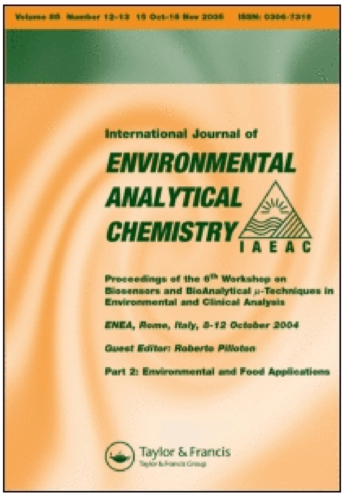

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Potentiometric determination of mercury(II) using a tribromomercurate–rhodamine B PVC membrane sensor

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The performance of a novel ion-selective membrane electrode for the determination of mercury(II) based on a tribromomercurate–rhodamine B (TBM–RB) ion-pair complex has been described. The developed electrode showed a linear, reproducible, and stable potentiometric response with an anionic super-Nernstian slope of 69.5 ± 0.5 mV per decade over a wide range of concentration, 10^{-5}–10^{-2} M $HgBr_3^-$, with a detection limit of 2.4×10^{-6} M of Hg^{2+}. The membrane showed a fast response time of 10–20 s and in a pH range of 1.5–7.5. The proposed sensor exhibited excellent selectivity for the tribromomercurate anion over anions: Br^-, Cl^-, SCN_4^{2-}, CrO_4^{2-}, acetate, oxalate, citrate, sulphate, phosphate, selenite, and nitrate. Also, there is a negligible interference from different cations such as, Ca^{2+}, Sr^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Pb^{2+}, Al^{3+}, and Zn^{2+}. The prepared sensor was used successfully as an indicator electrode for potentiometric titrations of mercury(II) with rhodamine B and thiosulphate. The analysis of mercury(II) ions in wastewater and microbial media with average recovery percentages of $100.6 \pm 1.8\%$ and $101.3 \pm 1.7\%$, respectively, using the developed sensor was in good agreement with the data obtained using the standard dithiazone spectrophotometric method.

Keywords: Tribromomercurate (TBM); Rhodamine B (RB); Potentiometry; PVC membranes; Microbial media

1. Introduction

Mercury(II) has a toxicity nature and harmful effects even at low concentrations in environmental, industrial, agriculture, and biological fields. The toxicological effects of mercury include neurological damage, irritability, paralysis, blindness, and insanity. Mercury(II) enters the environment from a large number of miscellaneous sources related to human use. Thus, the determination of mercury(II) ion in different matrix has received considerable attention in recent years [1–3].

The current techniques cited in the literature for determination of Hg(II) include spectrophotometry [4–8], cyclic voltammetry [9, 10], X-ray fluorescence [11, 12], atomic absorption [13], emission spectrometry [14], and mass spectrometry [15].

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Most of these methods require expensive instruments and multi-steps for the chemical separation and determination.

Several ion-selective electrodes for Hg(II) determination have been published [1–3]. Some of these electrodes are based upon the heterogeneous membrane of antimony(III) arsenate [16], chalcogenide glass solid-state electrodes [17–19], liquid membrane electrodes incorporating mercury(II) complex [20–23], and PVC membrane sensors based on synthetic ionophores [24–30]. Anionic trichloromercurate and triiodomercurate modified carbon paste electrode have also been successfully used for the potentiometric determination of mercury(II) [31, 32]. Most of these sensors suffer from a lack of reproducible response, interferences from a number of metal cations and short life time [2, 33].

In the present study, a novel PVC membrane sensor for mercury(II) determination in wastewater and microbial media has been developed. The proposed method is based upon the use of the complex ion associate of tribromomercurate–rhodamine B (TBM–RB) as an ionophore in the PVC-membrane. The sensor showed anionic super-Nernstian response $69.5 \pm 0.5\,\text{mV}$ per decade over a wide range of pH with significant selectivity of Hg(II) over many common anions and cations.

