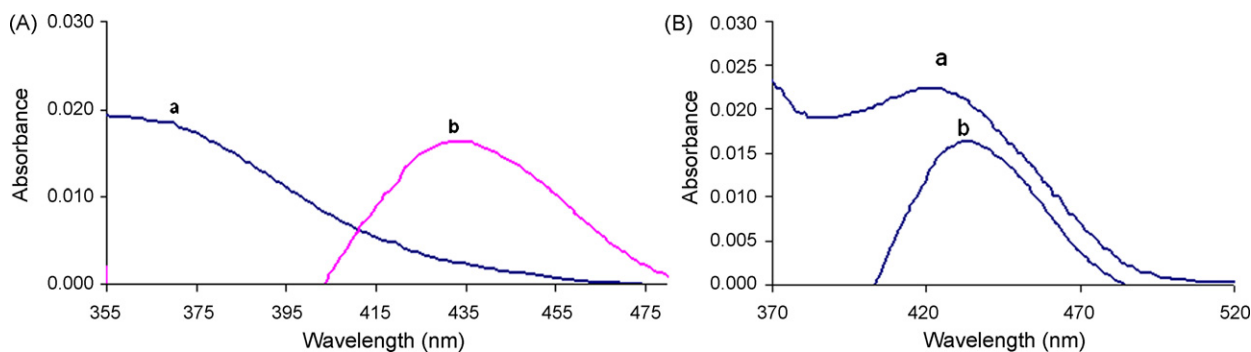

Fig. 3. Possible schemes of reaction between 4-hydroxy Salophen with activated membrane.

Fig. 4. (A): Absorbance spectra of the (a) 5.7×10^{-4} mol L^{-1} 4-hydroxy-salophen in triacetylcellulose membrane, and (b) 1.0×10^{-4} mol L^{-1} Pb(II) with 4-hydroxy-salophen complex. (B): (a) The complex in a solution and (b) The complex as immobilized on the hydrolyzed cellulose acetate film. Conditions: hydrolysis time, 24 h; Treated with a mixture of 0.60% (w/v) thiourea and 0.50% (w/v) polyvinyl alcohol solution for 24 h; Immobilization at pH 6.2; Measuring at pH 3.1.

indicator shows that the loss of a proton after the covalent binding influences charge distribution during the dissociation of the immobilized dye. Bathochromic shifts about 11 nm was observed for the immobilized form when compared to 4-hydroxy salophen in aqueous solutions. The reason for the transition interval shift is possibly the new covalent binding and thus enhanced the conjugation of the system [35–37]. In addition, that result confirms the structural conformation of the immobilized dye is more planar than that of its solution analogue [36,37].

The influence of pH on the immobilization of the ligand on the activated cellulose acetate was studied using 5.7×10^{-4} mol L^{-1} 4-hydroxy salophen with different pH values. The hydrolyzed films were immersed into a stirred solution containing the ligand at the desired pH for a fixed time of 24 h. The hydrolyzed films were washed with distilled water and then dried. The absorbance of each of the films (for different pH values) was measured according to λ_{max} of the ligand in the pH value (Fig. 5). The results show that the best pH for immobilization was 6.2. This pH was selected for the preparation of the membrane sensor.

3.1. Effect of pH

The equilibrium of the complexation reaction of the ligand with Pb(II) is strongly affected by the solution pH; this is expected as the 4-hydroxy salophen has –OH and –NH groups which are protonated during complexation. The effect of pH was investigated by measuring the absorbance of the optode membrane at different pH levels when Pb(II) concentration was fixed at 1.0×10^{-4} mol L^{-1}. Fig. 6 shows the effect of pH on the absorbance intensity. The absorbance intensity of the membrane is actually independent of pH within the pH range of 4.0–8.0, and can be quickly restored. The response time was the shortest within this same pH range. However, absorbance
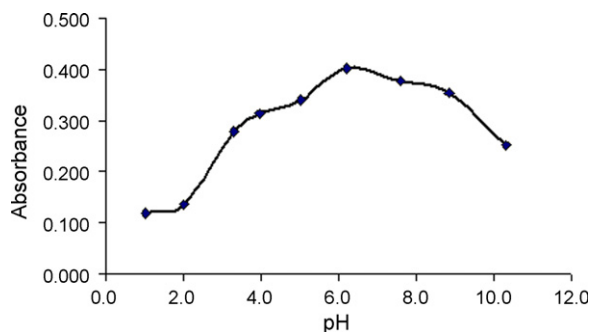
intensity was pH-dependent and both response and recovery times were comparatively longer when pH was <3.0, whereas for pH of 3.1 it was reached to the maximum value. Therefore, we chose a pH of 3.1 for the determination of Pb(II) in aqueous solutions in subsequent experiments.

