

## All Solid State Graphene Based Potentiometric Sensors for Monitoring of Mercury Ions in Waste Water Samples

Ganjali, M.R.<sup>1,2\*</sup>, Faridbod, F.<sup>1</sup>, Davarkhah, N.<sup>1</sup>, Shahtaheri, S.J.<sup>3</sup> and Norouzi, P.<sup>1,2</sup>

<sup>1</sup>Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran

<sup>2</sup>Biosensor Research Center, Endocrinology & Metabolism Molecular-Cellular Sciences Institute, Tehran University of Medical Sciences, Tehran, Iran

<sup>3</sup>Departments of Occupational Health, School of Public Health, and Institute for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran

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**ABSTRACT:** In this work, all-solid-state potentiometric PVC membrane sensor was introduced for fast and simple monitoring of mercury ions in waste water samples. The all solid state electrode is made based on a conductive composite of graphite, reduced graphene oxide, epoxy resin on a copper wire. A thin layer PVC membrane is then coated on the surface of the new conducting transducer. PVC membrane is composed of 30% PVC, 62% NPOE as plasticizer, 3% ionic liquid, and 5% Hg<sup>2+</sup> ion imprinted polymer (IIP). The sensing element of the sensor is an artificial host which is imprinted by vinyl pyridine and a suitable cross-linker. The sensor shows a Nernstian response of 29.4±0.3 mV/decade. Dynamic linear range of the sensor is 1.0×10<sup>-8</sup>-1.0×10<sup>-3</sup> mol/L of the mercury concentration and detection limit of 3.2×10<sup>-9</sup> mol/L. The interference of different ionic species with the response of the electrode shows a good selectivity of the proposed sensor. The proposed sensor is successfully applied in determination of mercury ions in some waste water samples.

**Key words:** All solid state, Mercury, Potentiometry, Sensor

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### INTRODUCTION

Monitoring of mercury ions is of great importance in environmental samples. Mercury and its compounds are one of the serious hazardous materials for human health. Mercury and its derivatives tend to bioaccumulate in the body which causes symptoms such as weakness, sleeplessness, paranoia, excessive salivation, skin itching and swelling, fever, memory loss, elevated blood pressure, tremors, gingivitis, excitability etc.

General instrumental methods for mercury analysis are complexometry, spectrophotometry, flameless or cold-vapour atomic absorption spectrometry, inductively coupled plasma (ICP), fluorimetry, and X-ray fluorescence (Kopysc, et al. 2000; Shetty and Shetty 2004; Drennan-Harris, et al. 2013, EPA, 2002).

However, having a portable device for online monitoring of the amount of mercury ions in water samples can offer an applicable and useful method of analysis.

Potentiometric ion-selective sensors are one of the extensive classes of electrochemical sensors

which have been used widely in analysis of various ionic species for many years (Faridbod, et al. 2013; Javanbakht, et al. 2008; Hosseini, et al. 2011; Zamani, et al. 2009a,b; Ganjali, et al. 2007a,b; 2008; 2009; 2010; 2013). In comparison with instrumental complex techniques, they offer advantages of fast, simple, and inexpensive method of analysis. They are portable devices which can be used easily to monitor the concentration of ionic species without consume or destructive the sample.

There are different types of potentiometric ion-selective electrodes including PVC membrane electrodes (PME), coated wire electrodes (CWE), carbon paste electrodes (CPE), all solid state electrodes (ASS) and field effective transistors (FET). Among them, general PVC membrane ion selective electrodes have not enough mechanical stability for long time usage. In addition detection limits of this kind of sensors are not too low (10<sup>-5</sup> to 10<sup>-7</sup> mol/L). Detection limits in CWE s, as asymmetric electrodes without internal filling solutions, were improved somewhat (10<sup>-8</sup> mol/L). CPE are very mechanically stable and offers the

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\*Corresponding author E-mail: ganjali@khayam.ut.ac.ir

advantages of renewability of the surface and ability to modify the composition of the paste. Although, CPE are more successful in voltammetric techniques, there are good reports on potentiometric methods.

