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Full Paper

A Novel Potentiometric Sensor for Trace Barium based on a 4,4′-Dinitrobenzil Derivative Ionophore Synthesized via Nano-Ionic Liquid Catalysis

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Abstract- Among the analytical methods for measuring small amounts of metal ions, potentiometric ion-selective sensors have high speed, precision, and accuracy and are more convenient to use. On the other hand, one-pot synthesis offers an attractive and sustainable approach by reducing waste, saving time, and simplifying complex multi-step reactions. Another important advantage of one-pot synthesis lies in its improved atom economy and reduced environmental footprint. In this research, a new Ba^{2+} ion-extracting potentiometric sensor based on 1,2-bis(4-nitrophenyl) ethane-1,2-dione (4,4'-dinitrobenzil) (BNED) ligand was prepared. The interaction between the ligand with barium ions and other metal ions were investigated through UV-Vis spectroscopy, which indicated the selectivity for Ba^{2+}. The optimal percentage composition for the present electrode membrane is 37:55:3:5, respectively for PVC:BA: NaTPB: BNED. This sensor has a Nernst slope of 24.9 mV/Decade in the linear range of $1\text{-}10^{-7}$ M to $1\text{-}10^{-2}$ M. The response of the electrode in the pH range of 4.0 to 10.5 is independent of the changes in the concentration of H^+ ions. The designed electrode has a lifespan of about 3 months and a response time of about 25 seconds. This sensor has good selectivity for Ba^{2+} over various cations (alkali metals, alkaline earth metals, heavy metals and transition metals). The electrode prepared in the present study was used as a detector electrode in the measurement of Ba^{2+} in real samples.

Keywords- Potentiometric sensor; 1,2-bis(4-nitrophenyl) ethane-1,2-dione (4,4'-dinitrobenzil); Ion-selective membrane electrode; Barium ion

1. INTRODUCTION

Heavy metals are recognized as one of the most persistent classes of environmental contaminants because of their high toxicity, long-term environmental persistence, and tendency to accumulate in biological systems. Among these pollutants, lead, thallium, cadmium, barium, and antimony are extensively utilized in a wide range of industrial activities, making them important contributors to environmental contamination [1]. Previous studies have identified arsenic, cadmium, chromium, nickel, lead, and barium as toxic elements capable of inducing molecular-level toxicity and causing adverse biological effects [2]. Barium (Ba), a naturally occurring alkaline earth metal, is widely employed in numerous industrial applications; however, its soluble compounds present considerable health hazards. Soluble barium salts, including barium chloride and barium nitrate, disrupt potassium ion transport by blocking cellular potassium channels, thereby causing a rapid decrease in serum potassium concentration (hypokalemia) [3]. Consequently, exposure to these compounds may result in progressive muscle weakness, hypertension, cardiac arrhythmias, and respiratory paralysis, all of which may become life-threatening in the absence of immediate medical treatment [3,4]. Human exposure mainly occurs through ingestion of contaminated drinking water and, to a lesser extent, through inhalation of airborne particles in occupational environments [3,5]. In contrast, the insoluble form of barium, namely barium sulfate, exhibits very limited bioavailability and is therefore safely employed as a radiographic contrast agent in medical imaging procedures [3]. Industrial operations such as mining, ore processing, and inappropriate waste management continue to increase environmental barium contamination, raising concerns regarding chronic exposure even at relatively low concentrations [5]. Recent toxicological investigations have consistently identified the cardiovascular and neuromuscular systems as the primary targets of barium toxicity, emphasizing the importance of strict monitoring and regulation of barium concentrations in drinking water and occupational environments [4,5].

Accurate determination of barium is of considerable importance in environmental monitoring, clinical toxicology, industrial quality control, and geochemical investigations [6]. The selection of an appropriate analytical method largely depends on factors such as the sample matrix, the required detection limit, and whether elemental concentration or isotopic composition is being determined. Conventional gravimetric analysis based on the precipitation of barium as barium sulfate ($BaSO_4$) provides reliable results but generally requires lengthy analytical procedures and is susceptible to various chemical interferences [7]. Instrumental techniques such as Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) are among the most frequently employed methods for trace barium analysis, with ICP-MS offering excellent sensitivity together with multi-element detection capability [6,8]. For applications requiring highly precise isotope ratio measurements, Multi-Collector ICP-MS (MC-ICP-MS) remains the preferred analytical technique because of its outstanding isotopic precision [9]. Nevertheless, the analytical

performance of plasma-based techniques strongly depends on complete digestion of the sample, which remains particularly challenging for highly stable barium-containing minerals such as barite ($BaSO_4$) [10,11].

