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Determination of Cobalt(II) by a New PVC Membrane Coated Graphite Electrode Based on 6-chloro-11- azabenzo[a]phenothiazin-5-one as a neutral ion carrier

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Abstract

Cobalt has great biological effects on human beings and also other living organisms, hence its determination is very important. In this regard, a novel coated graphite electrode was designed for determination of Co^{2+} ions by exploiting 6-chloro-11- azabenzo[a]phenothiazin-5-one as a neutral ion carrier, for the first time. The foremost function was witnessed from the membrane composition of PVC (29%), Potassium tetrakis (4-chlorophenyl) borate (2%) as an ionic additive,6-chloro-11-azabenzo[a]phenothiazin-5-one (9%) as ionophore and Dioctylphthalate (60%) as Plasticizer. The linearity domain of the membrane sensor was from 5×10^{-7} to 1×10^{-2} Mol L^{-1} with the Nernstian slope value of 30.1 mV.Decade^{-1}. The potential response of the designed electrode was also investigated in non-aqueous mediums and it was found out that the electrode is also able to be used in systems that are entailed of 20% of ethanol and acetone organic solvents. The response time and lifespan of the electrode was 5 S and 3 months respectively. The sensor selectivity was also evaluated by match potential method over other cations and it shows an eminent selectivity towards Co^{2+} over all of the inspected ions. The applicability of the electrode in the potentiometric titration with EDTA was also investigated. In the end, the proposed electrode was utilized for determination of Co^{2+} in four aqueous specimens as real samples.

Keywords: *Cobalt (II), 6-chloro-11- azabenzo[a]phenothiazin-5-one, Ion selective electrode, Potentiometry.*

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Introduction

Cobalt is a white transition metal which is represented in the periodic table by Co symbol [1]. On the one hand, this hard and brittle element is a valuable nutrient for the body, because it is one of the main constituents of vitamin B_{12} that is essential to growth, cell production, hematopoiesis and myelin synthesis. And the deficiency of this vitamin is attached to pernicious anemia, delayed growth and vitiligo [2-4]. But on the other hand, in high doses cobalt can be too toxic and poisonous. Prior studies have proved that cobalt poisoning could eventuate to high blood pressure, cardiovascular diseases, diarrhea, ulcer, vomiting, pulmonary edema and severe allergies [5-9]. Moreover, the international agency of cancer researches has categorized cobalt as carcinogenic substances. And it should be noted that 500 mg of this metal is enough for killing a person and its daily dietary uptake must not exceed from 10 ppm [10-16]. Despite the fact that harmful effects of cobalt and also other heavy metals on humans and other living organism have been revealed to the international community, but it is still widely utilized in various industries including alloy production, manufacturing of dyesand electroplating. Therefore, this metal can be a potential contaminant that can affect the health of human beings adversely. And its determination is of a great importance in the environmental and medicinal analysis [17-19].

Different analytical techniques such as colorimetry, atomic absorption spectroscopy with both flame and graphite furnace atomizers, neutron activation analysis and inductively coupled plasma optical emission spectroscopy (ICP-OES) have been developed for the determination of cobalt [20-25]. Unfortunately, the referred methods have tangible drawbacks such as being time consuming, needing to expensive and intricate instrumentations, destruction of sample matrices, requiring experienced operators and including pre-concentration and sample preparation steps. But fortunately, ion selective electrodes can be a prominent alternative for the aforementioned techniques owing to their simplicity, wide concentration range, and portability, applicability in opaque and colored samples, strong selectivity and being economical. And these matters explain why many researchers focus on this group of electrochemical sensors [26-33]. Although many ISEs have been constructed for determination various ionic compounds and some of them have also become commercialized, but there are only a few reports about Co^{2+} and most of them suffer from noticeable downsides like narrow working range, limited pH scope, high limit of detection, short lifetime and poor selectivity. Hence, it can be inferred that research in this field should be ongoing in order to achieve better potentiometric sensors and boost the place of ISEs in routine analyses [34-40].

The structure of 6-chloro-11- azabenzo[a]phenothiazin-5-one is given in (Figure 1) as it can be observed from the figure, this compound is a non-linear phenothiazine derivative which has 2 nitrogen, 1 sulfur,1 chlorine and 1 oxygen heteroatoms in its chemical structure [41]. Moreover, its solubility in water and polar solvents is poor. So, it can be expected that 6-chloro-11-azabenzo[a]phenothiazin-5-one act as an exquisite ionophore in the construction of ion selective electrodes. In this regard, 6-chloro-11- azabenzo[a]phenothiazin-5-one was utilized in the development of a new coated graphite electrode for determination of Cobalt (II) for the first time, in this research.

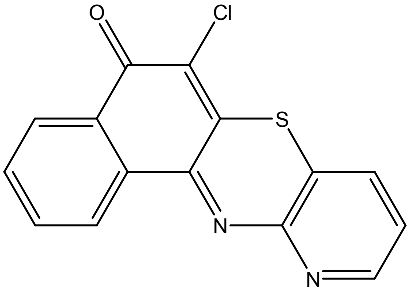

Figure 1. Chemical structure of 6-chloro-11- azabenzo[a]phenothiazin-5-one.

