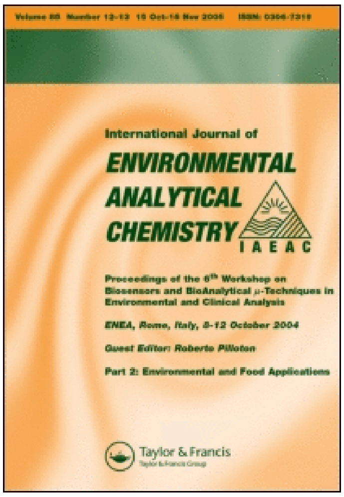

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Development of a cobalt (II) optical sensing film based on *N*^{5}-(2, 4-dinitro-phenyl)-*N*^{1},*N*^{1}-diethyl-penta-1,3-diene-1,5-diamine

Majid Arvand[a]; Tahereh M. Gholizadeh[a]; Nosratollah Mahmoodi[a]
[a] Faculty of Science, Department of Chemistry, University of Guilan, Rasht, Iran

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Development of a cobalt (II) optical sensing film based on N^5-(2, 4-dinitro-phenyl)-N^1,N^1-diethyl-penta-1,3-diene-1,5-diamine

Majid Arvand*, Tahereh M. Gholizadeh and Nosratollah Mahmoodi

Faculty of Science, Department of Chemistry, University of Guilan, Rasht, Iran

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An optical sensing film has been proposed for sensitive determination of cobalt (Co) (II) ion in aqueous solutions. The cobalt sensing membrane was prepared by incorporating N^5-(2, 4-dinitro-phenyl)-N^1,N^1-diethyl-penta-1,3-diene-1,5-diamine (HDDA) as ionophore in the plasticised PVC membrane containing *o*-nitrophenyl octyl ether as plasticiser. The membrane responds to cobalt ion by changing colour irreversibly from yellow to green in acetate buffer solution at $pH = 5.5$. The proposed sensing film displays a linear range of 0.028–29.68 $\mu g\,mL^{-1}$ with a limit of detection 0.012 $\mu g\,mL^{-1}$. Moreover, upon the introduction of a negatively charged lipophilic additive (oleic acid) into the membrane, the optode displayed enhanced sensitivity. In addition, satisfactory analytical sensing characteristics for determining Co(II) ion were obtained in terms of the selectivity, stability and reproducibility. The response time of the optode was about 15–25 min, depending on the concentration of Co(II) ions. The optode membrane has been applied to determine Co(II) in various water samples and copper-free alloys.

Keywords: optical sensing film; cobalt (II) ion; ionophore; UV–Vis spectrophotometry

1. Introduction

Pollution caused by heavy metals is a major environmental problem in the world. Mining and industrial operations discharge large quantities of effluents into water bodies. Thus, rivers, lakes and estuaries are polluted with heavy metals to different degrees. Cobalt (Co) is one of such type of metals. Co is widespread in nature in meteorites, fresh waters, soils, plants and animals.

Cobalt is a component of cyanocobalamin or vitamin B12; in fact, it is the only vitamin known to contain a heavy metal. Vitamin B12 as a coenzyme has important role in many biochemical processes, such as erythrocyte formation, and its deficiency can lead to pernicious anaemia [1]. Thus, the importance of detection and monitoring of Co ions in environmental, waste and drinking waters is unquestionable [2,3].

The development of optical sensors has become a rapidly expanding area of analytical chemistry, because they offer the advantages of simple preparation, reasonable selectivity and sensitivity and no need for separate reference devices [4–6]. Optical sensors required simple instrumentation and are suitable for multi-sensor array fabrication. In comparison

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*Corresponding author. Email: arvand@guilan.ac.ir

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with ion-selective electrodes, they do not require internal and external reference devices, long preconditioning time is not a pre-requisite for use, and are not subjected to electrical noise [7].

Optical sensors that make use of plasticised polymer membrane containing a reagent that reacts with the analyte to produce a distinctive colour change are of great interest for, among other applications, the trace analysis of heavy metal ions [8–10].

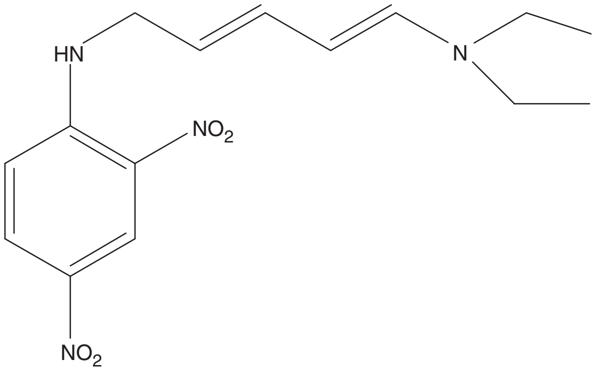
However, despite the suitability of optical sensors for the optical monitoring of Co^{2+} ions, there have been several number reports on Co^{2+} ion optical sensors in literature [11–15].