Although modern instrumental techniques provide excellent analytical performance, several practical challenges continue to limit their routine application in barium determination. One of the most critical issues is the sample preparation step [11]. Because barium readily forms highly insoluble compounds with sulfate and several other anions, incomplete dissolution or precipitation during sample preparation may lead to analyte loss and reduced analytical accuracy [11]. Furthermore, barite, one of the most stable barium minerals, exhibits remarkable resistance toward conventional acid digestion methods, making alkaline fusion necessary for complete dissolution. However, this procedure increases the concentration of dissolved salts in the sample and consequently enhances matrix effects during ICP-MS analysis [10,11]. Instrumental interferences also represent a significant source of analytical uncertainty. In ICP-MS measurements, the major isotopes of barium may suffer from spectral overlap caused by polyatomic oxide species derived from lighter elements, thereby necessitating the use of collision/reaction cell systems or high-resolution mass spectrometers to ensure reliable quantification [6,11]. Likewise, accurate isotope ratio determination by MC-ICP-MS requires rigorous correction of instrumental mass bias before precise isotopic data can be obtained [9]. Besides these analytical limitations, the high acquisition and maintenance costs of sophisticated plasma-based instruments, together with their dependence on skilled operators, considerably restrict their availability for routine laboratory analysis [6,9].

Ion-selective electrodes (ISEs) constitute one of the most widely used classes of potentiometric sensors for the selective determination of ionic species. These sensors operate by converting the activity of a target ion directly into an electrical potential through a stable electrochemical system incorporating an appropriate reference electrode. Owing to their simple operating principle, rapid response, wide linear concentration range, excellent selectivity, relatively low detection limits, low operational cost, and portability, ISEs have attracted considerable attention for monitoring trace heavy metals in environmental, industrial, and biological samples [12-14]. Continuous efforts to improve their analytical performance have stimulated the development of a broad variety of membrane materials, including neutral ionophores, inorganic ion exchangers, chelating ligands, intercalation compounds, and advanced nanostructured composites. Moreover, potentiometric sensing offers additional practical advantages such as rapid analysis, low energy consumption, straightforward instrumentation, and convenient integration into automated analytical systems designed for continuous monitoring applications. Recent progress in electrochemical sensing technology, together with advances in membrane fabrication and microelectronic devices, has significantly expanded the applicability of ISEs for portable and real-time determination of hazardous heavy metal ions under field conditions [15,16]. In recent years, our research group has also reported

several ion-selective electrodes for the determination of different cationic and anionic species, demonstrating the effectiveness of this analytical approach [17-28].

Among the various synthetic strategies developed in recent years, one-pot synthesis has become an attractive and efficient methodology because it enables multiple reaction steps to be completed within a single reaction vessel without isolating intermediate products [29]. This synthetic approach substantially decreases reaction time, solvent consumption, and purification procedures while simultaneously improving atom economy and overall process sustainability [30]. Elimination of intermediate isolation not only minimizes material loss but also reduces experimental variability and frequently enhances product yield and reproducibility [29,30]. Consequently, one-pot methodologies have found widespread application in the synthesis of structurally complex compounds for medicinal chemistry, materials science, and large-scale industrial production [30,31]. These characteristics are fully consistent with the principles of green chemistry, emphasizing environmentally friendly, economical, and resource-efficient synthetic processes [31]. In the present work, 1,2-bis(4-nitrophenyl)ethane-1,2-dione (4,4′-dinitrobenzil) was synthesized using a nanomaterial-functionalized ionic liquid organosilica catalyst and subsequently employed as a neutral ionophore for fabricating a potentiometric membrane sensor capable of the selective determination of trace concentrations of barium ions. The analytical applicability of the proposed sensor was further verified through successful determination of barium in real samples.

2. EXPERIMENTAL SECTION

2.1. Reagents

Analytical-grade nitrophenyl octyl ether (NPOE), dibutyl phthalate (DBP), benzyl acetate (BA), sodium tetraphenylborate (STPB), oleic acid (OA), tetrahydrofuran (THF), and high-molecular-weight poly (vinyl chloride) (PVC) were supplied by Fluka and used without any additional purification. The nitrate salts of all investigated cations were obtained from Merck at the highest commercially available purity and, except for vacuum drying over P_2O_5, were employed as received. Triply distilled deionized water was utilized for the preparation of all solutions and throughout the experimental work. The remaining chemicals and reagents were either synthesized in our laboratory or procured from Fluka, Aldrich, or Merck.

2. 1. 1. Preparation of Solution

A 1.0×10^{-2} M barium stock solution was prepared by accurately dissolving the appropriate amount of analytical-grade barium nitrate ($Ba(NO_3)_2$) in deionized water. Working standard solutions covering the concentration range of 1.0×10^{-7}–1.0×10^{-2} M were freshly prepared by serial dilution of the stock solution with deionized water.

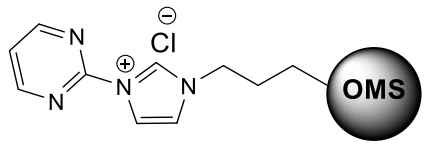
The internal reference solution of the ion-selective electrode consisted of 1.0×10^{-3} M $Ba(NO_3)_2$, which was prepared by dilution of the stock solution. Before each potentiometric

measurement, the electrode was conditioned by soaking in a 1.0×10^{-3} M Ba^{2+} solution for 24 h.

To investigate the influence of pH, dilute hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions were used for pH adjustment. The pH values were monitored using a calibrated digital pH meter. All aqueous solutions were prepared with freshly produced deionized water (resistivity ≥18.2 MΩ·cm) and stored in clean polyethylene containers at room temperature.