Here, we are going to design a new mercury ion selective potentiometric sensor based on all solid state technology. In this type, a conductive polymeric composite of graphite-(here reduced graphene oxide is also added)-loaded epoxy resin is used as internal contact and transducer. A layer of general PVC membrane is then coated on the surface of the conductive composite. Ion imprinted polymer (IIP) technology is used for synthesized the sensing element of the sensor. In our previous study (Ganjali, et al. 2011), we used the same IIP in a carbon paste electrode. However, ASS PVC membrane sensor shows a remarkable performance than CPEs.

## MATERIALS & METHODS

Tetrahydrofuran (THF), dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), nitrophenyloctylether (NPOE) and sodiumtetrapenyl borate (NaTPB) were purchased from Merck Co. (Germany). High-molecular weight polyvinylchloride (PVC) was from Fluka Co. Room temperature ionic liquids, 1-n-butyl-3-methylimidazolium tetrafluoroborate ( $[bmim]BF_4$ ), 1-n-butyl-3-methylimidazolium hexafluorophosphate ( $[bmim]PF_6$ ), and 1-octyl-3-methylimidazolium tetrafluoroborate ( $[omim]BF_4$ ) were taken from Iran Petroleum Industry Institute.  $Hg^{2+}$  IIP was synthesized following a literature method published previously (Alizadeh, et al. 2011). 1 mmol  $Hg(NO_3)_2$  and 4 mmol 4-vinyl pyridine were dissolved in 20 mL of DMSO. Then, 0.15 g of the initiator (2,2-azobisisobutyronitrile) and cross-linker (Ethylene glycol dimethacrylate, EDMA), dissolved in 3mL DMSO, and was mixed with the previous solution and purged with  $N_2$  gas for 10 min. The polymerization was carried out in a water bath at 70 °C for 24 h. The obtained polymer were firstly washed with ethanol and then washed with a 0.1M HCl solution. Finally, the particles were washed with distilled water and dried at 60 °C.

Epoxy (macroplast Su 2227) from Henkel (Germany) and hardener (desmodur RFE) were from Bayer Ag (Germany). Graphite powder with a 1–2  $\mu m$  particle size was from Merck Co. Graphene oxide (GO) was prepared by a modified Hummers method using expandable graphite flake as the original material (Sun, et al. 2008). Chemical reduction of GO (RGO) was done in distilled water with  $NaBH_4$  (Wojcik and Kamat, 2010).

All solvents and all salts (nitrate or chloride form) were analytical reagent grade obtained from Merck Co. (Germany).

The sensor was constructed as typical all-solid-state PVC membranes. For the construction of a conductive polymer composite (graphite-loaded epoxy resin) used as internal contact and transducer, the powdered graphite, RGO, epoxy, and hardener were mixed in various proportions. The best all solid-state contact material was prepared by mixing 0.35 g (35% w/w) of epoxy resin, 0.15 (15% w/w) of hardener, 0.47 g (47% w/w) of powdered graphite and 0.03 g (3% w/w) of RGO in THF solvent and after mixing, the solution was left to stand about 20-30 min in air for aging. The epoxy resin mixture is used to bind the graphite. After obtaining appropriate viscosity, a shielded copper wire (0.5 mm diameter and 15 cm length) was polished and dipped in to the solution about 10 times. The wire was covered with the mixture, and let it dried for 10 hours. Using RGO in composition of conductive solid-state improve the performance of the transducer. The solid-state contact material was then immersed into the membrane cocktail for 3 times and then allowed to dry in air for 24 h. PVC membrane cocktail was composed of 5% w/w IIP, 63% w/w plasticizer (NPOE), 30% w/w PVC, and 2% w/w RTIL. The prepared membrane electrodes were conditioned in a  $10^{-3}$  mol/L solution of  $Hg^{2+}$  ion (Isildak and Asan 1999; Isildak 2000; Kemer and Ozdemir 2008). The PVC membrane was prepared as follow: different amounts of IIP with appropriate amounts of PVC, plasticizer and additive (IL) were dissolved in tetrahydrofuran (THF), and the solution was mixed well into a glass dish of 2 cm diameter. Then, THF was evaporated slowly until an oily concentrated mixture was obtained.