In this article, we described an optode for sensitive determination of Co with low detection limit using a recently synthesised N^5-(2, 4-dinitro-phenyl)-N^1,N^1-diethyl-penta-1,3-diene-1,5-diamine (HDDA) as complexing agent. This ionophore can extract Co^{2+} from aqueous sample solution into organic membrane phase and form a complex, which results a decrease in the ionophore absorbance and produce two new absorbance peaks. To the best of our knowledge, this compound has not previously been used in the development of a Co(II) optical sensing film or in any other optical sensors.

2. Experimental

2.1 *Reagents*

Relative high molecular weight poly (vinyl chloride) (PVC), nitrobenzene (NB), acetophenone (AP), *o*-nitrophenyl octyl ether (*o*-NPOE), *o*-nitrophenyl phenyl ether (*o*-NPPE), dibuthyl sebacate (DBS), bis(2-ethylhexyl) sebacate (DOS), oleic acid (OA), sodium tetraphenylborate (NaTPB), tetraethylammonium perchlorate (TEAP), tetrahydrofuran (THF), methanol (MeOH) and all other reagents were obtained from Merck (Darmstadt, Germany). A stock solution of $150\,\mu g\,mL^{-1}$ Co^{2+} was prepared by dissolving appropriate amount of $CoCl_2 \cdot 6H_2O$ in 100 mL volumetric flask and diluted with doubly distilled water. Working solutions with lower concentrations were prepared by suitable dilution of the stock solution. The pH adjustments were made with acetate buffer solution (1×10^{-4} M $CH_3COOH + 5.5 \times 10^{-4}$ M CH_3COONa) to achieve the desired pH, but in studying of pH effect, the pH of solutions was adjusted with either HCl or NaOH solutions. The structure of ionophore is depicted in Scheme 1.



Scheme 1. Structure of HDDA used as ionophore.

2.2 *Synthesis of the ionophore HDDA*

The ionophore HDDA (Scheme 1), used in this effort, was synthesised according to the reported method with some modification in the described procedure [16]. To prepare the compound, (0.3 g, 1 mmol) of premade *N*-2,4-dinitrophenyl pyridinium chloride was dissolved in 5 mL of absolute MeOH and was cooled to 10°C as well as allowed to stirred for 15 min at this temperature. To this was added dropwise solution of (0.073 g, 1 mmol) diethyl amine in 2 mL absolute MeOH over period of 10 min (the exact quantity of diethyl amine is important). The colour change of solution due to the addition of first drop of diethyl amine verifies that the reaction is completed. The crude participate was filtered and several times recrystallised from *n*-hexane affording 0.2 g, 62% yield (m.p. = 156–159°C). The product has IR (DMSO solvent): 3291, 2995, 2912, 1660, 1436, 1408, 1311, 700, 669 cm^{-1}. ^1H-NMR (500 MHz, $CDCl_3$): δ; 1.25 (t, $J = 7.2$ Hz, 6H), 3.3 (q, $J = 7.2$ Hz, 4H), 4.12 (d, $J = 9.9$ Hz, 2H), 5.13 (t, $J = 12.6$ Hz, 1H), 6.54 (dd, $J = 9.9, 14$ Hz, 1H), 6.7 (d, $J = 12.6$ Hz, 1H), 6.78 (dd, $J = 12.6, 14$ Hz, 1H), 6.92 (d, $J = 9.9$ Hz, 1H), 8.33 (dd, $J = 2.5, 8.8$ Hz, 1H), 8.7 (d, $J = 2.5$ Hz, 1H), 10.41 (br, 1H) ppm; $C_{15}H_{20}N_4O_4$ (320.34): Calcd C 56.24, H 6.29, N 17.49, O 19.98; Found C 56.38, H 6.43, N 17.15, O 20.04.

2.3 *Apparatus*

A Cary 100 UV–Vis spectrophotometer with a 1 cm cell was used for recording all spectra and absorbance measurements. A Metrohm pH meter (model 827) with a combined double junction glass electrode was used for monitoring pH values. All measurements were made in the absorbance mode.

2.4 *Membrane preparation*

The optode membranes were prepared from 4 mg of ionophore, 140 mg of *o*-nitrophenyl octyl ether as plasticiser, 6 mg of oleic acid as additive and 70 mg PVC. The membrane components were dissolved in 1.5 mL freshly distilled THF in a glass vial. The solution was immediately shaken vigorously to achieve complete homogeneity. An aliquot of 50 µL of this solution was poured and uniformly spread on a dust free glass plate (8 mm × 25 mm) which mounted on a spin device (rotating frequency ~2600 rpm). After a spinning time of about 15 s, the glass support plate with sensing membrane was removed and allowed to stand in ambient air for 24 h before use. The thickness of dry membrane was estimated to be ≈4 µm.

