New PVC Membrane-Based Ion-Selective Electrode for Ultrasensitive Detection of Bismuth(III) with Sudan I

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Summary: Accurate and dependable measurement of bismuth is vital for ensuring the safety of drugs, managing industrial processes, and evaluating environmental pollution. In this study, a new potentiometric sensor that uses Sudan I as the electroactive material within poly(vinyl chloride) (PVC) membrane structure was designed. The sensor displayed a broad linear concentration range of 1.0×10^{-3} to 1.0×10^{-10} M, an ultra-low detection limit of 4.0×10^{-11} M, and a response time of 30 seconds. It retained stable performance across a pH range of 2.0–7.0 and had an operational lifetime of about one month. When compared to existing literature, the sensor's selectivity and detection limit were significantly enhanced. It was successfully utilized to determine bismuth species in pharmaceutical formulations. Potentiometric methods provide clear advantages over other analytical techniques, such as simplicity, cost-effectiveness, quick response, and high selectivity. This developed sensor is a valuable tool for bismuth(III) determination, especially in quality control and pharmaceutical analysis.

Keywords: PVC membrane electrode, Potentiometric determination, Pharmaceutical analysis, Bi(III)-selective sensor, Ion-selective electrode.

Introduction

Bismuth, a versatile element with a wide range of applications, has garnered substantial interest in the research community due to its distinct features and potential uses. In the pharmaceutical industry, it is found in bismuth subsalicylate which is used to treat stomach ailments and as an antibacterial agent [1,2]. As for electronics, bismuth is used in thermoelectric materials and superconductors [3]. It is needed in the field of metallurgy with its application through lead-free solders [4] and low melting point alloys [5]. In cosmetics, bismuth oxychloride is used to give a pearlescent effect [6] while in nuclear and defense industries, it is employed to replace lead in radiation shielding [7]. Additionally, bismuth compounds are used as a catalyst [8], in fire safety systems [9], and in the glass and ceramics industry [10]. Adverse effects of bismuth compounds on human organism have been described, including nephropathy, osteoarthropathy, hepatitis and neurological disorders [11]. Hence, accurate determination of bismuth levels is essential for monitoring environmental pollution, analyzing food and water quality, and ensuring the safety of medical procedures.

In this regard, several detection methods such as atomic absorption spectroscopy (AAS) [12-17], inductively coupled plasma-mass spectrometry (ICP-MS) [18,19], spectrophotometric methods [20-26], colorimetric methods [27,28], inductively coupled plasma-atomic emission spectroscopy (ICP-AES) [29,30] volumetric methods [31], neutron activation analysis method [32], voltammetric methods [33,34] have been suggested for the quantification of bismuth in multiple sample types. The proposed methods have advantages and disadvantages when compared to each other. The choice of method is usually based on factors like the detection limit, sample complexity, simplicity, analysis cost and the availability of the instrument for particular analysis. Although modern methods for bismuth determination provide high sensitivity, they often involve complicated equipment, extensive sample preparation, and significant costs. Conversely, potentiometric ion-selective electrodes (ISEs) offer a straightforward, affordable, and quick alternative for determination of bismuth.

A potentiometric method that uses ion-selective electrodes (ISEs) offers many benefits, making it an effective and dependable analytical technique. This method is well-known for its straightforward sample preparation, which makes it suitable for a variety of applications. Moreover, ISEs are durable, needing little maintenance and featuring a simple operational process. These electrodes are recognized for their quick response time, enabling fast data collection, which is essential in numerous real-time monitoring systems [35,36]. The excellent selectivity of ISEs allows for precise

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measurements even in complicated matrices, and their broad linear response range guarantees reliable ion quantification across a wide concentration range. Additionally, ISEs are cost-efficient, presenting an affordable option compared to other analytical methods without sacrificing performance or accuracy. Their adaptability, along with the ease of integration into different systems, underscores their considerable potential in both research and industrial settings. Given these notable advantages, numerous studies in the literature have been also conducted by researchers focusing on Bi(III)-selective electrodes. More recently, Sanati et al. [37] fabricated a carbon paste electrode (CPE) tailored for Bi(III) ion detection, formulating it with carbon-based nanomaterials as a modifier, a binder, graphite powder, and a synthetic imine compound ionophore. Subsequently, a novel screen-printed ion-selective electrode for Bi(III) ion determination in various authentic samples was designed by Aglan et al [38], employing cerium zirconium phosphotungstate as the key sensing material. Lastly, Deligonul et al [39] introduced a polymer membrane electrode, integrating Green Fluorescent Protein-doped elastomeric multi-walled carbon nanotubes as a biocompatible sensing tool, embedded within a conductive plasticized PVC matrix for efficient Bi(III) determination.