A glass cell where the ASS PVC membrane sensor as an indicator electrode was placed; consisted of a Ag/AgCl double junction reference electrodes (Azar-Electrode Co., Iran) as external reference electrodes. Both electrodes were connected to an ion analyzer with a 250 pH/mV meter with  $\pm 0.1$  mV precision.

Following cell assembly for potentiometric measurements were used:

Cu wire/ASS layer/ion selective PVC membrane | sample solution || Ag-AgCl, KCl (satd.)

These measurements were done using calibration method with several standard solutions.

## RESULTS & DISCUSSION

Most of the reported potentiometric ion-selective electrodes are of symmetrical membrane.

Symmetrical ion selective electrodes are classical ion selective electrodes in which the ion selective membrane is placed between two solutions. In asymmetrical ion selective electrodes, one side of the membrane is in contact with a solid phase while the other is exposed to the measured solution (Scheme 1). Symmetrical sensors contain an inner reference solution for the development of potential gradient across the membrane (Ganjali, et al. 2008). The presence of liquid inside the electrode restricts their applications up to some extent. Also, for robustness and miniaturization, it is desirable to eliminate the liquid phase of inner reference solution from the conventional electrochemical cells to enhance their practical suitability for medicinal, biological sciences and technology, and in vivo experiments.

All solid state ion-selective polymeric membrane electrodes are of particular interest because they are free from the above limitations (Kumar, et al. 2013). The application of conductive epoxy supports in membrane sensors has allowed the construction of PVC membrane all-solid-state electrodes. Changing shape and size, miniaturized and flow-through electrodes for use in flow-injection analysis are the advantages of these types (Machado, 1994).

PVC matrix, a suitable plasticizer and an ion-pair compound are the main components of a membrane sensor. Each one plays a special role in the sensor response. Some of the important optimizations of the membrane ingredients are shown in Table 1. As a general procedure a plasticizer/PVC ratio about 2.2 is the best amount for making the membrane (Faridbod, et al. 2012; Shamsipur, et al. 1999; Zamani, et al. 2006; 2008a,b). Thus, for all the membranes presented in Table 1, 30% wt. PVC has been selected and not shown. Besides the PVC matrix, a water-immiscible organic solvent should be used to plasticize the membrane. It helps the mobility of the ion-pair complex inside the membrane (Abedi, et al. 2007; Zamani, et al. 2010; 2012) The plasticizer should have a low vapor-pressure, compatible with PVC, no functional groups which can undergo protonation reactions. General plasticizers with a variety of dielectric constants, dibutyl phthalate (DBP with DC of 6.4), nitrophenyloctyl ether (NPOE with DC of 24), nitrobenzene (NB with DC of 35.7) and benzylacetate (BA with DC of about 5.7) were used. Among them, NPOE showed better responses. Since mercury ion is rather a polar ion, polar plasticizer help to extract it better in the organic phase of the membrane. Although plasticizer helps the better extraction and exchanging the ions, sometimes it cannot be very successful. In this case,

adding small amount of ionic additive can be improve the exchange mechanism and reduce the ohmic resistance. A new recent approach for optimization of the response of the sensor is using a water-immiscible room temperature ionic liquid in the membrane composition. RTILs can be act as an ionic additive and besides decreasing the membrane Ohmic resistance; they can also improve the ion-exchanging. As it can be seen in Table 1, three room temperature ionic liquids were used in the composition of the membrane no. 7 to no. 11. Results shows that using [bmim]PF<sub>6</sub> helps the Hg<sup>2+</sup> ions better exchange from the aqueous solution to the organic phase of the membrane (Faridbod, et al. 2013).

As it can be seen from Table 1, a blank membrane, the membrane without the sensing element (IIP), responds too poor (membrane no. 12). Hence, membrane no. 9 showed the best Nernstian slope (29.4±0.3 mV/decade) was selected for further studies.