3.2. Response time, repeatability, and reversibility

An important analytical feature of any optode is its response time. The response time of the present optode is controlled by the time required for the analyte to diffuse from the bulk of the solution to the membrane interface and to associate with the indicator. Fig. 5 depicts the response versus time profile of the Pb(II) optode. The dynamic response time of the optode was of the order of 10 min for 95% attainment of the final value for a 1.0×10^{-4} mol L^{-1} Pb(II) concentration. The results showed that the response time for each measurement was less than 10 min. The sensor was, therefore, considered a potentially useful sensor for Pb(II) measurement.

Optode repeatability and reproducibility are two of their important characteristic features, both of which were investigated in the present work. The repeatability and reproducibility of immobilization of 4-hydroxy salophen on the membranes was evaluated by performing 32 determinations with 32 sensors (4 days, with eight sensors each day). The eight results showed that the repeatability of the membrane preparation and dye leaching on each day was at least 98.4% and ANOVA test showed no significant differences among the membranes produced on different days. The relative standard deviations (RSD) for the determination of 2.5×10^{-6} mol L^{-1} and 1.0×10^{-6} mol L^{-1} of Pb(II) standard solutions were 3.7% and 2.1%, respectively (Fig. 7).
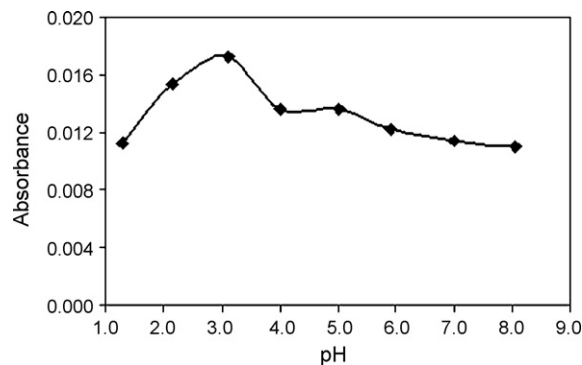

Fig. 5. Influence of pH on immobilization of the ligand on triacetylcellulose membrane. Conditions: time of hydrolysis, 24 h; time of immobilization, 5 h; 4-Hydroxy-salophen, 0.020% (w/v); pH of immobilization, 6.2; Pb(II), 1.0×10^{-4} mol L^{-1}.

Fig. 6. Influence of pH of the sample solution on the sensitivity of sensor. Conditions: time of hydrolysis, 24 h; time of immobilization, 5 h; pH of immobilization, 6.2; Pb(II), 1.0×10^{-5} mol L^{-1}; 4-Hydroxy-salophen, 0.020% (w/v).
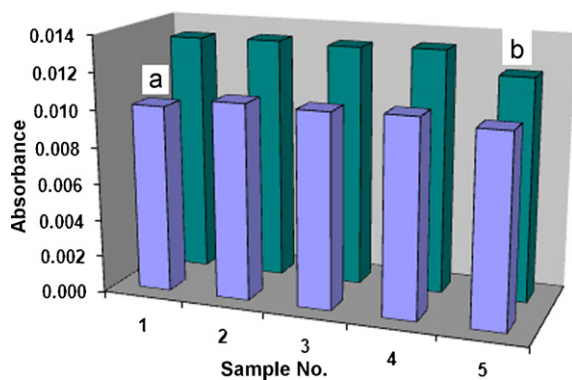
Fig. 7. The optode signals used for evaluation of the relative standard deviation for (a) 1.0×10^{-6} mol L^{-1}, and (b) 2.5×10^{-5} mol L^{-1} Pb(II) at the optimum conditions.

Fig. 8. Absorbance curve for determination of Pb(II) using the optode; (a) 1.0×10^{-3} mol L^{-1}, (b) 3.0×10^{-4} mol L^{-1}, (c) 1.0×10^{-5} mol L^{-1}, and (d) 1.0×10^{-7} mol L^{-1} Pb(II) at the optimum conditions.