Experimental

Reagent and Materials

Dioctyl phthalate (DOP), Nitrobenzene (NB), Potassium tetrakis (4-chlorophenyl) borate (KTY), Sodium hydroxide, Acid nitric, Acetone and Ethanol were purchased from Sigma Aldrich. 6-chloro-11- azabenzo[a]phenothiazin-5-one was synthesized and purified from the method that was explained in [41]. Nitrate salts of various metals, Poly vinyl chloride (PVC) and Tetrahydrofurane were bought from Merck and Fluka. All of the mentioned chemicals were utilized as received without any further purification. All of the solutions were supplied with doubly distilled deionized water (Kimia Tehran acid, Iran) and their activities were calculated by Debye-Huckel equation.

Apparatus

EMF measurements took place by SA-8515 potentiometer (which was procured from Sairan Company, Iran) at 25ºC ±0.1. A saturated Calomel electrode (that was bought from Azar electrode company, Iran) was used as the reference electrode and a Graphite rod (Karen atlas pazhooh, Iran) of 3 cm length and 3mm diameter was employed for the preparation of the coated Graphite electrode. The pH of solutions was adjusted by the glass electrode (Sentek Company, England). A Shimadzu 670/G atomic absorption spectrometer was utilized for determination of cobalt in real samples.

Membrane preparation

Different amounts of plasticizers (NB and DOP), PVC, ionophore (6-chloro-11-azabenzo[a]phenothiazin-5-one) and KTY as the ionic additive were weighed in a Petri dish. Then, 3ml of THF was added to the mixture in order to solve all of the ingredients in it. Afterward, the obtained solution was put under a hood and by lapse of time the solvent was evaporated gradually and an oily viscous solution was formed. In this step, the Graphite bar was plunged in the obtained solution for 15 S and a thin membrane of about 0.4 mm thickness was created on the surface of the Graphite. Then, in order to dry the membranes, the acquired electrode was put in the room temperature for 12 hours. In the end, the electrode was conditioned by drenching in a 1×10^{-3} Mol L^{-1} Co $(NO_3)_2$ solutions for 1 day.

Results and discussion

Evaluating the tendency of the used ionophore towards various cations

Finding the most appropriate cation that has the best interaction with the utilized ionophore is one of the main steps in developing an ion selective electrode because the selectivity of the proposed sensor is contingent on this inspection. For this purpose, a membrane with the composition of 5% (ionophore), 2% (KTY), 30% (PVC) and 63% (DOP) was prepared. And after the conditioning step, it's potential response to 10 different cations including Cu^{2+}, Mn^{2+}, Ag^{+}, Fe^{3+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mg^{2+}, Pb^{2+} and Cd^{2+} was investigated and the obtained Nernstian plots are depicted in (Figure 2). As it can be witnessed from the curves, cobalt has the widest linear working range from 1×10^{-6} to 1×10^{-2} Mol L^{-1} with a relatively high Nernstian slope among all of the evaluated cations. Whereas, other cations have a narrow working range with a slope which is much lower than that is predicted by the Nernst equation. Therefore, it could be concluded that cobalt (II) forms the strongest and most stable complex with the used ligand as a neutral ion carrier. And the membrane can show a selective trend toward this ion.

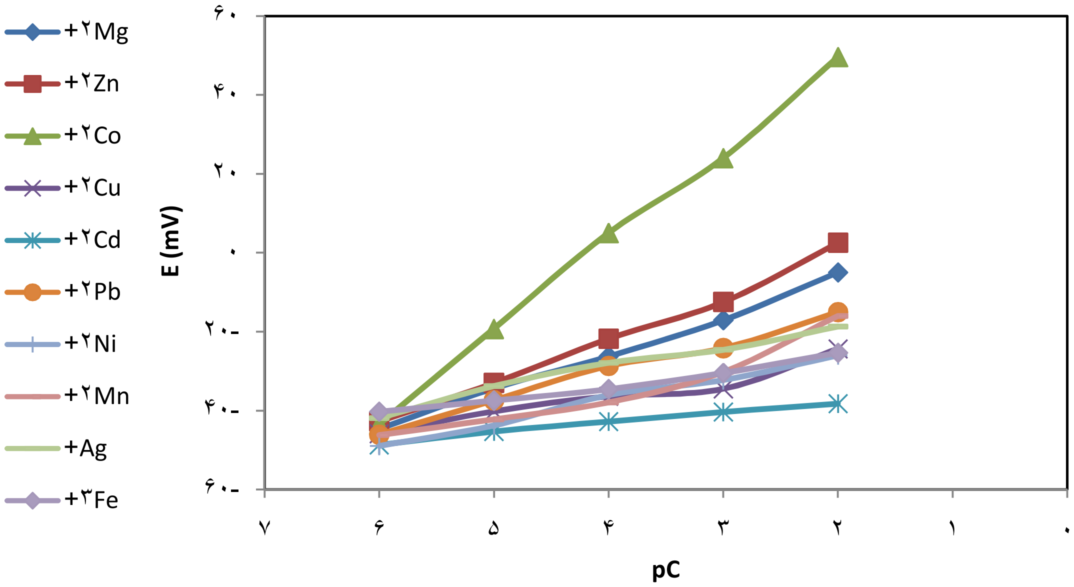

Figure 2. Investigating the interaction of 6-chloro-11- azabenzo[a]phenothiazin-5-one with different cations.

