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Research Article

DEVELOPMENT AND CHARACTERIZATION OF A NEW COBALT OPTICAL SENSOR BASED ON INCORPORATTING OF SALOPHEN IN A PVC MATRIX

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ABSTRACT

A new optical sensor is described for determination of cobalt ions. The optode membrane is based on interaction of salophen (N,N′-bis (salicylidene)-o-phenylenediamine) with cobalt ions in plasticized polyvinyl chloride (PVC) membrane, supported on a glass plate. In the fabricated optode, salophen acts as sensing component. Color of the sensing membrane in contact with Co^{2+} ions at pH 5.5, was changed from yellow to orange. The membrane composition and other affecting variables were optimized. Under the optimum conditions (i.e. 29.1% PVC, 63.1% DOS, 3.9% NaTPB, 7.8% salophen and response time of 5 min.), the proposed sensor displayed a linear range of 0.1–10 μg mL^{-1} with a detection limit of 0.016 μg mL^{-1}. Also the precision (RSD %) was better than 1.34% for 7 replicate determinations of 2.5 μg mL^{-1} cobalt (II) in various membranes. The sensor showed good selectivity for Co^{2+} ions with respect to several common alkali, alkaline earth and transition metal ions. The proposed optode was used for determination of Co^{2+} ions in water samples.

Keywords*:* Optode, Poly (vinyl chloride) membrane, Cobalt ions, Salophen

INTRODUCTION

Cobalt is an important element for industry and biological systems as well[1-3]. Nowadays Cobalt is used in high-temperature alloys, in permanent magnets and its salts are useful in paint dryers as catalysts, abrasion resistant glasses, ceramics, batteries and in production of numerous pigments like cobalt blue and cobalt green, in ground coats for porcelain enamels and in electroplating industry[2]. Cobalt is a component of vitamin B_{12} which has important role in many biochemical processes, such as erythrocyte formation, and its deficiency can lead to pernicious anemia. The recommended dietary allowance (RDA) for vitamin B_{12} for adults is 2.4 mg day^{-1}, which contains 0.1 mg of cobalt[4]. However, in larger amounts it is toxic and has been reported to produce pulmonary disorders, dermatitis, nausea, vomiting, diarrhea, blood pressure, slowed respiration, giddiness cardiomyopathy, hyperglycemia and so on[1]. Thus, due to the clear need for determining of Co^{2+} ions in many industrial, environmental medicinal and food samples, recently there are a lot of techniques being developed for Co sensing. Many sensitive techniques such as spectrofluorimetry, X-ray fluorescence spectrometry, neutron activation analysis, atomic absorption spectrometry, ICP-AES, capillary electrophoresis[5] and chemiluminescence have been widely applied to the determination of cobalt[1]. The determination of trace concentration of elements usually requires separation and preconcentration steps. Several modern methods including cloud point extraction[6,7], microextraction[8,9], ion exchange[10] and solid phase extraction[11] have been applied for the preconcentration of cobalt.

Progress in the field of optical hardware has initiated the development of many chemical optical sensors (optodes or optrodes), which comprise a rapidly expanding area of analytical chemistry[12]. They offer the advantages of simple, safe, reasonable selectivity and sensitivity, ease of miniaturization and remote sensing[13,14]. Also by application of optodes possibility of simultaneous preconcentration and quantification of a target analyte with a minimum sample manipulation is available[15]. In most optical sensors, a reagent is immobilized in a solid matrix usually in the form of a monolith or a thin film. The reagents immobilized into the sensor are responsible for the extraction of the analyte into the sensing material and generating an optical signal which is proportional to the change in the concentration of the analyte[16]. Different methods including absorption, reflectance, fluorescence, scintillation, refractive index and etc. can be used for the detection and quantification of the target analyte[17]. In recent years, six optode have been developed for the detection of cobalt[4,18-22].

Salophen, which is one of the most popular symmetrical tetradentate ligands, forms complexes with various metal ions[23]. The structure of salophen is depicted in fig.1.

