Design and Optimization of a PVC Membrane Sensor for Enhanced Selectivity and Sensitivity Towards Co (II) Ions

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Abstract— A novel PVC membrane-based potentiometric sensor was designed for the selective detection of Co²⁺ ions, Schiff ligand 3-chloro-N'utilizing the base (2-hvdroxvbenzvlidene) benzo hvdrazide (S-2) as the neutral ionophore. The ionophore's unique ability to exist in two tautomeric forms-amide and imidol-is pivotal to its high affinity for Co²⁺ ions. The hydroxyl group in the imidol form significantly enhances chelation, making S-2 an effective candidate for cobalt sensing. The sensor exhibits a wide linear detection range from 1.0×10^{-1} to 1.0×10^{-1} mol L⁻¹, with an impressive detection limit of 4.0×10^{-7} mol L⁻¹. It demonstrates near-Nernstian sensitivity, characterized by a slope of 29.7 mV per decade. The electrode delivers a rapid response time of approximately 10 seconds and remains stable for up to 12 weeks without significant performance degradation. High selectivity for Co²⁺ was observed, even in the presence of commonly interfering cations, and the sensor maintains optimal functionality across a pH range of 5.0 to 12.0. The practical performance of the sensor was validated through its application in potentiometric titrations of Co²⁺ with EDTA and the direct determination of cobalt concentrations in environmental samples. This study underscores the potential of the developed sensor for accurate and reliable cobalt ion detection, with broad applications in environmental analysis and industrial monitoring.

Index Terms— Cobalt ion-selective electrode, PVC membrane, Potentiometry, Schiff base.

1. Introduction

Cobalt is only required in trace levels by the human body. A lack of trace metals in the diet causes health issues. In order to produce vital enzymes that act as catalysts, animals utilize trace minerals [1]. These enzymes accelerate the body's natural changes. Living cells require enzymes to function correctly. For instance, cobalt is required for the synthesis of B-12 vitamins naturally. B-12 vitamins guarantee the production of sufficient red blood cells in the human body. Due to its absence in the soil, cobalt also has an impact on other animals. For instance, a cobalt shortage becomes infected with a disease known as coast disease, caused by cobalt deficiency. Moreover, too much cobalt can cause health issues. Cobalt dust can cause respiratory issues, diarrhea, and vomiting in those who work near it. Cobalt can cause skin irritation and rash if it is present.

Cobalt is found in a variety of biological and environmental samples due to its extensive use. Given its harmful consequences, the determination of the cobalt (II) ion becomes significant.

Narendra Kumar, Department of Chemistry, Maharaj Singh College, Saharanpur, India, https://orcid.org/0009-0009-0825-4068 (Dr. Narendra Kumar) The increasing need to quantify cobalt (II) ions in various environmental matrices has driven the advancement of diverse analytical techniques. These methods include capillary electrophoresis (CE) [2], liquid chromatography [3], flow injection analysis [4,5], and spectrophotometry [6,7]. Furthermore, advanced techniques such as inductively coupled plasma-atomic emission spectrometry (ICP-AES) inductively coupled plasma-optical [8], emission spectrometry (ICP-OES) [9,10], inductively coupled plasma-mass spectrometry (ICP-MS) [11], and atomic absorption spectrometry (AAS) [12,13] have been employed for cobalt (II) determination. Solid-phase extraction [14,15], voltammetry [16,17], photoacoustic methods [18], and X-ray fluorescence spectrometry [19,20] have also been utilized for this purpose. Recent studies have focused on developing innovative cobalt ion-selective electrodes incorporating various neutral ion carriers [21-24]. While several cobalt ion-selective electrodes have been documented [25-28], there remains a significant demand for highly selective sensors to facilitate cobalt monitoring. Notably, some of these carriers, containing sulfur and nitrogen donor atoms, have been integrated into polyvinyl chloride (PVC)-based membrane sensors for the selective detection of transition and heavy metal ions [29-33].

