Design and Evaluation of a Lead (II) Optical Sensor Based on Immobilization of Dithizone on Triacetylcellulose Membrane

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Abstract: In present study characterization of an optical sensor membrane is described for the determination of lead (II) ions based on the immobilization of dithizone on a triacetylcellulose membrane. The membrane responds to lead ions by changing color reversibly from red to green at pH 5.0. Under optimum conditions, the proposed membrane displayed a linear range of 0.5-5.5 μg mL^{-1} with a limit of detection of 0.15 μg mL^{-1} at a wavelength of 612 nm. The response time of the optode was about 11-15 min, depending on the concentration of lead (II) ions. The relative standard deviation (RSD) of the sensor response for 3.5 μg mL^{-1} of lead (II) was 2.8% and the RSD between seven membranes was 3.2%. The sensor can readily be regenerated with the ethylene diamine solution. The optode is fully reversible and the selectivity of optode to lead (II) ions in universal buffer at pH 5 is relatively good with Ag$^+$ ion as interferences. The proposed optode was successfully applied for the determination of lead (II) in soil and petrochemical waste samples.
Keywords: Optical sensor, Lead (II), Dithizone, Triacetylcellulose, Ethylene diamine.

Introduction

Lead is a ubiquitous environmental pollutant widely dispersed in the environment through the car batteries, ceramic glazes, in some candles, cables, solders and radiating shielding[1], paint, gasoline and printing material[2], as well as some industries such as mining and the refining of plants[3]. In car engines lead is burned, enter the environment through the exhausts of cars and pollute soils and air[1]. So, it has caused lead pollution to be a worldwide issue.

Lead is one of four metals that have the most damaging effects on human health. Lead induces a broad range of physiological, biochemical, and behavioral dysfunctions such as; disruption of the biosynthesis of haemoglobin and anaemia, a rise in blood pressure, kidney damage, miscarriages and subtle abortions, disruption of nervous systems, brain damage, declined fertility of men through sperm damage, diminished learning abilities of children, behavioral disruptions of children, such as aggression, impulsive behavior and hyperactivity[1, 4].

Therefore, it is very important to monitor the trace levels of it in environments. The most common analytical methods for the lead trace determination are the flame atomic absorption spectrometry (FAAS)[5, 6], the electrothermal atomic absorption spectrometry (ETAAS)[7,8,9] and the inductively coupled plasma emission

spectrometry (ICP)[10]. Although these methods have good sensitivity, but they require expensive instruments, well-controlled experimental conditions and profound sample-making.

In this regards, optical sensors have attracted the attention of many researchers because of easy fabrication, freedom from electrical interference, low cost, safety, good selectivity and sensitivity and the possibility of remote sensing. In optochemical sensors (so called optrodes)[11, 12] or optodes[13], the sensing element consists of reagent dyes immobilized in organic or inorganic matrices. The indicator dye undergoes a binding reaction with the ions. This reaction is accompanied by a change in the optical properties. The optical properties measured can be absorbance, reflectance, florescence, and refractive index[14, 15]. The measurement of the change in the optical property of the solid phase can be used for the detection and quantification of the target analyte[16,17]. Immobilization of dyes into or onto a solid support is a key issue for their application in optical sensing[18]. Covalent attachment to a functionalized support[19] and physical entrapment[20] are two commonly employed techniques. Organic dyes and metalochromic indicators, which are used in the spectrophoto metric determination of various metals, play a main role in the design of optodes[21]. The number of reagents available for the spectrophotometric determination of lead is relatively small. The main reagents are dithizone[22, 23], diethyldithiocarbamate[24], 4-(2-pyridilazo) resorcinol[25], diphenylcarbazone[26], 2-(2-thiazolyzo)-*p*-cresol[27]. Dithizone contains azo and hydrosulfides groups, has many characteristics required as an ionophore. This ionophore reacts with transition metals to form highly colored complexes. The complexes can be reversed to form again the ionophore over a large number of repetitions[28]. DeOliveira and co-workers introduced dithizone immobilized on XAD-4 resin as a sensor element of an optical sensor for lead using a flow-cell. They observed that the immobilized dithizone was susceptible to photodecomposition caused by the light from the quartz-halogen lamp. This resulted, with time, in an increase in signal which affected the accuracy of the measurements[29].

In present study, a lead optical sensor based on immobilization of metallochromic reagent, dithizone, on a triacetylcellulose membrane is introduced. The membrane responds to lead (II) ion by changing color reversibly from red to green which is spectroscopically detected in the absorbance mode. The proposed method offers a selective and sensitive method for lead (II) analysis in real samples.