2.5 *Preparation of real samples*

The analyses of alloy samples were conducted by weighing 1.4 g of the sample to the nearest 0.1 mg and transferring the sample into a 250 mL Erlenmeyer flask. Then 20–25 mL of HNO_3–HCl (1 : 3) was added. The mixture was heated until dissolution is complete. The solution was heated to dryness. Then the residue was dissolved in water and diluted with water to 100 mL in a 100 mL volumetric flask. An appropriate volume of each sample solution was diluted further with water so that the concentration of cobalt ion in the final solution was within the working range [11]. Water samples were used directly after filtration with a filter paper (Whatman No. 1).

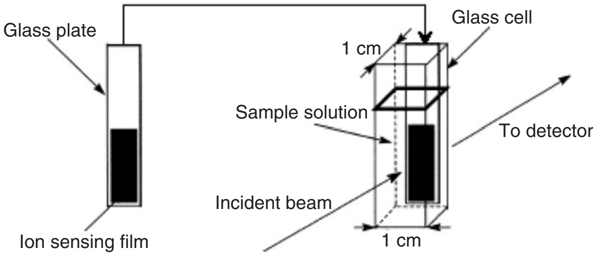


Figure 1. Absorbance measuring system for the film optode.

2.6 *Procedure*

An easily handled, small, and low-cost ion-sensing film optode that can be utilised as a handy sensing tool has been developed [10]. These film optodes were a plasticised PVC-matrix membrane containing a lipophilic ionophore. For simple and easy use of this ion-sensing film, the PVC membrane was attached to the surface of an 8 mm × 25 mm thin glass plate whose size fits into a conventional glass vessel used as a standard optical cell for a spectrophotometer as shown in Figure 1. Consequently, the determination of an analyte ion using the film optode can be achieved by simply immersing it into the glass vessel for monitoring the absorbance change as the response of the optode [5,17,18].

The prepared membrane was put vertically inside the sample cell containing 3 mL acetate buffer solution with $\mathrm{pH} = 5.5$, and a membrane (without ionophore) at the same conditions was used as a blank membrane. The standardised metal ion solutions were added to the sample cell and the absorbance value of the system was measured after 30 min (required to reach the equilibrium) at $\lambda_{\max} = 610\,\mathrm{nm}$. The limiting absorbances A_0 and A_c were determined with the optode membrane in contact without and with $58.93\,\mu\mathrm{g\,mL^{-1}}$ Co^{2+}. By plotting the calibration curve of the absorbance signal value α (Equation (3)) *versus* the logarithmic concentration of Co ion (pCo), the unknown Co concentration can be read. All measurements were carried out at room temperature.

3. Results and discussion

3.1 *Spectral characteristics of ionophore in the solution*

In preliminary experiments, it was found that the addition of proper amounts of Co^{2+} to an ethanol solution of HDDA resulted in a slow change in the colour of the solution from yellow to green, while the presence of alkaline earth and transition-metal ions, such as Bi^{3+}, Ni^{2+}, Pb^{2+}, Al^{3+}, Ag^{+}, Zn^{2+}, Be^{2+}, Sn^{2+}, Mn^{2+}, Cr^{3+} and Cd^{2+}, showed no observable colour change in the ligand solution. This is most possibly indicative of strong complex formation of the ligand with Co^{2+} ions in the ethanol solution. Figure 2 shows the spectral change. As can be seen, the complexation was accomplished by a relatively strong decrease of the absorption band of the ligand HDDA, with $\lambda_{\max}$ at 470 nm and creation of new absorption bands, 577 and 610 nm, for the Co–HDDA complex. The results showed that the wavelength 610 nm has high correlation coefficient and sensitivity compared with the 577 nm. Then, 610 nm was selected for further studies.

In order to determine the stoichiometry of the resulting complex, the absorption spectra containing 1.0×10^{-4} M of the ligand solution at a fixed ionic strength of 0.05 M

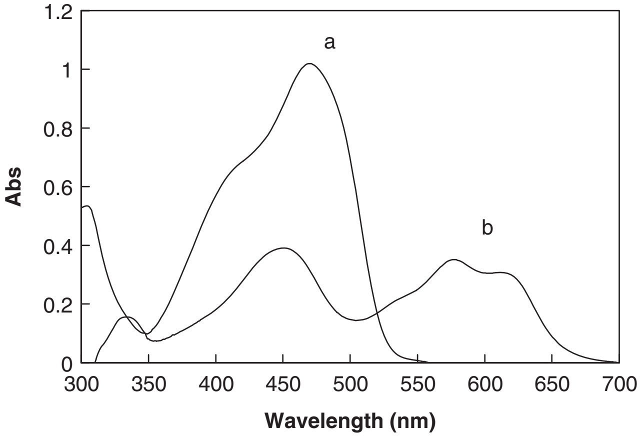


Figure 2. Absorption spectra for ethanol solution of HDDA in the absence [a] and presence of $3\,\mu g\,mL^{-1}$ Co^{2+} [b] at pH = 5.5.