The compound 3-chloro-N'-(2-hydroxybenzylidene) benzohydrazide (S-2) has been extensively investigated for its biological properties, particularly as a selective inhibitor of LSD1 and as an iron-chelating agent in anticancer therapies [34]. While its iron-chelating capabilities imply potential applications in metal ion sensing, the literature lacks comprehensive studies exploring its utility as a metal ion sensor. Notably, Schiff base compounds with structural similarities to S-2 have demonstrated efficacy in metal ion detection [35]. For instance, the analogous compound (E)-N'-[2-hydroxybenzylidene]benzohydrazide, differing only by the absence of the chloro substituent, has been reported to form stable complexes with metals such as VO(II), Mn(II), Co(II), Ni(II), and Cu(II). This structural resemblance suggests that 3-chloro-N'-(2-hydroxybenzylidene) benzohydrazide may similarly interact with various metal ions, indicating its potential for applications in metal ion sensing [36].

In this study, we synthesized and characterized the hydrazine-based Schiff base ligand 3-chloro-N'- (2-hydroxybenzylidene) benzohydrazide (S-2) (Figure 1). For the first time, this compound was employed as an ionophore to develop a potentiometric sensor with high selectivity for Co^{2+} ions, demonstrating its novel application in metal ion detection.

2. Materials and Methods

2.1. Chemicals and reagents

All reagents and solvents used in this study were of analytical grade and were applied without any further purification. 3-chlorobenzohydrazide and salicylaldehyde were sourced from Alfa Aesar. High molecular weight poly(vinyl chloride) (PVC), plasticizers including dibutyl phthalate (DBP), o-nitrophenyloctylether (o-NPOE), and bis(2-ethylhexyl)sebacate (BEHS), along with the anion-excluding agent potassium tetrakis(p-chlorophenyl)borate (KTpClPB), which were essential for the fabrication of polymer membrane sensors, were obtained from Sigma-Aldrich.

2.2. Instrumentation

A Perkin-Elmer Model 3100 atomic absorption spectrophotometer (AAS) with a graphite furnace and an inductively coupled plasma atomic emission spectrometer (ICP-AES) were employed for the analyses. Electrochemical potential measurements were conducted using a PH5652 digital pH meter/millivoltmeter (manufactured by ECIL, Hyderabad, India) and a CVM30 microvoltmeter from Century Instruments, Chandigarh, India. The pH values were recorded using a digital pH meter, Model pH5642A, also produced by ECIL, India.

2.3. Synthesis of 3-chloro-N' -(2-hydroxybenzylidene) benzo hydrazide (S-2)

The Schiff base 3-chloro-N' -(2-hydroxybenzylidene)benzo hydrazide (S-2) was synthesized by the reported method [37] as shown in Figure 1.

A solution containing salicylaldehyde (10 mmol) [B] and 3-chlorobenzohydrazide (10 mmol) [A] was prepared in 250 mL of ethanol and subjected to reflux for 2 hours. The reaction mixture was then allowed to cool to ambient temperature. The resulting clear solution was exposed to air for approximately 15 days, during which the majority of the solvent evaporated. This method produced needle-like single crystals of S-2, which were then collected by filtration and allowed to air dry. Yield 2.55 g (95%). Anal. Calcd for C₁₄ H₁₁ClN₂O₂ (%): C, 61.2; H, 4.0; N, 10.2. Found (%): C, 60.9; H, 4.1; N, 10.3. IR (KBr, max/cm1): 3446 (OH), 3164 (NH), 1650 (C ¹/₄ O), 1622 (C ¹/₄ N).



Figure 1. Synthetic pathway for the preparation of the Schiff base, 3-chloro-N'-(2-hydroxybenzylidene)benzohydrazide (S-2).

