

## 고 선택성 수은(II) 이온 막 센서

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## A Highly Selective Mercury(II) Ion-Selective Membrane Sensor

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**요 약.** 수은(II) 이온 센서로 이온투과 담체로서 bis(benzoylacetone) propylenediimine ( $H_2(BA)_2PD$ )을 근간으로 하는 새로운 이온 선택 PVC 막 전극이 개발하였다. 이 전극은 좋은 감응 특성을 보였고,  $29.8 \pm 0.75$  mV/10의 Nernstian 기울기로 부터  $1.0 \cdot 10^{-6}$ - $1.0 \cdot 10^{-1}$  M 수은(II) 이온 농도 범위에서 선형 Emf vs.  $\log[Hg^{2+}]$ 를 보였다. pH 2.5-11.5에서 검출한계는  $2.2 \cdot 10^{-7}$  M Hg(II)를 보였다. 다수의 전위 간섭이온에의 수은(II)이온 대한 선택 농도에 대해 역시 연구되었다. 이 센서는 다른 전하와 함께 많은 수의 양이온에 있어 수은(II)이온에 대해 고선택성을 보였다. 이 센서는 60초 안에 빠른 감응을 보이며 화학적으로 불활성인 것을 알아 내었고 3개월 동안 좋은 재현성을 보였다( $S=0.27$  mV). 이 전극은 실제 시료에서 수은(II)이온의 분석에 대해 서도 만족할 만한 결과를 얻었다.

**주제어:** Bis(benzoylacetone)propylenediimine, 이온 선택성전극 PVC, Hg(II)

**ABSTRACT.** A new ion selective PVC membrane electrode is developed as a sensor for mercury(II) ions based on bis(benzoylacetone) propylenediimine ( $H_2(BA)_2PD$ ) as an ionophore. The electrode shows good response characteristics and displays, a linear Emf vs.  $\log[Hg^{2+}]$  response over the concentration range of  $1.0 \cdot 10^{-6}$  to  $1.0 \cdot 10^{-1}$  M Hg(II) with a Nernstian slope of  $29.8 \pm 0.75$  mV per decade and with a detection limit of  $2.2 \cdot 10^{-7}$  M Hg(II) over the pH range of 2.5-11.5. Selectivity concentrations for Hg(II) relative to a number of potential interfering ions were also investigated. The sensor is highly selective for Hg(II) ions over a large number of cations with different charge. The sensor has been found to be chemically inert showing a fast response time of 60 s and was used over a period of 3 months with a good reproducibility ( $S=0.27$  mV). The electrode was successfully applied to determine mercury(II) in real samples with satisfactory results.

**Keywords:** Bis(benzoylacetone)propylenediimine, Ion selective electrode, PVC, Hg(II)

### INTRODUCTION

Mercury is a poisoning metal, cause ill effects on human nervous system and other body systems due to the over exposure of mercury. Mercury exposure is still an occupational hazard for people in many industries and mercury is present in the environment.<sup>1</sup> Hence, the need for mercury(II) ions determination in clinical analysis and environmental monitoring

has led to a number of methods for Hg(II) determination.

The available methods for low-level determination of Hg(II) in solutions include AAS, but it involves expensive instrumentation and sample pretreatment, which is time consuming and inconvenient. Potentiometric detection based on ion-selective electrodes (ISEs), as a simple method, offers several advantages such as speed and ease of prep-

aration and procedures, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity, and low cost. These characteristics have inevitably led to grow the list of available electrodes substantially over the last few years.<sup>2</sup> The procedure for the construction of the PVC membrane electrode is easy to implement, inexpensive and reliable.<sup>3</sup> Thus, the development of a selective sensor for mercury(II) has been a subject of investigation to analytical chemists. To improve the analytical selectivity, it is essential to search carrier compounds that would react with mercury with high selectivity. Several organic and inorganic compounds have been tested as an ionophore in producing ISEs for Hg(II), including amides,<sup>3</sup> crown ethers,<sup>4</sup> oxamides,<sup>5</sup> borondipyrromethane dye,<sup>7</sup> and thia compounds,<sup>7-9</sup> but these ISEs have short life time, and are prone to interference by a number of metal ions such as silver, iron and cadmium ions. Recently V.K. Gupta et al.<sup>10</sup> have been reported an Hg(II) ISE based on diamine donor ligand with a linear range of  $1.2 \times 10^{-5}$  to  $1.0 \times 10^{-1}$  M. The sensor has thin linear dynamic range and sodium plus ammonium ions are also interfered.