Experimental

Reagents

All chemicals were prepared from analytical reagent grade and were supplied from Merck Company. All aqueous solutions were prepared with double distilled water. Universal buffer solutions were prepared from boric acid/citric acid/phosphoric acid (0.04 M each). The final pH was adjusted by the addition of 0.1 M sodium hydroxide. A stock solution of 1000 μg mL^{-1} lead (II) ion was prepared by weighing 0.159 g of $Pb(NO_3)_2$ (Merck) and adjusting the volume to 100 mL. Working standard solutions of lead (II) were prepared from the stock solution by suitable dilution with water.

Apparatus and measurement procedures

A Perkin-Elmer λ35 UV-Vis spectrophotometer with a 1cm cell was used for recording the visible spectra and absorbance measurements. A Jenway 3510 pH-meter was used to check the pH of the solutions. A Hamilton syringe (10 μl) was used to inject small volumes of reagent into the cell. The constructed membrane was placed vertically in a disposable plastic cuvette and all measurements were performed in a batch mode. The membrane was first exposed to the universal buffer solution at pH 5 for some minutes and the absorbance was measured at 612 nm. Then the lead solution was injected into the cell and after mixing, the absorbance was measured at 612 nm after 15 min.

Procedure for the determination of lead in soil and waste samples

Soil sample (from Bandare Emam Petrochemical Company, Ahvaz, Iran) was homogenized and dried at 105° C. After that, 1.0 g of soil was taken and 3 mL of $HNO_3/H2O_2$ mixture (2/1) were added to the soil. The mixture was slowly shake and dried on a hot plate. After cooling, 2 mL of 0.75 M nitric acid were added to the residual and centrifuged. The clear digests were analyzed by the proposed method[30]. Petrochemical waste samples (from Bandare Emam Petrochemical Company, Ahvaz, Iran) did not need previous treatment and were analyzed for lead (II) ion concentration using the proposed optode.

Preparation of the sensor membrane

The transparent triacetylcellulose membranes were produced from waste photographic film tapes that were previously treated with commercial sodium hypochlorite for several seconds in order to remove colored gelatinous layers. The films were treated with a clear solution of dithizone (0.02 g) in 20 mL ethylene diamine for 7 min at ambient temperature. Then they were washed with water for removing ethylene diamine and loosely trapped indicator. The membranes were finally washed with detergent solutions and water. Prepared membranes were kept under water when not in use[31].

Results and Discussion

Spectral characteristics

Fig.1 shows the absorption spectra of immobilized dithizone, which was obtained after being equilibrated in buffer solution (pH 5) containing different concentrations of lead (II) ions. The spectral change is result of increase of lead (II) ions concentration in the membrane, which is due to the extraction of lead (II) ion into the membrane and complex formation with dithizone. The absorbance maxima of the immobilized dithizone are located at 612 and 444 nm. The wavelength of 612 nm was selected for further studies because of higher selectivity and sensitivity at this wavelength.
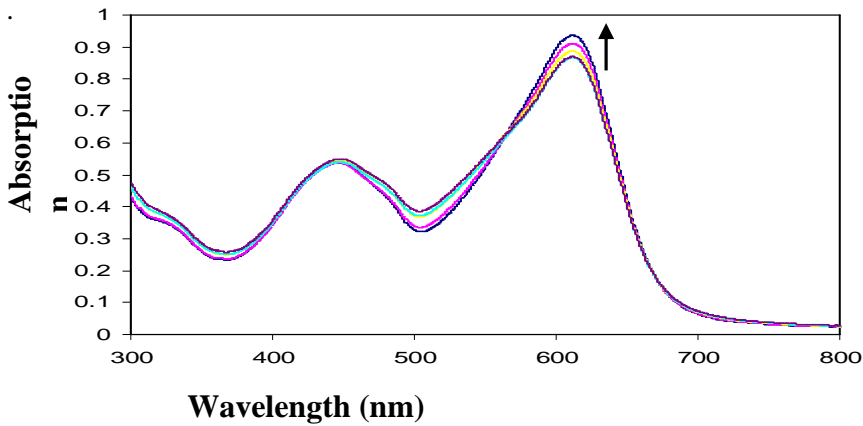

Fig.1. Absorption spectra of optode film in the presence of 0.5-7 μg mL^{-1} lead (II) at pH 5.