Table 1
Effect of possible interfering ions on the determination of 1.0×10^{-5} mol L^{-1} Pb(II) at pH 3.1 using the proposed optode.

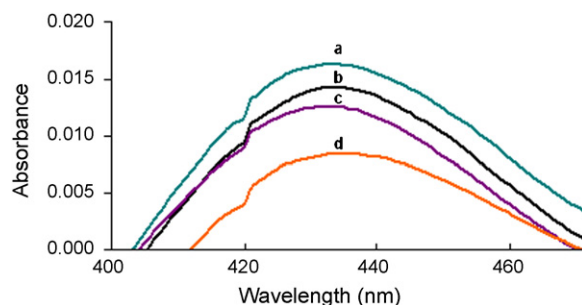| Species	Tolerance limit ($W_{ion}/W_{Pb(II)}$)
Na$^+$, Mg^{2+}, Ca^{2+}, Co^{2+}, Cd^{2+} Cs$^+$, K$^+$, Mn^{2+}, Al^{3+}, Zn^{2+} Cu^{2+}, Cr^{3+}, V^{3+}, Zn^{2+}, Zr^{4+}, Hg^{2+} SO$_3^{2-}$, SO$_4^{2-}$, C$_2$O$_4^{2-}$, NO$_3^-$, NO$_2^-$, CO$_3^{2-}$, BrO$_3^-$, CH$_3$COO	1000*
Fe^{3+}, Fe^{2+}	100

* Maximum concentration of ions tested.

3.3. Life time of optical sensor

The absorbance signals at 434 nm for the sensing membrane in contact with a 1.0×10^{-4} mol L^{-1} Pb(II) was recorded over a period of 10 min. During this period, there was no evidence of leakage of the reagent from the membrane. When the film was exposed to light, no drift in signal occurred and the optode was stable over the experiment with no leaching of the indicator. However, prepared membranes were kept under water when not in use to prevent them from drying out. When the optode was immersed in deionized water for a week, the signal value of the sensor did not change appreciably.

4. Selectivity

The interference of some common species on the absorbance determination of Pb(II) was investigated. The experiments were carried out by fixing the concentration of Pb(II) at 1.0×10^{-5} mol L^{-1} Pb(II) at pH 3.1. We recorded the absorbance

before and after adding the interference ions into the lead(II) ions solution. Tolerance limit was taken as the concentration causing an error of ±5% in the determination of Pb(II). The results are given in Table 1. The results confirmed that the optode membrane exhibited excellent selectivity toward Pb(II) with respect to the other coexisting interference ions. Therefore, it seems feasible to use this sensor for practical lead ions assays.

5. Analytical figures of merit

The response of the optode to various concentrations of Pb(II) ions in the range of 1.0×10^{-1}–1.0×10^{-8} mol L^{-1} was studied under the optimum conditions. Absorbance measurements were expressed as absorbance difference, which is defined as the difference between the absorbance of the immobilized 4-hydroxy salophen alone and the absorbance of the Pb(II)-4-hydroxy salophen complex at 434 nm. As can be seen, the response curve obtained for different concentrations of Pb(II) showed a semi-log calibration curve (Fig. 8). This phenomenon can be explained along the same lines discussed by Oehme and Wolfbeis [38]. When a metal ion reacts with an indicator at a molar ratio of 1:1 (neglecting the activity coefficient), the conditional stability constant can defined as:

$$K_f = [MI]/\{[M][I]\}$$

where, [MI], [M], and [I] denote the equilibrium concentration of the complex, metal ions, and the free indicator, respectively. If the metal-indicator complex, [MI], is the absorber being measured, absorbance varies with analyte concentration along the following lines [39]: $[MI] = \{K_f[M]/(1 + K_f[M])\}c_i$ where, c_i is the sum of free and combined indicator molecules. Therefore, at low concentrations of analyte (i.e., where $[M] < 1/K_f$), the response

Table 2
Determination of Pb(II) in real samples ($n = 3$).