2.4. Electrode Fabrication

Membranes were fabricated following a procedure adapted from earlier work [38,39]. The performance characteristics, including sensitivity, selectivity, and linearity of a specific ionophore, are strongly dependent on the membrane formulation and the choice of plasticizer. PVC-based membranes were prepared by dissolving the required quantities of Schiff base (S-2), an anion excluder (NaTPB), and different plasticizers (DBP, DEHA, BEHS), along with PVC, in 5 mL of tetrahydrofuran (THF). Once the components were fully dissolved, the solution was concentrated by evaporating THF. This concentrated mixture was then poured into polyacrylate rings placed on a smooth glass surface. To ensure reproducibility, both the viscosity of the solution and the rate at which the solvent evaporates were closely monitored, as these factors can impact the uniformity and morphology of the final Variations in these parameters could membrane. significantly impact the sensor response. Membranes with a thickness of 0.4 mm were carefully affixed to one end of a "Pyrex" glass tube following their detachment from the glass surface. A variety of membrane compositions were prepared and evaluated for their electrochemical properties.

2.5. Equilibration of membranes and potential measurements

The membranes were subjected to equilibration in a 0.1 M $Co(NO_3)_2$ solution for a duration of 72 hours to achieve ion exchange equilibrium. To assess the sensor's response, the concentration of $Co(NO_3)_2$ in the test solutions was systematically varied within the range of 1.0×10^{-8} to 1.0×10^{-7} M. Standard solutions of $Co(NO_3)_2$ were prepared by sequentially diluting a 0.1 M $Co(NO_3)_2$ stock solution. All potential measurements were performed at a controlled temperature of 25°C, utilizing an Ag/AgCl reference electrode in combination with the fabricated Co(II) ion sensor. The setup of the potentiometric cell used for these experiments is detailed as follows:

Ag|AgCl(3.0M KCl)|Co(II) (0.1M) |membrane|test solution|Ag|AgCl (3.0M KCl)

The activity coefficients were determined using the Debye-Hückel equation, which is expressed as follows:

log y = 0.511
$$z^2$$
 [$\mu^{1/2}$ / (1+ 1.5 $\mu^{1/2}$) - 0.2 μ]
(1)

Where μ ionic strength, and z valency

3. Results and Discussion

3.1. Selection of Ionophore

The compound 3-chloro-N'- (2-hydroxybenzylidene) benzohydrazide (referred to as S-2) has been employed as the ionophore in the membrane electrode in the present study. This selection was based on its ability to form highly stable chelates with metal ions of environmental significance as discussed earlier. The molecular structure of S-2 allows it to exist in two tautomeric forms, as illustrated in Figure 2. The hydroxyl group in the imidol tautomer plays a critical role in its chelation mechanism by facilitating the formation of two chelate rings: one six-membered and one five-membered (see Figure 3). These structural features significantly enhance its affinity for Co²⁺ ions. Furthermore, the presence of two hydroxyl groups in the imidol form contributes to stabilizing the +2 charge of Co²⁺ ions, resulting in the formation of highly stable complexes. Owing to these properties, the S-2 ligand demonstrates excellent suitability for coordinating with transition metal ions such as cobalt.

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S= Solvent molecule

Figure 3. Two tautomeric forms (amide and imidol) of ligand S-2 and its chelate formation with Co^{2+} ion.

3.1. Working Concentration Range and Slope

The potential responses of the Co²⁺-selective electrodes, particularly for the (S-2) ion-selective membrane, are illustrated in Figure 4. The figure illustrates the potential response slopes for Co²⁺ ions. In most cases, the observed slopes are marginally lower than the theoretical values predicted for metal ions with single, double, or triple charges. The Co²⁺ sensor, in particular, achieves a Nernstian response across a concentration range of 1.0 \times 10^{-7} to 1.0×10^{-1} M. The composition of the membrane, along with the type of additives used, significantly influences the ionophore's sensitivity and selectivity towards the target ion [40-42]. Therefore, a summary of the performance characteristics of various membranes with different component ratios is provided in Table 1. Among these, membrane number 6, with a composition ratio of PVC:NPOE:S2:KTpClPB as 30:62:5:3, exhibits Nernstian behavior across a broad concentration range for Co²⁺ ions. Among the three plasticizers evaluated, NPOE demonstrated the greatest sensitivity, outperforming DBP and BA. This superior performance can be attributed to the polar solvent characteristics of NPOE which enhance the extraction of Co²⁺ ions with relatively high charge density from the aqueous phase into the organic membrane phase.



ion-selective electrodes incorporating S-2.