2. Experimental

2.1 *Reagents and materials*

All chemicals used were of analytical grade reagent, and the solutions were made with doubly distilled water. Mercuric chloride and potassium bromide were obtained from Aldrich. Tetrahydrofuran (THF) and rhodamine B (RB) were obtained from (Riedel De-haën). *o*-Nitrophenyloctyl ether (*o*-NPOE), dioctylphthalate (DOP), dibutylsebacate (DBS) and high-molecular-mass poly vinyl chloride (PVC) were purchased from Fluka. A stock solution (10^{-2} M) of tribromomercurate (TBM) was prepared by mixing an accurate weight of mercuric chloride (0.271 g) and potassium bromide (0.416 g) in 100 mL 10^{-2} M acetate buffer of pH 4. Dilute solutions (1×10^{-3} to 1×10^{-6} M) of $HgBr_3^-$ were freshly prepared by diluting the stock solution with acetate buffer of pH 4. A stock solution of rhodamine B (1×10^{-2} M) was prepared by dissolving an accurate weight of the reagent in a minimum volume of distilled water followed by filtration and dilution to 100 mL. Luria–Bertani (LB) broth biological fluid was prepared by dissolving tryptane (10 g), yeast (10 g), and sodium chloride (10 g) in water, and the pH was then adjusted to pH 7.0 with NaOH.

2.2 *Apparatus*

Potentiometric measurements were carried out at $25 \pm 1^\circ$C with an Orion microprocessor ionanalyser model (420A pH/mV meter) using a tribromomercurate–rhodamine B-PVC membrane sensor in conjunction with an Orion double Junction Ag/AgCl model (90-02) reference electrode containing 10% (w/w) potassium chloride solution in the outer compartment. An Orion model (81-82) glass electrode and a Perkin–Elmer Lambda 15 UV/VIS spectrophotometer were used for the pH and absorbance measurements, respectively.

2.3 *Preparation of the tribromomercurate–rhodamineB (TBM–RB) ion pair*

A 20 mL (10^{-2} M) portion of an aqueous solution containing $HgBr_3^-$ (TBM) was mixed with 20 mL (10^{-2} M) of rhodamine B (RB) (figure 1). The mixture was then shaken for 10 min, and the produced precipitate was filtered off through a Whatman No. 42 filter paper, washed with deionized distilled water, dried at room temperature, and finally ground to a fine powder.

2.4 *Construction of the (TBM–RB) PVC membrane sensor*

A 10 mg portion of the $HgBr_3^-$–RB^+ ion pair was thoroughly mixed with PVC powder (0.19 g) and *o*-NPOE (0.35 g) in a glass Petri dish (5 cm diameter). The cocktail was dissolved in 7 mL of THF, covered with a filter paper, and left to stand overnight to allow slow evaporation of the solvent at room temperature. The master PVC membrane (~ 0.1 mm thick) was sectioned with a cork borer (10 mm diameter) and glued to polyethylene tubing as previously described [34, 35]. The electrode was filled with a mixture of an equal volume of $HgBr_3^-$ (1×10^{-2} M) and potassium chloride (1×10^{-2} M) solutions in the presence of Ag/AgCl as an internal reference wire electrode (1.0 mm diameter). The external reference electrode was an Ag/AgCl double-junction. The prepared sensor was conditioned by soaking in $HgBr_3^-$ solution (1×10^{-2} M) for 2 h and stored in the same solution when not in use.

2.5 *Sensor calibration*

A 10 mL portion of an aqueous solution of $HgBr_3^-$ (1×10^{-2} to 1×10^{-6} M) was transferred to a 50 mL beaker. The sensor in conjunction with a double-junction Ag/AgCl reference electrode was immersed in the test solution. The potential readings were recorded after stabilization to ± 0.2 mV, and the emf was then plotted as a function of the logarithm of the $HgBr_3^-$ concentration. The produced calibration graph was used in subsequent work for determination of unknown Hg^{2+} concentrations. The detection limit was taken at the point of intersection of the extrapolated linear segments of the calibration curve. The potentiometric selectivity coefficients ($K^{pot}_{HgBr_3,B}$) were determined by both the separate solution method (SSM) and the fixed interference method (FIM) [34, 43] using 10^{-3} M aqueous solutions of $HgBr_3^-$ and the interferents.

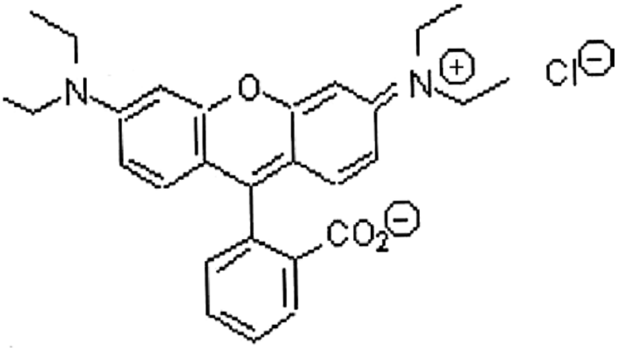

Figure 1. Chemical structure of the reagent rhodamine B.