2.2. Ligand Synthesis

A multi-step synthesis of pyrimidyl imidazolium ionic liquid confined in SBA-15 framework (Pyrm-OMS) was prepared via sol-gel process by hydrolysis and co-condensation of 3-(pyrimidin-2-yl) 1-(3-(trimethoxysilyl) propyl) 1H-imidazol-3-ium chloride and tetraethoxy silane was recently reported by our research group (Figure 1) [32]. According to this report, the surface area of Pyrm-OMS nanomaterials was 574 m^2/g, with a pore volume of 0.59 mL/g and an average size of 5.5 nm. The hexagonal mesostructured ordering and thermal stability of Pyrm-OMS nanocatalyst were confirmed by X-Ray diffraction and thermogravimetric analysis, respectively. The present study aims to further explore the catalytic potential of Pyrm-OMS in the environmentally friendly one-pot synthesis of 1,2-bis(4-nitrophenyl) ethane-1,2-dione (4,4'-dinitrobenzil) from 4-nitrobenzaldehyde under mild conditions.



Pyrm-OMS

Figure 1. Chemical structure of Pyrm-OMS nanomaterials

2.2.2. General procedure for synthesis 1,2-bis(4-nitrophenyl) ethane-1,2-dione (4,4'-dinitrobenzil) catalyzed using Pyrm-OMS nanomaterials

In a typical reaction, a mixture containing 4-nitrobenzaldehyde (5 mmol), Pyrm-OMS nanomaterials (0.01 g), trimethylamine (1 mL), ethanol (3 mL), and water (5 mL) was charged into a three-necked round-bottomed flask equipped with a magnetic stir bar. The corresponding benzoin formation was completed after reaction at 80°C for 8 h under constant stirring, as indicated by TLC analysis. After that, hydrogenperoxide (30%, 1 mL) was added via syringe to the reaction mixture subsequently. The reaction mixture was stirred for 10 h at the same temperature.

After completion of the reaction (TLC), the reaction mixture was filtered and concentrated. Then hot chloroform (10 mL) was added to the filtrate, and heterogeneous Pyrm-OMS nanomaterials were washed and recovered for the next reaction run. The combined concentrated filtrate and chloroform washing was washed with water (2×10 mL) and dried over sodium sulfate. The solvent was removed under vacuum. The obtained solid was purified by recrystallization in ethanol to afford pure 4,4'-dinitrobenzil characterized by ^{1}H & ^{13}C NMR.

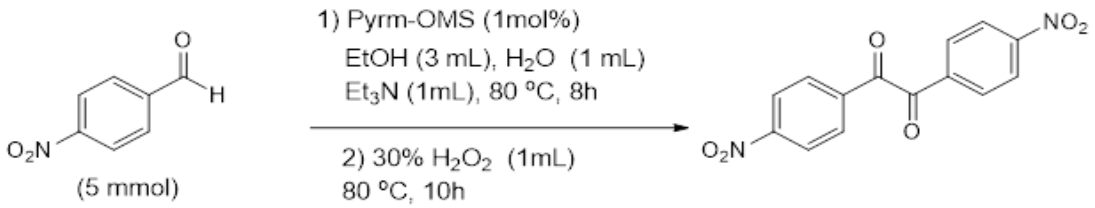


Figure 2. One-pot synthesis of 1,2-bis(4-nitrophenyl) ethane-1,2-dione (4,4'-dinitrobenzil) catalyzed by Pyrm-OMS nanomaterials

2.3. Electrode preparation

To prepare the PVC membrane, 30 mg of powdered PVC, 60 mg of nitrophenyl octyl ether (NPOE) as the plasticizer, 3 mg of potassium tetrakis(4-chlorophenyl) borate (KTCPB) as the lipophilic additive, and 7 mg of the ionophore L were dissolved in 4 mL of freshly distilled tetrahydrofuran (THF). The mixture was stirred thoroughly until a uniform solution was obtained and then transferred into a 2 cm diameter glass dish. The solvent was allowed to evaporate gradually at room temperature until a viscous membrane cocktail was formed. A Pyrex tube (3–5 mm o.d.) was carefully dipped into the membrane solution for approximately 5 s, producing a transparent membrane layer with an approximate thickness of 0.3 mm. The coated tube was subsequently removed and left to dry under ambient conditions for nearly 24 h. After complete drying, the electrode body was filled with an internal solution containing 1.0×10^{-3} M $Ba(NO_3)_2$. Before potentiometric measurements, the fabricated membrane electrode was conditioned by immersion in a 1.0×10^{-2} M $Ba(NO_3)_2$ solution for 24 h [17–28]. An Ag/AgCl electrode was employed as the internal reference electrode.

2.4. The emf measurements

Potentiometric measurements were carried out using polymeric membrane electrodes configured in the following electrochemical cell:

Ag/AgCl | 3.0 M KCl | internal filling solution (1.0×10^{-3} M Ba^{2+}) | PVC membrane | test solution | Hg/Hg_2Cl_2, saturated KCl.