Although some of the proposed Bi(III) selective sensors exhibit some satisfactory potentiometric performance properties when looking at the above-mentioned studies, investigating sensors with better performance properties is essential to fill the present gaps in this field and to meet possible future requirements. In this context, we described a potentiometric sensor for sensitive and highly selective detection of Bi(III) in this work. A typical azo dye Sudan I was incorporated into the PVC membrane as electroactive sensing element and utilized to attain selective and sensitive response to Bi(III). The unique host-guest coordination chemistry between the Sudan I molecule, the active ionophore Sudan I, and the bismuth(III) ions is responsible for the developed sensor's potentiometric response. Two essential electron-rich coordination sites are present in the Sudan I molecule, which is immobilized in the lipophilic PVC matrix: the oxygen atom of the hydroxyl group (-OH) and the nitrogen atom of the azo group (-N=N-). By functioning as efficient Lewis bases, these sites enable a reversible and selective complexation with the corresponding Lewis acid, the bismuth(III) cation. A clear phase boundary potential is established by this important interaction at the sample-membrane interface, which results in the production of a stable [Bi(Sudan I)n]$^{3+}$ charge-transfer complex. According to the Nernst equation, the activity of bismuth(III) in the sample solution controls the amplitude of this potential. The main reason for the electrode's strong selectivity for bismuth(III) ions over other possible interfering cations is thought to be the distinct stereochemical and electronic structure of the cavity formed by the Sudan I ionophore. With advantages of easy fabrication process, low-cost, wide linear response range, good sensitivity and selectivity, and ultra-low detection limit, the developed sensor will be a good choice as an effective and efficient tool for the determination of Bi(III).

Experimental

Chemicals and Instruments

Tetrahydrofuran (THF), bis(2-ethyl)hexyl sebacate (DOS), dibutylphthalate (DBP), high-molecular-weight polyvinyl chloride (PVC) and o-nitrophenyloctylether (NPOE) were acquired from Sigma-Aldrich (Germany). The hardener (Desmodur RFE) and epoxy resin (TP3100) required to construct the solid contact were procured from Bayer (Germany), and Denlaks (Turkey) respectively. The pharmaceutical Bizmopeptol (262 mg bismute subsalicylate) (Aytaç Muhittin Dinçer Dinçtaş, Ankara-Türkiye) employed in analytical application was purchased from a local pharmacy. Furthermore, all of the chemicals used to prepare the solutions were at reagent-grade and were acquired from Sigma-Aldrich (Germany). The deionized water (18.3 MΩ) used in the investigation was attained from Human Corporation Zeener Power II (Korea) water purification system. Potentiometric measurements were executed using a custom-built, digitally controlled potentiometric measurement apparatus. A Gamry (USA) brand saturated Ag/AgCl electrode was preferred as the reference electrode along the study.

Fabrication of the Electrode

The fabrication of the sensors commenced with the coating of copper wires using a conductive solid-contact material. This material was formulated by blending tetrahydrofuran with epoxy (35% w/w), hardener (15% w/w), and graphite (50% w/w) to achieve a homogeneous mixture. The exposed ends of the copper wires were then repeatedly dipped into this mixture, ensuring uniform coverage, before being allowed to dry in a dark environment at room temperature for 24 hours. Following this step, sensing membranes were assembled and subsequently mounted onto the solid-contact-coated surfaces and left to dry under the same conditions for 24 hours. The membrane components were blended in THF at a proportion of 100 mg/mL. As a final step, the fabricated sensors underwent a conditioning process by immersion in a 1.0×10^{-2} M Bi(III) solution for 12 hours.

Potentiometric Measurements

The potentials were measured at ambient temperature (22±2 °C) implementing the electrochemical cell configuration described below:

Ag/AgCl Ref E. ‖ Bi(III) solution | PVC membrane | solid contact | copper wire

Potentiometric measurements were collected by immersing the fabricated sensor and reference electrode into 25 mL of test solutions under continuous agitation. After each measurement, both the reference electrode and the working electrode were rinsed well with pure water and carefully wiped with a soft absorbent tissue to prevent contamination.

Results and Discussion

Membrane Optimization

Optimizing the PVC membrane composition in ion-selective electrodes enhances their selectivity, sensitivity, and stability, leading to more accurate ion detection. Therefore, a series of membranes, the compositions of which are given in the Table-1, were evaluated potentiometrically in order to determine the optimum membrane formulation by examining the ionophore ratio, plasticizer type and ionic additive effect. Some of the potentiometric performance features belonging to the studied membrane formulations were epitomized in Table-2. To demonstrate the effectiveness of Sudan I dye as an electroactive substance, membrane formulations without Sudan I (Sensors 11 and 12) were also included in the evaluation. A comparative evaluation of the potentiometric data presented in Table-2 indicates that Sensor 1 exhibits the most favorable membrane formulation in terms of linear range, detection limit, and Nernstian behavior. Consequently, the subsequent sections of this study primarily focus on Sensor 1.

