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Utilization of a plasticized PVC optical sensor for the selective and efficient detection of cobalt(II) in environmental samples

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A novel sensitive, selective, and reversible cobalt(II) ion optical sensor was prepared by the incorporation of 5-[*o*-carboxyphenylazo]2,4-dihydroxybenzoic acid [CPDB] and sodium tetraphenylborate (NaTPB) in a plasticized polyvinyl chloride (PVC) membrane containing dioctyl adipate (DOA) as a plasticizer. The influence of several parameters such as pH, base matrix, solvent mediator and reagent concentration was optimized. A comparison of the obtained results with those of previously reported sensors revealed that the proposed method, in addition to being fast and simple, provided a good linear range (0.05–45.20 μM) and low detection limit (0.015 μM). Low detection and quantification limits and excellent selectivity in the presence of interfering ions such as Fe^{3+}, Cu^{2+}, Ni^{2+}, Ag^{+}, Au^{3+}, Cr^{3+}, Cd^{2+}, Zn^{2+}, Hg^{2+}, and SO_4^{2-} make it feasible to monitor Co^{2+} ion content accurately and repeatedly in environmental samples with complicated matrices. The optode was regenerated successfully using 0.3 M nitric acid (HNO_3) solution while its response was reversible with a relative standard deviation (RSD) lower than 1.9% for seven replicate determinations of 20 μM Co^{2+} in various membranes. The optode was stable and was stored for at least 15 days without observing any change in its sensitivity.

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Introduction

Environmental pollutants have attracted attention due to their ability to gradually accumulate in the human body through the food chain and cause diseases and additional complications. In recent years, all over the world, heavy metal pollution has become a serious concern due to the increase in urban development and industry. As a constituent of vitamin B_{12}, cobalt is a critical metal in the environment, having important roles in the body. Depending on its concentration, it can be an essential metal but can also be toxic for many living beings.[1] In the medicine and toxicology fields, the assessment of trace levels of Co^{2+} ions plays a significant role in environmental sample evaluation.[2] Owing to its inexpensive procedures, colorimetry is a frequently used analytical technique for assessing ultra-trace metals in biological samples. Preliminary preconcentration and sample clean-up procedures are required to determine trace metals because of their low abundance and high complexity.[3,4]

A variety of sensitive and selective analytical methodologies such as electroanalysis,[5] atomic absorption spectrometry (AAS),[6] flame atomic absorption spectrometry (FAAS),[2,7–12] electrothermal atomic absorption spectrometry (ET-AAS),[13,14] chemiluminescence,[15] X-ray fluorescence,[16] laser-induced thermal lens spectrometry,[17] neutron activation analysis (NAA),[18] inductively coupled plasma optical emission spectroscopy (ICP-OES),[19,20] inductively coupled plasma mass spectrometry (ICP-MS),[21] and spectrophotometry[22–30] have been demonstrated for the assessment of cobalt in various samples. However, many of these methods involve the risk of sample contamination and analyte loss due to the sample preparation and preconcentration steps. Among these techniques, spectrophotometry is the most convenient one due to its simplicity, availability, specificity, and low cost.

Many types of samples in their natural state cannot be analyzed due to the presence of analytes at ultra-trace levels. Furthermore, due to a great demand for analytical techniques in the environmental field, the established sample number has also been increased by these labs. The methodologies of optical sensor optodes have been prescribed to separate and/or preconcentrate the analyte, thereby defining the detection limits of current instrumentation. To achieve high sensitivity and productivity, coupling between optical sensor optodes and colorimetry has been shown to be an effective strategy.

To ensure operator safety and environmental preservation, green analytical chemistry studies various analytical procedures that minimize toxic substance consumption, reagent use, waste generation and waste decontamination.[31] Recently, optical sensors have been of great interest in analytical chemistry.[32–35] In clinical and environmental monitoring, optodes have played a significant role owing to their miniaturization potential, good flexibility, electrical interference freedom, low cost and remote

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sensing potential. Moreover, it is possible to develop optical sensors for species that cannot be sensed in other ways.

These sensors usually consist of diverse reagents that are immobilized by applying diverse procedures within appropriate membranes, wherein analyte mass transport into the membrane changes its optical characteristics. The ideal sensor must possess a rapid response time, long lifetime and reversibility, which are affected by the immobilization technique used.[36–39]

Lately, many optodes have been synthesized with diverse membranes. In most of these sensors, the reagent is immobilized by simple adsorption onto the membranes, covalent bonding or entrapment.[40–43] Transparent triacetyl-cellulose has been extensively applied for chemical reagent immobilization as a polymeric membrane. Many spectrophotometry-based optodes have several drawbacks such as high detection limits, vast interfering effects of ions, and narrow ranges of assessment. To exhibit good sensitivity and selectivity toward Co^{2+} ions, the 5-[*o*-carboxyphenylazo]2,4-dihydroxybenzoic acid (CPDB)[44] ionophore has been applied, which well enhances the detection limits, decreases the effect of interference, and widens the concentration range. Previously reported optical sensors depending on a one-at-a-time approach have various limitations such as high experiment number (which is expensive due to costly reagent consumption) and possible errors in the optimum value attainment of variables and their consequences.