The effect of buffer solution on the optode membrane response

The effect of the pH of the sample solution on the membrane response was studied in the pH range of 3-7 by changing the universal buffer pH. Fig.2 shows the effect of pH values on the absorbance intensity of the optode membrane at the fixed wavelength of 612 nm. The absorbance measurements were made for 2.5 μg mL^{-1} lead (II) ion at different pH values.
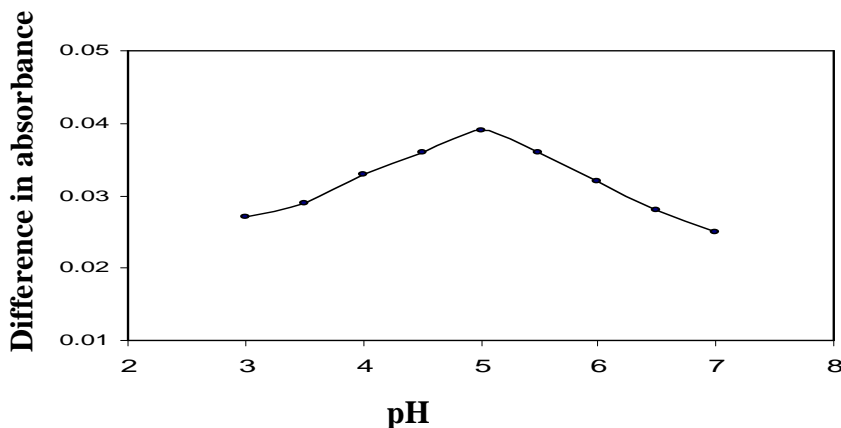

Fig.2. Effect of pH on the optode film response.

As it can be noticed in Fig.2, with increase in the pH of the solution, ΔA (difference between the absorbance of the immobilized dithizone alone and the absorbance of the lead-dithizone complex) reaches a maximum value at pH 5, and then decreases. This phenomenon might be due to the fact that at lower pH values (pH<5), complexation is weak. At pH values higher than 5, lead (II) forms different hydroxide species which make it unable to form complex with dithizone[28]. Thus, pH 5 was selected for further studies.

Dynamic range

Fig.3 depicts the response of the proposed lead (II) optode under optimum conditions to various lead (II) ion concentrations in the range 0-7 μg mL^{-1}. The plot of the difference in absorbance against lead (II) ion concentration can be used as a calibration plot for determination of lead (II) ions.

As can be seen, the calibration graph exhibited a linear range from 0.5 to 5.5 μg mL^{-1} , with a correlation coefficient of 0.9997, which described by the equation:

$$\Delta A = 0.0156 C_{Pb^{2+}} - 0.0004$$

ΔA is the absorbance difference (difference between the absorbance of immobilized dithizone alone and the absorbance of the lead-dithizone complex) and $C_{Pb}{}^{2+}$ is concentration of lead (II) ion (μg mL^{-1}).

In this case, 6.5 μg mL^{-1} was found as the concentration of lead (II) ion that saturates the film. Detection limit of the lead optode, defined as that concentration of the sample yielding a signal equal to the blank signal plus three times of its standard deviation, was found to be 0.15 μg mL^{-1}.
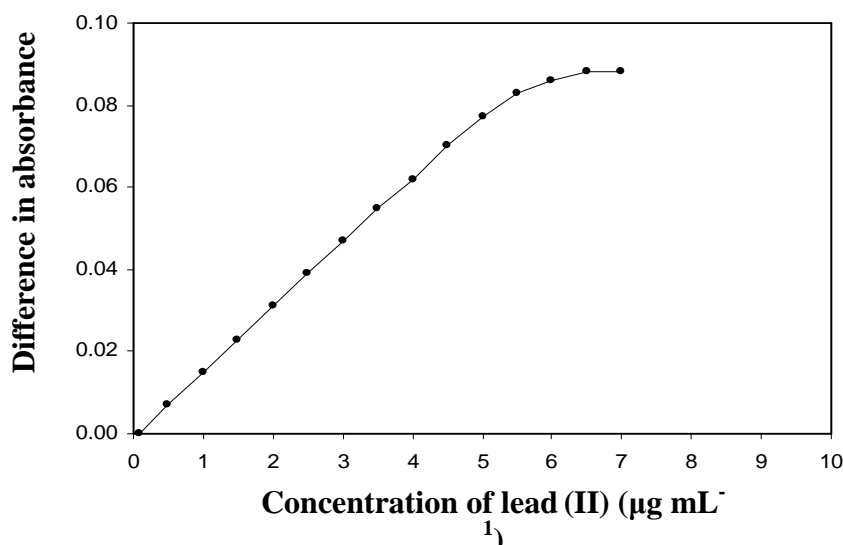

Fig.3. The optode film response vs. lead (II) ion concentration in the range of 0-7 μg mL^{-1} at pH 5.