Membrane optimization

The potential response of the electrode can be influenced by different variables such as the amount and nature of ion carrier, the dielectric constant of the used plasticizer, the amount of ionic additive and the ratio between PVC and solvent mediator. Therefore, optimizing the composition of the PVC membrane is a pivotal step in the development of a potentiometric sensor. For this purpose, 16 different compositions were prepared and their potential response was investigated. The amount of ionophore was the first examined parameter. As the provided data in Table 1, demonstrate obviously, the 12th composition that is composed of 9% ionophore, 2% KTY, 60% DOP and 29% PVC, has shown the best function. As it can be witnessed, the linearity domain and the slope of the Nernstian plots have been improved remarkably by increasing the amount of the 6-chloro-11-azabenzo[a]phenothiazin-5-one. With a closer look, it can be realized that the free ionophore membranes (no. 1 and 2) do not have any sensitivity because their slopes (7.1±0.3 and 11.2±0.4 mV.Decade^{-1}) are non-Nernstian and their working range is too narrow (1×10^{-4}-1×10^{-2} Mol L^{-1}). Whilst by gradual incrementing the amount of the ligand until the value of 9%, the dynamic range and Nernstian slope of the designed electrode have become ameliorated drastically (no. 4-12). This evidence proves that 6-chloro-11- azabenzo[a]phenothiazin-5-one forms a strong and stable complex with Co^{2+}. It is worth noting that by enhancing the amount of ion carrier from the value of 9%, a noticeable decrease has happened in the slopes of calibration curves (no. 12,15-16). This phenomenon can be related to the saturation of the membrane. So, 9 mg was chosen as the most appropriate amount of ionophore, in this research.

The quiddity and mount of plasticizer is the next factor which can have a great impact on the characteristics of an ion selective electrode. In order to investigate the effect of plasticizer, 6 different membranes (no. 8-10,12-13) were constructed. The ingredients of these membranes were competently similar to each other. And the nature of solvent mediator was the only discrepancy between them. Afterward, their potential responses were recorded. The achieved results indicate that the DOP is a better plasticizer than NB, because the eventuated membranes from DOP exhibit higher sensitivity and better Nernstian slopes. It seems this matter is pertinent to the dielectric constant and polarity of DOP, since DOP is less polar than NB and its dielectric constant is 5.1, that is considerably lower than the dielectric constant of NB (36.1). This fact implies that NB is more susceptible to extract other interfering ions that are present in the test solution and consequently can affect the designed sensor's function adversely. On the other hand, DOP is able to ameliorate the sensitivity and selectivity of the electrode owing to its lower polarity and dielectric constant. Thus, DOP was selected as the plasticizer in this step [42,43].

Owing to the fact that lipophilic anions play an important role in defusing the performance of cation selective membrane sensors, the effect of KTY presence on the features of the membrane potential response was also studied. Former researches have shown that ionic additives in neutral ion carriers' based electrodes canhave a positive impression on the performance of sensors by decreasing the ohmic resistance of the membrane. Moreover, in some cases that the utilized ionophore has a weak interaction with the analyte, ionic additives can facilitate the extraction procedure [44]. In this regard, 4 compositions were prepared (no. 3, 11-12, 14) and their performance was inspected. As it is obvious from the table, the third membrane does not have any KTY and its slope is 27.4±0.3 mV.Decade^{-1}. But by increasing the amount of KTY until 2 mg, the sub-Nernstian slope of the membrane has defused to the Nernstian slope value of 30.1±0.2 mV.Decade^{-1}. It is worth mentioning that further addition of KTY leads to a decline in the slope of the calibration curve. Thus, 2mg of KTY is completely reasonable for the convenient performance of the suggested electrode (Table 1).

Table 1. Optimization of the membrane composition.