The electromotive force (emf) of the cell was measured at 25.0 °C with a Corning Ion Analyzer Model 250 pH/mV meter. Ion activities corresponding to the measured potentials were estimated according to the Debye–Hückel equation [33].

3. RESULTS AND DISCUSSION

3.1. UV–Vis Spectroscopic Studies and Mechanistic Considerations

The UV–Vis spectrum of the free ionophore, 1,2-bis(4-nitrophenyl) ethane-1,2-dione (4,4′-dinitrobenzil), recorded in acetonitrile exhibited an intense absorption maximum at approximately 290 nm. This absorption band is attributed to the π→π* electronic transition arising from the conjugated aromatic system together with the diketone chromophore. Owing to its sensitivity toward changes in the electronic environment of chromophoric molecules, UV–Vis spectroscopy provides an effective approach for investigating ligand–metal interactions, where even weak coordination processes can produce detectable spectral variations [33].

Progressive addition of Ba^{2+} ions to the ligand solution caused a continuous reduction in the absorbance intensity at 290 nm, resulting in a distinct hypochromic effect. Throughout the titration experiment, no new absorption bands appeared within the investigated wavelength range. This observation indicates that coordination with Ba^{2+} primarily perturbs the intrinsic electronic transitions of the ligand instead of producing a new charge-transfer band. Such spectral behavior is consistent with metal coordination through carbonyl oxygen donor atoms, where complex formation modifies the electronic distribution responsible for the π→π* transition [34].

The observed decrease in absorbance is attributed to the interaction between Ba^{2+} and the oxygen atoms of the 1,2-diketone moiety. Coordination of the metal ion is expected to alter the electron density around the carbonyl groups while partially reducing the conjugation within the aromatic–carbonyl system. These electronic changes decrease the transition probability of the π→π* excitation, thereby producing the experimentally observed hypochromic response. Moreover, the strongly electron-withdrawing para-nitro substituents enhance molecular polarization, increasing the donor ability of the carbonyl oxygen atoms toward hard metal ions. Comparison of the spectral responses obtained for other investigated cations, including alkali and alkaline earth metal ions, demonstrated that Ba^{2+} produced the largest change in absorbance. This enhanced affinity can be explained by both steric and electronic considerations. The relatively large ionic radius of Ba^{2+} is well suited to the spatial arrangement of the two carbonyl donor sites, facilitating effective coordination. In addition, according to the HSAB principle, Ba^{2+} behaves as a hard Lewis acid and therefore exhibits a stronger preference for oxygen-containing donor atoms than many competing cations. Consequently, smaller or more strongly hydrated metal ions display less favorable interactions under identical experimental conditions [34].

Application of the Benesi–Hildebrand equation to the spectrophotometric titration data, assuming a 1:1 ligand-to-metal binding model, afforded a formation constant on the order of 10^4 M^{-1}. The excellent linear relationship obtained from the Benesi–Hildebrand plot further confirms the proposed complex stoichiometry [35]. Considering that the ligand is a neutral molecule without a preorganized macrocyclic structure, the calculated stability constant indicates sufficiently strong interaction with Ba^{2+} while maintaining the reversible binding characteristics required for potentiometric sensing. The calculated formation constants for Ba^{2+} together with those obtained for the remaining investigated cations are listed in Table 1, clearly demonstrating the preferential affinity of the synthesized ionophore toward Ba^{2+}.

Overall, the UV–Vis results provide convincing evidence for selective recognition of Ba^{2+} by the synthesized ionophore in solution. The combination of a distinct and selective spectral response together with a moderately high formation constant confirms that 1,2-bis(4-nitrophenyl) ethane-1,2-dione is an appropriate neutral carrier for Ba^{2+} recognition. Verification of this solution-phase complexation behavior provides a solid foundation for incorporating the ligand into a polymeric membrane for fabrication of a potentiometric barium-selective electrode [36].

Table 1. Formation constants of various cations with BNED

Cation	*Log* K_f	Cation	*Log* K_f
Ba^{2+}	3.95±0.05	Al^{3+}	1.85±0.02
Ni^{2+}	3.01±0.07	Ag^{+}	1.79±0.05
Pb^{2+}	2.94±0.04	Co^{2+}	1.66±0.10
La^{3+}	2.22±0.03	Mg^{2+}	1.52±0.08
Mn^{2+}	2.14±0.09	K^{+}	1.50±0.07
Cr^{3+}	1.98±0.05	Na^{+}	1.33±0.09
Cu^{2+}	1.91±0.07	Ca^{2+}	1.30±0.08

3.2. Membrane Composition

The analytical performance of ion-selective membrane electrodes, including their selectivity, detection limit, and linear dynamic range, is strongly influenced not only by the characteristics of the analyte ion but also by the composition, nature, and physicochemical properties of the membrane components.

Following the spectroscopic confirmation of the most suitable metal ion for complexation with the synthesized ionophore, the membrane composition was optimized using a one-variable-at-a-time strategy. During this optimization process, three membrane constituents were maintained at constant levels while the remaining component was systematically varied. For each optimization step, twenty individual membrane electrodes were fabricated. After an appropriate conditioning period, the potential of each electrode was measured with a voltmeter and the corresponding values were recorded. Calibration curves were subsequently

constructed, and the slope of each electrode response was calculated. Comparison of the highest slope obtained at each optimization stage (Table 2) allowed identification of the membrane composition that produced a response closest to the theoretical Nernstian slope for divalent ions (29.6 mV per decade). This optimized membrane formulation was then selected for all subsequent potentiometric studies.