The potential response of the electrochemical cell in different concentrations of the Hg<sup>2+</sup> ion (one decade difference; from 1.0×10<sup>-8</sup>-1.0×10<sup>-1</sup> mol/L) was recorded. According to the Nernst equation, the potential vs. -log [Hg<sup>2+</sup>] was plotted as shown in Fig. 1. The linear part of this curve indicates the linear range of the sensor. In conventional PVC membrane sensors, the measuring linear range can extend from 0.1 to 10<sup>-5</sup> or even 10<sup>-6</sup> mol L<sup>-1</sup>. But in ASS PVC membrane sensor lower detection limits can be achievable. Due to the saturation of the active sites of the electrode surface (smaller surface), the upper limit of detection is 10<sup>-3</sup> mol/L. The slope of the linear part of the sensor which is 29.4 mV/decade of the Hg<sup>2+</sup> ion concentration shows a Nerstian behavior and confirms the performance of the proposed sensor. Standard deviation of five replicate measurements was then calculated ±0.3 mV. A linear response towards the Hg<sup>2+</sup> concentration was from 1.0×10<sup>-8</sup>-1.0×10<sup>-3</sup> mol/L. By extrapolating the two segments of the calibration curves, detection limit of the PVC membrane sensor was obtained 3.2×10<sup>-9</sup> mol/L.

Dynamic response time of a sensor is the required time for the sensor to achieve values within ±1 mV of the final equilibrium potential, after successive immersions in the sample solutions (Zamani, et al. 2006; 2008a,b; 2010). Its calculation involved the variation and the recording of the Hg<sup>2+</sup> ion concentration in a series of solutions from 1.0×10<sup>-8</sup> to 1.0×10<sup>-3</sup> mol/L. Sensor was able to quickly reach its equilibrium response in the whole concentration range. As can be seen in Fig. 2, this time for the ASS PVC membrane sensor was about 10 s in the whole solutions.

**Table 1. Various membrane ingredients used in making ASS-PVC membrane sensor**

No	PVC	Plasticizer	IIP	RTIL	Slope* (mV/decade)	LR (mol/L)*	DL (mol/L)*	Response time	R <sup>2</sup>
1	30	NPOE,67	3	-	13.5±0.6	5.0×10 <sup>-6</sup> - 1.0×10 <sup>-4</sup>	5.0×10 <sup>-6</sup>	1 min	0.845
2	30	NPOE,65	5	-	23.8±0.4	1.0×10 <sup>-7</sup> - 1.0×10 <sup>-3</sup>	8.0×10 <sup>-8</sup>	32 s	0.986
3	30	NPOE,63	7	-	21.2±0.5	5.0×10 <sup>-7</sup> - 5.0×10 <sup>-3</sup>	3.5×10 <sup>-7</sup>	45 s	0.934
4	30	NB,65	5	-	18.6±0.5	1.0×10 <sup>-7</sup> - 1.0×10 <sup>-3</sup>	1.0×10 <sup>-7</sup>	53 s	0.954
5	30	DBP,65	5	-	12.2±0.4	1.0×10 <sup>-6</sup> - 5.0×10 <sup>-3</sup>	1.0×10 <sup>-7</sup>	57 s	0.922
6	30	BA,65	5	-	14.7±0.6	1.0×10 <sup>-6</sup> - 1.0×10 <sup>-3</sup>	8.0×10 <sup>-7</sup>	55 s	0.931
7	30	NPOE,64	5	1[bmim]PF <sub>6</sub>	25.2±0.4	1.0×10 <sup>-7</sup> - 1.0×10 <sup>-3</sup>	1.0×10 <sup>-7</sup>	36 s	0.992
8	30	NPOE,64	5	2[bmim]PF <sub>6</sub>	27.8±0.4	1.0×10 <sup>-8</sup> - 8.0×10 <sup>-3</sup>	1.0×10 <sup>-8</sup>	18 s	0.994
9	30	NPOE,63	5	3[bmim]PF <sub>6</sub>	29.4±0.3	1.0×10 <sup>-8</sup> - 1.0×10 <sup>-3</sup>	3.2×10 <sup>-9</sup>	10 s	0.998
10	30	NPOE,63	5	4 [bmim]PF <sub>6</sub>	29.1±0.4	1.0×10 <sup>-8</sup> - 1.0×10 <sup>-3</sup>	1.0×10 <sup>-8</sup>	27 s	0.990
11	30	NPOE,65	5	3 [bmim]BF <sub>4</sub>	28.5±0.5	1.0×10 <sup>-8</sup> - 1.0×10 <sup>-3</sup>	1.0×10 <sup>-8</sup>	15 s	0.995
12	30	NPOE,62	-	3[bmim]PF <sub>6</sub>	5.1±0.8	1.0×10 <sup>-6</sup> - 1.0×10 <sup>-3</sup>	1.0×10 <sup>-6</sup>	2.5 min	0.798

