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Fabrication of a New Selective Optical Sensor for Cobalt Determination Using 1-Nitroso-2-naphthol and Monitoring of Cobalt in Water Samples

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In this study, the researcher has focused on manufacturing a new, highly selective, and simple optical membrane for determining cobalt(II) ions in aqueous solutions. The cobalt(II) is first oxidized when using hydrogen peroxide (H₂O₂) solution to eliminate the effect of the concomitant species and increase the selectivity in the determination of cobalt(II) in real samples. The cobalt(II) ions were determined by recording the absorbance intensity of the new selective and sensitive thin optically transparent sensor. 1-Nitroso-2-Naphthol (1N2N) is used as a sensitive, selective, and stable complexing ligand to change the absorbance of the transparent membrane in the presence of cobalt(II). The ready-made optical sensor indicated good reproducibility, a relatively long lifetime, and stability with an appropriate linear response from 0.1 to 5.0 mg l⁻¹. The detection limit was calculated as 0.03 mg l⁻¹. Further investigations were evaluated intra-day and inter-day precision (RSD%) 2.76-4.46% and 0.89-5.39%, one after another, and the average percentage of relative error (RE%) was in the range of 1.89 to 3.41. The results indicate that the utilized method successfully determined cobalt(II) in different water samples containing tap water, seawater, and spring water, without pretreatment.

Keywords: Cobalt, Optical sensor, 1-Nitroso-2-naphthol, Spectrophotometry, Ion-selective film

INTRODUCTION

Cobalt is a rare metal with a variety of commercial, industrial, and military usages, and it is also an essential element in the performance of many biological processes, as in the molecular structure of vitamin B12 [1-3]. However, a large amount of this metal harms human health and may cause some diseases such as lung and heart disorders [4]. There are various sensitive and selective, fast methods here to be used for determining and evaluating cobalt ions in environmental samples, such as inductively coupled plasma atomic emission spectroscopy (ICP-AES) [5] and flame atomic absorption spectroscopy [6]. These expensive instruments incur high running costs and must be under well-controlled experimental conditions. In recent years, chemical

sensors containing ion-selective electrodes and optical sensors are simple, cheap, and fully portable devices for evaluating cobalt [7-21]. Optical chemical sensors (optodes) are suitable and sensitive tools and the cheapest, efficient, insoluble chelating agents. The ligand immobilized in the sensor is responsible for extracting the target ions into the sensing material [22-25]. Since most ligands are soluble in water, lipophilization by forming ion pairs is commonly used to slow the leaching process [26-29]. Signals made with ligands that can minimize the interference of the real sample matrix are measured with this method. Some metal ions that form stable complexes with 1-nitroso-2-naphthol of ligand can selectively react with cobalt under specific conditions [30]. However, no report has yet been published on its use for developing a photosensor method. This study describes the preparation and responsive characteristics of a new susceptible optical sensor based on the immobilization of

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1-nitroso-2-naphthol in a PVC membrane to determine Co(III) ions. According to this method, cobalt(II) ions are first oxidized by hydrogen peroxide solution (H_2O_2) at 60 °C, and then the absorbance intensity of the transparent membrane is changed into the obtained cobalt(III) ions by complexing the selective immobilized 1N2N ligand.

EXPERIMENTAL

Instruments and Apparatus

A UV-Vis spectrophotometer model S2150 SERIES (China) was used to record the spectra and absorbance of a transparent membrane coated on glass slides. The 1N2N ligand was immobilized with PVC on a glass substrate as a selective optical sensor, and the batch method was used for all measurements. The pH meter model HANNA HI 8314 (Romania) with combined glass electrode was performed for pH measurement after calibration against standard Merck buffers. The heating and stirring was performed using a hot plate R-50 (Iran) heater.

Reagents and Solution

Cobalt(II) nitrate.6H₂O, 1-nitroso-2-naphthol, dioctyl phthalate, sodium tetraphenylborate, polyvinyl chloride, Tetrahydrofuran (THF) and all other chemicals used were of analytical grade and were purchased from Merck Company. Deionized water was used all over the experiments. A 1000 mg l⁻¹ of cobalt(II) stock solution was prepared by dissolving the appropriate weight of cobalt(II) nitrate.6H₂O and diluting it to 100 ml in a volumetric flask. Its working solution was prepared freshly by diluting the stock solution with deionized water. Hydrogen peroxide (35%) and 1-nitroso-2-naphthol (1N2N) were used as oxidants and complexing agents, respectively. The acetate/acetic acid buffer solution was prepared by dissolving 5 g of Sodium Acetate (CH₃COONa.5H₂O) and 10 ml of acetic acid and then diluting to 40 mL with deionized water. The certified reference materials (CRMs) analyzed by the presented method were NCS DC 73301 (Rocks constituents) and JSd-3 (stream sediments from the geological survey of Japan).