Figure of Merit

A fresh PVC membran sensor was fabricated using the optimized component ratios and was used to construct the potentiometric response curve. Standard Bi(III) solutions were chosen within the concentration range of 1.0×10^{-3}-1.0×10^{-12} M. The obtained potentiometric responses of the electrode to these standard Bi(III) solutions and regarding response curve were demonstrated in Fig. 1. With a slope of 23.8 mV per decade, the sensor demonstrated a linear operating range from 1.0×10^{-3} to 1.0×10^{-10} M (Fig 2). Following IUPAC recommendations [40], the detection limit was calculated as 4.0×10^{-11} M.
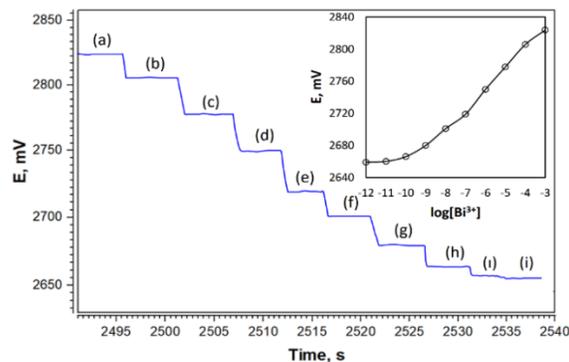

Fig. 1: The recorded real-time potentiometric responses and the corresponding response curve (inset) derived from standard Bi(III) solutions. (a) 1×10^{-3} (b) 1×10^{-4} (c) 1×10^{-5} (d) 1×10^{-6} (e) 1×10^{-7} (f) 1×10^{-8} (g) 1×10^{-9} (h) 1×10^{-10} (ı) 1×10^{-11} (i) 1×10^{-12} M.
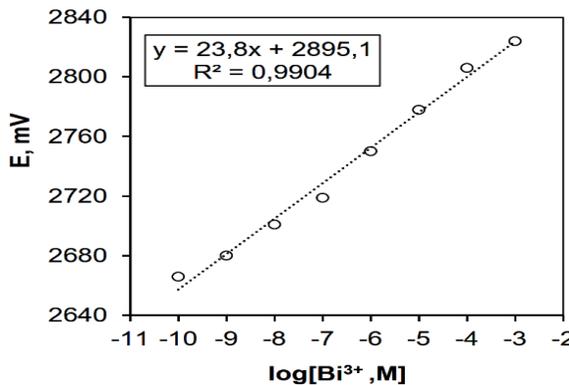

Fig. 2: The calibration plot corresponding to the linear operating range of the proposed Bi(III)-selective sensor.

Table-1: The membrane compositions (w/w %) investigated in the course of the optimization study.

Sensor	PVC	Plasticizer			Ionophore	Ionic Additive
		o-NPOE	DBP	DOS	Sudan I	KTpClPB
Sensor 1	32.0	64.0	-	-	3.0	1.0
Sensor 2	32.0	65.0	-	-	3.0	-
Sensor 3	32.0	-	64.0	-	3.0	1.0
Sensor 4	32.0	-	65.0	-	3.0	-
Sensor 5	32.0	-	-	64.0	3.0	1.0
Sensor 6	32.0	-	-	65.0	3.0	-
Sensor 7	32.0	66.0	-	-	1.0	1.0
Sensor 8	32.0	67.0	-	-	1.0	-
Sensor 9	32.0	62.0	-	-	5.0	1.0
Sensor 10	32.0	63.0	-	-	5.0	-
Sensor 11	32.0	67.0	-	-	-	1.0
Sensor 12	32.0	68.0	-	-	-	-

Table-2: Potentiometric characteristics of certain sensor compositions presented in Table-1.

Sensor	Slope (mV/decade)	Detection limit (M)	Linear range (M)	R²
Sensor 1	23.8	4.0×10^{-11}	$1.0 \times 10^{-10} - 1.0 \times 10^{-3}$	0.9904
Sensor 2	39.0	1.0×10^{-6}	$1.0 \times 10^{-6} - 1.0 \times 10^{-3}$	0.9909
Sensor 3	38.0	1.0×10^{-7}	$1.0 \times 10^{-6} - 1.0 \times 10^{-3}$	0.9945
Sensor 4	37.9	1.0×10^{-6}	$1.0 \times 10^{-6} - 1.0 \times 10^{-3}$	0.9905
Sensor 5	39.5	5.0×10^{-7}	$1.0 \times 10^{-6} - 1.0 \times 10^{-3}$	0.9978
Sensor 6	37.5	5.0×10^{-6}	$1.0 \times 10^{-6} - 1.0 \times 10^{-3}$	0.9985
Sensor 7	26.5	5.0×10^{-6}	$1.0 \times 10^{-5} - 1.0 \times 10^{-3}$	0.9884
Sensor 8	32.7	1.0×10^{-6}	$1.0 \times 10^{-5} - 1.0 \times 10^{-3}$	0.9909
Sensor 9	28.4	1.0×10^{-6}	$5.0 \times 10^{-5} - 1.0 \times 10^{-3}$	0.9923
Sensor 10	16.9	5.0×10^{-7}	$1.0 \times 10^{-6} - 1.0 \times 10^{-3}$	0.9911
Sensor 11	13.2	1.0×10^{-5}	$1.0 \times 10^{-5} - 1.0 \times 10^{-3}$	0.9842
Sensor 12	8.4	5.0×10^{-5}	$1.0 \times 10^{-5} - 1.0 \times 10^{-3}$	0.9718