\*The results are based on five replicate measurements.

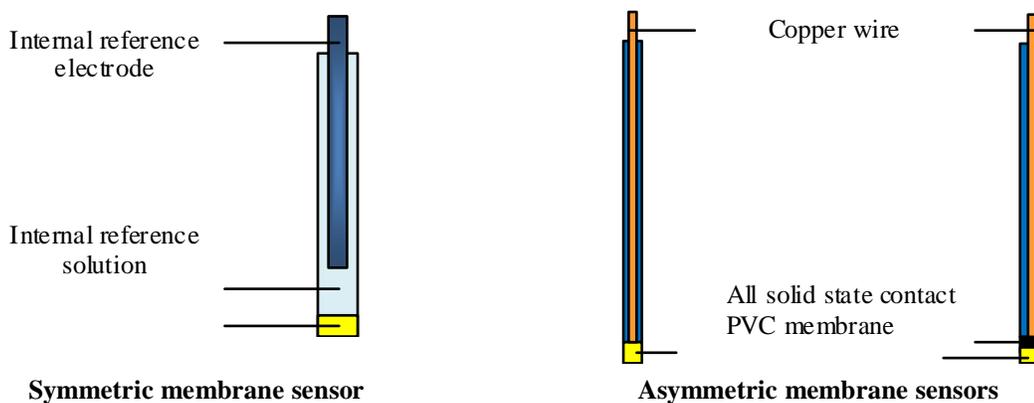
To examine the effect of pH on the sensor responses, the potential was measured at specific concentration of the Hg<sup>2+</sup> ion solution (1.0×10<sup>-5</sup> mol/L) from the pH value of 1.0 to 10.0 (concentrated NaOH or HCl solutions were employed for the pH titrations). The results showed that the potential remained constant despite the pH change in the range of 3.0 to 5.0, which indicates the applicability of this electrode in the specified pH range. Relatively noteworthy fluctuations in the potential vs. pH behavior took place below and above the formerly stated pH limits. In detail, the fluctuations above the pH value of 5.0 might be justified by forming Hg(OH)<sup>+</sup> or Hg(OH)<sub>2</sub> and decrease the solubility of the ions in aqueous solution. Fluctuations below the pH value of 3.0 were caused by protonation of the active sites (heteroatoms) of IIP.

Lifetime of the sensor was estimated by the calibration curve, periodical test of a standard solution and calculation of its response slope. For this estimation, three electrodes were employed extensively (1 hour per day) for 12 weeks. The average lifetime for the conventional PVC membrane potentiometric sensors is in the range of 4–10 weeks (Ganjali, et al. 2008; 2009; 2010; 2013; Faridbod, et al. 2013). Here, after 10 weeks utilization of the sensor,

a slight gradual decrease in the slope and an increase in the detection limit were observed. It is well known that the loss of plasticizer, sensing element, or ionic site from the polymeric film due to leaching into the sample solution after several times of usage, is a primary reason for limited lifetimes of the sensors. Using RTILs in the composition of the membrane causes a longer lifetime of the sensor. ASS PVC membrane sensors show a longer life-time than traditional PVC membrane sensors.