In this paper, we reported a Hg(II)-ISE based on  $H_2(BA)_2PD$  as an ionophore. The developed sensor is selective, has a wide working concentration range, fast response time with reproducible results. The present ISE based on  $H_2(BA)_2PD$  is comparable and superior in many results (such as selectivity, working linear range, response time, and working pH) than those reported papers in literature as shown in Table 1.

## EXPERIMENTAL

### Reagents

Bis(benzoylacetone) propylenediimine is used as the ionophore which was prepared according to the reported method in literature<sup>11</sup> and its structure is shown in Fig. 1. PVC of high relative molecular weight, dibutyl phthalate (DBP), dioctyl phthalate (DOP), sodium tetraphenyl borate (NaTPB) and tetrahydrofuran (THF) and all other chemicals were of highest purity available from Merck, and were used without further purifications, except THF, which was distilled before using. All solutions were prepared by dissolving the salts of metal nitrates in distilled deionized water.

### Potential measurements

Potentials were measured by direct potentiometer at  $25 \pm 0.1^\circ\text{C}$  with the help of ceramic junction calomel electrodes and the cell set-up was as follow:

Hg/Hg<sub>2</sub>Cl<sub>2</sub>, KCl (sat.)/Internal electrolyte 0.1(M) Hg<sup>2+</sup>/Membrane/Sample solution Hg/Hg<sub>2</sub>Cl<sub>2</sub>, KCl (sat.)

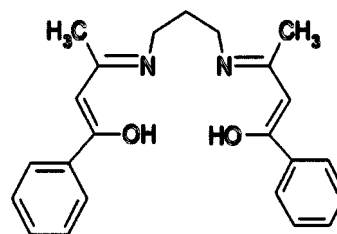


Fig. 1. Structure of  $H_2(BA)_2PD$ .

Table 1. Comparison studies of the proposed ISE with previously reported in literature (since 2000)

Ionophore	Response time (s)	Linearity (M)	logK				Reference
			Co <sup>2+</sup>	Pb <sup>2+</sup>	Cd <sup>2+</sup>	Mg <sup>2+</sup>	
Bis[5-(4-nitrophenyl)azo salicylaldehyde]	<10	$7.0 \times 10^{-7} - 5.0 \times 10^{-2}$	-4.49	-4.29	-4.30	-5.12	[1]
2-mercaptobenzimidazole	100	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	---	-1.08	-2.66	-1.53	[7]
Tetrathia-diazaocyclotetradeca-2,9-diene	18	$1.4 \times 10^{-6} - 1.0 \times 10^{-1}$	-3.16	-1.70	-3.50	-4.53	[8]
Salicylaldehyde thiosemicarbazone	<30	$1.8 \times 10^{-6} - 1.0 \times 10^{-1}$	-3.5	-3.23	-0.4	-2.70	[9]
(H <sub>2</sub> NCHMeCH <sub>2</sub> NH <sub>2</sub> )(H <sub>2</sub> O) <sub>2</sub> HgCl <sub>2</sub>	10	$1.3 \times 10^{-5} - 1.0 \times 10^{-1}$	-1.05	-1.30	-1.10	-1.67	[10]
1,4-Dithia-12-crown-4calixarene derivative containing the thiazole azo group	Not reported	$5.0 \times 10^{-6} - 1.0 \times 10^{-2}$	-3.8	-2.6	-4.6	-4.5	[23]
Ethyl-2-benzoyl-2-phenylcarbamoyl acetate	Not reported	$1.0 \times 10^{-6} - 1.0 \times 10^{-3}$	<-6	<-6	<-6	<-6	[24]
Bis(benzoylacetone)propylenediimine	60	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	-5.44	-4.26	-3.55	-2.04	This work

All potentiometric measurements were made with a pH/mV meter (Coning, Model 140). All EMF measurements were carried out in a 50-ml double walled glass cell with a constant magnetic stirring of the test solution. Activities were calculated according to Debye–Huckel procedure.<sup>12</sup> Response times were determined after the potential of one mercury solution had become constant, and similar measurements were carried out in another solution of 100-fold lower concentration. The response time is defined as the time taken to reach a potential of 95% the potential difference in the two measurements.