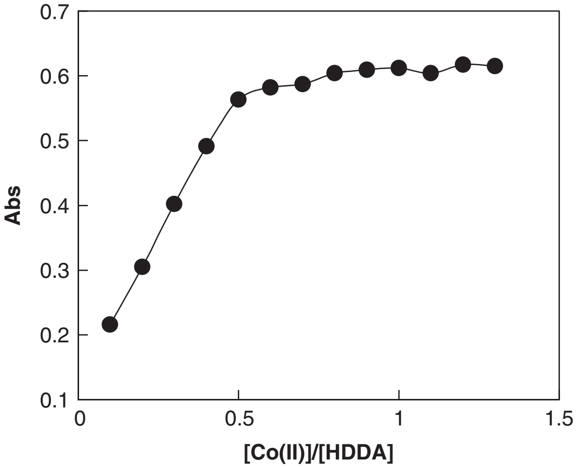


Figure 3. Mole ratio plot of complexation of HDDA with Co^{2+} in ethanol at $\lambda_{max} = 610$ nm.

(maintained by TEAP) and varying amounts of the Co ion were obtained. The absorbance *versus* $[Co^{2+}]/[HDDA]$ mole ratio plot obtained at 610 nm in ethanol solution is shown in Figure 3. The plot revealed an inflection point at $[Co^{2+}]/[HDDA]$ mole ratio of about 0.5 emphasising the formation of a 1 : 2 (metal-to-ligand) complex in the solution.

3.2 *Spectral characteristics of ionophore in the membrane*

After HDDA incorporated in the PVC membrane, the spectral properties of the ligand in the membrane remained the same as those measured in ethanol/water solvent (Figure 4). This is the basis of the optical sensing device in this investigation. Therefore, the wavelength 610 nm has been used in all subsequent measurements of absorbance.

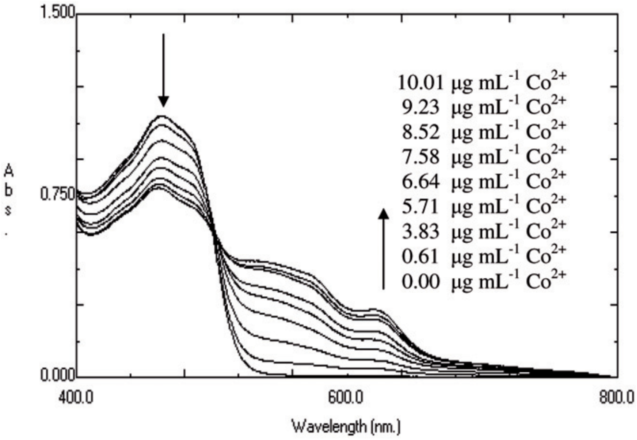


Figure 4. Absorption spectra for the ionophore HDDA incorporated into membrane and varying amounts of Co^{2+} ions in aqueous solution with pH = 5.5 (membrane composition: 4 mg of HDDA, 140 mg of *o*-NPOE, 6 mg of OA and 70 mg PVC).

3.3 *Measuring principle*

When Co(II) ion is extracted into the optical membrane, it forms a complex with HDDA and increases its absorption at $\lambda_{\max}$ 610 nm. To achieve electro-neutrality, a counter ion for the anionic site is necessary. A bulky additive, NaR, was added. If the complex equilibrium between Co^{2+} ions in the aqueous sample solution (aq) and HDDA in the plasticised PVC membrane phase (org) will form a $m:n$ complex, the overall equilibrium will be expressed as follows:

$$m\mathrm{Co}^{2+}_{(\mathrm{aq})} + n\mathrm{HDDA}_{(\mathrm{org})} + \mathrm{NaR}_{(\mathrm{org})} \rightleftharpoons \mathrm{Co}_m(\mathrm{DDA})^{(2m-n)+}_{n(\mathrm{org})} + n\mathrm{H}^{+}_{(\mathrm{aq})} + \mathrm{R}^{-}_{(\mathrm{org})} + \mathrm{Na}^{+}_{(\mathrm{aq})} \tag{1}$$

The law of mass action can describe the corresponding equilibrium constant K_{exch} of the system for Co^{2+} ions that is expressed in Equation (2), in which it is assumed that the activities of species in the membrane are proportional to their concentrations [19]:

$$K_{\mathrm{exch}} = \frac{\left[\mathrm{Co}_m(\mathrm{DDA})_n^{(2m-n)+}\right]_{\mathrm{org}}[\mathrm{H}^+]^n_{\mathrm{aq}}[\mathrm{R}^-]_{\mathrm{org}}[\mathrm{Na}^+]_{\mathrm{aq}}}{[\mathrm{Co}^{2+}]^m_{\mathrm{aq}}[\mathrm{HDDA}]^n_{\mathrm{org}}[\mathrm{NaR}]_{\mathrm{org}}}. \tag{2}$$