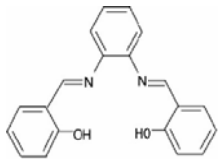

Fig. 1: Salophen's structure

Gholivand et.al reported an optode for Cu^{2+} based on this ionophore[24]. To the best of our knowledge, it has not previously been used in the development of a optical sensing film or any other techniques for Co (II) determination.

In this paper, we report a new optical sensor based on salophen as both ionophore and chromoionophore into a PVC plasticized membrane supported on a glass plate for selective, sensitive and accurate monitoring of cobalt (II) ions. The proposed optode showed good physical properties and selectivity toward Co (II) ions and was used for determination of cobalt ions in water samples successfully.

EXPERIMENTAL

Apparatus

A PerkinElmer model lambda 25 double beam UV–Vis spectrophotometer with a 1 cm quartz cells was used for recording all spectra and absorbance measurements. A Metrohm 827 pH meter (Laboratory talk company, UK) equipped with a Metrohm glass electrode was used to monitor pH.

Reagents

All reagents used were of the highest purity available and used as received. High molecular weight poly (vinyl chloride) (PVC), dioctyl phthalate (DOP), Dibutyl phthalate (DBP), Tributylphosphate (TBP), Dioctyl adipate (DOA), Dioctyl sebacate (DOS), sodium tetraphenylborate (NaTPB) and tetrahydrofuran (THF) were from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland). Demineralized water (DMW) was used throughout the experiments. Standard cobalt (II) solutions were prepared by serial dilution of a 1000 mg L^{-1} standard (Fluka, Cobalt Standard for AAS) with water. The pH was adjusted with the following solutions: HCl/KCl for pH 1

and 2, Na_2HPO_4/citric acid for pH 3, CH_3COOH/CH_3COONa for pH 4–6, KH_2PO_4/NaOH, for pH 7–8.

Synthesis of N, N′ -bis (salycilidene)-1, 2-phenylenediamine

An ethanol solution (10 mL) containing 1,2-phenylenediamine (approx 3 g) was transferred into a 150 mL quick fit round-bottomed flask, fitted with a quick fit condenser and then salycilaldehyde (approx 5 mL) was added drop wise. The mixture was refluxed for 10 h, filtered and recrystalized twice in ethanol[25].

Membrane preparation

The optode was prepared from a coating solution containing 30.0 mg PVC, 65.0 mg plasticizer (DOS), 4.0 mg anionic additive (NaTPB) and 8 mg salophen in 2 mL THF. The solution was immediately shaken vigorously to achieve complete homogeneity. Then 30 µl of coating membrane solution by glass syringe was injected onto the dust free glass plates (9 mm ×30 mm) and spread quickly by aiding of a capillary glass tube. The membrane was allowed to dry in air for a few minutes. The coating solutions is stable for several weeks if kept in a tightly closed vial in refrigerator and can be used for the construction of new membranes[26].

Absorbance measurement

Spectrophotometric measurements were performed as follows, the sensing membrane was placed vertically inside the spectrophotometer quartz cell already filled with 2.5 mL of acetate buffer of pH=5.5. Then the sample containing Co^{2+} ions in appropriate amounts was injected into the cell and absorption spectrum was recorded or absorbance was measured at 475 nm against reference glass support membrane (membrane without salophen) after 5 min (time required to reach equilibrium). Difference in absorbance which is defined as the difference between optode spectra in any time during titration and in the buffer solution were used for calculations[27].

Analysis of water samples

Water samples (Tap, mineral, river and seawater) were collected from Tehran, Damavand (damavand, east north of Tehran), Gheshlagh (Sanandaj) and Caspian sea (Zibakenar) in Iran respectively. Each sample was filtered using a 0.45 µm PTFE filter, and adjusted to approximately pH 5.5 by adding NaOH\HNO3. Then 2.5 mL of each sample first directly and then spiked with appropriate amount of Co^{2+} ions subjected to analysis by the proposed optode according to recommended procedure.

RESULTS AND DISCUSSION

Spectral characteristics

The proposed optical sensor is a bulk optode, because there is a reversible mass transfer of analyte from the sample into the bulk of the sensing layer[28]. In this optode salophen acts as both ionophore and chromoionophore. When cobalt ions diffuse into the membrane, it forms a complex with salophen and a change in the absorbance of membrane is occurred.