Sample	Pb(II) added (mol L^{-1})	Pb(II) found[a] (mol L^{-1})	Recovery (%)	FAAS method (mol L^{-1})
River water	–	<Detection limit	–	<Detection limit
River water	1.00×10^{-6}	$(1.04 \pm 0.16) \times 10^{-6}$	104.0	$(0.96 \pm 0.19) \times 10^{-6}$
River water	5.00×10^{-5}	$(5.04 \pm 0.34) \times 10^{-5}$	101.0	–
Tap water	–	<Detection limit	–	<Detection limit
Tap water	1.00×10^{-6}	$(9.89 \pm 0.17) \times 10^{-7}$	99.0	$(1.05 \pm 0.23) \times 10^{-6}$
Tap water	5.00×10^{-5}	$(4.90 \pm 0.31) \times 10^{-5}$	98.0	–
Industrial wastewater	–	<Detection limit	–	<Detection limit
Industrial wastewater	1.00×10^{-6}	$(9.60 \pm 0.28) \times 10^{-7}$	96.0	$(1.08 \pm 0.32) \times 10^{-6}$
Industrial wastewater	5.00×10^{-5}	$(5.04 \pm 0.34) \times 10^{-5}$	101.0	$(4.98 \pm 0.54) \times 10^{-5}$
NIST-1640				
Natural water[b]	–	$27.23 (\pm 0.68)$ μg kg^{-1}	98.8	–

[a] ± in parenthesis show the standard deviation for three replicates analysis.
[b] Actual Pb(II) value, 27.89 ± 0.14 μg kg^{-1}.

is proportional to the analyte concentration [M]. As concentration increases, the response becomes curved, reaching a limiting value when $[M] > 1/K_f$. This corresponds to the saturation of the indicator with analyte. There is a linear correlation between absorbance of the sensor and $\log[Pb(II)]$ for the interval range of $1.0 \times 10^{-3} – 1.0 \times 10^{-7}\,mol\,L^{-1}$ of Pb(II), with a regression equation of $A = 0.0072\log[Pb(II)] + 0.0556$ with a correlation coefficient of 0.9955 ($n = 5$), where C is $\log(Pb(II))$ concentration in the solution.

The detection limit of the sensor film, which is defined as the concentration of the sample yielding a signal equal to the blank signal plus three times of its standard deviation, was found to be $8.6 \times 10^{-8}\,mol\,L^{-1}$ Pb(II).

6. Determination of lead ions in natural water samples

Natural river water and wastewater samples were used to test the practical application of the present sensor. Water samples spiked with different amounts of Pb(II) were analyzed and the concentration of Pb(II) ions was measured using the proposed optode membrane. In addition, the lead contents were measured using flameless atomic absorption spectrometry (FAAS). Moreover, a SRM 1640 natural water standard sample, containing a known amount of lead(II), was purchased to further test the accuracy and recovery of the method. The results are given in Table 2. The recoveries were at least about 96–104% (Table 2), showing that the optical sensor developed in this work is useful for the determination of lead(II) ions in water samples. From the results of three replicate measurements given in Table 2, it is immediately obvious that there is a satisfactory agreement between the results obtained by the Pb(II)-selective optode and the results obtained from furnace atomic absorption spectrometry (FAAS).

7. Conclusion

The optode described in this work provides a simple means for the determination of Pb(II) ions. A waste cellulose material with good optical and mechanical properties is used as a matrix for immobilization. The color changeable optode for the detection of Pb(II) ions in aqueous samples was developed by the immobilization of 4-hydroxy salophen in the cellulose triacetate matrix. While being more sensitive, the proposed sensor has a good linear dynamic range and a lower response time than previously reported optical sensors for Pb(II) ions determination. The optical sensor has a good selectivity toward Pb(II) versus other metal ions. The optode was found to be stable and reliable for use in tap water, river and wastewater samples. Application of this optode to determine Pb(II) in water samples plus a standard reference material sample showed high accuracy and precision of the optode for lead(II) determination. The results of this study confirm that the optode can be successfully used for routine analysis with portable equipment.