Table 1 indicates that the membrane without KTpClPB shows a slope of 20.9 mV per decade (entry 7, Table 1), which is below the anticipated Nernstian response. However, when KTpClPB is included, the membrane exhibits a favorable Nernstian behavior with a slope of 29.7 mV per decade (entry 6, Table 1). The incorporation of lipophilic, immobilized ionic additives plays a crucial role in modifying membrane resistance and, in some cases, refining the selectivity profile of ion-selective PVC membranes, thereby enhancing their performance. It is widely

recognized that lipophilic additives are key to achieving the desired membrane selectivity in ion-selective electrodes. Without these additives, the electrodes fail to exhibit the expected response behaviour [43,44].

Table 1. Optimization of Membrane Components.

No. of Com.	PVC	Ion.	KTpClPB	BESH	NPOE	DBP	Slope
1	30	4	2	70	65	-	25.5
2	30	4	2	-	64	-	26.7
3	30	4	2	-	63	-	31.5
4	30	3	1.5	-	63	64	24.8
5	30	6	2	-	63	-	27.1
6	30	5	3	-	62	-	29.7
7	30	4	0	-	65	-	20.9
8	30	3	2	-	65	-	19.7

The inclusion of such additives not only reduces the ohmic resistance, enhancing the response behaviour and selectivity, but also improves the sensitivity of the membrane electrode when the ionophore's extraction efficiency is limited. Furthermore, the performance of the developed sensor was evaluated at various concentrations of the internal reference solution, ranging from 1.0×10^{-3} to 1.0×10^{-1} M. The results demonstrated that changes in the internal solution concentration did not significantly affect the corresponding potential response, except for a slight modification in the captured Nernstian plot. A concentration of 1.0×10^{-1} M for the reference solution was found to be optimal for stable sensor performance. The contact time and the concentration of the equilibrating solution were optimized to achieve stable and repeatable potentials with rapid response times. The optimal equilibration period in a 1.0×10^{-1} M Co $(NO_3)_2$ solution was determined to be 72 hours.

3.2. Calibration Curve

The typical calibration graph characteristics of cobalt sensor based the Schiff base on ligand 3-chloro-N'-(2-hydroxybenzylidene) benzo hydrazide (S-2) as an ionophore is reported in Figure 5. Within the concentration range of 1.0×10^{-7} to 1.0×10^{-1} M, the electrode exhibited a linear response to Co^{2+} ion activity (Figure 5). At 25°C, the calibration curve showed a slope of 29.0 ± 0.5 mV per decade of activity change. The detection limit was established by identifying the intersection point of the extended linear segments of the calibration plot, which indicated a concentration of 4.0×10^{-8} M.



Figure 5. Calibration curve of the Co (II) sensor at the membrane.

3.3. Dynamic Response and Lifetime

Additionally, we recorded the average time required for the Co(II) ion-selective electrode to stabilize within ± 1 mV of the final equilibrium potential after several immersions in solutions with cobalt ions, each differing in concentration by a factor of ten. For every concentration, the membrane electrode's static response time was approximately 10 s (Figure 6). Potentials were steady for almost five minutes, with a standard deviation of 0.3 mV across ten replicate measurements. The electrode's performance characteristics remained consistent when the potentials were recorded across concentrations, regardless of whether they were tested from low to high or the other way around.



Figure 6. Electrode's response over time to fluctuations in the Co(II) solution concentration.