In our laboratory, CPDB was synthesized and used to determine cobalt in synthetic mixtures and in pharmaceutical formulations.[44] The goal of the present study is to successfully incorporate this reagent in plasticized PVC film to construct a novel optical sensor for Co^{2+} determination. The sensor response time and pH value were optimized separately. The influence of several parameters such as pH, base matrix, solvent mediator, and reagent concentration were optimized.

Experimental

Chemicals

All the chemicals were of analytical grade. Low molecular weight polyvinyl chloride (LPVC, mol wt $\approx$ 48 000 g mol^{-1}), tetraphenylborate (NaTPB), dioctyl adipate (DOA), sodium dibutylphthalate (DBP), tributylphosphate (TBP), dioctylphthalate (DOP), *o*-nitrophenyloctyl ether (*o*-NPOE) and tetrahydrofuran (THF) were used without purification.

5-[*o*-Carboxyphenylazo]-2,4-dihydroxybenzoic acid (CPDB) was prepared as described in our previous work.[44] Universal, thiel, phosphate, borate and acetate buffer solutions at different pH values of 2.0–12 were prepared as described previously.[45] 0.01 M stock solutions of interfering ions were prepared by dissolving appropriate amounts of suitable salts in double-distilled water.

Stock solutions of Co^{2+} (1.7×10^{-3} M) were prepared by dissolving 0.4947 g of the respective pure nitrate salt $Co(NO_3)_2 \cdot 6H_2O$ (Merck, Darmstadt, Germany) in the minimum amount of deionized water, completed to the mark of a 100 mL measuring flask with water, and standardized volumetrically against EDTA. Working standard solutions were obtained daily by the suitable stepwise dilution of the stock solutions with deionized water and shaking them just before use.

Instrumentation

An Orion research model 601 A/digital ionalyzer pH meter was used to check the pH of the solutions. A Shimadzu model 670 atomic absorption spectrometer with flame atomization was used. The operating parameters were set as recommended by the manufacturer. Atomic absorption measurements were carried out in a nitrous oxide-acetylene flame. A UV-vis spectrophotometer model V-670 from JASCO (Tokyo, Japan) was used to record the spectra and the absorbance measurements. The absorbance measurements were obtained by mounting optical membrane sensor samples ($1 \times 9 \times 50$ mm^3) inside a quartz cuvette. The absorbance measurements of the optical membrane sensor samples were obtained with respect to air as well as the blank optode sample. The film thicknesses of the sensing slides were measured using a digital microscope (Ray Vision Y 103) that was coupled to a video camera (JVC TK-C 751 EG) and a digital micrometer (Mitutoy, Japan) with an accuracy of $\pm$0.001 mm.

Membrane preparation

The transparent glass slide membranes were purchased from microscope slides in sizes of $1 \times 9 \times 50$ mm^3 and were kept in a $HNO_3 : H_2O_2$ (3 : 1) volume ratio solution. The optical sensor was washed with THF and double-distilled water before use. The sensing mixture was prepared by dissolving 5.0 mg NaTPB, 8.0 mg CPDB, 30 mg PVC and 75 mg DOA in 2.0 mL THF. The mixture was stirred with a magnetic stirrer to obtain a homogeneous solution. Glass plates were placed in the spin-on device and spin-coated onto a glass plate at 1000 rpm for 30 s. The thickness of the obtained membrane was estimated to be about 0.005 mm. The membrane was placed in ambient air and allowed to dry in air for 5.0 min, and the optode was maintained in a buffer solution of pH 7.5.

General procedure

The sensing membrane (optode) was placed in a beaker filled with 25 mL of the test solutions containing different levels of Co^{2+} (0.05–45.20 μM) and 5.0 mL of pH 7.5 buffer. After 5.0 min, the optode was mounted into the spectrophotometer directly and its net absorbance was assessed at $\lambda_{max} = 595$ nm against a blank membrane prepared in the same manner except for cobalt ions.

Procedure for pharmaceutical formulations

A suitable weight of vitamin B_{12} powder or 5.0 mL of the injectable was placed in a 25 mL crucible and digested with a few drops of HNO_3 at 500 °C. The residue was heated in a water bath after dissolving in 3.0–5.0 mL HNO_3 for 2.0 min. Then, it was diluted with 5.0–10.0 mL double-distilled water and filtered if necessary. Three 5.0 mL portions of double-distilled water were used to wash the crucible and the filter paper. The cobalt content of the prepared solution was assessed as stated according to the previous procedure.

Water samples

Water samples were directly used after filtration with a filter paper (Whatman No. 1). The analyses of the alloy samples were conducted by weighing about 1.8 g of the sample to the nearest 0.1 mg and transferring the sample into a 250 mL Erlenmeyer flask with 10–12 mL HNO_3 : HCl (1 : 3) and a few drops of concentrated HF. The mixture was heated until dissolution was complete. The solution was heated to dryness. The residue was dissolved in water and diluted to 100 mL in a 100 mL volumetric flask. The solution was used for analysis.