The response curves of optical sensors are usually depicted as the normalised absorption α, as a function of the metal-ion concentration. The measured absorption is converted into α by Equation (3), in which A_0 is the absorption of free ligand, A_c the absorption of the complex and A is the measured absorbance at 610 nm. At this wavelength, the only absorbing species is the complex C, so that α is equal to the molar fraction of the complex. From the Beer's law, we assume the normalised absorbance value α which is the ratio of the concentration of free complex [C], to the total amount of HDDA, C_{HDDA}, is related to the measured absorbance as follows:

$$\alpha = \frac{[\mathrm{C}]}{\mathrm{C}_{\mathrm{HDDA}}}, \quad [\mathrm{HADDA}] = (1-\alpha)\mathrm{C}_{\mathrm{HDDA}}, \quad \alpha = \frac{\mathrm{A}-\mathrm{A}_{\mathrm{o}}}{\mathrm{A}_{\mathrm{c}}-\mathrm{A}_{\mathrm{o}}} \tag{3}$$

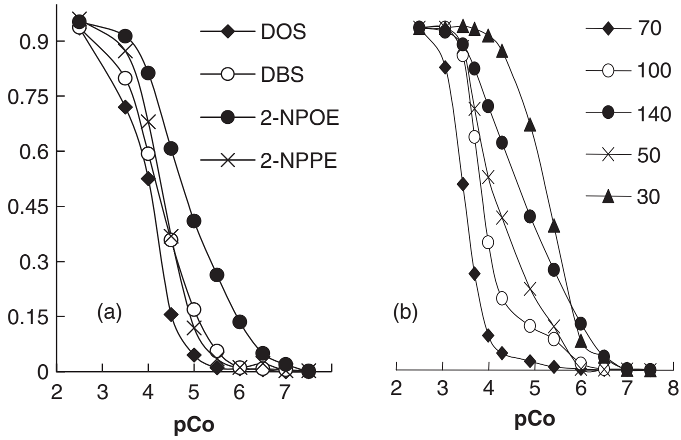


Figure 5. Effect of the type (a) and content (b) of plasticiser on the response of the optical sensing film.

From Equations (2) and (3), with the condition of electro-neutrality $C_R = [NaR]_{org} + [R^-]_{org}$ and $[R^-]_{org} = [C]_{org}$, at constant concentrations of H^+ and Na^+ and if all constants are summarised in K_{exch}, we can obtain the relationship between α and $[Co^{2+}]$:

$$K_{exch} = \frac{\alpha^2 C_{HDDA}^2}{[Co^{2+}]_{aq}^m [(1-\alpha)C_{HDDA}]^n (C_R - \alpha C_{HDDA})} \tag{4}$$

Equation (4) can be used to find the theoretical data, to fit observed absorptions and to calculate K_{exch} [18]. Equation (4) is the basis of quantitative determination of Co(II) using the proper optical membrane.

3.4 *Effect of membrane composition*

3.4.1 *Choice of solvent mediator (plasticiser)*

The membrane composition and the nature of the plasticiser largely influence the response characteristics and the working concentration range of the optical sensors [20]. Optode films with a high amount of plasticiser have optimum physical properties and ensure relatively high mobility of their constituents. In order to give a homogeneous organic phase, the membrane solvent must be physically compatible with the polymer, i.e. have plasticiser properties. Otherwise, it exudes, yielding membranes of unstable composition. For various reasons, it also has an influence on the selectivity behaviour. Six plasticisers such as DBS, *o*-NPOE, DOS, *o*-NPPE, NB and AP were tested as potential plasticisers for preparing the membrane. The membranes were prepared from a mixture of PVC (70 mg), plasticiser (140 mg), additive (6 mg) and ionophore (4 mg) in THF (1.5 mL). The membranes containing *o*-NPOE revealed the best physical properties with maximum sensitivities and wide concentration range (Figure 5a). Membrane obtained from AP as plasticiser did not show any absorption change against Co ion and membrane with NB was not stable on glass support plate, as well.

For determination of the effect of plasticiser amount on the optode response, membranes that contain different amounts solvent mediator *o*-NPOE (30, 50, 70, 100, 140 mg) were prepared. Absorption measurements showed that membrane containing 140 mg *o*-NPOE revealed the best physical properties and wide concentration range (Figure 5b).

3.4.2 *Effect of the PVC amount*

In general, the thickness and hardness of the membrane depend on the amount of PVC used. At lower PVC contents, the membrane becomes mechanically weak and swells up easily in aqueous solution and leaching of the membrane is significant. By increasing the amount of PVC, the membrane becomes dense, that it prevents the leaching of ionophore from membrane into aqueous solution [21]. In this work, we examined the various amounts of PVC on the response characteristic of membrane. The results illustrated that increasing the amount of PVC (more than 70 mg) did not improve the sensitivity and were not suitable due to the decreasing of ion diffusion into the bulk of membrane.

3.4.3 *Effect of amount of the ionophore*

Ionophores play a key role in the selectivity of ion-selective optodes. The rational design of synthetic carriers takes advantages of the different elements of molecular recognition. The creation of suitable binding sites and proper topology in the ionophore that are complementary to the size and charge of a particular ion can lead to very selective interaction [22].