Response time

The response time of the 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[32]. The response time was tested by recording the absorbance change from a pure buffer (pH 5) to a buffered lead solution of 3.5 μg mL^{-1}. The membrane was found to reach 95% of the final signal at 11-15 min depending on the concentration of lead (II) (Fig. 4).

At high lead (II) concentrations, a rapid response was achieved, which resulted in a large change in response. At low lead (II) concentrations, a longer response time was produced by the optode film. This is due to the fact that the response time of the optode film is governed by three processes: (1) diffusion in the film (2) the rate of complex formation between metal ion and ligand, and (3) the rate of complex dissociation[33].
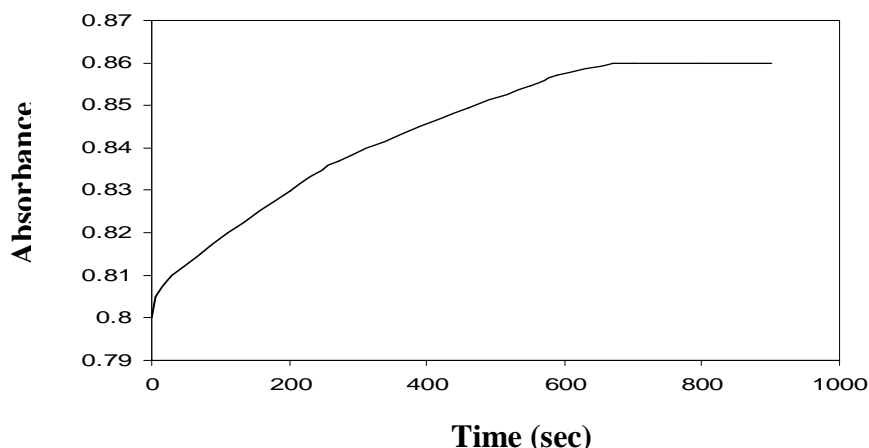
Fig.4. Typical response curve of the film optode at 612 nm as a function of
time when film was exposed to 3.5 μg mL^{-1} lead (II) ions.

Life time and stability

The lifetime of the optode membrane was determined by immersing the membrane into the cell containing the buffer solution (pH 5). The absorbance signals were recorded at wavelength of 612 nm over a period of about 10 h. During this period, there was no evidence of leakage of reagent from the membrane and no drift in signal was observed and the sensing phase was stable over the experiment. The prepared membranes were kept under water, while were not in use, to prevent them from being drying out. Additionally the stability of response of the film was investigated over six weeks under water, which indicated that the film was stable over this period.

Regeneration of the optode

A good sensor should be regenerated at a short period of a time. The regeneration time was defined as the time taken for the sensor to reach the baseline signal (the signal observed in the buffer solution at pH 5). Some reagent including EDTA (0.1M), HNO$_3$ (0.1M), ethylene diamine and HCl(0.1M) were studied as regenerating reagents. Ethylene diamine was concluded to be the best reagent, which gave short membrane regeneration times (10-30 S). After this regeneration and for the next lead concentration measurements, the optode should be placed in buffer (pH 5) for 10-15 min.

Reproducibility and reversibility

These parameters of the sensing phase membrane in the determination of lead was evaluated by repeatedly exposing the sensing phase membrane to a 3.5 μg mL^{-1} lead solution and a 0.1mol L^{-1}ethylen diamine solution. The repeatability of the membrane response at 612 nm using a single membrane was tested by performing seven replicate measurements for 3.5 μg mL^{-1} of lead solution. The relative standard deviation (RSD) of sensor response for these determinations was found to be 2.8%. Fig. 5 shows the absorbance changes versus time for the optode membrane. The reproducibility of the response of different membranes was also studied (Fig. 6). Reproducibility was evaluated by carrying out similar procedure on seven individual membranes at different periods of time, so that the RSD for the measurement of 3.5 μg mL^{-1} lead (II) was 3.2%. The results show that the reproducibility is satisfactory.

