

Determination of Cadmium Ions by Designing an Optode Based on Immobilization of Dithizone on a Triacetylcellulose Membrane in Polluted Soil and Water Samples

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요약. 카드뮴이온 검출을 위한 optode를 triacetylcellulose 막에 있어 dithizone을 고정에 의하여 디자인 되었다. Optode 막이 카드뮴을 포함하는 611 nm 에서 흡수 변화가 가능한 실제 시료에 도입 되었을 때 녹색에서 붉은 색으로 색 변화가 일어났다. Cd^{2+} 이온 검출은 검출한계가 $0.025 \mu g ml^{-1}$ ($25 ng ml^{-1}$)이고 $0.3-3 \mu g ml^{-1}$ ($2.67-26.67 \mu M$) 범위에서 가능하였다. Optode의 반응 시간은 Cd^{2+} 이온에 의존하여 15분 안에서 일어났다. 다른 간섭종의 효과에 대해 시험되었고 좋은 선택성을 보였다. 제안된 optode를 사용하여 오염된 토양과 물 시료에서 Cd^{2+} 이온의 검출 결과는 잘 확립된 원자흡수법과 동등하게 얻을 수 있었다.

주제어: Optode 막, Triacetylcellulose 막, Dithizone, 분광법, 카드뮴 이온

ABSTRACT. An optode for cadmium ion determination has been designed by immobilization of dithizone on triacetylcellulose membrane. When the optode membrane is introduced into a real samples containing cadmium, there is a color change from green to red, making it possible to use the change in absorbance at 611 nm as the analytical signal. The sensor could be used in the range of $0.3-3 \mu g ml^{-1}$ ($2.67-26.67 \mu M$) of Cd^{2+} ions with a limit of detection of $0.025 \mu g ml^{-1}$ ($25 ng ml^{-1}$). The response time of optode is within 15 min depending on the concentration of Cd^{2+} ions. It can be easily and completely regenerated by dilute EDTA solution. The effect of different possible interfering species has been examined and was shown the optode has a good selectivity. The results obtained for the determination of cadmium ion in polluted soil and water samples using the proposed optode was found to be comparable with the well-established atomic absorption method.

Keywords: Optode membrane, Triacetylcellulose membrane, Dithizone, Spectrophotometry; Cadmium ion

INTRODUCTION

The development of sensors with an optical transduction of the chemical recognition process (optical sensors, optodes) has become a highly relevant and rapidly expanding area in analytical chemistry.¹⁻⁴

So recent decades have been an increase in the development and quick growth of optodes as viable alternatives to other types of sensors that's because of it's advantages of easy fabrication, good sensitivity and selectivity and low cost of such these optodes.⁵⁻⁹

These optical sensing devices are based on

absorption, reflection, fluorescence or chemiluminescence's, and they commonly make use of chemical compounds that drastically change their optical properties as the result of the actual recognition process.¹⁰⁻¹³

Toxic effects of heavy metals have been well studied.^{14,15} Heavy metals may enter the food chain as a result of their uptake by edible plants. So, determination of heavy metals in environmental samples is very important. Some of these metals such as cadmium have significantly toxic and hazardous effect on human health. Excessive cadmium exposure may give rise to renal, pulmonary, hepatic, skeletal, reproductive effects and cancer.¹⁶ On the other hand, Cadmium and it's salts are used in numerous and varied industrial processes. Electroplating is the major use of the metal itself. It is utilized in such different applications as process engraving, amalgam in dentistry, and nickel-cadmium storage batteries as well.¹⁷ Cadmium's level in the environment varies widely. Cadmium emissions to the environment are normally transported continually between the three main environmental compartments: air, water and soils. The World Health Organization (WHO) reported tolerably weekly intakes of Cd as 0.007 mg/kg body weight for all human groups. Briefly, it is seen that this metal can dangerously affect human health even at ultra trace concentrations.¹⁸ So determination of cadmium is very important for environmental protection. Several methods such as graphite furnace atomic absorption spectrometry (GF- AAS),¹⁹ Flame atomic absorption

spectrometry,²⁰ inductively coupled plasma atomic emission spectrometry (ICP-AES),²¹ Isotope dilution inductively coupled plasma mass spectroscopy (ID-ICPMS),²² Differential pulse anodic stripping voltammetry (DPASV)²³ have been used to determine the cadmium ions.

Although these methods have good sensitivity but they require expensive instrument, well-controlled experimental conditions and profound sample-making.