Table 2. Optimization of membrane ingredients

Membrane No.	Composition (%)				Slope (mV/decade)	Dynamic range (M)
	Matrix (PVC)	Plasticizer	Additive	Ionophore (BNED)		
1	40	60	-	-	~0	-
2	38	NPOE, 60	2	-	~0	-
3	35	NPOE, 60	2	3	10.5	1.0×10^{-3} -1.0×10^{-5}
4	33	NPOE, 60	2	5	18.1	3.0×10^{-2} -1.0×10^{-6}
5	31	NPOE, 60	2	7	16.4	4.0×10^{-2} -1.0×10^{-6}
6	32	NPOE, 60	3	5	21.5	1.0×10^{-2} -1.0×10^{-6}
7	31	NPOE, 60	4	5	20.0	5.0×10^{-2} -5.0×10^{-6}
8	37	NPOE, 55	3	5	23.9	1.0×10^{-1} -1.0×10^{-5}
9	27	NPOE, 65	3	5	19.3	1.0×10^{-1} -1.0×10^{-6}
10	**37**	**BA, 55**	**STPB,3**	**5**	**24.9**	**1.0×10^{-2} -1.0×10^{-7}**
11	37	BA, 55	Ktetrakis*,3	5	23.1	1.0×10^{-2} -5.0×10^{-7}
12	37	DOP, 55	Ktetrakis,3	5	22.2	5.0×10^{-1} -1.0×10^{-5}

**Potassium-tetrakis-(4-chlorphenyl)-borat*

Since previous investigations have demonstrated that a plasticizer-to-PVC ratio of approximately 2 generally provides desirable electrochemical characteristics for PVC-based ion-selective membranes, the optimization procedure was initiated using this ratio. The final optimized membrane consisted of 4,4′-dinitrobenzyl as the ionophore, benzyl acetate as the plasticizer, sodium tetraphenylborate as the lipophilic ionic additive, and poly(vinyl chloride) (PVC) as the supporting polymer matrix.

3.2.1. Effect of the Ionophore (Carrier)

As presented in Table 2, the concentration of the ionophore (4,4′-dinitrobenzyl) had a pronounced effect on the membrane response. Increasing the ionophore content up to 5% enhanced the calibration slope, whereas further addition resulted in a gradual decrease in electrode sensitivity. At lower ionophore concentrations, the membrane contains an insufficient number of active complexation sites for barium ions, leading to a diminished analytical response. In contrast, excessive ionophore loading may promote non-uniform distribution throughout the membrane or partial saturation of the polymeric phase. Moreover, an

overabundance of ionophore can disrupt favorable polymer–polymer interactions and reduce carrier mobility within the membrane, ultimately deteriorating the potentiometric performance of the electrode [25].

3.2.2. Effect of the Ionic Additive

The incorporation of ionic sites into the membrane is essential for achieving desirable performance in ion-selective electrodes. In membranes containing neutral carriers, the addition of lipophilic ionic additives bearing a charge opposite to that of the target ion enhances selectivity, lowers membrane resistance, and improves the overall stability of the electrode, provided that both the ionophore type and its concentration are properly optimized. The optimum molar ratio between the ionic additive and the carrier is governed by the charge of the primary and interfering ions as well as the stoichiometry of their complexes with the ionophore [25].

Numerous investigations have shown that lipophilic ionic additives substantially improve the operational behavior of polymeric membrane sensors. Their incorporation decreases membrane resistance, suppresses interference from counter ions, and consequently enhances both selectivity and sensitivity [25]. In addition, these additives accelerate ion-transfer kinetics across the membrane–solution interface. Their principal function is to impart selective ionic permeability to the PVC membrane, and in their absence many membrane electrodes fail to exhibit satisfactory potentiometric characteristics.

As summarized in Table 3-2, membranes containing 3% sodium tetraphenylborate (NaTPB) exhibited superior analytical performance, providing enhanced sensitivity and a calibration slope that approached the theoretical Nernstian value more closely than the other investigated membrane formulations.

3.2.3. Effect of the Plasticizer

An ideal plasticizer should exhibit high lipophilicity, relatively high molecular weight, low volatility, limited leaching from the polymer matrix, and excellent compatibility with all membrane constituents. Appropriate viscosity and dielectric constant are likewise essential. The plasticizer plays a pivotal role in determining the overall characteristics of the membrane sensor, particularly its selectivity, because it influences both the dielectric properties of the membrane phase and the mobility of the carrier and ionic species within the membrane [25].

The optimization experiments demonstrated that benzyl acetate, possessing a dielectric constant of approximately 5, effectively retained the ionophore within the membrane while providing favorable conditions for stable complex formation with barium ions. As indicated in Table 2, decreasing the plasticizer content to 55% resulted in an increase in the electrode slope toward the expected Nernstian response.