Membrane No.	**Ionophore (%wt)**	**KTY (%wt)**	**PVC (%wt)**	**Plasticizer (%wt)**		**Slope (mV.Decade^{-1})**	**Working range (Mol L^{-1})**
				DOP	NB		
1	0	0	35	65		7.1±0.3	1×10^{-4}-1×10^{-2}
2	0	3	35	62		11.2±0.4	1×10^{-4}-1×10^{-2}
3	9	0	31	60		27.4±0.3	1×10^{-6}-1×10^{-2}
4	3	2	30	65		17.3±0.4	1×10^{-5}-1×10^{-2}
5	4	2	30	64		20.6±0.2	1×10^{-6}-1×10^{-2}
6	5	2	30	63		22.9±0.2	1×10^{-6}-1×10^{-2}
7	6	2	32	60		23.8±0.3	1×10^{-6}-1×10^{-2}
8	6	2	32		60	21.2±0.4	1×10^{-6}-1×10^{-2}
9	8	2	30	60		25.3±0.4	1×10^{-6}-1×10^{-2}
10	8	2	30		60	23.6±0.3	1×10^{-6}-1×10^{-2}
11	9	1	30	60		28.5±0.3	1×10^{-6}-1×10^{-2}
12	9	2	29	60		30.1±0.2	5×10^{-7}-1×10^{-2}
13	9	2	29		60	28.6±0.2	5×10^{-7}-1×10^{-2}
14	9	3	29	59		28.1±0.2	5×10^{-7}-1×10^{-2}
15	10	2	30	58		27.8±0.3	5×10^{-7}-1×10^{-2}
16	12	2	30	56		27.5±0.3	5×10^{-7}-1×10^{-2}

Applicable pH range

Due to the fact that the utilized ion carrier is not able to form a complex with the analyte in every pH, therefore, the potential response of ISEs can be independent of pH only in a limited pH scope. Because, in acidic solutions, the concentration of hydronium ions is so high and it can compete with the main cation in forming a complex with the used ligand. On the other hand, in basic solutions, the main cation starts forming the complex with hydroxyl ions. As a consequent, both of the cited matters can create noticeable oscillations in the potential of the electrode. Hence, investigating the useful pH range is an inevitable step in the development of an ion selective electrode. For this purpose, a 1×10^{-4} Mol L^{-1} Co $(NO_3)_2$ solution was made and its pH was modified by using small volumes of highly concentrated nitric acid and sodium hydroxide solutions in the range of 1.0-12.0. Then, the potential values were recorded. As the obtained results that are depicted in (Figure 3) demonstrate obviously, the constructed coated graphite electrode has an independent potential response from pH in the range of 3.5-8.5.

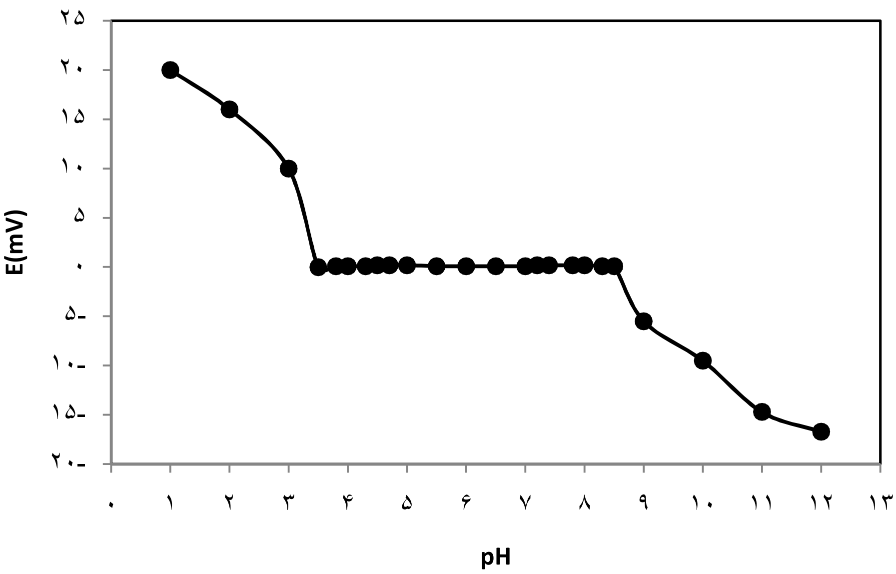

Figure 3. The influence of pH on the potentiometric sensor based on 6-chloro-11-azabenzo[a]phenothiazin-5-one.

Calibration curve and detection limit

Most of the analytical methods are based on depicting of the calibration curve. Because calibration curve shows linearity domain, limit of detection and sensitivity of analytical techniques. For this purpose, several standard solutions of $Co(NO_3)_2$ was made and their potential was recorded by the proposed electrode system in optimum conditions. Afterward, the potential values were depicted versus the activity of the solutions. As it can be observed from the (Figure 4), the designed Co^{2+} selective coated graphite electrode has a linear relationship with the activity of Cobalt(II) from 5×10^{-7} to 1×10^{-2} Mol L^{-1} with an admissible Nernstian slope value of 30.139 mV.Decade^{-1}. The electrode's limit of detection is 4×10^{-7} Mol L^{-1} that was calculated by extrapolating two segments of the calibration graph.