In order to evaluate the sensor's dynamic response time, when the concentration of Bi(III) was varied from 1.0×10^{-5} M to 1.0×10^{-4} M, the real-time potentials were recorded continuously. The data shown in Fig 3 demonstrates that the sensor achieved a stable potential, fluctuating by no more than ± 1.0 mV from the final equilibrium value, within 30 seconds after per tenfold increase in Bi(III) ion concentration.
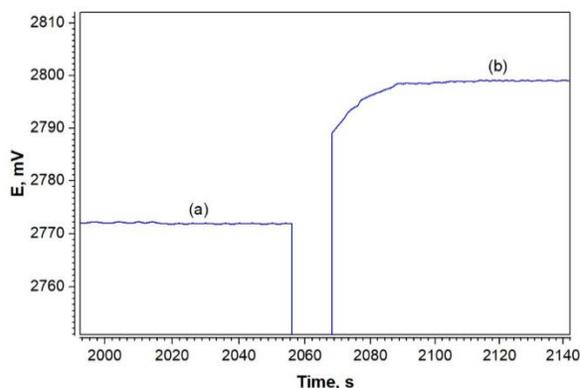

Fig. 3:   Dynamic response time of the proposed Bi(III)-selective sensor measured in (a) 1×10^{-5} M and (b) 1×10^{-4} M Bi(III) solutions.

The sensor's selectivity was assessed by comparing its potentiometric response in Bi(III) solutions to its response in solutions with various interfering species at different concentrations. As shown in Fig 4, the sensor demonstrates significantly greater selectivity for Bi(III) compared to other species. The selectivity coefficient ($K_{A/B}$) is an important parameter for evaluating how well a membrane can identify a primary ion (A) in the existence of a competing ion (B). A lower $K_{A/B}$ value indicates greater selectivity. In this study, the selectivity coefficient $K_{A/B}$ was determined using separate solution and mixed solution methods [41] for charged and neutral species, respectively. The calculated selectivity coefficients for studied interfering substances were listed in Table-3.
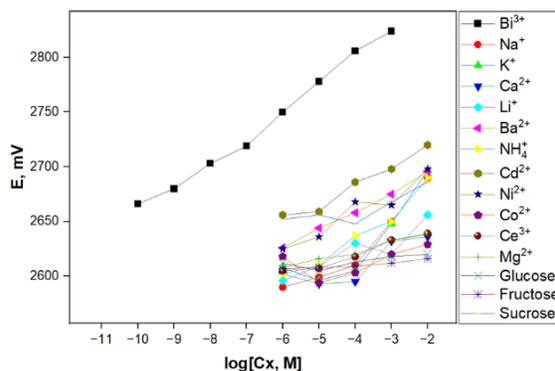

Fig. 4:   Response profiles generated from potential readings of Bi(III) and various interferents' solutions at different concentrations.

Table-3: Selectivity coefficients of the developed Bi(III)-selective sensor for a range of potential interferents.

Interferents	$K_{Bi(III)/B}$	$-\log K_{Bi(III)/B}$
Na⁺	1.78×10^{-3}	2.75
K⁺	3.55×10^{-3}	2.45
Ca²⁺	7.76×10^{-9}	8.11
Li⁺	5.75×10^{-5}	4.24
Ba²⁺	3.23×10^{-6}	5.49
NH₄⁺	1.77×10^{-3}	2.75
Cd²⁺	3.63×10^{-5}	4.44
Ni²⁺	3.98×10^{-6}	5.40
Co²⁺	3.89×10^{-9}	8.41
Ce³⁺	1.05×10^{-9}	8.97
Mg²⁺	9.55×10^{-9}	8.02
Glucose	1.55×10^{-6}	5.81
Fructose	1.05×10^{-6}	5.98
Sucrose	1.17×10^{-3}	2.93

Establishing the pH working range of an ion-selective electrode is essential for achieving precise and consistent potentiometric measurements, since extreme pH levels can affect the electrode's response and result in inaccurate outcomes. The impact of pH on the potential of the sensors was evaluated by monitoring their emf while gradually altering the acidity through the precise addition of HCl or NaOH. The potentiometric responses depending on solution pH was illustrated in Fig 5. The graph in Fig. 5 confirms a linear response across the pH range of 2.0-

7.0. The decrease in electrode potential at pH levels above 7 can be explained by the precipitation of Bi(III) ions, which occurs as the concentration of OH^- ions in the solution rises. As a result, the effective concentration of Bi(III) in the solution gradually diminishes.
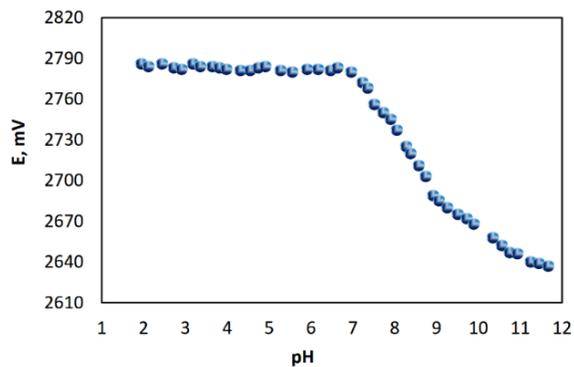

Fig. 5:   The impact of pH on the measured potential of a 10^{-5} M Bi(III) solution.