3.2.4. Effect of the Polymer Matrix

Poly(vinyl chloride) (PVC) served as the polymer matrix for membrane fabrication in the present study. Although PVC is commonly considered an inert structural support, it has a significant influence on the physicochemical properties of the membrane. Compared with many other polymeric materials, PVC-based membranes generally provide greater operational stability, longer service life, and stronger adhesion to the electrode substrate. Furthermore, PVC forms a microscopic network capable of accommodating both the plasticizer and ion exchanger, promoting membrane swelling and facilitating ion transport, which contributes to a potentiometric response close to the theoretical Nernstian behavior.

Based on the optimization experiments and the results summarized in Table 2, the optimum membrane formulation for the proposed barium-selective sensor consisted of 37:55:3:5 (PVC:BA:NaTPB:L, respectively).

3.3. Response Characteristics of the Ba^{2+}-ISE

The analytical performance of the fabricated Ba^{2+}-selective electrode was assessed according to the recommendations of IUPAC [37]. The emf response of the prepared polymeric membrane electrode (Figure 3) exhibited a well-defined Nernstian behavior across a wide concentration range.

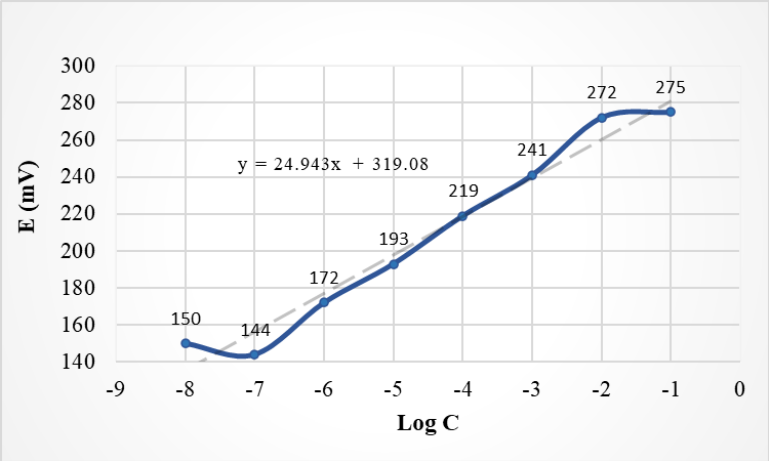


Figure 3. Calibration graph PME electrode

As illustrated in Figure 3, the electrode displayed a linear response toward Ba^{2+} over the concentration interval of 1.0×10^{-7}–1.0×10^{-2} M, with a Nernstian slope of 24.9±0.3 mV $decade^{-1}$. The detection limit, estimated from the intersection of the extrapolated linear sections of the calibration curve, was found to be 9.1×10^{-8} M.

The response time, which is an important parameter for practical sensing applications, was determined by measuring the time required for the electrode potential to reach within ±1 mV

of its final equilibrium value following successive tenfold changes in Ba^{2+} concentration. As shown in Figure 4, the fabricated polymeric membrane electrode attained a stable potential in less than 25 s, indicating a rapid dynamic response.

The long-term operational stability of the proposed barium-selective electrode was further investigated over a period of 15 weeks. During this evaluation, the sensor was used routinely for approximately 2 h per day, demonstrating satisfactory durability throughout the testing period.

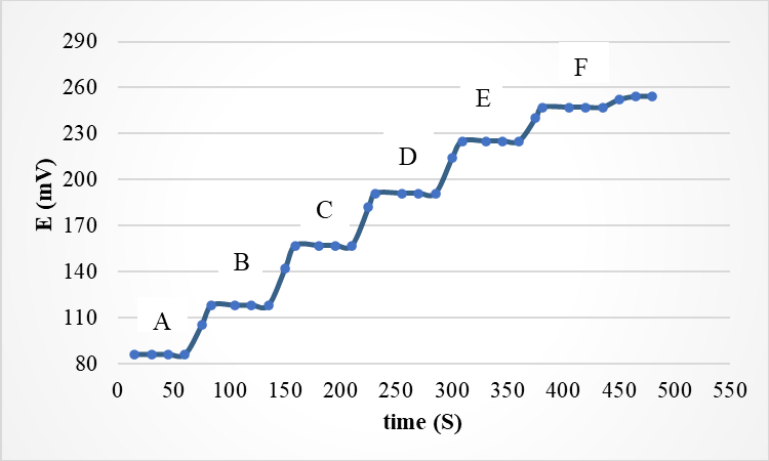


Figure 4. Typical dynamic response of the proposed electrode for step change concentrations from low to high: A) 1.0×10^{-7}, B) 1.0×10^{-6}, C) 1.0×10^{-5}, D) 1.0×10^{-4}, E) 1.0×10^{-3}, F) 1.0×10^{-2} M