Effect of foreign ions

One of the most important characteristics of an optical membrane sensor is its relative response towards the primary ion over other ions present in the solution. For this purpose, a study of the effect of foreign ions was made by adding different amounts of other ions including Na(I), Mg(II), Sn(II), Ni(II), Cu(II), Zn(II), Ag(I), Co(II), Mn(II), Cd(II), Sr(II)and Cr(III) to solutions containing 0.5 μg mL^{-1} of lead (II) ion. The tolerance limit was taken as the concentration of the interfering species causing an error less than ±5%. The results showed at the applied pH value the following ions did not interfere even a 100 fold excess of these ions: Na(I) , Mg(II) , Sn(II), Ni(II), Cu(II), Zn(II), Co(II), Mn(II), Cd(II), Sr(II)and Cr(III). The main interfering species in the determination of lead was Ag$^+$. However, the interference from this ion can be eliminated by using 0.1 M Cl$^-$ solution as the masking agent.
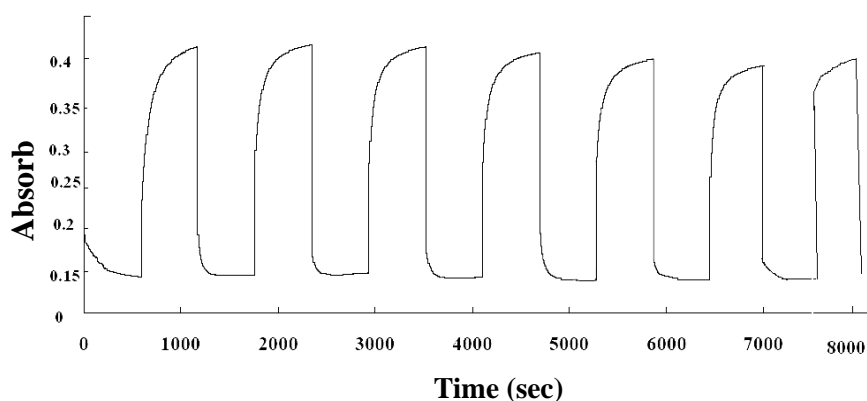
Fig.5. Variation of the absorbance of the membrane at 612 nm for repeatedly exposing into 3.5 μg mL^{-1} lead (II) solution and 0.1 mol L^{-1} ethylene diamine solution.
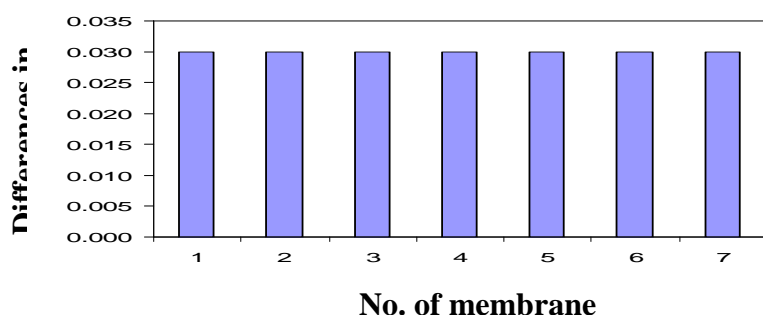

Fig.6. Reproducibility of the response of different membranes exposing into 3.5 μg mL^{-1} lead (II) solution.

Determination of lead (II) in soil and waste samples

In order to test the analytical validity of the proposed optode, this optode was applied to the determination of lead (II) in soil and petrochemical waste samples. The results are given in Table 1. For this purpose, 2.5 mL of buffer solution (pH 5) poured in to cell and 100 µL of the sample was added to the buffer solution. The lead content of soil and petrochemical waste samples were assayed by standard addition method and then determined by the proposed optode. From the data given in Table 1 of this work is readily seen that the present optical sensor is useful for the determination of lead in real samples.

Table 1. Determination of lead (II) ions in soil and petrochemical waste samples.

Sample	Concentration of lead (II) (μg mL^{-1})		Recovery%	R.S.D%
	Added	Found		
P. W. 1	-	0.5	-	-
P. W. 2	2	2.52	101.0	2.7
P. W. 3	3	3.51	100.3	2.3
P. W. 4	4	4.49	99.75	1.5
P. W. 1	-	ND*	-	-
P. W. 2	2	2.11	105.5	2.7
P. W. 3	3	3.10	103.3	1.3
P. W. 4	4	4.05	101.2	1.5
Soil1	-	0.5	-	-
Soil2	2	2.51	100.5	2.7
Soil3	3	3.52	100.6	2.3
Soil4	4	4.53	100.7	1.5

* Not detected.; P.W.: Petrochemical Waste

Conclusions

The new lead optode reported in present study is easily prepared and provides a simple, fast and inexpensive means for determination of lead (II) ions. The membrane responds to lead (II) ion by changing color reversibly from red to green. The sensor can be regenerated readily with a solution of ethylene diamine and has a long lifetime. The response of the optode was reproducible. The optical sensor has a good selectivity toward lead (II) versus other metal ions except for Ag^+ which can be omitted by using 0.1M Cl^- solution as masking agent. It has wide dynamic range and low cost. This optical sensor can be applied for the determination of lead (II) ions in various samples such as polluted soil and petrochemical waste samples.

Acknowledgment

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