2.6 *Application of the proposed sensor*

2.6.1 Analysis of mercury in industrial wastewater. A 10 mL aliquot of Hg(II) test solution containing 10–50 µg/mL of mercury(II) was added to an industrial wastewater solution obtained from an electroplating plant, followed by the addition of an excess quantity of potassium bromide 10^{-2} M solution and accurately transferred to a 25 mL calibrated flask. The solution was then made up to the mark with acetate buffer solution at pH 4 and shaken well, and the mercury(II) content finally determined by the proposed method. The standard addition (spiking) method was used by measuring the potentials displayed by the test solutions of the $HgBr_3^-$ before and after addition of a 1.0 mL aliquot of standard $HgBr_3^-$ solution (1×10^{-3} M). The change in electrode potential (ΔE) was then recorded and used for the analysis of mercury(II) in the tested sample.

2.6.2 Analysis of mercury in microbial media. The microbial media LB broth was prepared by dissolving 10 g of tryptane, 10 g of yeast, and 10 g of sodium chloride in 1 L, as described previously [36]. Different concentrations of mercury(II) ranging from 10 to 50 µg/mL were added to the LB broth media in a 25 mL calibrated flask, made up with acetate buffer, pH 4, and then tested for mercury(II) content using the standard addition method.

3. Results and discussion

3.1 *Membrane composition and performance characteristics of the (TBM–RB) sensor*

In the present investigation, five membrane compositions were employed in the preparation of the ion-selective electrodes by mixing 33.2–35 wt% PVC, 63–65 wt% *o*-NPOE and 0–3.8 wt% of the TBM–RB ion pair. The results are summarized in table 1 and show the dependence of the characteristic responses of the TBM–RB sensor on the membrane composition. The data revealed a good sensor response and lower limit of detection of the TBM–RB ion-selective PVC membrane sensor at a membrane composition of 1.9 : 63.1 : 35 wt% of TBM–RB ion pair, *o*-NPOE and PVC, respectively. The proposed membrane sensor is electrochemically evaluated under static and hydrodynamic modes of IUPAC operating recommendation [37]. The thickness of the membrane depends on the content of PVC powder, and a good correlation between membrane thickness and PVC content was found. The detection

Table 1. Composition of membranes and their potentiometric response characteristics.

	Composition (%)					
No.	PVC	Plasticizer *o*-NPOE	$HgBr_3$–RB ion pair	Slope (mV per decade)	Dynamic range (M)	LLD (M)
1	35.0	65.0	–	15.2	1×10^{-3} to 1×10^{-2}	–
2	35.0	64.5	0.5	52.2	1×10^{-4} to 1×10^{-2}	1.0×10^{-4}
3	35.0	64.0	1.0	65.5	5×10^{-5} to 1×10^{-2}	2.5×10^{-5}
4	35.0	63.1	1.9	69.5	1×10^{-5} to 1×10^{-2}	2.4×10^{-6}
5	33.2	63.0	3.8	69.5	1×10^{-5} to 1×10^{-2}	8.0×10^{-6}

limit of the sensor decreases with decreasing PVC content, but if the membrane is too thin, it loses its mechanical strength and is easily broken as previously reported [38]. Also, increasing the PVC content leads to an increase in the ohmic resistance of the membrane, so the exchange kinetic at the surface of membrane is diminished at a low concentration of Hg(II). The critical response characteristics of the electrode based on the TBM–RB ion pair are summarized in table 2, and representative data are shown in figure 2. The data indicate that the sensor exhibited a super-Nernstian response in the range of 10^{-2}–10^{-5} M of $HgBr_3^-$ with an anionic slope of 69 ± 0.5 mV per decade. This behaviour is probably attributed to a quasi-steady-state accumulation of the anion $HgBr_3^-$ in the boundary layer of the membrane phase. Thus, the quasi-steady-state fluxes of the anions across the membrane interface are achieved, even if the sum of the current carried by all ions is zero, and the strong ion fluxes of $HgBr_3^-$ in the direction of the inner solution lead to a progressive deviation from the Nernstian response [39–41]. A detection limit of

Table 2. Performance characteristics of TBM–RB PVC membrane sensor plasticized with *o*-NPOE.