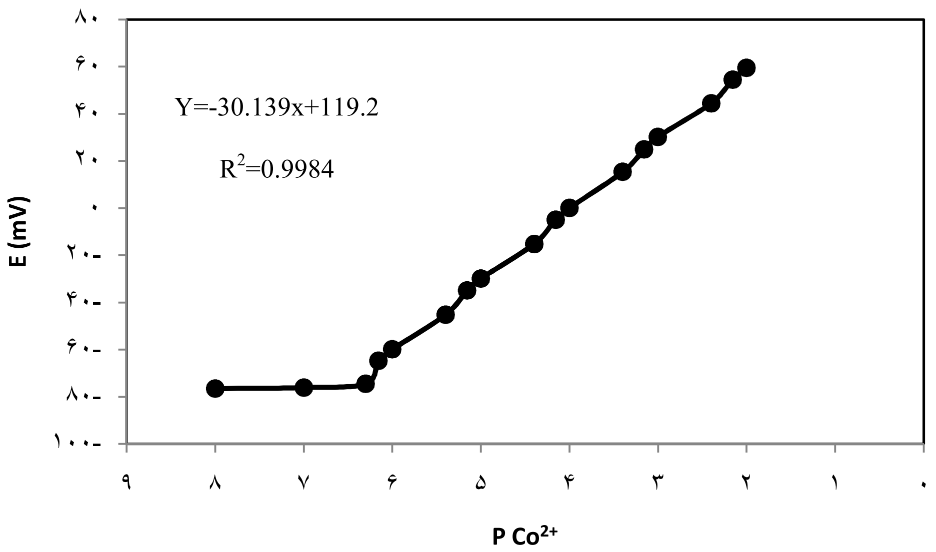

Figure 4. Calibration graph of the Co^{2+} selective coated graphite electrode.

The effect of organic solvents

Owing to the fact, that many real samples such as wastewaters consist of organic materials. Therefore, evaluating the function of ion selective electrodes in partially non-aqueous mediums can predict the capability of the designed electrode for determination of the desired analyte in real samples. In this regard, three series of $Co(NO_3)_2$ solutions with various contents of ethanol, acetone and mixture of ethanol and acetone (50:50) were supplied. And in the next step, the dynamic range and slope of calibration curves were inspected and the achieved results were tabulated in Table 2. As it is obvious from the table, the constructed sensor keeps its sensitivity and wide working range up to 20% of the non-aqueous content. However, by further increasing the proportion of organic solvent to water a significant fall has seen in the slopes of calibration graph. In addition, the limit of detection has risen considerably after incrementing the ratio of organic solvent further than 20%. It seems this phenomenon is relevant to the leakage of the ionophore from the membrane to the matrix of the test solutions due to the decreasing of the solutions" polarity in the high concentration of organic solvents.

Table 2. The influence of organic solvents on the performance of the potentiometric sensor.

Non-aqueous content (%v/v)	Dynamic range ($Mol\ L^{-1}$)	Slope ($mV.Decade^{-1}$)
0	5×10^{-7}-1×10^{-2}	30.1±0.2
Ethanol		
5	5×10^{-7}-1×10^{-2}	29.9±0.2
10	5×10^{-7}-1×10^{-2}	29.6±0.3
15	5×10^{-7}-1×10^{-2}	29.2±0.4
20	5×10^{-7}-1×10^{-2}	28.8±0.3
25	1×10^{-6}-1×10^{-2}	26.9±0.4
Acetone		
5	5×10^{-7}-1×10^{-2}	29.8±0.3
10	5×10^{-7}-1×10^{-2}	29.5±0.4
15	5×10^{-7}-1×10^{-2}	29.1±0.5
20	5×10^{-7}-1×10^{-2}	28.5±0.4
25	3×10^{-6}-1×10^{-2}	27.1±0.5
Mixed 50:50 (Ethanol+ Acetone)		
5	5×10^{-7}-1×10^{-2}	29.6±0.2
10	5×10^{-7}-1×10^{-2}	29.3±0.5
15	5×10^{-7}-1×10^{-2}	29.0±0.3
20	5×10^{-7}-1×10^{-2}	28.3±0.3
25	5×10^{-6}-1×10^{-2}	25.9±0.4

Selectivity

Lack of selectivity is the main problem of some potentiometric ion selective electrodes. The sensor's discrimination ability between different ions is contingent on the utilized ionophore tendency towards various ionic species. And due to the fact that selectivity issue can influence the accuracy and reproducibility of every analytical technique dramatically, hence, its evaluation is essential for each novel designed analytical method. In this regard, the selectivity of the suggested electrode was inspected over 15 different cations by matched potential method (MPM). If the obtained selectivity coefficient K_{MPM} value is close to 1, it shows that the membrane sensor has an equal potential response towards the analyte and interfering ion [45,46]. Whereas, closer selectivity coefficient values to zero connotes that the electrode has a poor affinity toward the interfering ion. In our case, all of the calculated K_{MPM} values that are tabulated in Table 3. Are about 100 to 1000 folds smaller than the value of 1. It indicates that the designed sensor has an eminent selectivity and is able to discriminate between Co^{2+} and other cations.