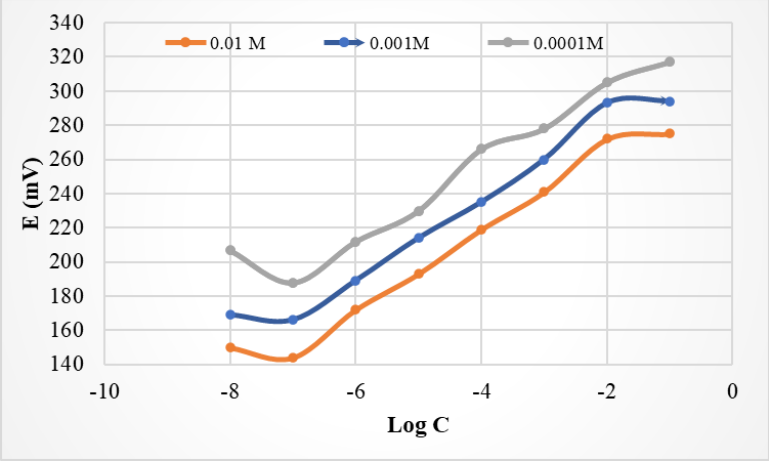


Figure 5. Effect of internal solution. a: 10^{-2} M, b: 10^{-3} M, c: 10^{-4} M of Ba^{2+}

3.4. Effect of the Internal Solution

According to the established theoretical description of ion-selective electrode behavior [37], the composition of the internal reference solution may influence the measured potential

when a significant diffusion potential develops across the inner membrane interface. To examine this effect, the electrode response was evaluated using different concentrations of the internal reference solution, as described in the Experimental section.

The results revealed that changing the Ba^{2+} concentration of the inner filling solution from 1.0×10^{-3} to 1.0×10^{-2} M produced no significant variation in either the slope or the linear working range of the calibration plot. As expected, the only noticeable effect was a shift in the intercept of the corresponding Nernstian calibration curves (Figure 5).

Among the concentrations investigated, an internal solution containing 1.0×10^{-3} M Ba^{2+} provided the most stable and reproducible electrode response and was therefore selected for all subsequent experiments.

3.5. Effect of Solution pH

The interaction between hydrogen ions and the target cation for complexation with the ionophore is one of the principal factors governing the potentiometric response of ion-selective electrodes [38]. Therefore, the influence of solution pH on the potential response of the fabricated sensor was investigated using a 1.0×10^{-3} M Ba^{2+} solution.

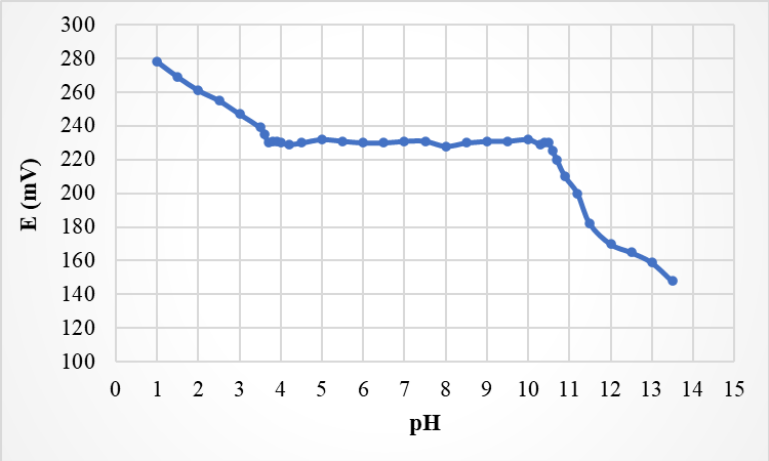


Figure 6. Influence of the test solution pH on the potential response of the electrode in the presence of 1.0×10^{-3} M Ba^{2+}

The pH was adjusted over the range of 1–14 by adding hydrochloric acid (HCl) to obtain acidic media and sodium hydroxide (NaOH) to produce alkaline conditions. The electrode potential was measured after each pH adjustment. As presented in Figure 6, the sensor exhibited a nearly constant potential throughout the pH range of 4.0–10.5, indicating that neither H^+ nor OH^- ions significantly interfered with the electrode response within this interval.

At pH values below 4.0, the electrode potential increased because hydrogen ions competed effectively with barium ions for the available ionophore binding sites. In contrast, at pH values

above 10.5, the potential gradually decreased, most likely owing to the formation of barium hydroxide species under strongly alkaline conditions, which reduced the concentration of free Ba^{2+} ions in solution.

3.6. Selectivity Coefficients

The selectivity coefficient is a fundamental parameter for evaluating the influence of interfering ions on the performance of ion-selective membrane electrodes. In this study, selectivity coefficients were determined using the separate solution method (SSM) in accordance with the IUPAC recommendations [39]. The obtained values are summarized in Table 3 and graphically presented in Figure 7.