Fabricated Optical Sensor

The optical sensor was made by immobilizing the selective ligand within the PVC membranes. For this

purpose, 2 mg of ligand (1N2N), 78 mg of DOP, 3 mg of Na-TPB, and 39 mg of PVC were added to a beaker (10 ml) and dispersed with 3 ml of THF to achieve a transparent and homogeneous gel solution mixture. Then, 25 microliters of the homogenized gel solution were placed on a small glass substrate (thickness 0.1 mm, width 9 mm, height 60 mm) to form a thin membrane film layer. The prepared membrane was dried at room temperature for 15 min and then in a clean dish for 12 h to completely evaporate the solvent. When membranes are not used, they are stored in a clean, dry environment. The glass substrate was first cleaned with a diluted solution of sulfuric acid and sodium hydroxide and then distilled water, respectively. Finally, the membrane was placed in an oven heated to 110 °C for 30 min.

Analytical Procedure

Ten milliliters of stock sample solution (in the linear range of concentration) of cobalt(II) and 1 ml of H₂O₂ as an oxidant were mixed into a beaker, and pH was controlled at 4.5 with an acetic acid/acetate buffer solution; the mixture was heated to 60 °C for 35 min, then cooled to ambient temperature. The optical sensor membrane was suspended in the solution, and the mixture was agitated for 15 min by stirring at 1500 rpm. The color of the membrane became red due to the formation of the Co(1N2N)₃ complex solution. After this step, the absorption spectrum was recorded against a blank reference membrane in the 400-700 nm wavelength region.

RESULTS AND DISCUSSION

To make a suitable optical sensor membrane, a sensor material must be selected according to different aspects, such as response rate, selectivity, sensitivity, stability, and lifetime. 1N2N is a sensitive and selective complexing agent for the spectrophotometric determination of cobalt(II). Figure 1 shows the absorption spectra of the cobalt complex, which has a maximum absorbance of 415 nm. With increasing concentrations of Co²⁺ to the 1N2N thin film membrane, the intensity of the absorption band increases at 415 nm, which is attributed to the formation of Co (1N2N)₃ complexes in the membrane and their subsequent complexation and chelation by ligand.

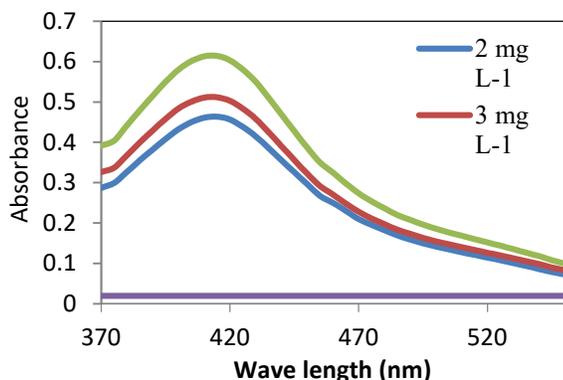


Fig. 1. The absorption spectra of cobalt complex. $\text{Co}(\text{1N2N})_3$ has a maximum absorbance at 415 nm.

Calibration Curve and Dynamic Response Time

The differential absorbance (DA) values of the proposed optical membrane (absorption difference after and before adding the metal ion solution to the membrane cell) were plotted at different concentrations of Co^{2+} . The results are shown in Fig. 2. It was found that the linear ranges were 0.1 to 5.0 mg l^{-1} for Co^{2+} , and as increasing the concentration of Co^{2+} up to 5 mg l^{-1} , the absorbance change was constant, and in most additions, the membrane was saturated, and the curved linear state disappeared. The calibration equation was $A = 0.123C + 0.033$ with a correlation coefficient of 0.9982, where C was the concentration of cobalt(II) in mg l^{-1} .