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.²⁴ Narayanaswamy and coworkers 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.²⁵

In this paper, we discuss the application of a metallochromic reagent, dithizone, immobilized on an optically transparent triacetylcellulose membrane to measure the cadmium ions. Experimental results showed that, this optode could be used as an effective tool in analyzing the cadmium content of various samples such as several soil and water. In *Table 1* we compare the present optode with other Cd analysis method.

Table 1. Comparison of the proposed method with other reported cadmium analyses methods

Method	DL or LDR	Recovery %	RSD%	Remarks	Ref.
TS-CV-AAS	DL= 18 ng L ⁻¹	94-103	2.1	Too expensive, sophisticate instrument	29
SPE	LDR= 0.0-1.0 µg mL ⁻¹	96-105	2.5-3.2	Multistep procedure	30
TS-FF-AAS	DL=0.03 µg L ⁻¹	-	4.6	Too expensive, sophisticate instrument	31
Optode	LDR= 0.03-3.0 µg mL ⁻¹	96-104	1.9	Fast, cheap, simple instrument	Proposed Method

EXPERIMENTAL

Chemicals

All chemicals were of the best available analytical reagent grade and all aqueous solutions were prepared with double distilled water and with salts of the highest purity available. The indicator dithizone (Sym-diphenylthio carbazone) and ethylene diamine were supplied from Merck. Universal buffer solutions were prepared from boric acid/ Acetic acid/phosphoric acid (0.04 M each). The final pH was adjusted by the addition of 0.02 M sodium hydroxide. A stock solution of 1×10^{-2} M Cd^{2+} ion was prepared by weighing 0.3085 gr of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck) and adjusting the volume to 100 ml.

Instruments and measurement procedure

UV/vis spectra were obtained with a Perkin-Elmer Model Lambda 2 spectrometer. The pH measurements were made with a Jenway 3510 pH meter. A SensAA GBC double beam atomic absorption spectrometer (AAS) with hollow cathode lamp operating at 4mA was used for the determination of cadmium in real samples, which was made at 228.8 nm. An adjustable-capillary nebulizer and supplies of acetylene and air were used for the generation of aerosols and atomization. Deuterium lamp background correction was employed to correct for the non-specific absorbance. Operation in a double beam-background correction mode was imperative due to the complexity of the aspirated sample. All measurements were performed in the integration mode. The membrane was placed vertically inside the cell containing, so, the optical path is straightly passed through into the membrane. All measurements were performed in a batch mode.

The sensor was first exposed to the universal buffer solution at pH 5 for some minutes and then the absorbance was measured at 611 nm (the maximum wavelength of the indicator). Then the cadmium solution was added to the membrane by a microliter syringe and after mixing, the absorbance at 611 nm was again measured after 15 min.

Membrane preparation

The immobilized indicator on the triacetylcellulose membrane was prepared according to the following procedure.

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 0.02 g dithizone in 10 ml ethylene diamine for 7 min at ambient temperature. Then they were washed with double distilled water for removing excess ethylene diamine and the loosely trapped indicator. The membranes were finally washed with detergent solutions and rinsed with double distilled water. Prepared membranes were kept under water when not in use.²⁶

Procedure for the determination of cadmium in soil and water samples

To make Cd analysis, firstly, each soil sample was homogenized and dried at 105 °C. After that, 1.0 g of soil was taken and 3 ml of $\text{HNO}_3/\text{H}_2\text{O}_2$ 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 remainder and centrifuged. The clear digests were analyzed by the proposed method.¹⁸

River water samples (from different locations of Kor River, Shiraz, Iran) did not need previous treatment and was analyzed for cadmium ion concentration using the proposed optode. All the real samples were prepared from locations which are near the Shiraz petroleum industry.

RESULT AND DISCUSSION

Spectral characteristics

Fig. 1 shows the absorption spectra of free and immobilized dithizone which were obtained after being equilibrated in buffer solution (pH 5) containing different concentrations of cadmium. The spectral characteristic of this optode showed two maxima at 500 and 611 nm. A decrease in the