Table 3. Selectivity coefficients of the designed electrode over various cations.

Ion	**K_{MPM}**
Cu^{2+}	1.8×10^{-3}
Mg^{2+}	1.9×10^{-2}
Ca^{2+}	7.6×10^{-4}
Fe^{2+}	4.8×10^{-3}
Fe^{3+}	6.9×10^{-3}
Zn^{2+}	5.2×10^{-2}
Cr^{3+}	2.7×10^{-3}
Na^{+}	9.9×10^{-4}
K^{+}	8.3×10^{-4}
Pb^{2+}	2.1×10^{-2}
Cd^{2+}	5.7×10^{-3}
Ag^{+}	6.2×10^{-3}
Hg^{2+}	9.1×10^{-3}
Ni^{2+}	1.3×10^{-3}
Al^{3+}	3.4×10^{-3}

Response time and lifespan

The response time of an ion selective electrode indicated to the time that takes for the electrode system to reach a 90% value of its stabilized potential after being put in the test solution. This parameter has a direct relationship with the exchange kinetics speed of complexation-decomplexation of analyte ions with the used ligand as an ionophore at the membrane surface. In order to evaluate this variable, the reference and indicator electrodes were plunged in a series of solutions of $Co(NO_3)_2$ with10 times discrepancy in the activity. And the electrode system's potential was recorded in every second. In the next step, the obtained potentials were depicted versus the time in (Fig. 5). As it can be observed, the response time of the electrode is about 5S in the entire working range that is extremely short. The lifespan of the sensor was also investigated by measuring the linear working, limit of detection and the slope of calibration graphs over a period of 16 weeks. This experiment was performed by calibrating the constructed coated graphite electrode three times a day. As the provided data in (Figure 6), exhibit clearly the designed Co^{2+} selective electrode is usable at least for three months with an admissible reproducibility and enough sensitivity. But after this time range, the slope of calibration graphs has fallen drastically and the linearity domain has become narrower due to the gradual rising of detection limit [47].

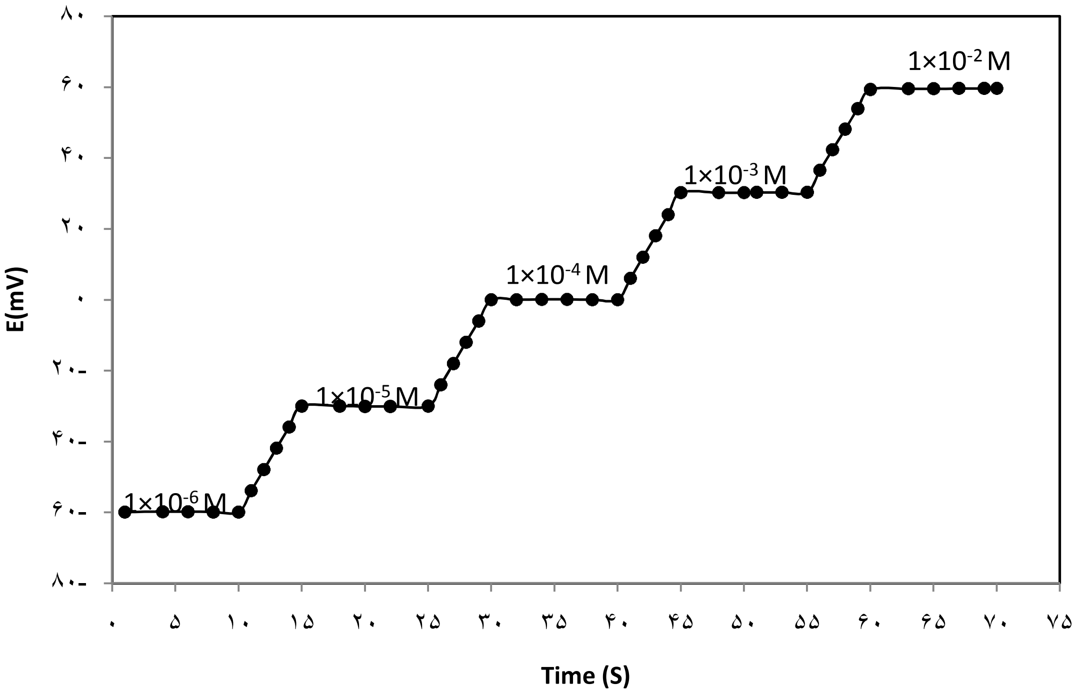

Figure 5. The dynamic response time of the Co^{2+} selective electrode for step alterations in the concentration of Co^{2+} over a concentration range from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}.