Parameter[a]	$HgBr_3$–RB PVC membrane sensor
Slope (mV per decade)	-69.5 ± 0.5
Intercept (mV)	-86 ± 0.4
Correlation coefficient (*r*) ($n = 5$)	0.997
Lower limit of linear range (M)	1×10^{-5}
Dynamic range of response (M)	1×10^{-5} to 1×10^{-2}
Lower limit of detection (M)	2.4×10^{-6}
Response time for 1×10^{-3} M (s)	10–20
Working pH range	1.5–7.5

[a] Average of five measurements ± SD.

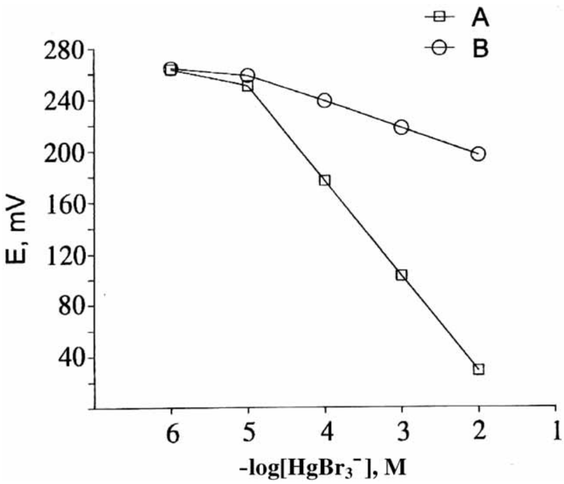

Figure 2. Potentiometric response of (A) $[HgBr_3^-]$ and (B) KBr using the $HgBr_3^-$–RB membrane sensor plasticized with *o*-NPOE.

approximately 2.4×10^{-6} M Hg(II) for the proposed TBM–RB membrane sensor was achieved successfully.

The typical dynamic response curve for the sensor was tested at 1×10^{-3} and 1×10^{-2} M of $HgBr_3^-$, and the sequence of the measurements from low to high concentrations was recorded. The time required for the sensor to reach values within ±0.5 mV of the final equilibrium potential was found to be 30–40 s in dilute solutions with $<1 \times 10^{-3}$ M of $HgBr_3^-$ and to improve to 10–20 s, at concentrations of $>1 \times 10^{-3}$ M. The lifetime of the sensor has a potential stability and fluctuation of the calibration slope not exceeding 0.6 mV per decade over a period of 2 months. The calibration slope and the linear range of the response after this period gradually decreased, and the response time was also increased to 1–1.5 min, probably due to the leaching of the ion pair from the PVC membrane sensor. The calibration graph for the sensor was found to be reproducible from day to day, provided the electrode was stored in the appropriate $HgBr_3^-$ solution before use.

It is well known that the type of plasticizer influences the dielectric constant of the membrane phase, the mobility of ionophore molecules, and the state of the ligands [33]. So, it was expected that the type of plasticizer will affect the performance characteristics of the sensor. Hence, three TBM–RB PVC matrix membranes containing the plasticizer DBS, DOP, and *o*-NPOE were prepared separately and tested for the calibration slope, linear range, and lower limit of detection. The performance characteristics of the TBM–RB sensor plasticized with *o*-NPOE, which has a polarity higher than that of DBS and DOP plasticizers, showed a high sensitivity (2.4×10^{-6} M) of mercury(II), a super-Nernstian slope (-69.0 ± 0.5 mV per decade), and a wide range of linear response from 1×10^{-5} to 1×10^{-2} M $HgBr_3^-$, this may be due to a very low charge density of the $HgBr_3^-$ anion. A narrow linear response range from 5×10^{-4} to 5×10^{-2} M $HgBr_3^-$, slopes of -45.8 ± 0.5 and -42.5 ± 0.5 mV per decade, and a lower limit of detection 1×10^{-5} M and 8×10^{-4} M $HgBr_3^-$ were achieved with the plasticizer DBS or DOP, respectively.