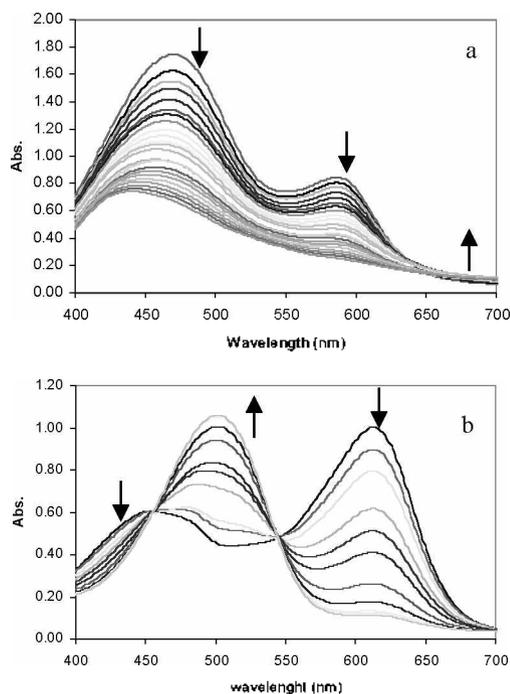


Fig. 1. (a) Absorption spectra for a 1.0×10^{-3} M dithizone solution in the presence of Cd^{2+} ($0.0 - 3.5 \mu\text{g ml}^{-1}$) at pH 5. (b) Absorption spectra of optode film response to Cd^{2+} in the range of $0.0 - 4.5 \mu\text{g ml}^{-1}$ at pH 5. Arrows indicate the spectral trends in changing Cd^{2+} concentrations.

absorption band at 611 nm and an increase in the absorption band at 500 nm were apparent as the cadmium concentration increases, due to the extraction of cadmium ion into the membrane. In fact the mechanism of the response of optode is believed to be based on complexation of dithizone and cadmium. Also, it is important to note that the absorption spectra of immobilized dithizone has a bathochromic shift in comparison to those of their soluble form (611 instead of 590 nm). This can suggest that the structured conformation of the immobilized indicators is more planar than that of its soluble analogue.²¹ The wavelength of 611 nm was selected for further studies because of higher selectivity and sensitivity at this wavelength.

Effect of pH

The equilibrium of the complexation reaction of dithizone with Cd^{2+} is affected by the solution pH.

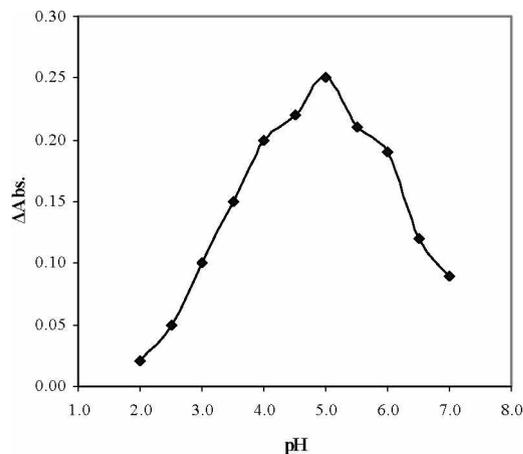


Fig. 2. Effect of pH on the response of membrane in the presence of $0.85 \mu\text{g ml}^{-1}$ mercury at 611 nm.

Fig. 2 shows the effect of pH on the absorbance intensity of the optode membrane. The absorbance measurements were made for $0.85 \mu\text{g mL}^{-1}$ cadmium ion in the pH range of 2.0 – 7.0 at 611 nm. The absorbance measurements were expressed as absorbance difference, which was defined as the difference between the absorbance of the immobilized dithizone alone and the absorbance of the Cd^{2+} - dithizone complex at 611 nm. As can be seen in *Fig. 2*, the pH increases from 2.0 to 5.0, the value of the difference in absorbance increases. At pH values more than 5, the response decreases. This phenomenon might be due to the fact that at lower pH values ($\text{pH} < 5$), complexation is weak as can be seen in *Fig. 2* the maximum difference in absorbance was occurred at pH 5. At pH values higher than 7, the ligand has leakage from the membrane and the membrane was not usable. Therefore pH 5 was selected for further studies.

Dynamic Range

The response of the proposed Cd^{2+} - optode under optimum experimental conditions to the various concentration of Cd^{2+} ion in the range of $0.0 - 4.5 \mu\text{g ml}^{-1}$ is shown in *Fig. 3*. The absorbance measurements were expressed as absorbance difference, which is defined as the difference between the absorbance of immobilized dithizone alone and the absorbance of the Cd-dithizone