3.4 Lifetime and Reproducibility Studies

The sensor membrane exhibited stable performance for a duration of 12 weeks, with no significant fluctuations in potential values. To preserve its functionality, the membrane was stored in a 0.001 M Co²⁺ solution and reconditioned in a 0.1 M Co²⁺ solution whenever potential deviations were observed. The reproducibility of the sensor was assessed by conducting 25 consecutive measurements at a Co²⁺ concentration of 1.0×10^{-3} M, resulting in a standard deviation of 0.5 mV, which reflects excellent repeatability and precision.

3.4. Effect of pH

The impact of pH on the potential response of the cobalt sensor was analyzed using a 1.0×10^{-3} M Co²⁺ solution over a pH range from 5.0 to 12.0, as depicted in Figure 7. The potential response remained stable between pH 5.0 and 10.0, but a significant shift occurred at higher pH levels. The significant shift in potential observed at elevated pH levels is likely attributed to the formation of hydroxy complexes of Co²⁺ ions in the solution. Conversely, at lower pH levels, a reduction in potential was noted, suggesting that the electrode began to exhibit a response to hydrogen ions as well [31].



Figure 7. Impact of pH on the potential response of the Co(II) ion-selective sensor

3.5. Potentiometric selectivity

Selectivity coefficients are commonly employed to quantify the influence of interfering ions on the response behaviour of ion-selective membrane electrodes. The potentiometric selectivity coefficients of the cobalt membrane sensor were determined using the matched potential method [45]. As indicated in the results presented in Table 2, the selectivity coefficients for all other cations were found to be 3.0×10^{-3} or lower, suggesting that these ions have a minimal effect on the performance of the Co²⁺ ion-selective electrode.

Table 2. Selectivity coefficients for various interferingcations for the membrane sensor.

Ion	K _{Sel}
La ³⁺	$5.0 imes 10^{-5}$
Fe ³⁺	$3.3 imes 10^{-4}$
Al^{3+}	$5.0 imes 10^{-4}$
Sr^{2+}	$7.0 imes 10^{-4}$
Cd^{2+}	$8.0 imes 10^{-5}$
Ni ²⁺	$3.0 imes 10^{-3}$
Cu ²⁺	$6.0 imes 10^{-5}$
K^+	3.1×10^{-5}
Na^+	$3.9 imes 10^{-4}$
Ag^+	$3.6 imes 10^{-4}$

3.6. Comparative Analysis of Co²⁺ Ion-Selective Membrane Sensor Performance with Reported Literature

Table 3 provides a detailed comparison of the performance of our Co^{2+} ion-selective membrane sensor with similar devices reported in the literature. Key metrics such as sensitivity, selectivity, response time, stability, and reproducibility are compared. Our sensor demonstrates excellent performance, with high selectivity for Co^{2+} , rapid response, long-term stability, and reproducibility, positioning it as a competitive option for real-world applications in environmental and industrial monitoring. **Table 3.** Comparison of the Co^{2+} selective sensor with the reported sensors.

R	Detect	Serious	Working		Slope
ef.	ion limit	interfering	concentration	р	(mV
no.	(M)	ions	Range (M)	Н	decade-1
				range	of
				-	$a_{Ce^{2+}})$
This	4.0 ×	No	1.0×10^{-7} to	5.0 -	29.7
work	10^{-8}	interference	1.0×10^{-1}	12.0	
24	8.0 x 10 ⁻⁶	Na^{+} , Ni^{2+} ,	$4.0 \times 10^{-6} - 1.0$	2.8	29.0
		Fe ³⁺	$\times 10^{-1}$	-7.3	
46	4.0 x 10 ⁻⁶	$Cu^{2+}, Zn^{2+},$	8.6 x 10 ⁻⁶ –	3.0 -	30.3
		Fe^{3+}, Cd^{2+}	1.0 x 10 ⁻²	11.0	
47	6.0 x 10 ⁻⁷	Ni ²⁺	2.0 x 10 ⁻⁶ –	3.0	29.0
			1.0 x 10 ⁻²	-8.0	
31	8.5 x 10 ⁻⁷	Ni ²⁺ , Cu ²⁺ ,	6.3 x 10 ⁻⁶ –	2.5	30.0
		Ag^+, Hg^{2+}	1.0 x 10 ⁻¹	-2.6	
27	3.9×10 ⁻⁷	Ni^{2+} , Cu^{2+} ,	6.3×10 ⁻⁷ - 1.0	3.3	29.0
		Ag^+	x 10 ⁻¹	-9.0	
48	3.0 x 10 ⁻⁷	No	1.0 x 10 ⁻⁶ –	6.0	28.6
		interference	1.0 x 10 ⁻¹	-10	