Fig. 2 shows the absorption spectra of salophen in acetonitril solution and immobilized salophen. The spectral change is a result of the addition of Co^{2+} and the complex formation. The absorbance maxima of the immobilized salophen are located at 335 and 475 nm and those in solution at 330 and 450 nm. Observed bathochromic shifts suggest that the structural conformation of the immobilized reagent is more planar than that of its solution analogue[29]. In subsequent studies, we selected 475 nm for absorbance measurement.

Effect of membrane composition

The membrane composition is well known to largely influence the response characteristics of the optode such as sensitivity, response time, working concentration range, detection limit and selectivity of the optical sensors[30].

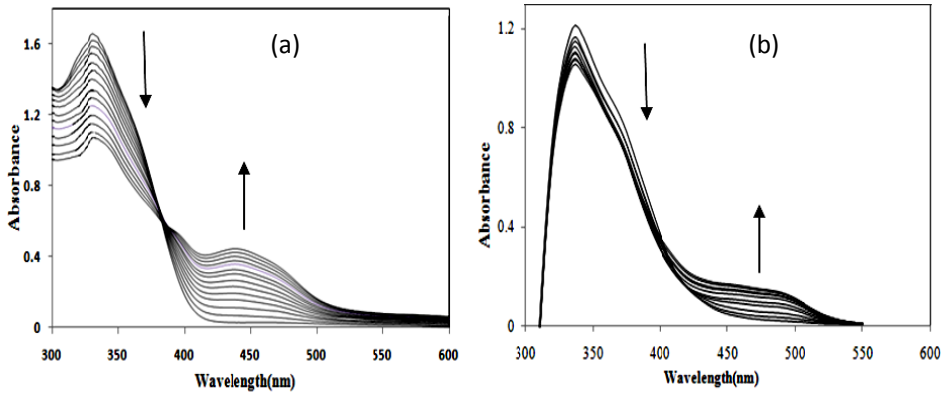

Fig. 2: (a) Absorption spectra for a 7×10^{-5} M salophen solution in the presence of Co^{2+} (0–10 ppm) in acetonitril. (b) Absorption spectra of optode film response to Co^{2+} in the range of 0–10 ppm at pH 5.5. (A–Z shows increase in concentration of Co^{2+}).

Thus the effect of membrane composition was investigated by varying proportion of the plasticizer, PVC, ionophore and lipophilic ionic additive as follows:

In order to have a homogenous organic phase, solvent mediators (plasticizer) must be physically compatible with the polymer used in membrane preparation. Several plasticizers with different polarities were tested as potential plasticizers, including DOP, DOS, DBP, TBP and DOA. The membranes were prepared from a mixture of 30 mg PVC, 60 mg of the plasticizer, 6 mg salophen and dissolved in 2 mL THF. The difference in absorbance of membrane in the presence of 2 µg mL^{-1} Co (II) at 475 nm was used as the analytical signal. Leakage% of membranes was determined by locating of membranes in buffer solution with pH=5.5 for 120 min. It was resulted that the membranes containing DBP or TBP had improper physical properties and showed leakage of the reagent at short times which indicates that these membrane solvents did not cause to a suitable signal for the proposed membrane sensor. Membranes containing DOA showed very low sensitivity.

Plasticizers such as DOP and DOS showed good sensitivity but leakage % of membranes containing DOP is higher than membrane containing DOS. DOS was the appropriate selection in order to both sensitivity and no leakage of salophen from the membrane. Results of optimization of the DOS amount have been shown in table 1. As can be seen, sensitivity of optode and leakage percent of salophen increases by higher amount of plasticizer and response time decreases. The leakage% < 10% for optode membranes are tolerable in literature[31]. Thus a membrane containing 65 mg DOS (63.1%) was selected as a suitable amount for plasticizer.