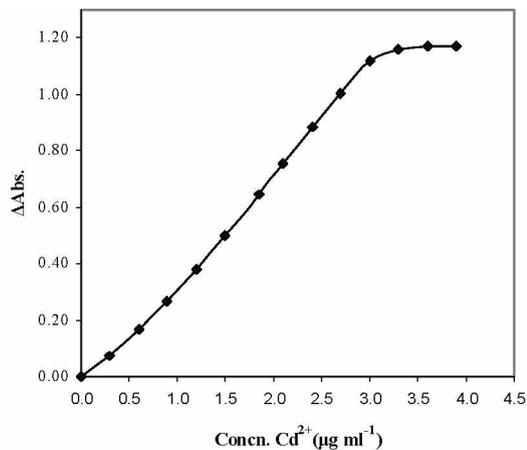


Fig. 3. The optode film response vs. Cd²⁺ ion concentrations in the range of 0.0–4.5 μg ml⁻¹ at pH 5.

complex. The plot of the difference in absorbance against Cd²⁺ ion concentration can be used as a calibration plot for determination of cadmium ions.

The calibration plot exhibited a linear range between 0.3 and 3 μg ml⁻¹ (2.67–26.67 μM) which gave the equation:

$$\text{Response} = 0.3918C_{\text{Cd}^{2+}} - 0.0799$$

Where the response is the difference in absorbance at 611 nm and $C_{\text{Cd}^{2+}}$ is concentration of Cd²⁺ (μg ml⁻¹), with a correlation coefficient of 0.9957. In this case, 3.3 μg ml⁻¹ was found as the concentration of Cd²⁺ ion that saturates the film. The limit of detection (LOD) based on 3 sigma of the blank was 0.025 μg ml⁻¹ (25 ng ml⁻¹).

Response time

An important analytical feature of any optode is 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. The response time was tested by recording the absorbance change from a pure buffer (pH 5) to buffered cadmium solutions of 2.8 μg ml⁻¹. The optode film was found to reach 95% of the final signal at 15 min depending on the concentration of Cd²⁺. Fig. 4 shows the time course of the absorp-

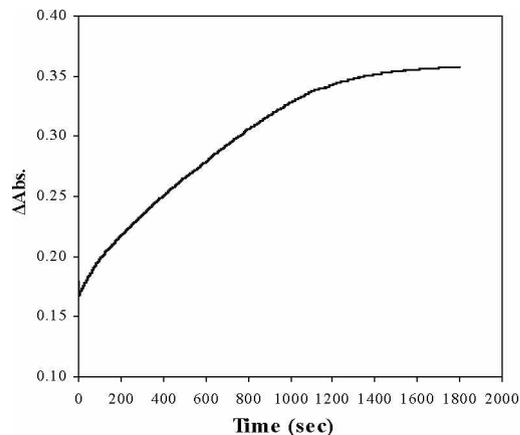


Fig. 4. Typical response curve of the film optode at 611 nm as a function of time when the film was exposed to 2.8 μg ml⁻¹ of Cd²⁺ ions.

tion intensity of the membrane at 611 nm. In general, the response time is lower in concentrated solutions than dilute solutions. 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.²⁸

Reproducibility

The repeatability and reproducibility of the proposed membrane optode were investigated. To evaluate discrepancies between responses in successive runs made using a single membrane sensor, the repeatability was studied by performing ten determinations with the same standard solution of cadmium ion. The coefficient of variation of sensor response for 1.5 μg ml⁻¹ Cd²⁺ was ±1.9%.

Differences between responses of individual sensors were evaluated by preparing ten membranes from the same mixture and the reproducibility was assessed by determination of 1.5 μg ml⁻¹ Cd²⁺ solutions (three determinations with each membrane). The coefficient of variation of response among membranes found to be ±3.4%. The results show that the reproducibility is satisfactory.

Short-term stability and life time

To study the short-term stability of the optode

membrane. its absorbance in contact with a $1.5 \mu\text{g ml}^{-1}$ solution of Cd^{2+} buffered at pH 5 was measured over a period of 6 h. From absorbance readings taken every 30 min ($n=12$) it was found that the response was almost complete with only 1.8% increase in absorbance after 6 h monitoring. The life time of membrane was determined by adding a buffer solution (pH 5) in a cuvette including the film. The signal was recorded at wavelength of 611 nm over a period of about 6 h. No significant loss of the indicator occurs during this time. When the membrane 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. Additionally the stability of response of the film was investigated over three weeks under ambient conditions, which indicated that the film was stable over this period.

Regeneration of the optode membrane

For an optode membrane to perform suitably, the color change must be reversible. For regenerating the sensor, anions such as I^- , Br^- , CrO_4^{2-} , SCN^- , $\text{S}_2\text{O}_3^{2-}$ were studied as regenerating reagents. None of the above reagents could regenerate the

membrane.