Biological samples

Urine and saliva samples were gathered from male and female volunteers aged 25 to 35 years, living in Benha (Egypt), without eating breakfast. In order to minimize the possibility of contamination with cigarette or food debris and airborne particles, the subjects were asked to thoroughly rinse their mouths three times with ultra-pure water. Human saliva samples were gathered between 8 and 9 h to minimize possible circadian contributions in Co-free polystyrene test tubes.[46] The samples (7.0 mL) were acidified with HNO_3 to pH 2.0 and placed in a graduated centrifuge tube and centrifuged for 20 min at 1500 rpm (377.2 g). Five milliliters of the supernatant were diluted to 25 mL with double-distilled water. Co^{2+} was assessed by the proposed method. Reasonable dilution for analysis is practical as the subsequent collection of great volumes may be tedious for the donors. Blanks were prepared with the same reagents without the samples, and underwent an identical procedure.

Urine samples were digested by UV-photolysis, as described previously.[3] Briefly, 5.0 mL of the sample was transferred in a decomposition glass beaker. 200 μL 30% (w/w) H_2O_2 was added. The mixture was irradiated for 45 min. Another 200 μL aliquot of 30% (w/w) H_2O_2 was added, and the irradiation process was continued for 45 min. Finally, 10 mL water was added, and the irradiation process was repeated for another 120 min. The digested sample volume was set to 25 mL after the completion of the irradiation method.

Food samples

Fifteen grams of flour and dried vegetable samples (obtained from Benha, Egypt) were first carbonized at a low temperature. The samples were burned in a muffle furnace for about 3.0 h at 600 °C. They were extracted after cooling at room temperature by adding 2.0 mL 9.0 M H_2SO_4 with heating. The mixture was filtered. The filtrate pH was adjusted to ≈7.5 with NaOH. A reasonable amount of EDTA for masking was added, and the sample was taken for analysis by the suggested technique.

Results and discussion

Preliminary investigations

5-[*o*-Carboxyphenylazo]-2,4-dihydroxybenzoic acid (CPDB) is described as a spectrophotometric reagent,[44] and it exhibits a pink color when it chelates with Co^{2+}. Owing to CPDB being an organic reagent, it is immobilized efficiently in the hydrophobic part of the membrane without prior lyophilization.[47] It was shown that by optimized fabrication, a sensor made by the incorporation of CPDB in a plasticized PVC membrane, including DOA, could be colorimetrically practical for the assessment of cobalt. When Co^{2+} ions diffuse into the membrane, it forms a complex with CPDB; thus, the membrane color varied from orange to pink. The absorption spectra of the CPDB control (λ_{max} = 444 nm) and cobalt-based optodes upon contact with 20 μM Co^{2+} at pH 7.5 (λ_{max} = 595 nm) are shown in Fig. 1.

Membrane composition

The response features and working concentration range of an optical sensor depend on certain ingredients such as the base matrix, solvent mediator, ionophore and additive applied in the membrane structure. Consequently, the sensor matrix must be optimized through the comparison of various polymers; low molecular weight PVC was found to be the best choice for the membrane base due to various factors such as its reasonable transmittance, appropriate immobilization of CPDB without any leakage, good mechanical stability and reliable permeability to Co^{2+} ions.

The plasticizer is essential and must be physically compatible with the polymer. To obtain a homogenous organic phase, plasticizers such as DBP, TBP, DOP, *o*-NPOE and DOA were screened. As shown in Fig. 2, it was established that the membranes including DBP, TBP, DOP and *o*-NPOE did not obtain a suitable band due to either improper physical features with LPVC or the leakage of CPDB from the membrane. It was established that DOA was the optimum choice due to its better physical characteristics as well as its maximum sensitivity and minimum leakage.

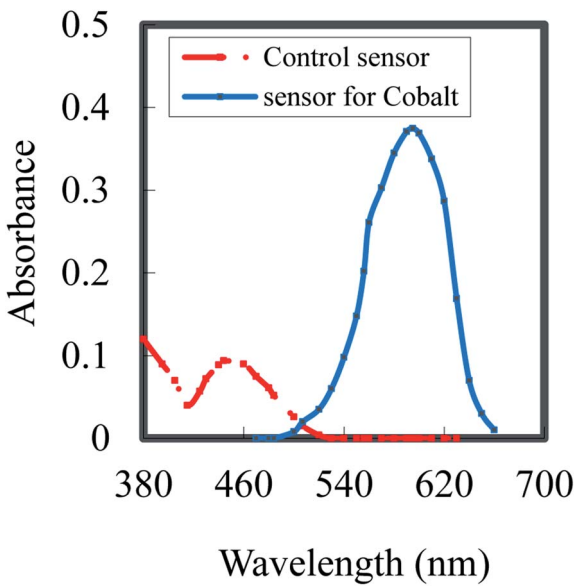

Fig. 1 Absorption spectra of a control sensor (PVC; DOA; NaTPB; CPDB) and cobalt based sensor upon contact with 20 mmol L^{-1} Co^{2+} at pH 7.5.

As listed in Table 1 (membrane no. 1–4), the sensors with a weight ratio of DOA to LPVC of 2.5 give the highest absorbance, and the results are highly concordant. Thus, 30 mg PVC and 75 mg DOA were selected as the optimum levels. The decrease in the Co^{2+} uptake efficiency at values lower than 75 mg is attributed to the improper solidity of the optode, which led to the low diffusion of analyte cations into the membrane. At quantities more than 75 mg, the flexibility of the optode increased, which led to ionophore leakage into the test solution.