Acknowledgment

References

[1] M.M.B. Paoliello, E.M. De Capitani, Environmental contamination and human exposure to lead in Brazil, Rev. Environ. Contam. Toxicol. 184 (2005) 59–96.
[2] D.M. Roundhill, Novel strategies for the removal of toxic metals from soils and waters, J. Chem. Educ. 81 (2004) 275–282.
[3] A.L.D. Comitre, B.F. Reis, Automatic flow procedure based on multicommutation exploiting liquid–liquid extraction for spectrophotometric lead determination in plant material, Talanta 65 (2005) 846–852.
[4] R. Seitz, in: O.S. Wolfbeis (Ed.), Fiber Optic Chemical Sensors and Biosensors, vol 2, CRC Press, Boca Raton, 1991, pp. 1–19, chapter 9.
[5] M. Kuramochi, K. Tomioka, M. Fujinami, K. Oguma, Rapid determination of lead extracted by acetic acid from glazed ceramic surfaces by flow injection on-line preconcentration and spectrophotometric detection, Talanta 68 (2005) 287–291.
[6] N. Rajesh, S. Manikandan, Spectrophotometric determination of lead after preconcentration of its diphenylthiocarbazone complex on an Amberlite XAD-1180 column, Spectrochim. Acta Part A 70 (2008) 754–757.
[7] O. Cankur, D. Korkmaz, O. Yavuz Ataman, Flow injection-hydride generation-infrared spectrophotometric determination of Pb, Talanta 66 (2005) 789–793.
[8] M. Soylak, L. Elçi, Y. Akkaya, M. Dogan, On-line preconcentration system for lead determination in water and sediment samples by flow injection-flame atomic absorption spectrometry, Anal. Lett. 35 (2002) 487–499.
[9] A.A. Ensafi, T. Khayyamian, H. Karbasi, On-line preconcentration system for lead(II) determination in wastewater by atomic absorption spectrometry using active carbon loaded with pyrogallol red, Anal. Sci. 19 (2003) 953–956.
[10] E. Espada-Bellido, M.D. Galindo-Riano, M. Garcia-Vargas, Sensitive adsorptive stripping voltammetric method for determination of lead in water using multivariate analysis for optimization, J. Hazard. Mater. 166 (2009) 1326–1331.
[11] M. Soylak, I. Narin, M.A. Bezerra, S.L.C. Ferreira, Factorial design in the optimization of preconcentration procedure for lead determination by FAAS, Talanta 65 (2005) 895–899.
[12] N.A. Badawy, A.A. El-Bayaa, A.Y. Abdel-Aal, S.E. Garamon, Chromatographic separations and recovery of lead ions from a synthetic binary mixture of some heavy metal using cation-exchange resin, J. Hazard. Mater. 166 (2009) 1266–1271.
[13] E. Eren, Removal of lead ions by Unye (Turkey) bentonite in iron, magnesium oxide-coated forms, J. Hazard. Mater. 165 (2009) 63–70.
[14] A.A. Ensafi, A. Zendegi Shiraz, On-line separation and preconcentration of lead(II) by solid-phase extraction using activated carbon loaded with xylenol orange and its determination by flame atomic absorption spectrometry, J. Hazard. Mater. 150 (2008) 554–559.
[15] A.A. Ensafi, A.R. Ghaderi, Preconcentration, separation and determination of lead(II) with methyl thymol blue adsorbed on activated carbon using flame atomic absorption spectrometry, J. Korean Chem. Soc. 52 (2008) 16–22.
[16] M.B. Arain, T.G. Kazi, M.K. Jamali, H.I. Afridi, N. Jalbani, R.A. Sarfraz, J.A. Baig, M.A. Memon, Time saving modified BCR sequential extraction procedure for the fraction of Cd, Cr, Cu, Ni, Pb and Zn in sediment samples of polluted lake, J. Hazard. Mater. 160 (2008) 235–239.
[17] T.G. Kazi, N. Jalbani, N. Kazi, M.K. Jamali, M.B. Arain, H.I. Afridi, A. Kandhro, Z. Pirzado, Evaluation of toxic metals in blood and urine samples of chronic renal failure patients before and after dialysis, Renal Failure 30 (2008) 737–745.
[18] I. Oehme, S. Praltes, O.S. Wolfbeis, G.J. Mohr, The effect of polymeric supports and methods of immobilization on the performance of an optical copper(II)-sensitive membrane based on the colourimetric reagent Zincon, Talanta 47 (1998) 595–604.