Regeneration with HCl can reverse the color but the membrane wasn't usable for further studies and HNO_3 decomposes the dye and wasn't useful.

The best result was obtained by applying EDTA which gave short membrane regeneration times (<10 min). It was observed that lower EDTA concentration, the generation time was longer while the higher EDTA concentration caused low response of the sensor. So 0.1 M EDTA concentration was selected as an optimum. After this regeneration and for the next cadmium concentration measurements, the optode should be placed in buffer (pH 5) for 10-15 min.

Effect of foreign ions

To study the selectivity of the proposed method. The effect of various species including Na^+ , Ba^{2+} , Ca^{2+} , Mg^{2+} , Mn^{2+} , Sn^{2+} , Zn^{2+} , Pb^{2+} , Fe^{2+} , Hg^{2+} , Al^{3+} , Bi^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} on the determination of cadmium was tested under optimum conditions. For this purpose samples containing a fixed concentration of cadmium ions, $1 \mu\text{g ml}^{-1}$ (8.89 μM), and different concentrations of other metal ions were analyzed by the method. A species was considered as interference if it causes a variation more than 1.6% in analytical signal when com-

Table 2. Determination of Cd (II) in real samples

Sample	Cd (II) Added ($\mu\text{g mL}^{-1}$)	Cd (II) found ($\mu\text{g mL}^{-1}$)		Standard Deviation (%)	RSD (%) (n=5)	Recovery (%)
		Optode ^a	AAS			
River water1	-	1.56	1.51	0.15	0.61	-
River water1	0.50	2.07	-	0.17	0.65	102
River water2	-	1.44	1.47	0.13	0.73	-
River water2	0.50	1.96	-	0.16	0.71	104
River water3	-	1.73	1.70	0.13	0.72	-
River water3	0.50	2.21	-	0.17	0.85	96
Industrial soil	-	1.38	1.45	0.45	1.11	-
Industrial soil	0.50	1.87	-	0.52	1.43	98
Farmland soil	-	0.35	0.35	0.64	1.35	-
Farmland soil	0.50	0.83	-	0.65	1.21	96
Playground soil	-	0.37	0.42	0.33	1.22	-
Playground soil	0.50	0.88	-	0.41	1.35	102
Roadside soil	-	0.62	0.59	0.65	1.48	-
Roadside soil	0.50	1.13	-	0.35	1.85	102

^aAfter addition of 0.10 M Murexide

pared to the analytical signal obtained in the absence of the interfering species. The results showed at the applied pH value the following ions did not interfere even a 100 fold excess of these ions: Na^- , Ba^{3+} , Ca^{2+} , Mg^{3+} , Mn^{2+} , Sn^{3+} , Zn^{2+} , Pb^{2+} , Fe^{2+} , Hg^{2+} , Al^{3+} , Bi^{3+} . The ions Cu^{2+} , Ni^{2+} , Co^{2+} were as interference for our method. However, as the system is similar to the extraction system, the interference from foreign metal ions can be reduced by prior extraction or by the use of masking agent. All these three interferences (Cu^{2+} , Ni^{2+} and Co^{2+}) can be eliminated by addition of 0.05 M murexide as a masking agent. Also it is apparent from this study that discrimination between different metals can be achieved by the control of several parameters including the absorption wavelength, the pH and the sample contact time in addition to the use of masking agents.

Determination of Cd^{2+} in polluted soil and water samples

To show the applicability of the method, it was applied to determine of cadmium in soil (industrial, farmland, playground and roadside) and water samples (river water, three samples from different of locations) under optimal experimental conditions. The results are given in Table 2. The cadmium content of the samples has determined by atomic absorption spectrometry (AAS). From the results of five replicate measurements given in Table 2, it is immediately obvious that there is good recovery (96-104%) and satisfactory agreement between the results obtained by the Cd^{2+} -selective optode and by AAS.

CONCLUSION

The optical sensor described in this work is easily prepared and provides a simple means for the determination of Cd^{2+} ions. The membrane responds to Cd^{2+} ions by changing color reversibly from green to red. The sensor can be regenerated readily with EDTA solution. It is fully reversible and has a long life time and can be used over long time after its preparation (2 months). The response

of the sensing phase was reproducible and the sensing phase presented a relatively good selectivity for Cd^{2+} ions. The proposed method is inexpensive and uses conventional instrumentation only. The sensor can be applied for the determination of Cd^{2+} ions in polluted soil and water samples which threaten human health.

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