3.2 *Effect of pH*

The behaviour of the TBM–RB PVC membrane sensor response at different pH values (0.8–10.0) of the test solution was critically studied. The emf of a cell of the type Ag/AgCl/10^{-2} M $HgBr_3^-$ to 10^{-2} M KCl (inner solution) ‖ plastic membrane ‖ and 10^{-3} M $HgBr_3^-$ (outer solution) ‖ Orion double junction reference electrode with 10% KCl in the outer compartment with varying acidity was measured. The results obtained show that the electrode has a wide pH range (1.5–7.5) (figure 3). At a pH higher than 7.5, the potential readings for the sensor increase sharply. This is mainly due to the interference from hydroxyl ions and/or the formation of hydroxyl species $Hg(OH)_2$ and $Hg_2(OH)_2$. At a pH of less than 1.5, the emf decreased slightly due to the interference by H^+ ions or probably from the expected dissolution of the $HgBr_3^-$–RB^+ ion pair [33, 41].

3.3 *Sensor selectivity*

The potentiometric selectivity ($K^{pot}_{HgBr_3^-,B}$) of the *o*-NPOE plasticized TBM–RB PVC membrane sensor was investigated using a separate solutions technique [42]

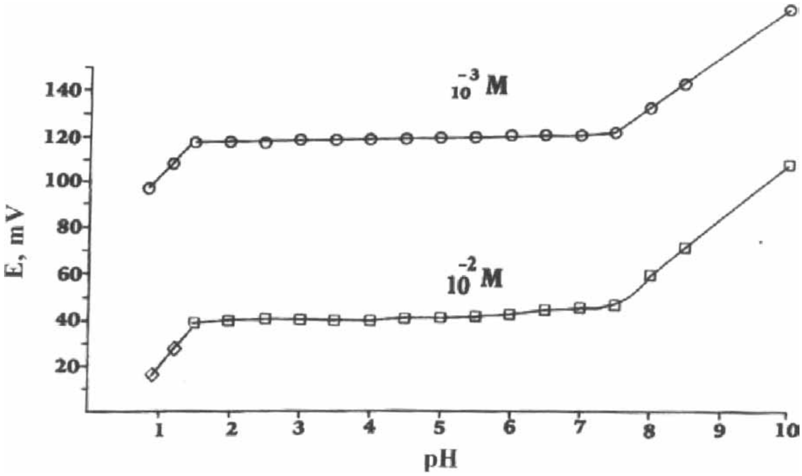

Figure 3. Effect of pH on the potential response of the $HgBr_3$–RB membrane sensor plasticized with *o*-NPOE.

in acetate buffer at pH 4. The selectivity coefficient was calculated from the rearranged Niclosky equation:

$$\log K^{\mathrm{pot}}_{\mathrm{HgBr}_3^-,\mathrm{B}} = \left[E_{\mathrm{HgBr}_3^-} - \frac{E_{\mathrm{B}}}{S}\right] + \left[\frac{1 + Z_{\mathrm{HgBr}_3^-}}{Z_{\mathrm{B}}}\right] \log \mathrm{HgBr}_3^-, \tag{1}$$

where $E_{\mathrm{HgBr}_3^-}$ is the potential measured in 10^{-3} M for $HgBr_3^-$, E_B is the potential measured in 10^{-3} M of the interfering anion, $Z_{\mathrm{HgBr}_3^-}$ and Z_B are the charges of the $HgBr_3^-$ and the interfering anions, respectively, and S is the slope of the electrode calibration curve plot [37]. The selectivity coefficient of the developed sensor ($K^{\mathrm{pot}}_{\mathrm{HgBr}_3,\mathrm{B}}$) was also determined using fixed interference method (FIM) [43]. This method was performed by adding incremental amounts of primary ion $HgBr_3^-$ to a solution containing 10^{-3} M of interfering ions until a Nernstian response slope to the $HgBr_3^-$ was observed. The linear portion of mercury anion calibration curve (obtained in the presence of 10^{-3} M of interfering ion) was extrapolated to the potential of the background interfering ion solution. The concentration of mercury anion at that point, $[C_{\mathrm{HgBr}_3^-}]$ was divided by the concentration of interfering ion, $[C_B]$, and the selectivity coefficient was calculated from the equation:

$$K^{\mathrm{pot}}_{\mathrm{HgBr}_3^-,\mathrm{B}} = \frac{[C_{\mathrm{HgBr}_3^-}]}{[C_{\mathrm{B}}]}. \tag{2}$$