The limit of detection (LOD) was evaluated at 0.03 mg l^{-1} by crossing over a point of the lines fitted to the linear parts of the DA vs. Co^{2+} concentration curve in Fig. 2. Therefore, the obtained detection limit shows that the selected optical sensors help determine small amounts of Co^{2+} in real samples without needing a pre-concentration method. The dynamic response time was followed by studying DA versus time by varying the concentration of Co^{2+} ions in solutions in the 0.1 to 5.0 mg l^{-1} range. It was found that the optical membrane takes 15 min to reach its equilibrium response values for Co^{2+} ions. A comparison of this method with other similar methods is given in Table 1.

Extraction Time and Stirring Rate

To achieve good precision and maximum sensitivity, the equilibrium of Co-1N2N complex formation between an optical sensor based on 1N2N complex (as acceptor) and

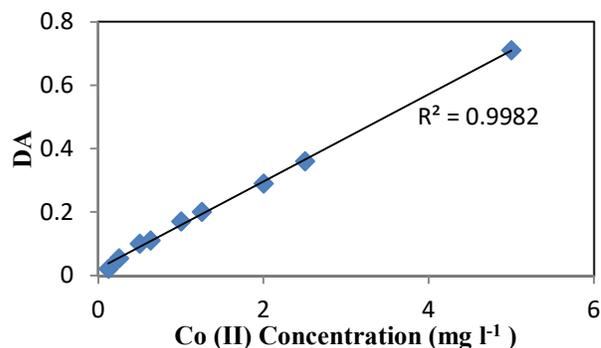


Fig. 2. Calibration plot of DA against Co^{2+} ion concentration (vs. mg l^{-1}) for the proposed optical membrane at 415 nm, pH = 4.5.

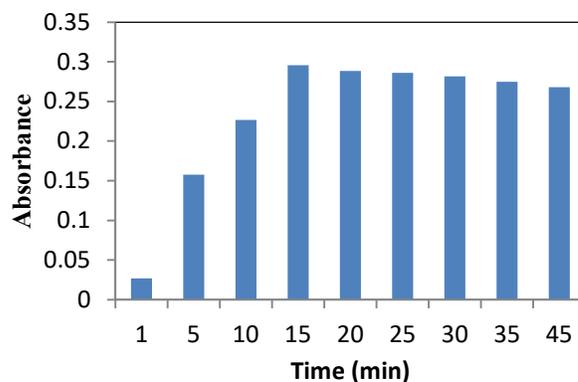


Fig. 3. Effect of extraction time on the absorbance of cobalt ions, conditions were: 2 mg l^{-1} Co^{2+} , acetate/acetic acid buffer at pH 4.5, and 9000 rpm stirring rate in ambient temperature.

aqueous oxidation solution (as donor phase) must be completed. So the extraction time was investigated from 1 to 45 min in optimal conditions for Co-1N2N complex formation. Figure 3 shows that the absorbance reaches its maximum value at 15 min and decreases slowly during longer extraction times. Therefore, after 15 min of stirring time, the equilibrium reaches up; this is considered the optimal extraction time for subsequent analysis. The stirring rate is one of the important factors that affect on equilibrium rate of Co-1N2N complex formation. Therefore, the agitator rotation range (200-1700 rpm) was investigated. The results show that it directly affects the adsorption, and by increasing the stirring rate, the adsorption increases to the maximum and

Table 1. Comparison of Optical Sensors Reported for the Determination of Cobalt(II) with Proposed Method

Reagent or indicator	Dynamic range (mg l ⁻¹)	Detection limit (mg l ⁻¹)	Ref.
Pyrogallol red	0.1-8.9	0.02	31
1-(2-Pyridylazo)-2-naphthol	0.1-2.0	0.07	32
2-(4-Pyridylazo)resorcinol	1.0×10^{-3} - 1.0×10^4	7.9×10^{-6}	33
Methyltriocetylammmonium chloride	0.5-5.6	0.35	28
Disodium-1-nitroso-2-naphthol-3,6-disulfonate	1.0-60.0 ^a	0.82	34
1-Nitroso-2-naphthol	0.1-5.0	0.03	Present work

^aVolume = 3 ml.

is inhibited by rotating the stirrer.

Temperature Effect

Since temperature is a significant factor in the reaction rate, its effect on the cobalt(II) oxidation rate has been carefully studied. For this purpose, the thermostat bath was programmed to gradually change and control the temperature in the 20-80 °C range and the oxidation rate of Co²⁺ to Co³⁺ with H₂O₂ at constant oxidation time (35 min) was investigated. The results in Fig. 4 confirm that temperature significantly influences the absorbance value. On the other hand, this is in agreement with a higher oxidation rate due to temperatures up to 60 °C. So, the oxidation process of Co²⁺ to Co³⁺ with H₂O₂ was performed at 60 °C.