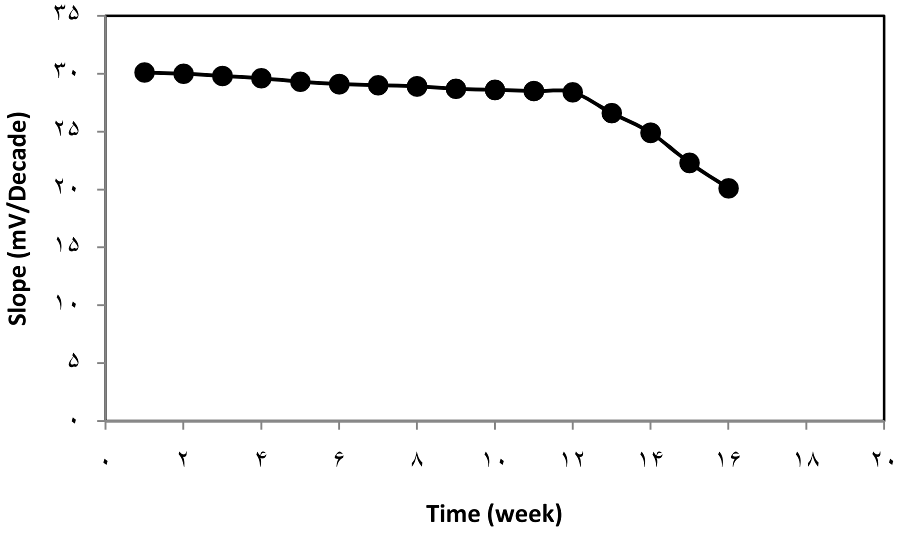

Figure 6. The lifetime of the designed Co^{2+} coated graphite electrode.

Potentiometric titration

For investigating, the performance of the proposed coated graphite electrode in indirect potentiometry, which is also known as potentiometric titration. 20 ml of a 1×10^{-5} Mol L^{-1} $Co(NO_3)_2$ solution was supplied and it was titrated with EDTA 1×10^{-3} Mol L^{-1}. The concentration of the EDTA solution was deliberately considered 100 times higher than the concentration of the

$Co(NO_3)_2$ solution, in order to minimize the errors that are originated from the volume alterations. The acquired normal and first derivative titration curves are presented in (Figures 7 and 8) respectively. As it can be witnessed the equivalent point and also the concentration of cobalt can be determined from both of the titration curves with a prominent accuracy. Therefore, it can be deduced that the constructed coated graphite electrode has the ability to be applied as an indicator electrode for the determination of low concentrations of Co^{2+} ions.

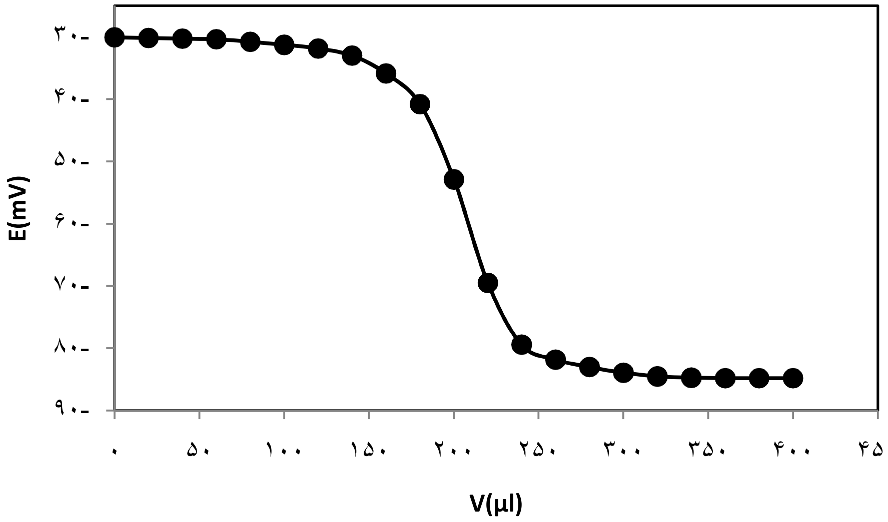

Figure 7. Normal titration curve of 20 mL 1.0×10^{-5} Mol L^{-1} Co^{2+} with 1.0×10^{-3} Mol L^{-1} EDTA, using the proposed sensor as an indicator electrode.