In order to assess the short-time repeatability of the Bi(III)-selective sensor, consecutive measurements were conducted in aqueous solutions of Bi(III) at concentrations of 1×10^{-4}, 1×10^{-5}, and 1×10^{-6} M. The potential-time graph representing these recordings is illustrated in Fig. 6. The average potential values recorded for 1×10^{-4}, 1×10^{-5}, and 1×10^{-6} M Bi(III) concentrations, along with their standard deviations, were calculated as 2802.0 ± 0.7 mV, 2774.4 ± 0.5 and 2739.6 ± 0.5 mV, respectively.
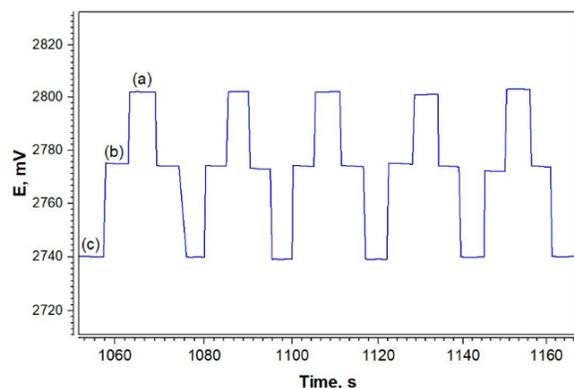

Fig. 6:   Repeatability of the Bi(III)-selective sensor in standard Bi(III) solutions at concentrations of (a) 1×10^{-4} M, (b) 1×10^{-5} M, and (c) 1×10^{-6} M.

In order to evaluate the sensor's lifespan, we closely monitored its slope variation over time. Prior to each measurement, the sensor was conditioned in a 1.0×10^{-2} M Bi(III) solution at room temperature for 30 minutes. Daily measurements were conducted in Bi(III) solutions ranging from 1.0×10^{-3} to 1.0×10^{-10} M to ensure the sensor maintained a linear response. The calculated slope values were then plotted against time (Fig. 7). As shown in Fig. 7, the sensor displayed stable slope values for the first 29 days. However, after this initial period, a significant decline in slope values was noted. Therefore, the effective operational lifespan of the Bi(III)-selective sensor is estimated to be around one month.
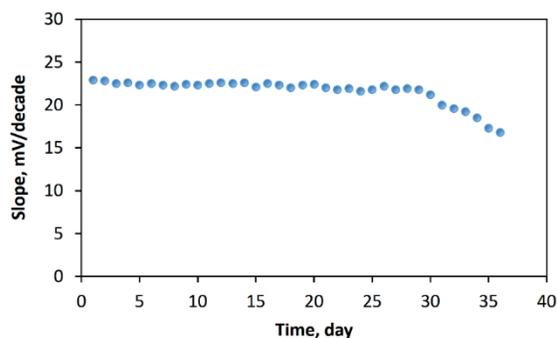

Fig. 7:   Time-dependent variation in the slope of the calibration plot over time for the Bi(III)-selective electrode.

Pharmaceutical Analysis

Ten Bizmopeptol (262 mg bismuth subsalicylate) tablets were ground in a mortar and a portion equal to the mass of a single tablet was weighed. This weighed mass was then added to a 8 mL mixture of concentrated HCl:deionized water (1:10 volume ratio). The obtained solution was then diluted with deionized water to obtain a 80 mL final volume. 2 mL of the resultant solution was again diluted to 20 mL final volume with deionized water for further analysis. The accuracy of the results obtained by the potentiometric method was determined by comparing them with the labeled value. Hence, the bismuth subsalicylate content of the drug was estimated three times using the proposed sensor based on the direct calibration method. While the labeled content is 262.0 mg per tablet, the potentiometric method yielded an estimated value of 264.2 ± 6.3 mg per tablet (N=3) (Fig. 8). Accordingly, the recovery rate and relative error (Er%) were calculated as 100.8% and +0.8, respectively. These findings demonstrate that the suggested sensor is a reliable tool for accurately determining the Bi(III) content in Bi(III)-based pharmaceuticals and monitoring their quality control processes.

Table-4: Evaluation of the potentiometric performance of the developed Bi(III)-selective sensor in comparison with previously reported Bi(III)-selective sensors.