In bulk membrane optodes, the membrane must be in thermodynamic equilibrium with the sample, a mass transfer of analyte into the membrane is required and presence of anionic additive facilitates the ion-exchange equilibrium[32]. The effect of NaTPB was investigated in the range of 0-6 mg. The results are given in table 1. As can be seen the presence of NaTPB cause to increasing of sensitivity significantly and highest absorbance is achieved by using 4 mg of NaTPB. At lower amounts, absorbances were decreased, and at higher quantities the leakage% of salophen is observed. Therefore, 4 mg NaTPB (3.88%) was selected as optimal amount in the membrane composition.

Salophen acts as sensing component in fabricated optode. Thus it is necessary to study the influence of its amount on the response of membrane. It was carried out using different concentrations of salophen in the range of 1–10.0 mg/2 mL and the difference in absorbance was measured for Co (II) in 2 μg mL^{-1} at 475 nm. Results were shown in Fig.3. As seen, the absorbance increased by increasing amounts of salophen up to 8.0 mg and higher amounts of salophen did not improve the sensitivity. Therefore 8.0 mg salophen (7.8 %) was selected as optimum value. The optimum membrane composition incorporates 30 % PVC, 63.1% DOS, 3.9% NaTPB, and 7.8% salophen.

Table 1: Effect of amount of DOS and NaTPB on the response of the proposed optode

Membrane	PVC (mg)	DOS (mg)	Salophen (mg)	NaTPB (mg)	Response time (min)	Absorbance (475 nm)	Leakage%
1	30	55	6	2	9	0.054	2.9
2	30	60	6	2	7	0.082	4.1
3	30	65	6	2	5	0.141	6.3
4	30	70	6	2	5	0.197	11.2
5	30	65	6	0	10	0.06	0.82
6	30	65	6	2	5	0.134	5.8
7	30	65	6	4	5	0.143	7.1

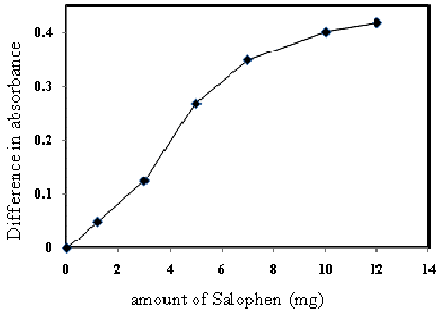

Fig. 3: Effect of salophen amount on the absorbance of membranes. [Co^{2+}]= 2 μg mL^{-1}, pH=5.5, time = 5 min, membrane layer contained = 30.0 mg of PVC, 65.0 mg DOS, and 4.0 mg NaTPB

Effect of pH

Effect of pH on cobalt ions uptake with optode was studied over the range of 2.5–9.0. In these studies membranes with optimum compositions was equilibrated with Co^{2+} (2.5 ppm) solutions for 5 min. Then the difference in absorbance of the membranes was measured at 475 nm. Results were shown in fig.4. As can be seen, by increasing pH, the response of membranes increases and the sensor response is maximum at pH= 5.5. At lower pH (<3.5) signal is low because of the extreme leakage of salophen. At higher pH values, the analytical signal decreases due to the possible formation of hydroxide species of Co (II). Thus a buffer of pH=5.5 was selected for further studies.

Other properties of membrane

The equilibrium response time is a very important factor in optical sensors. It is controlled by the time required for the analyte to diffuse from the bulk of the solution toward the membrane interface to associate with ligand[33]. If the diffusion of the complex in the membrane phase is the limiting step, $t_{95\%}$ is given approximately by[34]:

$$t_{95\%} = \frac{1.13d^2}{D_m} \quad (1)$$

Where d and D_m are the membrane thickness and the mean diffusion coefficient of the species in the membrane phase, respectively. In order to determine the response time of the proposed optode, the difference in absorbance of optimized membrane was recorded in the presence of Co^{2+} ions in 1.5, 3 and 8 ppm at pH=5.5 during the time of 0-25 min in 475 nm. Results depicted in fig. 5. It is obvious from figure that the 95% of maximum absorbance achieves within 5 min. We used 5-10 min equilibration time in subsequent experiments.