#### Electrode preparation

A number of membranes incorporating the ionophore, plasticizers and ion excluder in different compositions in PVC matrix fabricated as follow: a mixture of 28.20 mg of PVC, 60.64 mg of DBP as a plasticizer, 2.50 mg of additive NaTPB and 8.66 mg of  $H_2(BA)_2PD$  was dissolved in a 5 ml of THF. The mixture was shaken well to dissolve and produce clear solution. The resulting homogeneous mixture was then poured into a 50 mm Petri dish and the THF was evaporated at room temperature. Semi-transparent PVC membranes were obtained with an average thickness of 0.2 mm. The membrane was cut to the size attached to the PVC tube (i.d.=3 mm)

with the help of PVC glue and conditioned with 0.10 M  $Hg(NO_3)_2$  solutions for one day. The lifetime of the sensor is 3 months when conditioned by soaking in  $1.0 \times 10^{-3}$  M  $Hg(NO_3)_2$  solution for 24 h before measurements and stored in air when not be in use.

## RESULTS AND DISCUSSION

Schiff base upon deprotonation make complexes with  $Cu^{2+}$  and  $Hg^{2+}$ , which act as charge carriers in the membrane matrix. Bis(acetylacetonate) propylenediimine is a Schiff base that has been used as a new ionophore to develop a selective membrane sensor for copper determination.<sup>13</sup>

Bis(benzoylacetonate) propylenediimine ( $H_2(BA)_2PD$ ) is a ligand containing C=N and OH sites (Fig. 1). This compound could make complex with soft metal ions such as  $Hg(II)$ . In preliminary experiments, this compound was used to prepare a PVC membrane ISE for a wide variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions. Among these cations,  $Hg^{2+}$  shows more sensitive potential responses than the others. A number of characteristics are required for a sensor to be considered a suitable sensor for determination of ions, including selectivity and life time. Those characteristics have been taken into account in

Table 2. Optimized membrane compositions and their potentiometric response properties in mercury-selective electrodes

No.	Composition (%)				Slope (mV)	Dynamic range (M)
	PVC	L	NaTPB	DBP/DOP		
1	27.41	4.98	3.99	63.62, DBP	No response	No response
2	27.74	6.79	2.59	62.88, DBP	29.2	$1.0 \times 10^{-1} - 1.0 \times 10^{-6}$
3	27.45	5.81	3.45	63.29, DOP	23.1	$1.0 \times 10^{-1} - 1.0 \times 10^{-6}$
4	27.88	3.63	7.56	60.93, DOP	16.1	$1.0 \times 10^{-1} - 1.0 \times 10^{-7}$
5	28.20	8.66	2.50	60.64, DBP	29.8	$1.0 \times 10^{-1} - 1.0 \times 10^{-6}$
6	28.21	3.79	5.19	62.81, DBP	33.5	$1.0 \times 10^{-1} - 1.0 \times 10^{-6}$
7	28.26	5.20	3.56	62.98, DBP	34.1	$1.0 \times 10^{-1} - 1.0 \times 10^{-6}$
8	28.42	4.95	4.00	63.33, DBP	32.4	$1.0 \times 10^{-1} - 1.0 \times 10^{-5}$
9	28.96	3.97	4.56	62.51, DBP	No response	No response
10	29.58	4.85	1.94	63.63, DBP	29.7	$1.0 \times 10^{-1} - 1.0 \times 10^{-6}$
11	30.61	4.85	0.97	63.57, DBP	No response	No response
12	32.27	5.06	1.86	60.81, DOP	13.8	$1.0 \times 10^{-1} - 1.0 \times 10^{-6}$
13	32.40	6.16	2.61	58.83, DBP	30.0	$1.0 \times 10^{-1} - 1.0 \times 10^{-6}$
14	33.47	5.60	-	60.93, DOP	36.7	$1.0 \times 10^{-1} - 1.0 \times 10^{-5}$

order to assertion the utility of  $\text{II}_2(\text{BA})_2\text{PD}$  as an ionophore, membrane composition and the properties of the additives employed.<sup>14,15</sup> Thus, the influence of the membrane compositions, nature, amounts of plasticizer, and lipophilic additions on the potential response of the membranes were investigated (Table 2). As it can be seen, in the case of 60.64% DBP, 2.50% NaTPB, 28.20% PVC, and in the present of 8.66% ionophore shows the best sensitivity with a Nernstian slope of 29.8 mV/decade of mercury concentration (Table 2, No. 5).

Since the nature of the plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligand, the influence of a plasticizer on the characteristics of the sensor was investigated. As can be seen from Table 2, in our work, two plasticizers of different polarity including DOP ( $\epsilon_r=5.0$ ), and DBP ( $\epsilon_r=6.42$ ) were used. The results showed that DBP gave the best sensitivity of the two plasticizers.