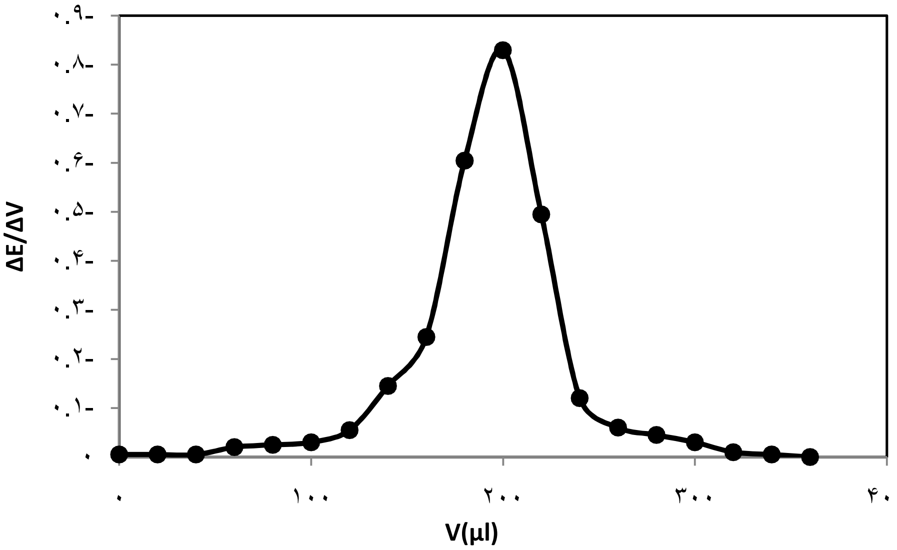

Figure 8. The first derivative titration curve of 20 mL 1.0×10^{-5} Mol L^{-1} Co^{2+} with 1.0×10^{-3} Mol L^{-1} EDTA, using the proposed sensor as an indicator electrode.

Analysis of real samples

In order to evaluate the capability of the recommended Co^{2+} coated graphite electrode, the concentration of this cation was determined in four aqueous samples including the Islamic Azad University of Yadegare-e- Imam Khomeini (RAH) laboratory sewerage, the Caspian sea, Karaj riverand Javaherdeh waterfall, water specimens. At first, all of the samples were filtered by a 0.45-µm pore size membrane filter. Then their pH was modified into the applicable pH range of the suggested electrode. Afterward, the concentration of cobalt(II) was determined by the designed sensor and also flame atomic absorption spectrophotometer (FAAS) and the acquired results were tabulated in Table 4. As it is obvious the obtained results from the sensor and FAAS are in an acceptable accordance with each other.

Table 4. Determination of Co^{2+} in four aqueous specimens.

Sample	**Measured with FAAS (ppm)**	**Measured with the recommended sensor (ppm)**
Laboratory sewerage	15.2 (±1.61)[a]	15.0(±2.14)
Caspian sea water	10.1(±2.12)	10.4(±2.43)
Karaj river water	7.6(±1.81)	7.3(±2.28)
Javaherdeh waterfall water	4.3(±2.34)	4.5(±2.05)

[a] %RSD based on five replicate analysis

Comparison of the designed Co^{2+} potentiometric ion selective electrode with some of the former reports

The main properties of the designed Co^{2+} selective electrode including detection limit, dynamic range, response time, lifespan and the slope of calibration graph have been compared with some of the prior reports in Table 5. As it can be witnessed, the recommended electrode has the highest slope, the lowest limit of detection and also the shortest response time among all of the cited previous sensors. Moreover, it should be noted that other features like dynamic range and also useful pH scope bear a lot of resemblance with the best antecedent former reported Co^{2+} selective sensors. Generally, it can be deduced that the designed coated graphite electrode in this study, is superior to other ones.

Table 5. Comparison of the proposed Co^{2+} selective electrode with some of the prior reports.

Lifetime (months)	**Detection limit (M)**	**Linear range (M)**	**Response time (S)**	**pH**	**Slope (mV/decade)**	**Ref.**
3	$10^{-6}\times4$	$10^{-1}\times1$ -$10^{-6}\times9$	25	4-7.2	29	38
2	$10^{-7}\times6$	$10^{-2}\times1$ -$10^{-6}\times2$	10	3-8	29.4	49
4	8.5×10^{-7}	$10^{-1}\times1$ -$10^{-6}\times6$	15	2.5-6.5	30	37
4	$10^{-6}\times8$	$10^{-1}\times1$ -$10^{-6}\times8$	20	2.8-7.3	29	48
4	$10^{-7}\times8$	$10^{-1}\times1$-$10^{-6}\times1$	25	3-7	29.6	36
2	$10^{-7}\times9$	$10^{-1}\times1$ -$10^{-6}\times1$	25	3.5-8	29.8	34
4	$10^{-6}\times3$	$10^{-1}\times1$ -$10^{-6}\times5$	10	2.5-6	30	40
3	$10^{-7}\times4$	$10^{-2}\times1$ -$10^{-7}\times5$	5	3.5-8.5	30.1	This work

Conclusion

In the recent years, the matter of heavy metals contamination has been very debatable. And cobalt is a mineral element which in little amounts is a crucial micronutrient for the body. But, in higher doses could even eventuate to the death of a person. And owing to its wide applications in various industries, its determination is very important for environmental and also clinical analysis. Therefore, a PVC membrane coated graphite electrode was constructed by using 6-chloro-11-azabenzo[a]phenothiazin-5-one as a neutral ion carrier, in this research. The designed potentiometric sensor shows a wide linearity domain, low detection limit, fast response time, superb selectivity and long lifetime. Due to the fact that the strong interaction of 6-chloro-11-azabenzo[a]phenothiazin-5-one with Co^{2+} ions has been proved in this research, the applicability of this ligand in the determination of cobalt (II) by extraction methods had better to be investigated by the experts of this field in the future.

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