| Ref	Slope (mV/decade)	Linear range (M)	Detection limit (M)	pH range	Response time
[35]	19.2	8.0×10^{-5}-1.0×10^{-1}	-	2-4	50 s
[36]	56.8	1.0×10^{-8}-1.0×10^{-1}	6.3×10^{-9}	4-11	36 s
[37]	20	1×10^{-5}–2×10^{-2}	1×10^{-5}	-	20-25 min
[38]	29.6	2.0×10^{-6}-1.0×10^{-2}	-	2.0-7.0	20 s
[39]	18.7	1.0×10^{-8}-1.0×10^{-4}	8.1×10^{-9}	0.5-2.5	20 s
[40]	53.0	1.0×10^{-6}-1.0×10^{-3}	2.0×10^{-6}	3.0-8.0	20-30 s
[41]	19.8	5.0×10^{-7}-1.0×10^{-2}	8.3×10^{-8}	3.0-6.0	6 s
[42]	19.9	1.0×10^{-7}-1.0×10^{-2}	1.4×10^{-8}	0.5-1.5	10s
[43]	19.2	4.8×10^{-7}-1.0×10^{-2}	1.45×10^{-7}	1.8-4.6	5 s
[44]	18.2	3.3×10^{-7}-1.0×10^{-1}	1.0×10^{-7}	3.5-8.0	7-10 s
[45]	19.1		4.3×10^{-6}		40-45 s
Current Study	23.8	1.0×10^{-10}-1.0×10^{-3}	4.0×10^{-11}	2.0-7.0	30 s
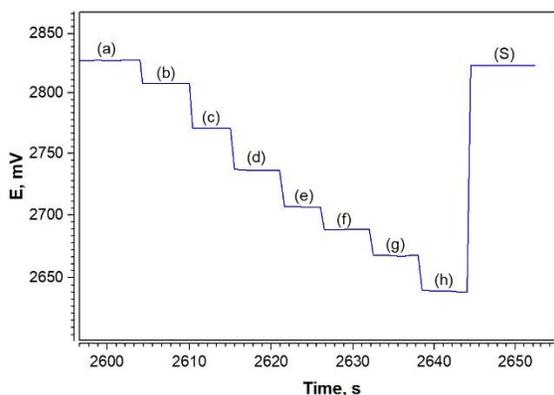
Fig. 8: Real-time potentiometric response profiles recorded for standard Bi(III) solutions: (a) 1.0×10^{-3} M, (b) 1.0×10^{-4} M, (c) 1.0×10^{-5} M, (d) 1.0×10^{-6} M, (e) 1.0×10^{-7} M, (f) 1.0×10^{-8} M, (g) 1.0×10^{-9} M, and (h) 1.0×10^{-10} M, along with pharmaceutical formulation S (Bizmopeptol, 262 mg bismute subsalicylate).

Conclusions

In this study, we successfully designed a new potentiometric sensor that uses Sudan I dye as the electroactive material within a PVC membrane for the selective and sensitive detection of bismuth. The optimization process confirmed that the membrane formulation consisted of 32.0% (w/w) PVC, 64.0% (w/w) o-NPOE, 3.0% (w/w) Sudan I and 1.0% (w/w) KTpClPB delivered superior potentiometric performance features. The sensor displayed a broad linear response range, a low detection limit, and a quick response time. It also exhibited excellent selectivity and stability across a wide pH range, maintaining reliable performance for about a month. The new sensor clearly outperforms a number of well-established techniques for determining bismuth. It provides portability and operational simplicity in contrast to expensive and intricate spectrometric

methods. Crucially, it has an ultra-low limit of detection (4.0×10^{-11} M) and a substantially larger linear range, outperforming the majority of bismuth potentiometric sensors that have been previously described (Table-4). Its moderate 30-second response time, which is a trade-off for its remarkable sensitivity, could be a drawback even though its pH stability and operating lifetime are on par with other electrodes. The effective application of the sensor for bismuth detection in a pharmaceutical sample further emphasizes its practicality and efficiency. With its cost-effectiveness, user-friendliness, high specificity, broad linear range and lower detection limit, this sensor presents a valuable alternative to traditional methods for monitoring bismuth in a wide range of applications.

Acknowledgments

References

1. E. Svensson Grape, V. Rooth, M. Nero, T. Willhammar and A. K. Inge, Structure of the Active Pharmaceutical Ingredient Bismuth Subsalicylate, *Nat. Commun.,* **13,** 1984 (2022)

2. D. T. Smoot, T. Hinds, H. Ashktorab, J. Jagtap, K. S. Kim and V. F. Scott, Effectiveness of Ranitidine Bismuth Citrate, Clarithromycin, and Metronidazole Therapy for Treating Helicobacter Pylori, *Am. J. Gastroenterol.,* **94,** 955 (1999)

3. T. Cao, X. L. Shi, M. Li, B. Hu, W. Chen, W. Di Liu, W. Lyu, J. MacLeod and Z. G. Chen, Advances in Bismuth-Telluride-Based Thermoelectric Devices: Progress and Challenges, *eScience,* **3,** 100122 (2023)

4. N. R. A. Razak, M. A. A. Mohd Salleh, N. Saud,

R. M. Said and M. I. I. Ramli, Influence of Bismuth in Sn-Based Lead-Free Solder – A Short Review, *Solid State Phenom.,* **273,** 40 (2018)

5.   G. P. Glasgow, The Safety of Low Melting Point Bismuth/Lead Alloys: A Review, *Med. Dosim.,* **16,** 13 (1991)–18.

6.   M. F. Mesko, D. L. R. Novo, V. C. Costa, A. S. Henn and E. M. M. Flores, Toxic and Potentially Toxic Eelements Determination in Cosmetics Used for Make-up: A Critical Review, *Anal. Chim. Acta* **1098,** 1 (2020).