The effect of varying amounts of CPDB on the response of the membrane is shown in Table 1. As shown by membrane no. 5–8, the absorbance increased with increasing amounts of CPDB up to 8.0 mg, while the absorbance decreased at greater levels owing to membrane leakage. Thus, 8.0 mg CPDB was the optimal value.

The presence of an anionic additive such as NaTPB leads to ion-exchange equilibrium due to the decrease in the response time and the complete mass transfer of Co^{2+} ions into the membrane.[48] The influence of NaTPB was demonstrated in the range of 2.0–7.0 mg (Table 1 membrane no. 9–12). It is found that the maximum absorbance is achieved by applying 5.0 mg NaTPB. Therefore, at this optimum concentration of NaTPB, the complete transfer of the Co^{2+} ion occurs only to the optode, in addition to the low response time and the complete equilibrium of ion-exchange.

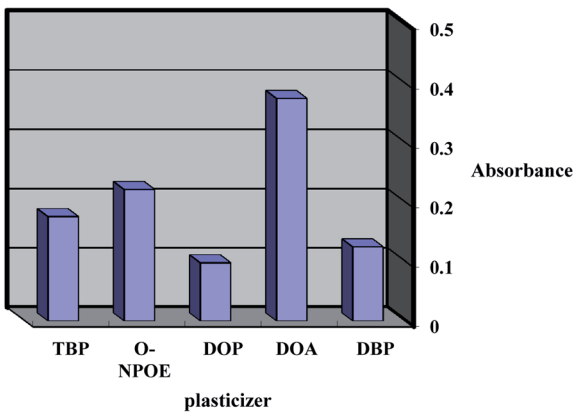

Fig. 2 Effect of Plasticizer types on the sensor formed to complexed with 20 mmol L^{-1} Co^{2+} at pH 7.5.

Response time of the optode

The response time of the optodes is defined as the diffusion time of the metal ions from the solution into the membrane (slowest step in the complexation process).[49] The influence of this factor on the optode response was determined (Table 1 membrane no. 13–16). The response time is affected by various factors, including Co^{2+} ion concentration, which controls its diffusion into the membrane; the ionophore loading technique;[50] and the membrane thickness. As observed, a time interval of at least 5.0 min is required for quantitative Co^{2+} uptake at 25 ± 2.0 °C. It was noted that the optode response remained constant for more than 15 days.

Effects of pH

Briefly, the ionophore structure indicates the presence of more reactive atoms such as the hydroxyl group and nitrogen atoms, which are used for binding Co^{2+} ions at high pH based on its complexation tendency. Consequently, the response of the optodes depends on the incorporation of the ionophore, which is significantly affected by the pH of the buffer. The influence of pH on the optode response (extent of complexation) in the pH range of 2.5–12 in buffer and non-buffer solutions was demonstrated, and the results are shown in Fig. 3. As shown, the optode absorbance increased at pH 7.5 and then decreased. At pH < 6.5, the protonation of the reagent prevents its reaction with Co^{2+} ions, while at pH > 9.5, the decrease in the response

Table 1 Effects of membrane composition on the absorbance of the proposed optode

Sensor	LPVC (mg)	DOA (mg)	CPDB (mg)	NaTPB (mg)	Response time (min)	Absorbance[a] (595 nm)
1	30	45	8	5	5.0	0.177 ± 0.021
2	30	60	8	5	5.0	0.268 ± 0.012
3	30	75	8	5	5.0	0.375 ± 0.005
4	30	90	8	5	5.0	0.323 ± 0.009
5	30	75	4	5	5.0	0.201 ± 0.017
6	30	75	6	5	5.0	0.327 ± 0.011
7	30	75	8	5	5.0	0.375 ± 0.005
8	30	75	10	5	5.0	0.337 ± 0.008
9	30	75	8	2	5.0	0.219 ± 0.024
10	30	75	8	4	5.0	0.326 ± 0.011
11	30	75	8	5	5.0	0.375 ± 0.006
12	30	75	8	7	5.0	0.292 ± 0.032
13	30	75	8	5	2.0	0.132 ± 0.023
14	30	75	8	5	4.0	0.279 ± 0.011
15	30	75	8	5	5.0	0.375 ± 0.004
16	30	75	8	5	10	0.366 ± 0.006

[a] Mean absorbance ± SD ($n = 3$) of each parameter is recorded from three solutions of 20 μM Co^{2+} at pH 7.5.

could be because of the hydrolysis of Co^{2+} ions, which is produced by the incomplete diffusion of Co^{2+} cations into the optode. Hence, a buffer with pH 7.5 was used in all further investigations. In comparison, the optimum pH for the Co–CPDB complex in aqueous solution has been reported as 9.5.[44]

Lifetime

The lifetime of the optode film was assessed by adding the buffer solution (pH 7.5) to the prepared membrane. The absorbance was measured at a wavelength of 595 nm over a period of time (about 10 h). During this time, no significant loss of the carriers occurred. A stable absorbance *versus* time plot was achieved through the exposure of radiation to the membrane. This may be attributed to the fixed composition of the membrane (the absence of significant carrier bleeding from the membrane to the bulk aqueous solution). No drift in the absorbance occurred. Nevertheless, the applied membrane was stored under water when not in use to protect it from drying out.