The optical sensing film proposed is based on the incorporation of HDDA with secondary amine functional group in its structure as an ion exchanger. This ionophore possesses a unique binding property towards Co^{2+} ion in sensing membrane and changes its colour from yellow to green as a result of the binding event. This ionophore (HDDA) is insoluble in water in its neutral form, while it is quite soluble in organic solvents. The effect of amount of the ionophore on the response of the membrane is illustrated in Figure 6(a). The blank membrane (membrane without ionophore in presence of Co ion with pH = 5.5) was taken as the reference. As it is seen from Figure 6, the presence of 4 mg

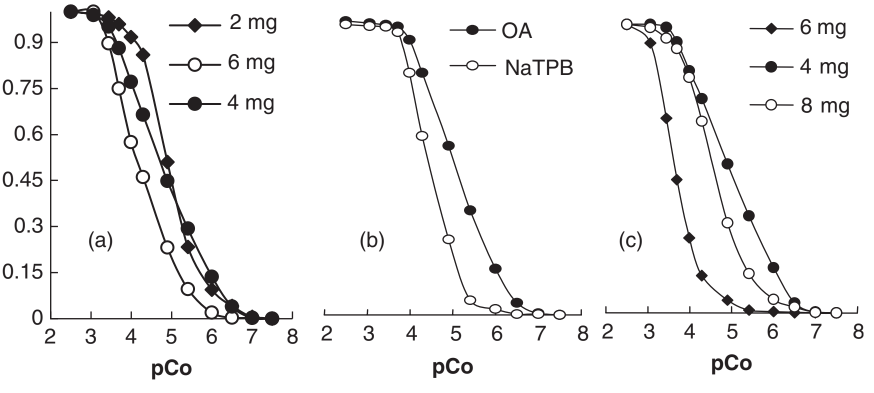


Figure 6. Effect of the amount of ionophore (a) and type (b) and also the amount of additive (c) on the response of the optical sensing film.

of ionophore (HDDA) in the PVC membrane resulted in the best optical response of the Co ion-sensing film. Higher amounts of HDDA (more than 4 mg) did not improve the sensitivity and were not suitable due to the leaching of HDDA.

3.4.4 *Effect of the additive*

In order to facilitate the establishment of a thermodynamic equilibrium between the bulk liquid membrane optodes and the sample solution of interest, a rather fast mass transfer of analyte from the sample into the membrane is required [23–25]. Thus, in this proposed Co optical sensing film containing HDDA as a neutral ionophore, the incorporation of a suitable additive was necessary to ensure the fast establishment of the corresponding ion-exchange equilibrium. OA and NaTPB were tested as additive for preparing the membrane. The membranes were prepared from a mixture of PVC (70 mg), plasticiser (140 mg), additive (4 mg) and ionophore (4 mg) in THF (1.5 mL). The results of Figure 6(b) show that the membrane containing OA revealed good response and transparency. The enhanced sensitivity may be attributed to the OA existing in the PVC membrane, changing the structure of the membrane and improving the passing efficiency of Co into the organic membrane. It favourably makes much more Co^{2+} extract into the membrane, and leads to a higher sensitivity. For study of the effect of additive amount on the optode response, membranes that contain different amounts OA (4, 6, 8 mg) were prepared. Absorption measurements showed that membrane containing 4 mg OA revealed best response (Figure 6c).

3.5 *Effect of pH on the membrane response*

The equilibrium of the complexation reaction of HDDA with Co ion is affected by the solution pH. Figure 7 shows the effect of pH values on response of the optode membrane. The absorbance measurements were made for 9 μg mL^{-1} Co ion at different pH values at 610 nm. Absorption value reached to the highest value at the pH = 5.5 and with increasing

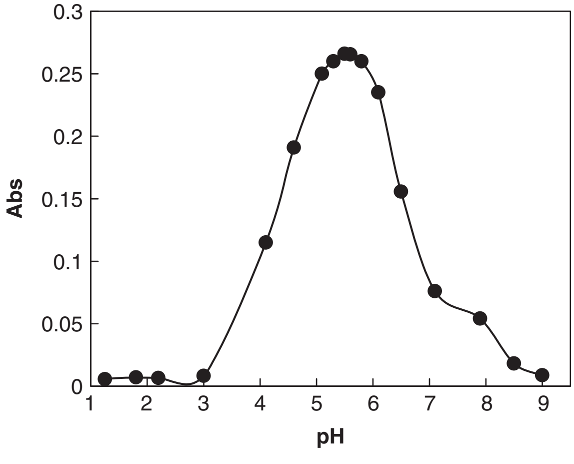


Figure 7. Effect of pH on the response of membrane in the presence of 9 μg mL^{-1} Co at 610 nm (membrane composition: 4 mg of HDDA, 140 mg of *o*-NPOE, 6 mg of OA and 70 mg PVC).

pH, absorption value decreased. Probably, when the pH increases to high values the Co (II) ions are converted to hydroxyl species or precipitated. Also at pH values under 4, the ionophore had leakage from the membrane. Thus, in subsequent experiments, a Co solution of $\mathrm{pH}=5.5$, adjusted by acetate buffer, was selected as an ideal experimental condition.