The results obtained are summarized in table 3. It is evident that the proposed sensor plasticized with *o*-NPOE sensor exhibited a higher selectivity towards Hg^{2+} ion in the presence of the cations Ca^{2+}, Sr^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Fe^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Cr^{3+}, and Pb^{2+}. The Ag^+ cation interfered with Hg(II) measurement due to precipitation of AgBr, which affected the formation of $HgBr_3^-$ anion. The anions: Br^-, Cl^-, IO_4^-, CN^-, SeO_3^{2-}, citrate, acetate, and oxalate did not interfere. While, I^-, $S_2O_3^{2-}$ and HgI_4^{2-} anions cause great interference, this behaviour is attributed to the formation of complex compounds with mercury(II) which are more stable than $HgBr_3^-$ anion [44].

Table 3. Selectivity coefficients ($K^{\mathrm{pot}}_{\mathrm{HgBr_3,B}}$) of TBM–RB PVC membrane sensor plasticized with *o*-NPOE.

Interferent (B)	$K^{\mathrm{pot}}_{\mathrm{HgBr_3,B}}$ (FIM)	Interferent (B)	$K^{\mathrm{pot}}_{\mathrm{HgBr_3,B}}$ (FIM)
I^-	~ 2	Ca^{2+}	6.5×10^{-4}
Br^-	2.6×10^{-3}	Sr^{2+}	6.4×10^{-4}
Cl^-	7.0×10^{-4}	Co^{2+}	6.2×10^{-4}
IO_4^-	9.5×10^{-3}	Ni^{2+}	7.1×10^{-4}
CN^-	9×10^{-2}	Cu^{2+}	2.1×10^{-3}
$K_2(SCN)_4^{2-}$	8×10^{-2}	Mn^{2+}	6.2×10^{-4}
CrO_4^{2-}	7.5×10^{-3}	Fe^{2+}	1.5×10^{-3}
$Hg\ (CN)_4^{2-}$	5×10^{-3}	Zn^{2+}	5.5×10^{-4}
HgI_4^{2-}	1.0×10^{-1}	Cd^{2+}	6.8×10^{-3}
Acetate	7.0×10^{-4}	Al^{3+}	3.5×10^{-3}
Oxalate	7.5×10^{-4}	Cr^{3+}	8.6×10^{-4}
Citrate	5.2×10^{-4}	Ag^+	1.0×10^{-1}
Sulphate	8.0×10^{-4}	Pb^{2+}	3.5×10^{-3}
Thiosulphate	~ 1.8		
Sulphite	6.0×10^{-3}		
Selenite	2.0×10^{-3}		
Nitrate	5.0×10^{-4}		

3.4 *Potentiometric titration of mercury(II)*

The prepared sensor was successfully used as an indicator electrode in potentiometric titration of 10 mL 10^{-3} M of $HgBr_3^{-2}$ vs. 10^{-3} M rhodamine B or 10^{-3} M sodium thiosulphate. The potential break for titration with rhodamine B was 70 mV at 1 : 1 ($HgBr_3$: RB) and 120 mV at 1 : 2 at (Hg(II) : $S_2O_3^{-2}$) due to the formation of the insoluble mercury(II) thiosulphate complex [45]. The results are shown in figures 4 and 5, respectively. The data revealed that the amount of mercury(II) ions can be determined quantitively using potentiometric titration with the developed sensor.

3.5 *Determination of mercury(II) in industrial wastewater and microbial media*

The proposed TBM–RB PVC membrane sensor was successfully employed for the analysis of mercury(II) in industrial wastewater and microbial media using the standard addition (spiking) technique. Results with an average recovery of 100.6% and relative standard deviation of ±1.8% (RSD) were found in industrial wastewater (table 4). The sensor was also used for the determination of mercury(II) in microbial media (LB broth media). The average recovery was 101.3%, and the relative standard deviation was ±1.7% (RSD) (table 5). These results were compared with data obtained using the dithiazone spectrophotometric method for determination of mercury(II) in industrial wastewater (average recovery 98.3% and relative standard deviation ±0.9%) and in microbial media (average recovery 97.1% and relative standard deviation ±1.1%) [4]. The *F*-test revealed no significant differences between the means and variances of the two sets of results. The good agreement between the potentiometric and spectrophotometric results shows that the proposed sensor can be used for routine analysis of real samples containing mercury(II) ions without prior separation.