Membrane properties

The characteristics of the optode membrane were obtained by assessing the change in the absorbance at 595 nm from individual solutions of 0.8, 1.6 and 3.2 μM Co^{2+}. In all of the three cases, the optodes reached 98% absorbance after 5.0 min. The membrane stability was studied for 10 h and during this period, the mean difference of absorbance for the tested solutions was ±0.009. Moreover, the membrane response was stable in air for 15 days.

The effect of the salting-out phenomenon on the response of the optode was examined by adding different concentrations of sodium nitrate. The results demonstrate that this factor had no influence on the response of the membrane up to 0.05 M $NaNO_3$ and it significantly decreased above this concentration due to the reduction in the activity of Co^{2+} ions at higher concentrations of the electrolyte, which reduces the interaction of Co^{2+} cations with the CPDB in the membrane.

Repeatability and regeneration

The repeatability of the membrane response at 595 nm was checked by performing various replicate measurements for a 20 μM solution. The RSD for these determinations was found to be less than 2.0%. It is essential that the sensor membrane be regenerated by an appropriate solution to prepare it for subsequent measurements. To select the best regeneration solution, mineral acids such as HNO_3, H_2SO_4, HCl, and H_3PO_4 as well as solutions of EDTA and KCl (all 0.3 M) were checked. To do this, the optode was put in 20 μM cobalt solution and after attaining equilibrium, it was taken out and put in a regenerating solution until the absorption of the membrane was stabilized. Nitric acid (0.3 M) showed the highest percentage of regeneration of the sensor.

Great regeneration was achieved for a Co^{2+} ion concentration of 20 μM. The corresponding RSD value was found to be ±1.95%. The short-term stability of the optodes was determined by their absorbance difference measurements in contact with a 20 μM Co^{2+} ion solution at pH 7.5 over a period of 10 h. From the absorbance readings taken every 15 min ($n = 40$), it was established that the response is almost complete with only a 1.7% increase in the absorbance after 10 h of monitoring. The lifetime of the membrane was checked over a period of two weeks, during which four prepared membranes were kept in 5.0% (v/v) ethanol at 4 °C. The mean absorbance differences of the sensors were found to be 0.043 (±0.002) and 0.055 (±0.003) before and after this period, respectively.

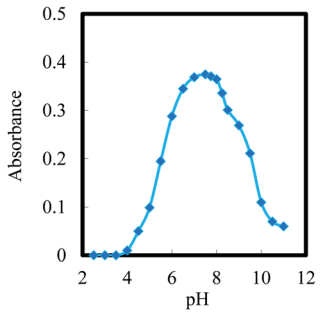

Fig. 3 Effect of pH value on the sensor response for 20 mmol L^{-1} of Co^{2+} at the optimum conditions.

Sensor selectivity

One of the most necessary parameters of a proposed sensor, which dictates its applicability for the analysis of real samples, is the selectivity coefficient. The influence of various cations and anions on the reactivity with the proposed optode at the optimum conditions was examined, revealing that there is no response to any of the examined ions and thereby indicating that no reaction occurs or there is no change in the color of the CPDB optode. The interference of various inorganic cations towards the proposed optical sensor was assessed using a 20 μM Co^{2+} solution in the presence of various concentrations of the interfering cations in a pH 7.5 buffer. The tolerance ratio was defined as the ratio of the interfering ion concentration to the Co^{2+} ion concentration, which causes a relative error of ±5.0%. The resulting tolerance ratios ($[M^{n+}]/[Co^{2+}]$) for the various interfering ions (M^{n+}) listed in Table 2 indicate that the Co^{2+} ion content can be distinguished selectively with high accuracy using the proposed optical sensor in the presence of excess levels of the investigated potential interferents. This moderate selectivity demonstrates the applicability of the proposed sensor for evaluating and monitoring the cobalt content of various real samples with complicated matrices in the presence of an excess of many other coexisting cationic species. The high selectivity in the presence of interfering ions such as Fe^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+}, Au^{3+}, Cr^{3+}, Cd^{2+}, Zn^{2+}, Hg^{2+}, and SO_4^{2-} make it possible to precisely and repeatedly monitor Co^{2+} ion content in environmental samples with complicated matrices.

Analytical characteristics

The optode response, in the form of a change in absorbance at 595 nm, towards Co^{2+} ion concentration was obtained within

Table 2 Interference by various ions on the proposed method for the determination of 150 ng mL^{-1} Co^{2+}

Foreign ion	Tolerance limit (μM)	Foreign ion	Tolerance limit (μM)
K^+, CH_3COO^-	20 000	Cr^{3+}, CO_3^{2-}	3500
Na^+, PO_4^{3-}	17 500	W^{6+}, Cl^-	3000
Ba^{2+}, NO_3^-, N_3^-	15 000	Cr^{6+}, SO_4^{2-}	2500
Al^{3+}, BrO_3^-	13 000	Fe^{3+}, I^-, Br^-, F^-	2000
Ca^{2+}, Mg^{2+}, SO_4^{2-}	11 000	Ti^{3+}, HCO_3^-	1500
Ag^+, Au^{3+}, citrate	10 000	Mo^{6+}, IO_4^-	1250
Fe^{2+}, Zn^{2+}, NO_2^-	8500	La^{3+}, Y^{3+}, Sc^{3+}	1000
Ni^{2+}, Cu^{2+}, NH_4^+	7000	V^{5+}, Be^{2+}	800
Zn^{2+}, Hg^{2+}, oxalate	5500	Th^{4+}, UO_2^{2+}	600
Cd^{2+}, Be^{2+}, $S_2O_3^{2-}$	4500	Pb^{2+}, Mn^2	500