Lifetime, Short-term Stability, Reproducibility, and Regeneration

The lifetime of the optical membranes was evaluated by preparing 10 different optical membranes simultaneously and storing them in a 20% ethanol vapor at 4 °C. After one week, the mean absorbance at 415 nm before and after this period was 0.45 ± 0.05 and 0.49 ± 0.08 , respectively. According to these results, when the optical membrane is not used, they should be carefully stored in 20% ethanol vapor at 4 °C, and they were stable for at least one week. To determine the short-term stability of the optical membranes, the absorption of optical membranes in contact with a 2.0 mg l⁻¹ Co²⁺ solution (pH = 4.5) was measured for 3 h after every 30 min (n = 6).

Responses were found to be approximately complete, with only a 2.01% increase in absorption after 3 h of monitoring. The reproducibility of proposed optical membranes was tested by preparing 12 different membranes

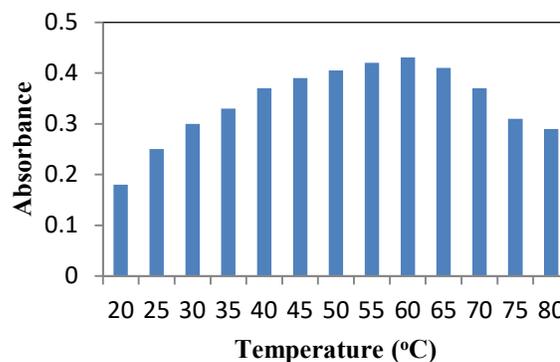


Fig. 4. Effect of temperature on oxidation of Co²⁺ ions (3.0 mg l⁻¹) with H₂O₂, conditions were: 2 mg l⁻¹ Co²⁺, acetate/acetic acid buffer at pH 4.5, and 9000 rpm stirring rate in ambient temperature.

under the same conditions, and the absorbance signal of prepared membranes was measured in 2.0 mg l⁻¹ Co²⁺ (pH = 4.5) solutions. The coefficient of variation for Co²⁺ concentration was $\pm 1.89\%$. The proposed optical membrane regeneration was investigated by monitoring optical membrane absorbance signals when the solutions change from high concentrations to low concentrations of Co²⁺ ions or after immersion of an optical membrane used in a chelating solution such as EDTA. The final absorption of the optical membrane has reached about 17% of the initial membrane absorption, indicating that the recovery is not complete.

Accuracy and Precision

To further investigate the accuracy and precision of the proposed optical membrane, a similar experiment was repeated four times on many produced membranes in one and

Table 2. Evaluation of Intra-day and Inter-day Accuracy and Precision

Co ²⁺ concentration ^a	Intra-day accuracy and precision (n = 4)			Inter-day accuracy and precision (n = 4)		
	Co ²⁺ mean measured ^a ± CL ^{a,b}	RSD% ^c	RE% ^d	Co ²⁺ mean measured ^a ± CL ^{a,b}	RSD% ^c	RE% ^d
1.00	1.02 ± 0.10	4.46	2.0	1.02 ± 0.14	5.39	2.0
2.00	2.04 ± 0.12	2.76	2.0	2.06 ± 0.21	4.81	3.0
3.00	3.09 ± 0.18	2.77	3.0	3.10 ± 0.60	0.89	3.3

^aThe values are in mg l⁻¹ range measured. ^bCL, confidence limits were calculated from $CL = \pm t.S/(n)^{1/2}$. The tabulated value of t is 4.303 at the 95% confidence level; S = standard deviation and n = number of measurements. ^cRSD%, relative standard deviation. ^dRE%, percent relative error, $\{RE\% = [(concentration\ found - known\ concentration) \times 100 / known\ concentration]\}$.

consecutive days for the three concentration levels of Certified Reference Materials (CRMs) to determine intra-day and inter-day accuracy and precision, respectively. Its significant digits were calculated for cobalt(II) solutions at three different concentration levels as shown in Table 2. The accuracy was evaluated based on the means percentage relative error (RE%) between the measured mean concentration and the validated concentration of Co²⁺ then calculated at each concentration as follows:

$$RE\% = [(validated\ concentration - known\ concentration) \times 100 / known\ concentration]$$

Values ranged between 1.89 and 3.41. Thus, the precision was defined as relative standard deviation values in percentage (%RSD) for intra-day and inter-day precision and was 2.76-4.46% and 0.89-5.39%, respectively. These results indicate a high accuracy, good precision, and reproducibility of the proposed optical sensor.