3.6 *Calibration range and detection limit*

The optical response of the proposed Co^{2+}-sensitive membrane under optimum experimental conditions was obtained. The plot of normalised absorbance value (taken after 25 min) against pCo can be used as a calibration plot for determination of Co ions in the concentration range 4.75×10^{-7}–5.04×10^{-4} M (0.028–29.68 $\mu\mathrm{g\,mL}^{-1}$) with equation of $Y=-0.3062X+1.9868$ ($R^2=0.9861$), where Y is α and X is negative logarithm of Co ion concentration in molars. A concentration of 58.93 $\mu\mathrm{g\,mL}^{-1}$ was found as the optimum concentration of Co^{2+} ion that saturates the optode membrane. Detection limit of the sensing film, which is defined as the concentration of the sample yielding a signal equal to the blank signal three times of its SD, was found to be 0.012 $\mu\mathrm{g\,mL}^{-1}$.

3.7 *Selectivity*

The selectivity of optical sensor, which reflects the relative response of the sensor for primary ion over divers ions present in solution, is perhaps the most important characteristics of an optical sensor. In order to access the possible analytical application of this sensing method, the effects of some alkali, alkaline earth and heavy metal ions were investigated. The experiment was carried out with a fixed concentration of Co^{2+} at 3 $\mu\mathrm{g\,mL}^{-1}$ and then measuring the changes in absorbance intensity before and after adding different foreign interferents in the Co solution buffered at $\mathrm{pH}=5.5$. The tolerance limit was set as the amount of foreign ion causing ±5% error in determination of Co. The results are summarised in Table 1. As can be seen from Table 1, several metal ions do not interfere even at high concentrations. In addition to Co, the sensing film also produces a response to some other metal ions ($\mathrm{Cu}^{2+}, \mathrm{Hg}^{2+}$) that form complex with HDDA at $\mathrm{pH}=5.5$. The results obtained may be important in terms of application of the sensing film to determination of other ions.

With the purpose of increasing selectivity, trials to eliminate the effects of interfering ions were made using some masking reagents such as diethylentriamine penta-acetic acid (DTPA), EDTA and oxime. But none of these reagents was suitable for complete elimination of interferences.

Table 1. Tolerance of diverse ions on determination of 3 $\mu\mathrm{g\,mL}^{-1}$ Co.

Foreign ions	Tolerance limit ($W_{\mathrm{ion}}/W_{\mathrm{Co(II)}}$)
K^+, Na^+, ZrO^{2+}, SCN^-, $\mathrm{PO_4}^{3-}$, Cl^-, I^-, Br^-, $\mathrm{SO_4}^{2-}$, Al^{3+}, Cs^+, Sn^{2+}, Mg^{2+}, Ag^+, $\mathrm{NH_4}^+$	1000
Ba^{2+}, Sr^{2+}, Ni^{2+}, Zn^{2+}	200
Mn^{2+}, Be^{2+}, Mo(VI), Fe^{2+}, Cr^{3+}, Fe^{3+}	100
Cu^{2+}, Hg^{2+}	10

3.8 *Reversibility, reproducibility, short-term stability and lifetime*

Some reagents including HCl, HNO_3, H_3PO_4, H_2SO_4, dithizone, EDTA, NaF and $Na_2C_2O_4$ were studied as regenerating and masking reagents. It was found that none of the above reagents or their mixtures could regenerate optode membrane completely and thus the membrane could be used as a probe for Co ion determination.

The short-term stability of the optical sensing film was determined by its absorbance intensity measurements in contact with a buffer solution (pH = 5.5) in a cuvette. The signal was recorded every 30 min at wavelength of 470 nm (λ_{max} of ionophore) over a period of about 5 h. It was found that no significant loss of the ionophore occurs during this time. When the membrane was exposed to light, no drift in signal occurred and the optode was

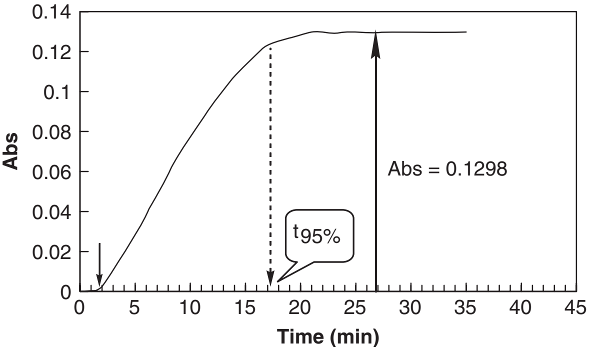


Figure 8. Response profile obtained with the Co(II)-optical sensing film for 2 μg mL^{-1} of Co^{2+} concentration in aqueous solution with pH = 5.5 (membrane composition: 4 mg of HDDA, 140 mg of *o*-NPOE, 6 mg of OA and 70 mg PVC).