7.   F. Bakri, P. L. Gareso and D. Tahir, Advancing Radiation Shielding: A Review the Role of Bismuth in X-ray Protection, *Radiat. Phys. Chem.,* **217,** 111510 (2024)

8.   E. Lopez, S. C. Thorp and R. S. Mohan, Bismuth(III) Compounds as Catalysts in Organic Synthesis: A Mini Review, *Polyhedron,* **222,** 115765 (2022)

9.   Q. Meng, X. Zhang, S. Li, S. Han, Y. Zhang, B. Wu and H. Kang, Bismuth Oxyiodide Nanorods Towards Improvements in Fire Safety and Mechanical Properties of Natural Rubber, *Polym. Degrad. Stab.,* **225,** 110770 (2024)

10.   D. Biswas, D. Patra, S. B. Hota, A. Das, N. Modak, R. Mondal and S. Kabi, Influence of Bismuth Content on the Properties of Glass-Ceramics with Composition xBi2O3-(0.40-x)B2O3-0.15ZnO-0.45P2O5: Synthesis, Structural, Thermal Analysis, and Dielectric Relaxation Process, *Phys. B Condens. Matter,* **697,** 416728 (2025)

11.   S.-I. Itoh, S. Kaneco, K. Ohta and T. Mizuno, Determination of Bismuth in Environmental Samples with Mg-W Cell-Electrothermal Atomic Absorption Spectrometry, *Anal. Chim. Acta,* **379,** 169 (1999)

12.   O. Acar, Z. Kilic and A. R, Turker, Determination of Bismuth, Indium and Lead in Geological and Sea-water Samples by Electrothermal Atomic Absorption Spectrometry with Nickel-Containing Chemical Modifiers, *Anal. Chim. Acta,* **382,** 329 (1999)

13.   J. L. Burguera, M. Burguera, C. Rivas, C. Rondon, P. Carrero and M. Gallignani, Determination of Bismuth in Biological Samples Using On-line Flow-Injection Microwave-Assisted Mineralization and Precipitation/Dissolution for Electrothermal Atomic Absorption Spectrometry, *Talanta,* **48,** 885 (1999)

14.   O. Cankur, N. Ertaş and O. Y. Ataman, Determination of Bismuth Using On-line Preconcentration by Trapping on Resistively Heated W Coil and Hydride Generation Atomic Absorption Spectrometry, *J. Anal. At. Spectrom.,* **17,** 603 (2002)

15.   R. Dobrowolski, J. Dobrzyńska and B. Gawrońska, Determination of Bismuth in Environmental Samples by Slurry Sampling Graphite Furnace Atomic Absorption Spectrometry Using Combined Chemical Modifiers, *Environ. Monit. Assess.,* **187,** 1 (2015)

16.   I. Kula, Y. Arslan, S. Bakirdere, S. Titretir, E. Kendüzler and O. Y. Ataman, Determination and Interference Studies of Bismuth by Tungsten Trap Hydride Generation Atomic Absorption Spectrometry, *Talanta,* **80,** 127 (2009)

17.   A. S. Ribeiro, M. Aurelio, Z. Arruda and S. Cadore, Determination of Bismuth in Metallurgical Materials Using a Quartz Tube Atomizer with Tungsten Coil and Flow Injection-Hydride-Generation Atomic Absorption Spectrometry, *Spectrochim. Acta Part B,* **57,** 2113 (2002)

18.   J. Kobayashi, H. Terada, H. Sugiyama, T. Matsukawa, M. Chiba and K. Yokoyama, Determination of Bismuth in Environmental Samples by ICP-MS and Basic Examination of Cell Toxicity for Their Compounds, *Bunseki Kagaku,* **60,** 357 (2011)

19.   Z. Ye, Y. Lei, X. Zeng, Z. Tang, X. Wang, P. Dai, X. Li, L. Chen, K. Hu and D. Ouyang, Sensitive Determination of Bismuth in Human Plasma by ICP-MS and Its Application to Pharmacokinetic Study of Potassium Bismuth Citrate in Healthy Chinese Subjects, *SSRN,* (2022)

20.   A. Afkhami, T. Madrakian and H. Siampour, Cloud Point Extraction Spectrophotometric Determination of Trace Quantities of Bismuth in Urine, *J. Braz. Chem. Soc.,* **17,** 797 (2006)

21.   A. S. Amin, Cloud-Point Extraction and Spectrophotometric Determination of Trace Quantities of Bismuth in Environmental Water and Biological Samples, *Spectrosc. Lett.,* **44,** 424 (2011)

22.   F. Bagheban-Shahri and A. Niazi, Chemometrics-Enhanced Simultaneous Spectrophotometric Determination of Aluminum and Bismuth with Hematoxylin in Vegetables and Water Using Multivariate Calibration, *J. Water Reuse Desalin.,* **6,** 137 (2016)

23.   S. A. Barakat and S. A. Barakat, Flow Injection Extraction-Spectrophotometric Determination of Bismuth with Di-(hydrogenated tallow alkyl) Dimethylammonium Chloride, *Turkish J. Chem.*, **26,** 345 (2002)