Table 3 Analytical features of the proposed optical sensor

Parameters	Proposed sensor
pH	7.5
λ_{max} (nm)	595
Beer's range (μM)	0.05–42.5
Ringbom range (μM)	0.2–40.5
Molar absorptivity (L mol^{-1} cm^{-1})	8.82×10^7
Sandell sensitivity (ng cm^{-2})	0.007
Detection limit (μM)	0.015
Quantification limit (μM)	0.048
Regression equation	
Slope (μg mL^{-1})	24.7
Intercept	0.09
Correlation coefficient (r)	0.999
RSD[a] (%)	1.9

[a] Relative standard deviation.

0.05–45.20 μM (Table 3). The blank absorbance at 595 nm was assessed after equilibrating the optode sample with a blank solution at pH 7.5. The absorbance changes linearly as a function of Co^{2+} ion concentration in the range of 0.05–45.20 μM. The minimum concentration of Co^{2+} ions required in the 25 mL equilibrating solution to establish a distinct color change of the optode was found to be 20 μM. However, the detection limit of Co^{2+} ion concentration can be further improved using a larger volume of the aqueous sample. The detection and quantification limits,[51] defined as $C_L = 3S_B/m$ and $C_Q = 10S_B/m$ (where C_L, C_Q, S_B, and m are the detection limit, quantification limit, standard deviation of the blank and slope of the calibration graph, respectively), were 0.015 and 0.048 μM, respectively.

Tables 4 and 5 demonstrate a comparison between the prepared optode and other previously reported sensors[3,35,40,42,43] or spectrophotometric[52–62] procedures for the determination of cobalt. It is clear that the achieved results are comparable with those of current sensors. The proposed optode provides a greater linear range and detection limit in some cases.

Analytical applications

The proposed sensor was applied to assess cyanocobalamin phosphate (vitamin B_{12}) in various pharmaceutical, serum, saliva and urine samples. Using the recommended method, the results of the analysis of capsules, syrups and ampoules showed a good correlation with those accomplished using the BP technique.[63] The relative standard deviation of the suggested procedure is established to be better than 1.9% (six determinations). The procedure performance was judged through the calculation of student's t- and F-values at a 95% confidence limit,[64] and the results show that the calculated values did not exceed the theoretical values (Table 6).

Cobalt is usually applied in dental cast alloys, orthodontic wires and implantable orthopedic instruments, releasing it into human tissue due to corrosion.[65] Saliva is a simple and low-cost sample to collect, and is used successfully to screen great populations;[66] it can therefore be applied to monitor Co^{2+} released from orthopedic devices. However, a major challenge for the assessment of chemical contaminants in saliva is that concentrations are often 1 or 2 orders of magnitude lower than in blood.[67] Consequently, blood and urine have been suggested as biomarkers of recent exposure to soluble Co^{2+} species.[1] Nevertheless, urine is favored for the monitoring of heavy metals because it allows for non-invasive sampling and simple collection.[66] To the best of our knowledge, there have been no reports on the optical sensor viability for metal preconcentration from non-invasive biological samples such as serum, saliva and urine. Consequently, after urine and saliva analysis, the results obtained are listed in Table 6. Moreover, analyte recovery in the presence of a biological matrix was examined. The applied procedure was used for six portions of both saliva and urine matrices, and the average concentrations of Co^{2+} were taken as the base values. Then, 1.0 μg L^{-1} Co^{2+} was added to the samples

Table 4 Comparison of some of the best previously reported Co^{2+} optodes based on various ionophores with the proposed one

Sensing material	Type of sensor (membrane)	Dynamic range (M)	Response time (min)	Detection limit (M)	Ref.
Methyltrioctylammonium chloride	Triacetyl cellulose	8.5×10^{-6} to 1.3×10^{-4}	7.0	5.9×10^{-6}	43
m-(Mercapto acetamido) phenol	Triacetyl cellulose	—	0.5–3.0	5.8×10^{-6}	2
Pyrogallol red	Triacetyl cellulose	1.7×10^{-6} to 1.52×10^{-4}	2.0	3.6×10^{-7}	40
1-(2-Pyridylazo)-2-naphthol	Cellulose acetate + poly(vinyl acetate)	0.02–0.5 mg L^{-1}	10	0.07 mg L^{-1}	42
Potassium thiocyanate	Polyvinyl chloride	1.0×10^{-6} to 1.0×10^{-3}	10	6.10×10^{-7}	35
5-[*o*-Carboxyphenylazo]2, 4-dihydroxybenzoic acid	Polyvinyl chloride	5.0×10^{-8} to 4.52×10^{-5}	5.0	1.5×10^{-8}	This work

Table 5 Comparative evaluation of various photometric reagents for the determination of cobalt