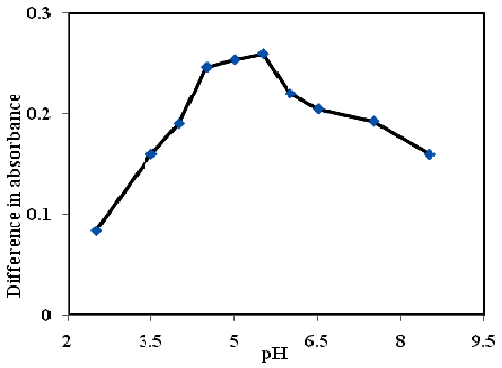

Fig. 4: Effect of pH on the absorbance of the proposed optode; conditions: [Co^{2+}] = 2.5 μg mL^{-1}, time= 5 min, membrane layer contained = 30.0 mg of PVC, 65.0 mg DOS, 8.0 mg salophen and 4.0 mg NaTPB.

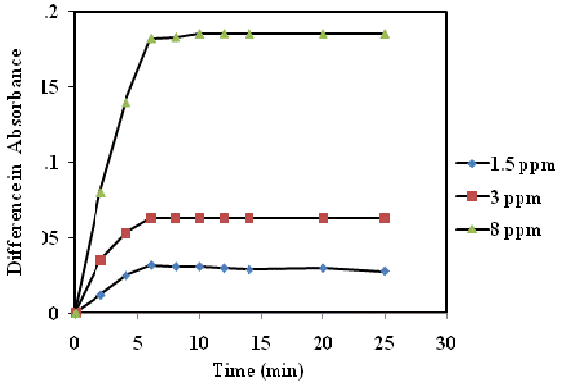

Fig. 5: Response time of the optode membranes in different concentration of Co^{2+} ions; conditions: membrane layer contained = 30.0 mg of PVC, 65.0 mg DOS, 8.0 mg salophen and 4.0 mg NaTPB, pH=5.5.

The relative standard deviation in this condition was 2.41%. This indicates that no significant leakage of the dye occurred during this period. When the membrane was exposed to light, no drift in signal occurred. The optode membrane was stable for 1 month in air.

One of the main characteristics of an optical sensor is its regeneration which allows using the sensor many times leading to consumption of small amount of reagent [35]. The regeneration of the proposed membrane sensor was studied by the use of different reagents including HCl, HNO_3, H_3PO4, NaF, EDTA, KSCN and salicylic acid in different concentrations. It was found that none of above reagents could regenerate optode membrane. In acidic media extreme leakage of membranes was seen and absorbance of optode was decreased. Therefore each optode can be used as a disposable sensor for solutions containing Co^{2+} ions.

Analytical characteristics

Analytical characteristics of the optimized membrane, including regression equation, linear range, limit of detection and reproducibility of cobalt determination were summarized in table. 2 The limit of detection estimated as the concentration of analyte producing an analytical signal equal to three times the standard deviation of the blank signal was 0.016 μg mL^{-1}. Also the relative standard deviation (RSD %) for 7 replicate determinations of 2.5 μg mL^{-1} Co in various membranes was 1.34 %. This indicates that the responses of manufactured membranes are reproducible and no significant difference of the individual measurements occurred during the experiments.

Selectivity

To determine the selectivity of the optode membrane, the experiments were carried out by fixing the concentration of Co (II) at 2 ppm under the optimized condition and recording the absorption spectra before and after adding the interference ions with varying concentrations. The interferences investigated were cations that may interaction with salophen in the membrane or species that may react with cobalt ions, and thus decreased the diffusion efficiency. Results were shown in Table. 3. The tolerance limit was defined as the concentration of added ion causing less than ±5٪ relative error. It is shown that presence of alkaline metals and anions such as nitrate, sulfate, chloride and others did not have any adverse effects on cobalt uptake. As can be seen, cations such as Cu^{2+}, Fe^{2+} and Fe^{3+} can interfere with the determination of Co^{2+} at different ratios. Response of the proposed optode for the copper (II) ions in lower mole ratios to the Co^{2+} ions is the formation of absorption band in 420 nm which do not have serious effect on absorption band of Co^{2+} in 475 nm. In the case of Fe^{2+} and Fe^{3+} extreme changes occurred in absorption spectra. Interference of them can be eliminated by the addition of appropriate amount of KSCN as masking agent.