4. ANALYTICAL APPLICATIONS

4.1. Analysis of Water Samples

Water samples were gathered, and the pH was adjusted to fall within the operational range of the sensor. The outcomes, presented in Table 4, were then compared with the results obtained using Atomic Absorption Spectroscopy (AAS). The comparison indicates that the sensor can effectively be utilized for the determination of Co(II) in real industrial wastewater samples.

Table 4. Analysis of water samples using AAS and the proposed sensor.

Sample	AAS (µg/mL)	Sensor (µg/mL)
Waste water 1	9.2	9.9
Waste water 2	1.7	2.1
Waste water 3	3.8	3.9

4.2. Potentiometric titration

The sensor demonstrated its utility not only in the direct determination of Co²⁺ ions but also for titrating Co²⁺ with various chelating and precipitating agents using the introduced Co²⁺-selective membrane electrode. For example, a 20.0 mL solution of Co^{2+} (1.0 × 10⁻³ M) was titrated with EDTA (1.0 × 10⁻² M). The resulting titration curve is shown in Figure 8. The data indicate that the electrode, with a concentration of $(1.0 \pm 0.03) \times 10^{-1}$ M, can be reliably used to determine the concentration of Co²⁴ ions in solution.



Figure 8. Potentiometric titration curve for 20 mL of 1.0 \times 10⁻³ M Co²⁺ with 1.0 \times 10⁻² M EDTA, conducted at a constant pH range.

5. CONCLUSIONS

The PVC-based membrane sensor, featuring the Schiff base 3-chloro-N'-(2-hydroxybenzylidene) benzo hydrazide (S-2) as the electroactive material, KTpClPB as the solvent mediator, and NaTPB as the anion excluder, demonstrated a broad operational concentration range. The sensor exhibited a rapid response time and maintained stable performance for up to three months without significant deviations in its response properties. It exhibited strong selectivity for Co(II), even in the presence of interfering ions commonly found in industrial waste. The electrode also displayed excellent reproducibility, making it ideal for use as an indicator electrode in potentiometric titrations and for the quantitative analysis of Co(II) in real waste samples.

For future work, we propose extending the lifetime studies beyond three months to further assess the sensor's long-term stability. Additionally, exploring alternative ionophores and membrane compositions could provide opportunities to enhance the sensor's selectivity and sensitivity. Further, testing the sensor in real-world industrial and environmental monitoring applications will be essential to fully evaluate its practical applicability and performance under diverse conditions.

Abbreviations

PVC= Polyvinyl Chloride EDTA= Ethylene Diamine Tetra Acetic Acid LSD 1= Lysine-Specific Histone Demethylase 1 DBP=Dibutyl Phthalate DEHA= Di(2-ethylhexyl) Adipate BEHS= Bis(2-ethylhexyl) Sebacate NPOE= 1-(2-Nitrophenoxy) octane Acknowledgements The author acknowledges M. S. College, Saharanpur, and

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Author Contributions

Narendra Kumar is the sole author. The author read and approved the final manuscript.

Conflicts of Interest

The author declares no conflicts of interest.

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