3.6 *Comparison with previously Hg(II) sensors*

A comparison of the response characteristics between the proposed sensor based on the TBM–RB ion-pair complex and several previously reported Hg(II) sensors is

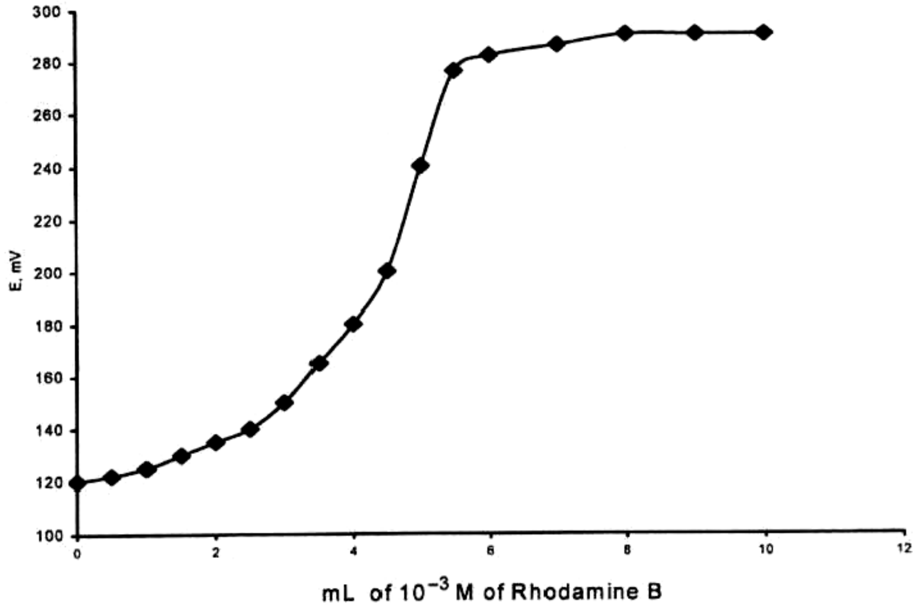

Figure 4. Typical potentiometric titration curve of 5 mL of 10^{-3} M $HgBr_3^-$ with 10^{-3} M of rhodamine B using the TBM–RB membrane sensor plasticized with *o*-NPOE.

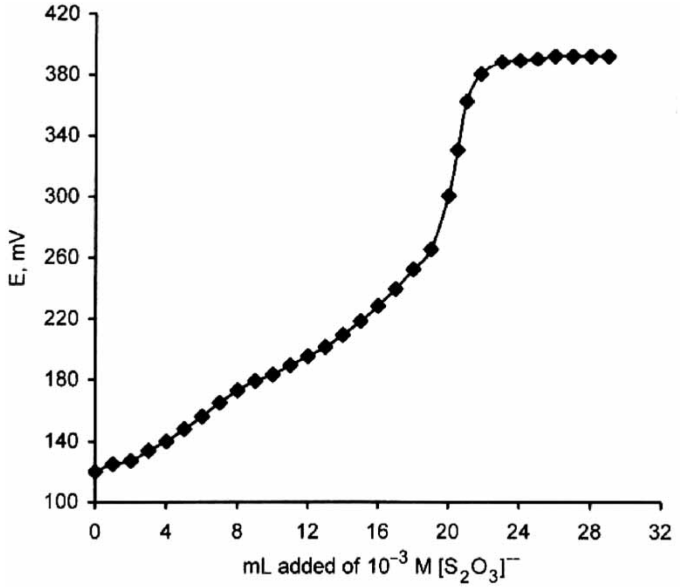

Figure 5. Typical potentiometric titration curve of 10 mL of 10^{-3} M $HgBr_3^-$ with 10^{-3} M sodium thiosulphite using the TBM–RB membrane sensor plasticized with *o*-NPOE.

Table 4. Analysis of mercury(II) in industrial wastewater using the TBM–RB PVC membrane sensor.

					Spectrophotometric method [4]		
Wastewater samples	Addition (µg/mL)	Recovery (µg/mL)	*R* (%)	RSD	Recovery (µg/mL)	*R* (%)	RSD
Sample 1	5.0	5.05	101.0	1.9	4.96	99.2	1.2
Sample 2	25	25.3	101.2	2.1	24.6	98.4	0.8
Sample 3	45	44.9	99.7	1.6	44.7	98.3	0.7
Sample 4	85	85.6	100.7	1.6	85.0	97.4	0.9

Table 5. Analysis of mercury(II) in microbial media (LB broth media) using the TBM–RB PVC membrane sensor.