Table 3. Selectivity coefficient of various interfering ions

Interfering ion	Selectivity coefficient	Interfering ion	Selectivity coefficient
Na^{+}	1.2×10^{-4}	Mn^{2+}	4.9×10^{-3}
K^{+}	6.6×10^{-4}	Co^{2+}	2.8×10^{-3}
Mg^{2+}	9.5×10^{-4}	Ni^{2+}	5.1×10^{-2}
Ca^{2+}	$<10^{-5}$	Cu^{2+}	3.9×10^{-3}
Al^{3+}	1.5×10^{-3}	Ag^{+}	2.5×10^{-3}
Pb^{2+}	3.5×10^{-2}	Zn^{2+}	$<10^{-5}$
Cr^{3+}	7.3×10^{-3}	La^{3+}	2.6×10^{-3}

As can be seen from Table 3, the proposed Ba^{2+}-selective electrode exhibited excellent discrimination against the majority of the investigated cations. The only noticeable exceptions were Ni^{2+} and Pb^{2+}, whose affinity toward the synthesized ionophore had previously been confirmed by spectrophotometric studies. For all other interfering ions, the selectivity coefficients were approximately 10^{-3} or lower, indicating negligible interference and confirming the high selectivity of the developed sensor toward barium ions.

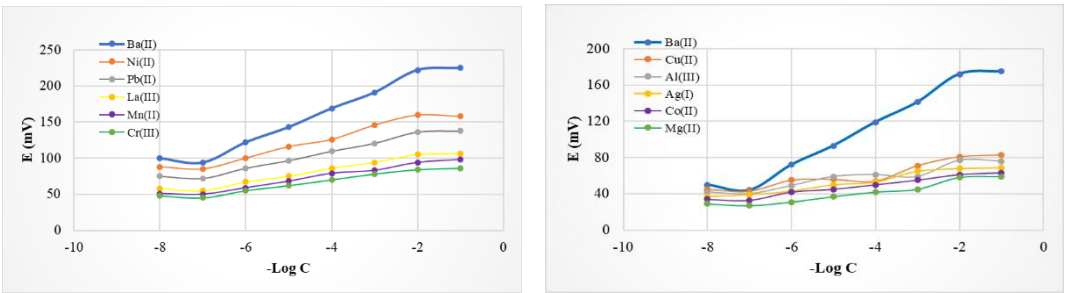


Figure 7. Selectivity coefficient of various interfering ions

3.7. Analytical Application

Calcium hydroxide pastes containing barium sulfate are widely used in endodontic therapy as temporary root canal dressings, intracanal medicaments, and materials for apexification

because of their antimicrobial properties and their ability to stimulate hard tissue formation [40,41]. The incorporation of barium sulfate provides sufficient radiopacity, allowing the material to be clearly visualized during radiographic examination of the root canal system [42]. One commercially available product containing this radiopaque additive is the MetaPaste syringe manufactured by Biomed Meta (South Korea).

To evaluate the analytical applicability of the proposed membrane-based potentiometric sensor, MetaPaste samples were first analyzed by atomic absorption spectroscopy (AAS). Approximately 0.5–1.0 g of paste from each syringe was accurately weighed and transferred into a 25 mL volumetric flask. Sample digestion was carried out by adding 5 mL of concentrated nitric acid (HNO_3) together with 1 mL of 30% hydrogen peroxide (H_2O_2), followed by heating at 80–90 °C under continuous magnetic stirring until complete dissolution and formation of a clear solution. After cooling to room temperature, the digest was diluted to volume with deionized water and filtered through a 0.2 μm membrane to remove suspended particles [33].

A series of Ba^{2+} standard solutions (0.1–2 ppm) was then prepared to construct the AAS calibration curve. The barium concentration of each sample was calculated from this calibration plot, and the corresponding barium content in the original paste was obtained using the following equation:

$$\text{wt\% Ba} = \frac{\text{Ba concentration (mg/L)} \times \text{solution volume (L)}}{\text{sample weight (mg)}} \times 100$$

The same digested samples were subsequently analyzed using the fabricated membrane-based potentiometric sensor after calibration under controlled pH and ionic-strength conditions. Potentiometric measurements were performed following established procedures for ion-selective electrodes [42]. The Ba^{2+} concentrations obtained with the proposed sensor were in close agreement with those measured by AAS, Table 4, confirming the accuracy, reliability, and practical applicability of the developed membrane sensor for the determination of barium in MetaPaste samples.

Table 4. Comparison of Ba^{2+} concentration determined by AAS and the membrane-based potentiometric sensor

Method	**Ba^{2+} Concentration (mM) (Mean ±SD, n= 3)**	**Relative Standard Deviation (RSD, %)**
Atomic Absorption Spectroscopy (AAS)	15.0±0.45*	3.0
Membrane-based Potentiometric Sensor	15.2±0.61	4.0

*Values are expressed as mean ±SD (n = 3). Student's t-test confirmed that no statistically significant difference existed between the two methods at the 95% confidence level ($p > 0.05$)

4. CONCLUSION

A novel Ba^{2+}-selective potentiometric sensor based on 4,4′-dinitrobenzil (BNED) as an ionophore was successfully developed and characterized. The optimized membrane exhibited a near-Nernstian response of 24.9 mV decade^{-1} over the concentration range of 1×10^{-7}–1×10^{-2} M, with a response time of about 25 s and satisfactory stability over three months. The sensor showed good selectivity toward Ba^{2+} over various interfering cations and maintained a stable response in the pH range of 4.0–10.5. The successful determination of Ba^{2+} in real samples demonstrates the potential of the proposed electrode as a simple, rapid, and reliable tool for trace barium analysis.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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