Table 2: Analytical characteristics of the proposed method

Characteristic	Value
Linear range (μg mL^{-1})	0.1–9.2
Regression equation (n = 7) (C, μg mL^{-1})	$A = 0.024C - 0.0065$
Correlation coefficient (R^2)	0.9994
Reproducibility (R.S.D., %) (n = 7, $[Co^{2+}]$=2.5 μg mL^{-1})	1.34
Limit of detection (μg mL^{-1}) (n=5)	0.016

Validation and application

In order to confirm the usefulness of the proposed method, it was applied to the determination of Co (II) in real water samples. The results were shown in Table. 4 The mean recoveries for the addition of different concentration of cobalt to water samples were in the range of 93-100.5%. The results showed that the proposed method could be successfully applied to determination of cobalt in real water samples.

Table 3: Tolerance limits of interfering ions in the determination of 2 ppm Co^{2+}

Ions	Interferent-to-analyte ratio
Li^+,Na^+,K^+,Mg^{2+},Ca^{2+}, Pb^{2+},Ni^{2+}, Sn^{2+},Al^{3+},Cd^{2+},Zn^{2+},Sb^{3+}, Cr^{3+}, F^-, Cl^-,SO_4^{2-} ,EDTA, NO_3^-, CH_3COO^-, PO_4^{3-}, ClO_4^-	1000:1
Cu^{2+}	10:1
Fe^{3+} , Fe^{2+}	2:1

Table 4: Determination of Co^{2+} in water spiked samples

Samples	Co^{2+} (ppm)		
	Added	Found	Recovery(%)
Tap water	0.0	0.03±0.01 [a]	-
	3	2.92±0.05	97.3
	8	8.04±0.01	100.5
River water	0.0	0.05±0.07	-
	3	2.82 ±0.06	94
	8	7.91±0.05	98.8
Sea water	0.0	0.08±0.05	-
	3	2.79 ±0.02	93
	8	7.88 ±0.03	98.5
Mineral water	0.0	0.03±0.02	-
	3	2.93 ±0.04	97.7
	8	7.95±0.03	99.3

a:Mean±S.D. (n = 3)

CONCLUSION

The proposed method gives a precise, sensitive, low cost and selective procedure for determination of cobalt, based on optical membrane sensor. A comparison of the proposed optode with the previously reported optical sensors for cobalt (table 5) reveals that the properties of proposed optode are comparable with others. It provides a wide dynamic range, reliable reproducibility and a good limit of detection and also its response time and selectivity toward cobalt among other cations and anions is satisfactory.

It is worthy to note that salophen has not previously been used in the development of an optical sensing film or any other techniques for cobalt determination and it can be applied to the water samples containing trace amounts of this element successfully.

Table 5: Optical sensors reported for the determination of Co (II).

Ref	Reagent	linear range (ppm)	LOD (ppm)	Measured signal	response time (min)
21	CHQMBDCD[1]	0.03-1200	0.006	fluorescence	5
18	pyrogallol red	0.102-9.12	0.022	absorption	2
19	PAN[2]	0.02–0.5	0.01	absorption	20
19	reagentless fiber-optic sensor	0.1–2	0.07	absorption	-
20	HDDA[3]	0.028–29.68	0.012	absorption	15–25
4	methyltrioctylammonium chloride	0.51–7.8	0.354	absorption	7
22	PAR[4]	0.001-10000	7.9×10^{-6}	reflactance	-
Present Work	salophen	0.1-9.2	0.016	absorption	5

[1.] 7-[(5-chloro-8-hydroxy-7-quinolinyl)methyl]-5,6,7,8,9,10-hexahydro-2H-1,13,4,7,10-benzodioxatriazacyclopentadecine -3,11(4H,12H)-dione.

[2.] 1-(2-pyridylazo)-2-naphthol

[3.] N^5-(2, 4-dinitro-phenyl)-N^1, N^1-diethyl-penta-1,3-diene-1,5-diamine

[4.] 2-(4-prydilazo) resorcinol

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