					Spectrophotometric method [4]		
Mercury(II) in microbial media	Addition (µg/mL)	Recovery (µg/mL)	*R* (%)	RSD	Recovery (µg/mL)	*R* (%)	RSD
Sample 1	10	10.1	101.0	1.7	9.7	97.0	1.3
Sample 2	35	35.4	101.2	1.9	34.8	97.1	1.2
Sample 3	50	50.9	101.8	1.6	48.7	97.4	0.9

presented in table 6. The data show that the proposed sensor is comparable and has a much better time of response (10–20 s), a wide pH range of application (1.5–7.5) when compared with other sensors [1, 2, 31–33], a lower limit of detection when compared with anionic mercury(II) electrodes [31, 32], and a better potentiometric selectivity for Hg(II) over Ag(I) and Cd(II) when compared with previously reported Hg(II) membrane sensors [16, 28].

3.7 *Characterization of the extracted ion-associate complex TBM–RB*

The composition of the produced complex ion associate of $\mathrm{HgBr_3^-}$ with $\mathrm{RB^+}$ was determined by the continuous variation method [47]. Equimolar 1×10^{-3} M solutions of $\mathrm{HgBr_3^-}$ and $\mathrm{RB^+}$ were mixed in complementary proportions to give a fixed total volume (10 mL). The pH of the solutions was then adjusted to pH 4. The mixtures were then allowed to equilibrate for 5 min, and the ion associate produced was then extracted into $\mathrm{CHCl_3}$ and its absorbance measured at 555 nm against a reagent blank. A plot of the absorbance of the extract vs. the mole fraction of $[\mathrm{HgBr_3^-}]$ produced a graph that indicated the formation of a complex ion associate with a $[\mathrm{HgBr_3^-}]$-to-RB molar ratio of 1 : 1. The elemental analysis of the isolated ion associate $\mathrm{HgBr_3}$-Rd shows 37.8% C, 3.5%, 3.1% N, in good agreement with the formation of $\mathrm{HgBr_3}$-Rd ion associate.

4. Conclusions

The proposed TBM–RB PVC membrane sensor for mercury(II) determination in industrial wastewater and microbial media has the advantages of simplicity, low cost, high accuracy, selectivity, fast response (10–20 s), reproducibility and lower detection limits of mercury(II) 2.4×10^{-6} M. The sensor has several advantages over other

Table 6. Response characteristics of different Hg(II) ion-selective electrodes.

Ionophore	Linearity (M)	Detection limit (M)	Slope (mV per decade)	Response time (s)	pH range	Reference
Ethyl-2-benzoyl-2-phenylcarbamoyl acetate	10^{-6} to 10^{-3}	$<10^{-6}$	30	120	2.0–4.5	[2]
Bis[5-(4-nitrophenyl)aza salicylaldehyde]	8.0×10^{-7} to 5.0×10^{-2}	2×10^{-7}	30	10	1.0–3.5	[23]
Dithia-12-crown-4	1×10^{-6} to 1×10^{-3}	$<10^{-6}$	30	60		[39]
Antimony (III) arsenate	5×10^{-5} to 1×10^{-2}	5×10^{-5}	28	–		[16]
Diaza-18-crown-6	1×10^{-5} to 1×10^{-3}	$<10^{-5}$	41	–		[28]
Salicylaldehyde-thiosemicarbazone	1.7×10^{-6} to 1.0×10^{-1}	1.0×10^{-6}	29	<30	1.0–3.0	[1]
Trichloromercurate	5×10^{-6} to 1×10^{-2}	2.3×10^{-5}	−58	–	1.5–6	[31]
Triiodomercurate	6×10^{-6} to 1×10^{-3}	4×10^{-6}	−55.5	30–50	4.0–9.0	[32]
Tribromomercurate–rhodamine B	1.0×10^{-5} to 1.0×10^{-2}	2.4×10^{-6}	−69.5	10–20	1.5–7.5	Present work

mercury(II) sensors in terms of time of response, a wide pH range and better selectivity of Hg(II) over Ag(I) and Cd(II) in comparison with other reported anionic membrane sensors [31, 32]. The main advantage of this work is its applicability for routine control analysis of mercury(II) without prior separation [4–8] in different real samples.

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