Reagent	Medium/solvent	λ_{max} (nm)	ε (L mol^{-1} cm^{-1}) × 10^4	Linear range (μg mL^{-1})	Ref.
Disodium 1-nitroso-2-naphthol-3,6-disulphonate	DMF/$CHCl_3$	—	1.33	0.84–1.44	52
Sodium diethyldithiocarbamate	Aqueous (CTAB[a])	324	2.17	0.0377 ± 0.0082[b]	53
N-Hydroxy-*N*,*N*-diphenyl benzamidine	Toluene	405	0.70	0.10–12	54
1-Hydroxy-2-carboxyanthraquinone	Ethanol–water	494.5	—	0.75–4.5	55
Diethyl thiocarbamate	Aqueous (ADS[c])	322	2.22	0.0493 ± 0.0018[b]	56
3-Hydroxy-2-methyl-1,4-napthoquinone 4-oxime	Naphthalene/DMF	430	2.09	0.12–1.8	57
Bis(2,4,4-trimethylpentyl)phosphinic acid	Benzene	635	0.03	0.295–2.36[d]	58
1-Nitroso-2-naphthol	Aqueous (TX-100[e])	420	3.18	0.0056–3.00 (1.68 × 10^{-3})[f]	27
2-(2-Benzothiazolyazo)-2-*p*-cresol	Aqueous (TX-100[e])	615	1.62	0.08–1.06 (10)[f]	59
2-Nitroso-1-naphthol-4-sulphonic acid	DMF	620	—	0.2–12	60
Phenanthraquinone monothiosemicarbazone	Water–methanol	550	1.24	0.8–4.0	61
3-(4-Phenyl-2-pyridinyl)-5-phenyl-1,2,4-triazine + picric acid	1,2-Dichloroethane	—	—	0.0072–0.50	62
5-[*o*-Carboxyphenylazo]2,4-dihydroxybenzoic acid	PVC NaTPB	595			This work

[a] CTAB: hexadecyltrimethylammonium bromide. [b] Units μg. [c] ADS: ammoniumdodecyl sulphate. [d] Units mg. [e] Triton X-100. [f] Detection limit.

and the same method was employed. The results achieved with the proposed technique were in great agreement with those previously described for urine samples,[68] while the Co^{2+} recoveries were highly satisfactory for all the cases.

The final test of the effectiveness of the sensor as an environmental monitoring device is to test real water samples and alloy samples since the system has been optimized with laboratory prepared samples. The recovery of spiked Co^{2+} in Nile River water (Benha) was established with the suggested optode. The results are given in Table 7. The standard deviations of the analysis and the recoveries of the added Co^{2+} to the samples indicate that the recommended procedure is capable of real sample analysis.

Table 6 Determination of vitamin B_{12} in various dosage forms and biological samples compared with the BP method[63]

Sample	Vitamin B_{12} content (mg)	Found[a]		*t*-Value[b]	*F*-Value
		Optode ± SD	Official ± SD		
Tablets					
Tri-B[c]	0.125	0.126 ± 0.07	0.122 ± 0.22	1.37	2.09
Mineravit[d]	1.000	0.997 ± 0.05	0.990 ± 0.18	1.56	2.35
Trivarol[e]	0.125	0.124 ± 0.10	0.129 ± 0.26	1.14	1.88
Beco forte[f]	12.00	11.98 ± 0.08	12.10 ± 0.17	1.22	2.03
Ampoules					
B_{12} Depot[g]	0.5 mg mL^{-1}	0.502 ± 0.12	0.494 ± 0.26	1.10	1.71
Trivarol[e]	1 mg per amp	1.008 ± 0.06	1.025 ± 0.20		
Tri-vitacid[h]	1 mg per amp	0.994 ± 0.11	1.028 ± 0.28		
Tri-B[c]	1 mg per amp	0.991 ± 0.14	1.031 ± 0.19	0.99	1.65
Serum ng mL^{-1}	—	75.0 ± 0.08	73.50 ± 0.23		
	25	103.6 ± 0.05	106.60 ± 0.14	1.43	
	50	127.2 ± 0.07	102.20 ± 0.13		2.26
Urine ng mL^{-1}		22.0 ± 0.10	23.00 ± 0.17		
	40	63.8 ± 0.07	61.20 ± 0.12	1.21	
	80	100.5 ± 0.09	106.40 ± 0.17		2.00
Saliva ng mL^{-1}	0	n.d.[i]			
	35	37.1 ± 0.10	36.70 ± 0.21	1.65	
	70	72.5 ± 0.12	68.40 ± 0.27		3.17

[a] Average of six determinations. [b] Theoretical values of *t*- and *F*- are 2.57 and 5.05, respectively, for five degrees of freedom and a 95% confidence limit. [c] The Nile Company for Pharmaceutical and Chemical Industries, Egypt. [d] Egyptian International Pharmaceutical Industries Company, Egypt. [e] The Memphis Chemical Company, Cairo, Egypt. [f] Misr Company for Pharmaceutical Industries, Cairo, Egypt. [g] The Arab Drug Company for Pharm. & Chem. Industries, Egypt. [h] Chemical Industries Development Company, Egypt. [i] Not detected.