The potentiometric response of the membranes was greatly improved in the presence of lipophilic anionic additives, NaTPB. It is known that lipophilic salts not only reduce the membrane resistance, but also enhance the response behavior and selectivity and reduce interference from sample anions.<sup>16,17</sup> Using 2.50% (W/W) NaTPB resulted in a Nernstian behavior of the electrode (Table 2, No. 5).

The behavior of the membrane electrode was examined with different concentrations of the inner reference solution from  $1.0 \times 10^{-3}$  to  $1.0 \times 10^{-1}$  M  $\text{Hg}(\text{NO}_3)_2$ . The results showed that change in the concentration of the reference solution causing a slight effect on the potential response of the sensor but it did not affect the slope of the line. Therefore, 0.10 M  $\text{Hg}(\text{NO}_3)_2$  was selected as an internal solution.

The influence of pH on the response of the membrane electrodes was examined with three different  $\text{Hg}^{2+}$  concentrations when the pH was adjusted with dilute nitric acid or sodium hydroxide solution. Typical results are shown in Fig. 2. Potential were found to stay constant from pH 2.5 to 11.5. The observed drift at higher pH values could be due to hydrolysis of  $\text{IIg}^{2+}$  and formation of some hydroxyl complexes of  $\text{IIg}(\text{II})$  in the solution. Therefore, we

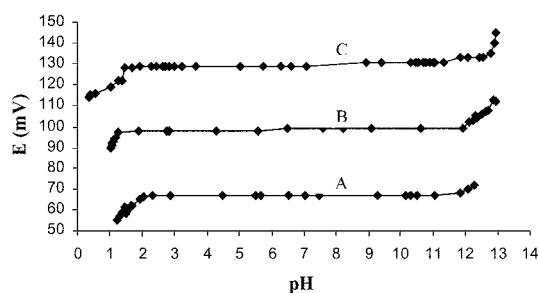


Fig. 2. pH response of the membrane. A) 0.0010 M; B) 0.00010 M; and C) 0.000010 M  $\text{IIg}(\text{II})$ .

did not adjust the pH of the solution for the next study, because long range of pH did not affect the signal. In acidic solution ( $\text{pH} < 5$ ) the fundamental cation is  $\text{IIg}^{2+}$ , whereas when the pH is nearly neutral, the fundamental cation is  $[\text{IIgOH}]^{18,19}$  which reacts with the ligand. The pH behavior of the electrode shows that the ionophore can reacts with both of  $\text{IIg}^{2+}$  and  $\text{IIgOH}^+$ .

For analytical applications, the response time of a sensor is an important factor. The response time of the electrode was tested by measuring the time required to achieve a steady state potential (within  $\pm 1$  mV), in  $1.0 \times 10^{-1}$  to  $1.0 \times 10^{-5}$  M  $\text{IIg}^{2+}$  solutions. All of the electrodes yielded steady potentials within 23 to 100 s. Typical potential time plots for the electrode are shown in Fig. 3. The steady potentials remained constant for about 5 min. The stability and reproducibility of the electrodes were also tested. The standard deviation of 10 replicate measurements at several mercury concentrations over

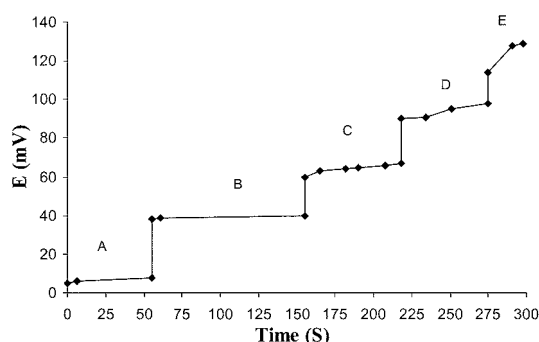


Fig. 3. Response time of the electrode. A) 0.10 M; B) 0.010 M; C) 0.0010 M; D) 0.00010 M; and E) 0.000010 M  $\text{IIg}(\text{II})$ .