Selectivity

To evaluate the selectivity of 1N2N ligand, several optical membranes were prepared under the same conditions. The optical sensor spectra were recorded for a 2.0 mg l⁻¹ Co²⁺ ion solution exposed to different levels of potential interfering mineral cations under optimal conditions. To this end, the tolerance ratio (RT) has been defined as follows:

$$TR = [M^{n+}] / [Co^{2+}]$$

Where the [Co²⁺] and [Mⁿ⁺] are the concentration of the target, the interfering ions cause a relative error of 5%,

Table 3. Tolerance Ratio (TR) for Different Interfering Ions in the Determination of Co²⁺

Interferent ^a	TR ^b	Interferent ¹	TR ²
Na ⁺	93.8	Cd ²⁺	214.3
K ⁺	39.5	Cu ²⁺	208.3
Mg ²⁺	241.9	Fe ³⁺	83.3
Ca ²⁺	192.3	Pb ²⁺	46.9
Zn ²⁺	107.1	Mn ²⁺	20.8

^aOptical sensor was examined using a 2.0 mg l⁻¹ solution of Co²⁺ ion and pH = 4.0-5.0. ^bTolerance Ratio: Ratio of the concentration of interfering ion over the concentration of Co²⁺ ion that caused a relative error of 5%.

respectively. The tolerance ratios obtained for the potentially interfering ions Mⁿ⁺ are presented in Table 3. These results indicate that the 1N2N ligand used in optical sensors interacts selectively with cobalt ions under optimum conditions. So Co(II) can be determined in excess amounts of potential environmental interactions of coexisting ions in industrial waste and environmental waters in real samples by using the proposed optical sensor.

Further Capability and Application

For further investigation, the accuracy and recovery of a proposed optical sensor was assessed for environmental samples and two certified reference material samples (NCS 73301 and JSd3) without any pretreatment techniques. In Table 4, the results were evaluated by using spike and real samples, including tap water, seawater, and spring water. The

validated values obtained for the analysis of CRMs are presented in Table 5. As shown by the results presented in Tables 4 and 5, the spike and CRMs values confirm the resulting method. In table 5, the results were treated using the statistical t value ($t_{\text{experimental}} = 3.06$ for NCS DC 73301 sample and $t_{\text{experimental}} = 3.76$ for JSd-3 sample, $t_{\text{critical}} = 4.3$) and no significant differences were observed at a 95% confidence level ($n = 3$).

CONCLUSIONS

A rapid, selective, well-stabled, and lifetime optical sensor which uses 1-nitroso-2-naphthol as ligand has been

Table 4. Results (Mean \pm Standard Deviation Based on Three Replicate Analysis) of Determination of Cobalt in Real Samples

Sample	Spiked (mg l ⁻¹)	Found (mg l ⁻¹)	Recovery (%)
Tap water ^a	0	ND	-
	2.0	2.04 \pm 0.06	102.0
	3.0	3.09 \pm 0.09	103.0
Spring water ^b	0	ND	-
	2.0	1.99 \pm 0.10	99.5
	3.0	3.10 \pm 0.06	103.3
Seawater ^c	0	ND	-
	2.0	1.95 \pm 0.06	97.6
	3.0	2.94 \pm 0.06	98.0

ND: not detected. ^aObtain from Mashhad, Iran. ^bObtain from Now Chah, Mashhad, Iran. ^cCaspian Sea, Iran.

Table 5. The Results (Mean \pm Standard Deviation Based on Three Replicate analyses) of the Analysis of the Certified Reference Materials (CRMs)

Sample	Certified (mg l ⁻¹)	Found (mg l ⁻¹)	Recovery (%)
NCS DC 73301	3.4	3.21 \pm 0.062	94.41
JSd-3	12.7	12.38 \pm 0.085	97.48

used to determine cobalt(II) ions in real samples. 1N2N is a selective ligand in optical membrane sensors to make stable complexes with cobalt(III) ions obtained by cobalt(II) oxidation. This method is able to determine the low concentration of cobalt(II) ions on various real samples such as tap water, seawater, and spring water with high accuracy, precision, and low costs.

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