Table 7 Determination of Co in water and biological samples (95% confidence interval; $n = 6$)

Sample	Added ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)		Recovery[a] (%)
		Sensor ± SD	FAAS ± SD	
River water	—	0.37 ± 0.03	0.40 ± 0.14	—
	1.00	1.40 ± 0.08	1.35 ± 0.21	102.19
	2 0	2.32 ± 0.02	2.55 ± 0.17	97.89
Tap water	—	0.25 ± 0.02	0.30 ± 0.14	—
	2.5	2.80 ± 0.07	2.70 ± 0.09	101.82
	5.0	5.15 ± 0.03	5.45 ± 0.18	98.10
Wastewater	—	1.05 ± 0.09	1.00 ± 0.25	—
	4.0	4.95 ± 0.11	5.15 ± 0.32	98.02
	8.0	9.15 ± 0.04	8.80 ± 0.27	101.10
SRM-12[b]	—	0.019 ± 0.02	0.020 ± 0.24	—
	0.2	2.02 ± 0.09	2.03 ± 0.16	99.06
	0.4	0.415 ± 0.13	4.41 ± 0.23	103.26
SRM-589[b]	—	0.112 ± 0.03	0.110 ± 0.17	—
	0.1	0.215 ± 0.09	0.220 ± 0.22	101.42
	0.2	0.310 ± 0.14	0.320 ± 0.28	99.36

[a] Nile River water (Benha City). [b] Certified reference standard materials with cobalt contents of 0.020% for SRM-12 and 0.110% for SRM-589.

The suggested procedure was used for the assessment of Co^{2+} in tap, waste and river water samples (Table 7). The recovery of Co^{2+} was between 98.02% and 103.26%. The Co levels were 0.37 $\mu g\ L^{-1}$ in the river water samples, 0.25 $\mu g\ L^{-1}$ in tap water and 1.05 $\mu g\ L^{-1}$ in wastewater. The results did not significantly vary compared to those previously described for river, tap and wastewater samples.[69]

Furthermore, the accuracy of the proposed methodology was estimated by analyzing the certified reference materials (CRMs) of SRM-12 and SRM-589 with Co^{2+} contents of 0.020% and 0.110%, respectively. These CRMs include many ions frequently present in such samples. Subsequently, the certified concentration values in the CRMs were greater than the upper limit of the linear range obtained by the proposed sensor; a dilution by a factor of 25 had to be employed for analysis. Applying the developed methodology, the Co contents present in the CRMs were 0.019% and 0.112%, respectively (95% confidence interval, $n = 6$).

The proposed optical sensor was applied for the assessment of cobalt in flour and vegetable samples after standard addition,

Table 8 Determination of cobalt in food samples

Samples	Added ($\mu g\ g^{-1}$)	Found ($\mu g\ g^{-1}$)		Recovery (%)
		Optode[a]	FAAS	
Tomato	—	1.45 ± 0.03	1.51 ± 0.20	—
	5.00	6.30 ± 0.05	6.30 ± 0.13	97.67
	10.0	11.60 ± 0.09	11.80 ± 0.21	101.31
Soybean meal	—	312.10 ± 0.12	314.20 ± 0.27	—
	25.0	335.80 ± 0.08	340.90 ± 0.32	99.61
	50.0	385.6 0.15	383.30 ± 0.24	99.94
Tea	—	101.60 ± 0.11	105.40 ± 0.19	—
	40.0	142.50 ± 0.07	147.70 ± 0.36	100.64
	80.0	180.30 ± 0.10	182.90 ± 0.29	99.28
Spinach	—	0.83 ± 0.03	0.91 ± 0.24	—
	4.00	4.65 ± 0.06	4.72 ± 0.34	96.27
	8.00	8.95 ± 0.08	9.20 ± 0.19	101.36
Mint	—	13.50 ± 0.11	14.20 ± 0.32	—
	10.0	22.90 ± 0.09	25.00 ± 0.27	97.45
	20.0	34.50 ± 0.12	33.60 ± 0.38	102.99
Cabbage	—	N.D.	N.D.	—
	15.0	14.91 ± 0.04	15.25 ± 0.33	99.40
	30.0	30.45 ± 0.12	29.60 ± 0.35	101.50
Flour	—	N.D.[b]	N.D.[b]	—
	12.5	12.55 ± 0.03	12.40 ± 0.23	100.40
	25.0	24.70 ± 0.07	25.25 ± 0.34	98.80

[a] Mean ± standard deviation ($n = 6$). [b] Not detected.

under the described procedure. The results recorded in Table 8 indicate that the concentrations of Co^{2+} ions assessed using the optical sensor are in good agreement with those obtained by the FAAS procedure.

Conclusion

The proposed optode is a precise, accurate, low-cost, sensitive and selective device for cobalt assessment based on a PVC membrane. Additionally, the suggested procedure is rapid and easy and provides a broader dynamic range, reliable reproducibility and better detection and quantification limits. A comparison with previously reported sensors demonstrates that the proposed method provides a wider linear range and lower detection and quantification limits in some cases. Finally, the fabricated sensor can be applied successfully for the monitoring of cobalt in various environmental samples. According to the best of our knowledge, no manufactured optode has been described in the literature for the determination of cobalt using the studied reagent.

Ethics approval and consent to participate

All biological studies were carried out in strict accordance with the animal welfare guidelines of the World Organization for Animal Health. All biological experiments were performed using protocols approved by the Laboratory Animal Ethics Committee of "Egypt" and the Commission on the Ethics of Scientific Research, Faculty of Medicine, Benha University. In all cases, informed written consent was obtained from each participant.

Conflicts of interest

The authors declare that they have no conflict of interest.

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