Table 2. Results of four replicate determination of Co in real samples.

Sample	Co (II) added	Co (II) found	Recovery (%)
Mineral water[a]	–	< Detection limit	–
Mineral water	4.42 μg mL^{-1}	(4.31 ± 0.11) μg mL^{-1}	97.5
Mineral water	12.55 μg mL^{-1}	(12.31 ± 0.13) μg mL^{-1}	98.1
River water[b]	–	< Detection limit	–
River water	3.83 μg mL^{-1}	(3.77 ± 0.09) μg mL^{-1}	98.4
River water	9.23 μg mL^{-1}	(9.02 ± 0.10) μg mL^{-1}	97.7
Tap water	–	< Detection limit	–
Tap water	4.42 μg mL^{-1}	(4.36 ± 0.13) μg mL^{-1}	98.6
Tap water	12.55 μg mL^{-1}	(12.28 ± 0.14) μg mL^{-1}	97.8
Permendur alloy[c]	–	(48.8 ± 0.3)%	97.6
Permendur alloy	10.0%	(58.7 ± 0.7)%	97.8
Rem alloy[d]	–	(11.8 ± 0.6)%	98.3
Rem alloy	10.0%	(21.58 ± 0.6)%	98.1

Notes: [a]The water obtained from Damavand spring (Lorestan, Iran).
[b]Obtained from Sefidroud river (Guilan, Iran).
[c]Co (50%), Fe (49%), Mn (0.4%).
[d]Co (12%), Mo (17%), Mn (3%), bal Fe.

Table 3. Comparisons of the proposed method and other methods for the determination of Co.

Method	Application	Dynamic range	Detection limit	Recovery (%)	RSD (%)	Reference
Optical sensor	Water samples and SRMs	0.1–8.96 μg mL^{-1}	0.021 μg mL^{-1}	98–105	2.5 ($n=3$)	[11]
Optical sensor	Wastewater, alloy and tablet	0.1–2 μg mL^{-1}	0.07 μg mL^{-1}	–	1.5 ($n=5$)	[12]
Flow cell optosensor	–	1.0×10^{-3}–1.0×10^{4} μg mL^{-1}	7.9×10^{-6} μg mL^{-1}	–	1.6	[13]
Fibre-optic sensor	Industrial, environmental and biological samples	0.1–2 μg mL^{-1}	0.07 μg mL^{-1}	–	1.5 ($n=5$)	[14]
Optical sensor	Food samples and vitamin B12	0.5–7.66 μg mL^{-1}	0.35 μg mL^{-1}	–	1.58 ($n=7$)	[15]
Optical sensing film	Water samples and alloys	0.028–29.68 μg mL^{-1}	0.012 μg mL^{-1}	>97.5	1.96 ($n=5$)	This article

stable over the experiment with no leaching of the ionophore. The membrane was stable over a period of 4 months when not in use (membrane was kept in air) and the signal value of the membrane did not change.

The difference in the response of individual membranes was evaluated by preparing five membranes from the same mixture and the reproducibility was obtained by determining the signal of the membrane to 9 μg mL^{-1} solution of Co^{2+}. The mean absorbance was found to be 0.269 ± 0.007 with $RSD = 1.96$. The results show that the reproducibility is satisfactory.

3.9 *Response time*

The response time of the present optical sensing film is controlled by the time of required for the analyte to diffuse from the bulk of the solution towards the membrane interface to complexation with ligand. We found 70 mg PVC including 140 mg plasticiser showed the shortest response time. The dynamic response time of the optode was of the order of 15 min for 95% attainment of the final value for 2 μg mL^{-1} Co^{2+} concentration (Figure 8). The response time depends on the concentration of Co ion.

3.10 *Analytical application*

As the system has been optimised with laboratory prepared sample, the final test on the effecting of the sensing film as an environmental monitoring device is to run real water samples and alloys. The known amounts of Co(II) were added into water samples and the recovery of spiked Co(II) in these samples was studied with the proposed optical sensing film. The results are given in Table 2. The SDs of the analysis and the recoveries of the added Co to the samples show that the proposed method has capability for water samples and copper-free alloys analysis without considerable error. Table 3 presents a comparison between the proposed method and other methods for the determination of Co [11–15].

4. Conclusion

In conclusion, we have shown that a recently synthesised ionophore HDDA can be used for the development of an optical sensing film for Co ions. On the basis of the results presented in this work, the proposed Co(II) ion optical sensing film has some advantages including: easy preparation, low cost, wide dynamic range, low detection limit, good reproducibility and suitable short-term stability. This sensing membrane has potential application for determination of Co in a variety of water samples, and copper-free alloys. The sensing film can also respond quantitatively to other metal ions (Cu^{2+}, Hg^{2+}). Thus, the system could be optimised for detection of other metals, or adopted to the detection of several metals in real sample.

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