Table 3. ANOVA test method for the reproducibility and repeatability of the sensor for Hg(II) concentration of  $1.0 \times 10^{-5}$  M

	Day 1	Day 2	Day 3	Day 4
Electrod 1	29.60	29.77	29.29	29.50
Electrod 2	29.80	29.83	29.60	30.02
Electrod 3	30.02	30.04	29.98	30.08
Electrod 4	30.14	30.30	30.06	30.12
RSD (%)	0.80	0.80	1.2	0.97
Repeatability of preparation sensors on any day (%)	99.20	99.20	98.80	99.03
Reproducibility of preparation sensors (%)		99.09		
Between-sample mean square		0.1412875		
Within -sample mean square		3.462575		
$F_{(2,3,12)}$		0.163		
$F_{(30,3,12)}$		3.490		

periods of 20 min and 2 h were 0.5%. ANOVA test method used to show the reproducibility and repeatability of the sensor for Hg(II) concentration of  $1.0 \times 10^{-5}$  M. The results are given in Table 3. The long-term stability of the electrode was studied by periodically recalibrating in standard solutions and calculating the response slope over the range of  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-1}$  M  $\text{Hg}^{2+}$ . The slopes of the electrode responses were reproducible to within 0.1 mV/decade over a period of 3 months, but the life time studies for more than 3 months have not been done. Therefore, the sensor can be used for at least 3 months, without a considerable change in their response characteristic towards  $\text{Hg}^{2+}$ .

#### Calibration range

Using the optimized membrane composition and conditions described above, the potentiometric response of the sensor system was studied in  $\text{Hg}^{2+}$  concentration range of  $1.0 \times 10^{-9}$  to  $1.0 \times 10^{-1}$  M at 25 °C. The calibration curve of the electrode is shown in Fig. 4. The results show a Nernstian response of 29.8 mV/

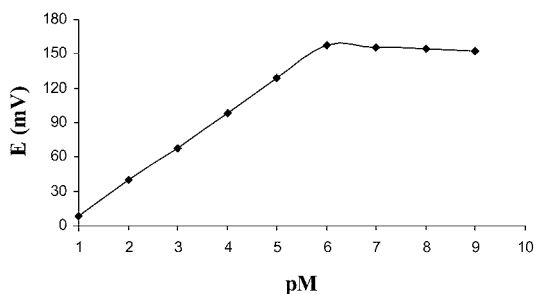


Fig. 4. Potentiometric response of the electrode.

decade of  $\text{Hg}^{2+}$  concentration, and the wide linear range within the concentration range from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M Hg(II), with a slope of 29.8 mV/decade.

The limit of detection defined as the concentration of mercury obtained when extrapolating the linear region of the calibration curve to the baseline potential was  $2.2 \times 10^{-7}$  M Hg(II).

#### SELECTIVITY OF THE ELECTRODE

The most important characteristics of any sensor are its response to the primary ion in the presence of other ions present in solution, which is expressed in terms of the potentiometric selectivity coefficient. ( $K_{\text{Hg},\text{M}}$ ),  $K_{\text{Hg},\text{M}}$  describes the preference by the membrane for an interfering ion M relative to Hg(II), were determined by the separate solution method.<sup>20</sup> In this method, calibration curves are obtained for primary and interfering ions and values of  $E_i^0$  and  $E_j^0$  are determined by extrapolating the response functions to 1 M activities according to the following equation:

$$K_{i,j}^{\text{pot}} = \frac{a_i}{(a_j)^{z_i/z_j}} \exp\left[\frac{E_j - E_i}{RT} z_j F\right] = \exp\left[\frac{E_j^0 - E_i^0}{RT} z_j F\right]$$

One of the problems in previous methods is that  $K_{i,j}^{\text{pot}}$  was originally introduced with the empirical Nicolsky–Eisenman equation,<sup>21</sup> which is known to be incorrect when two ions of different charges significantly contribute to the EMF response of the

Table 4. Values of selectivity coefficients of  $\text{Hg}^{2+}$ -selective electrode

Interfering ion	$\log K_{Li}^{pot}$
$\text{Cd}^{2+}$	-3.55
$\text{Hf}^{4+}$	-3.72
$\text{La}^{3+}$	-4.17
$\text{Ag}^+$	-3.11
$\text{Co}^{2+}$	-5.44
$\text{Mg}^{2+}$	-2.04
$\text{Pt}^4$	-5.14
$\text{K}^+$	-3.49
$\text{Sr}^{2+}$	-3.91
$\text{Ti}^{3+}$	-5.13
$\text{Fe}^{3+}$	-2.74
$\text{V}^{3+}$	-5.02
$\text{Al}^{3+}$	-3.10
$\text{Li}^+$	-3.66
$\text{Na}^+$	-3.14
$\text{Th}^{4+}$	-5.37
$\text{Ca}^{2+}$	-3.42
$\text{Ni}^{2+}$	-4.38
$\text{Cr}^{2+}$	-4.17
$\text{Cu}^{2+}$	-4.61
$\text{Zn}^{2+}$	-3.55
$\text{Tl}^+$	-3.29
$\text{Cs}^+$	-3.49
$\text{Pb}^{2+}$	-4.26
$\text{Mn}^{2+}$	-4.03

electrode.<sup>22</sup> In these conditions, the new modified separate solution method can be used to obtain selectivity coefficients that are near to the thermodynamically concepts.