[19] A.A. Ensafi, A. Aboutalebi, A versatile stable cobalt optical sensor based on pyrogallol red immobilization on cellulose acetate film, Sens. Actuators B 105 (2005) 479–485.
[20] J.E. Lee, S.S. Saavedra, Evanescent sensing in doped sol–gel glass films, Anal. Chim. Acta 285 (1994) 265–269.
[21] L. Rivera, D. Izquierdob, I. Garcésb, I. Salinasb, J. Alonsoa, M. Puyol, Simple dip-probe fluorescence setup sensor for in situ environmental determinations, Sens. Actuators B 137 (2009) 420–425.
[22] W.H. Chan, R.H. Yang, T. Mo, K.M. Wang, Lead-selective fluorescent optode membrane based on 3,3′,5,5′-tetramethyl-N-(9-anthrylmethyl)benzidine, Anal. Chim. Acta 460 (2002) 123–132.
[23] I. Klimant, M. Otto, A fiber optical sensor for heavy metal ions based on immobilized xylenol orange, Mikrochim. Acta 108 (1992) 11–17.
[24] W.A. de Olivera, R. Narayanaswamy, A flow-cell optosensor for lead based on immobilized dithizone, Talanta 39 (1992) 1499–1503.
[25] M. Lerchi, E. Bakker, B. Rusterhols, W. Simon, Lead-selective bulk optodes based on neutral ionophores with subnanomolar detection limits, Anal. Chem. 64 (1992) 1534–1540.
[26] N.A. Yusof, M. Ahmad, A flow-through optical fibre reflectance sensor for the detection of lead ion based on immobilised gallocynine, Sens. Actuators B 94 (2003) 201–209.
[27] E. Antico, M. Lerchi, B. Rusterholz, N. Achermann, M. Badertscher, M. Valiente, E. Pretsch, Monitoring Pb^{2+} with optical sensing films, Anal. Chim. Acta 388 (1999) 327–338.
[28] S. Haron, A.K. Ray, Optical biodetection of cadmium and lead ions in water, Med. Eng. Phys. 28 (2006) 978–981.
[29] B.S.V. de la Riva, J.M.C. Fernandez, R. Pereiro, A.S. Medel, Flow-through room temperature phosphorescence optosensing for the determination of lead in sea water, Anal. Chim. Acta 395 (1999) 1–9.
[30] Q. He, E.W. Miller, A.P. Wong, C.J. Chang, A selective fluorescent sensor for detecting lead in living cells, J. Am. Chem. Soc. 128 (2006) 9316–9317.
[31] P. Chen, B. Greenberg, S. Taghavi, C. Romano, D. van der Lelie, C. He, An Exceptionally selective lead(II)-regulatory protein from ralstonia metallidurans: development of a fluorescent lead(II) probe, Angew. Chem. Int. Ed. 44 (2005) 2715–2719.
[32] M. Amirnasr, K.J. Schenk, A. Gorji, R. Vafazadeh, Synthesis and spectroscopic characterization of [CoIII(salophen)(amine)$_2$]ClO$_4$ (amine = morpholine, pyrrolidine, and piperidine) complexes, the crystal structures of [CoIII(salophen)(morpholine)$_2$]ClO$_4$ and [CoIII(salophen)(pyrrolidine)$_2$]ClO$_4$, Polyhedron 20 (2001) 695–702.

[33] A.A. Ensafi, Z.N. Isfahani, Determination of lead ions by an optical sensor based on 2-amino-cyclopentene-1-dithiocarboxylic acid, IEEE Sens. J. 7 (2007) 1112–1117.

[34] Y. Kostov, S. Tzonkov, L. Yotova, M. Krysteva, Membranes for optical pH sensors, Anal. Chim. Acta 280 (1993) 15–19.

[35] A.A. Ensafi, A. Kazemzadeh, Optical pH sensor based on chemical modification of polymer film, Microchem. J. 63 (1999) 381–388.

[36] T.P. Jones, M.D. Porter, Optical pH sensor based on the chemical modification of a porous polymer film, Anal. Chem. 60 (1988) 404–406.

[37] A. Safavi, M. Bagheri, Design of a copper(II) optode based on immobilization of dithizone on a triacetylcellulose membrane, Sens. Actuators B 107 (2005) 53–58.

[38] I. Oehme, O.S. Wolfbeis, Optical chemical sensors for the determination of heavy metal ions, Mikrochim. Acta 126 (1997) 177–189.

[39] W.R. Seitz, design of a fiber-optic pH sensor with rapid response, Anal. Chem. 56 (1984) 16A–34A.