24. S. Rastegarzadeh, N. Pourreza and A. Larki, Dispersive Liquid-Liquid Microextraction for the Microvolume Spectrophotometric Determination of Bismuth in Pharmaceutical and Human Serum Samples, *Anal. Methods,* **6,** 3500 (2014)

25. C. Verma, K. Tapadia, A. B. Soni and A. Sharma, Determination of Bismuth(III) in Environmental and Pharmaceutical Samples Using An Organic Reagent, *Anal. Methods,* **9,** 3682 (2017)

26. N. Chanawungmuang, M. Sukwattanasinitt and P. Rashatasakhon, Fluorescence Sensors for Bismuth (III) Ion from Pyreno[4,5-d]imidazole Derivatives, *Photochem. Photobiol.,* **97,** 301 (2021)

27. P. A. Bizirtsakis, M. Tarara, A. Tsiasioti, P. D. Tzanavaras and G. Z. Tsogas, Development of a Paper-Based Analytical Method for the Selective Colorimetric Determination of Bismuth in Water Samples, *Chemosensors,* **10,** 265 (2022).

28. P. C. A. Jerónimo, A. N. Araújo, M. C. B. S. M. Montenegro, D. Satinský and P. Solich, Colorimetric Bismuth Determination in Pharmaceuticals Using A Xylenol Orange Sol-Gel Sensor Coupled to a Multicommutated Flow System, *Anal. Chim. Acta,* **504,** 235 (2004)

29. O. Dachraoui, A. Atyaoui, F. Manaii, H. Maghraoui-Meherzi and C. Loukil, Bismuth Mass Fraction Determination in Thin Films by an ICP-AES Validated Method and Uncertainty Estimation, *J. Biochem. Biophys.,* **5** (n.d.)

30. Y. Okamoto, T. I. Fujiw Ara and H. Notake, Determination of Bismuth in Nonferrous Alloys by Inductively Coupled Plasma Mass Spectrometry Combined with Use of Solid-Phase Methylation and Electrothermal Vaporization Technique, *Appl. Spectrosc.,* **55,** 514 (2001)

31. P.-J. Sun, Coxecutive Chelatometric Determination of Bismuth and Lead Using Gallein as Indicator, *J. Chinese Chem. Soc.,* **8,** 314 (1961)

32. R. De Boeck, F. Adams and J. Hoste, Determination of Bismuth in Lead by Neutron Activation Analysis, *J. Radioanal. Chem.,* **2,** .109 (1969)

33. A. Yazdanipour, A. Niazi, S. K. Foladi and R. Tajik, Determination of Trace Amounts of Bismuth in Pharmaceutical and Water by Adsorptive Cathodic Stripping Voltammetry in the Presence of Xylenol Orange, *Orient. J. Chem.* **28,** 1353 (2012)

34. E. Hasdemir and K. Karaboduk, Simultaneous Determination of Bismuth and Copper by Square Wave Voltammetry in The Presence of Ethylenediaminetetraacedic Acid, *Gazi University Journal of Science,* **23,** 33 (2010)

35. S. Tian, L. Huang, Y. Gao, Z. Yua and D. Tang, A Nucleic Acid-Based Magnetic Potentiometric Aptasensing Platform for Indirect Detection of Prostate-Specific Antigen with Catalytic Hairpin Assembly, *Sens. Diagn.*, **2**, 707 (2023).

36. S. Lv, Z. Lin, K. Zhang, M. Lu, D. Tang, Polyion Oligonucleotide-Decorated Gold Nanoparticles with Tunable Surface Charge Density for Amplified Signal Output of Potentiometric Immunosensor, *Anal. Chim. Acta*, **964**, 67 (2017).

37. M. Sanati, M. Masrournia, H. Behmadi and A. Beyramabadi, Determination of Bismuth Ion in Biological and Water Samples with A Potentiometric Sensor Using Carbon Paste Electrode as A Straightforward and Simple Indicator Electrode, *J. Iran. Chem. Soc.* **19,** 3337 (2022)

38. R. F. Aglan, M. M. Hamed and H. M. Saleh, A New Screen-Printed Electrode for Selective Determination of Bismuth in Different Authentic Samples, *J. Iran. Chem. Soc.* **20,** 1481 (2023)

39. N. Deligonul, I. Yildiz, S. Bilgin, I. Gokce and O. Isildak, Green Fluorescent Protein-Multi Walled Carbon Nanotube Based Polymeric Membrane Electrode for Bismuth Ion Detection, *Microchem. J.* **190,** 108710 (2023).

40. R. P. Buck and E. Lindner, Recomendations for Nomenclature of Ion-Selective Electrodes (IUPAC recommendations 1994), *Pure Appl. Chem.,* **66,** 2527 (1994)

41. Y. Umezawa, P. Bühlmann, K. Umezawa, K. Tohda and S. Amemiya, Potentiometric Selectivity Coefficients of Ion-Selective Electrodes Part I. Inorganic Cations (Technical report), *Pure Appl. Chem.,* **72,** 1851 (2000)