Since the selectivity coefficients for monovalent, bivalent and trivalent ions are considerably lesser than unity, the electrode is highly selective to  $\text{Hg}(\text{II})$  ions over those potential interfering ions. The results are given in Table 3. Those selectivity values show that the ions, listed in Table 4, would not cause any

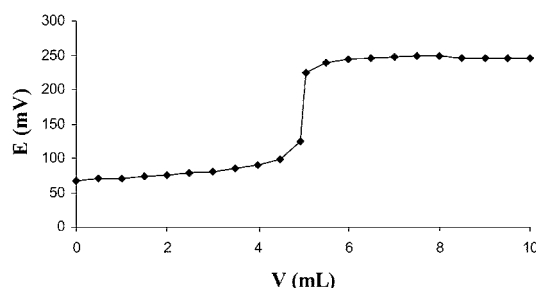


Fig. 5. Application of the mercury electrode based on  $\text{H}_2(\text{BA})_2\text{PD}$  to the potentiometric titration of 50.0 ml 0.0010 M  $\text{Hg}^{2+}$  with 0.010 M EDTA.

significant interference in the determination of  $\text{Hg}(\text{II})$  ions by the electrode sensor.

### ANALYTICAL APPLICATIONS

The sensor was successfully applied as an indicator electrode in the potentiometric titration of  $\text{Hg}^{2+}$  solution with EDTA. Typical results for the titration of a 50 ml of  $1.0 \times 10^{-3}$  M  $\text{Hg}(\text{II})$  solution with 0.010 M EDTA is shown in Fig. 5. A very good inflection point, showing perfect stoichiometry, is observed in the titration plot. As it is shown in Fig. 5 the resulting titration curve is unsymmetrical. Before the titration end point, the measured potential shows a usual logarithmic change with amount of the titrant added, while the potential response after the end point was almost constant, due to the low concentration of free  $\text{Hg}(\text{II})$  ions in the solution could be determined accurately by extrapolation of the two linear portions of the titration plot.

To assess the applicability of the proposed sensor to real samples, an attempt was made to determine  $\text{Hg}(\text{II})$  in industrial wastewater, river water and some synthetic sample. The samples were collected by a routine technique, preserve by acidification

Table 5. Recovery of mercury ions from different water sample

Sample type	$\text{Hg}^{2+}$ Added (M)	$\text{Hg}^{2+}$ Found (M)	Recovery(%)
Tap water	$5.00 \times 10^{-5}$	$4.84(\pm 0.05) \times 10^{-5}$	98.8
Tap water	$3.00 \times 10^{-5}$	$2.95(\pm 0.08) \times 10^{-5}$	98.3
River water (zayandehrood)	$5.00 \times 10^{-5}$	$5.01(\pm 0.02) \times 10^{-5}$	100.2
River water (zayandehrood)	$3.00 \times 10^{-5}$	$3.02(\pm 0.04) \times 10^{-5}$	100.7
Waste water	$5.00 \times 10^{-5}$	$5.12(\pm 0.09) \times 10^{-5}$	102.4
Waste water	$3.00 \times 10^{-5}$	$3.02(\pm 0.02) \times 10^{-5}$	100.7

with  $\text{HNO}_3$ , and stored in polyethylene bottles and analyzed within 12 h of collection. Each sample was analyzed in triplicate using the sensor by standard addition method. The results are given in Table 5, which shows that the amount of mercury recovered with the help of the sensor are in good, thereby reflecting the utility of the proposed method.

### CONCLUSION

This paper demonstrates that  $\text{H}_2(\text{BA})_2\text{PD}$  can be used in the development of a PVC membrane based sensor for  $\text{Hg}(\text{II})$  as a new ionophore. The sensor shows high selectivity, good detection limit, and wide linear dynamic range incorporated with low response time, stability and long life time. The sensor was successfully applied to the determination of  $\text{Hg}(\text{II})$  in real samples.

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