Selectivity, which describes an ion-selective electrode's specificity toward the target ion in the presence of interfering ions, is the most important characteristic of these devices. The potentiometric selectivity coefficients of the sensor were evaluated by the matched potential method (MPM) (Zamani, et al. 2006; 2008a,b; 2010). The resulting values of the selectivity coefficients are shown in Table 2. Note that all selectivity coefficients shows that the interferences negligible in the performance of the electrode assembly. This good selectivity of the sensor is the result of the ion imprinted polymer used as a sensing material of the sensor.

For repeatability experiment, 3 standard synthetic samples were measured by calibration



Symmetric membrane sensor Asymmetric membrane sensors  
 Scheme 1. Symmetric and asymmetric PVC membrane sensors

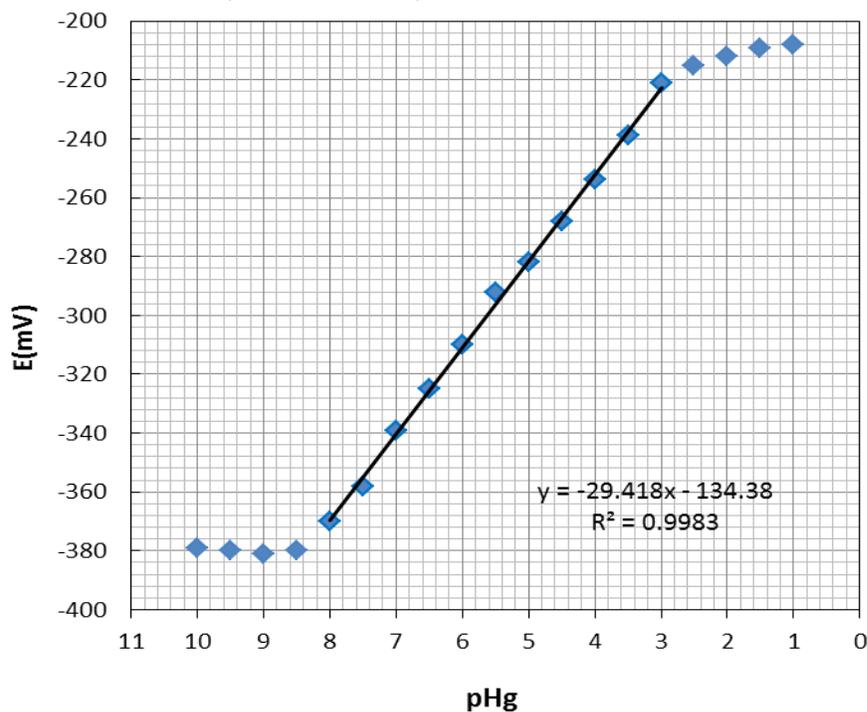


Fig.1. Calibration curve of Hg ASS PVC membrane sensor; the results are based on 5 replicate measurements

Table 2. The selectivity coefficients of various interfering cations for Hg<sup>2+</sup> ASS pVC membrane sensor

Cation	Selectivity Coefficients
Na <sup>+</sup>	<10 <sup>-4</sup>
K <sup>+</sup>	<10 <sup>-4</sup>
Mg <sup>2+</sup>	<10 <sup>-4</sup>
Ca <sup>2+</sup>	<10 <sup>-4</sup>
Cu <sup>2+</sup>	2.3×10 <sup>-4</sup>
Zn <sup>2+</sup>	3.2×10 <sup>-4</sup>
Co <sup>2+</sup>	1.0×10 <sup>-4</sup>
Cd <sup>2+</sup>	4.9×10 <sup>-4</sup>
Pb <sup>2+</sup>	3.0×10 <sup>-4</sup>
Ag <sup>+</sup>	1.0×10 <sup>-4</sup>
Fe <sup>3+</sup>	4.5×10 <sup>-4</sup>
Ni <sup>2+</sup>	1.0×10 <sup>-4</sup>
La <sup>3+</sup>	2.5×10 <sup>-4</sup>
Al <sup>3+</sup>	3.0×10 <sup>-4</sup>

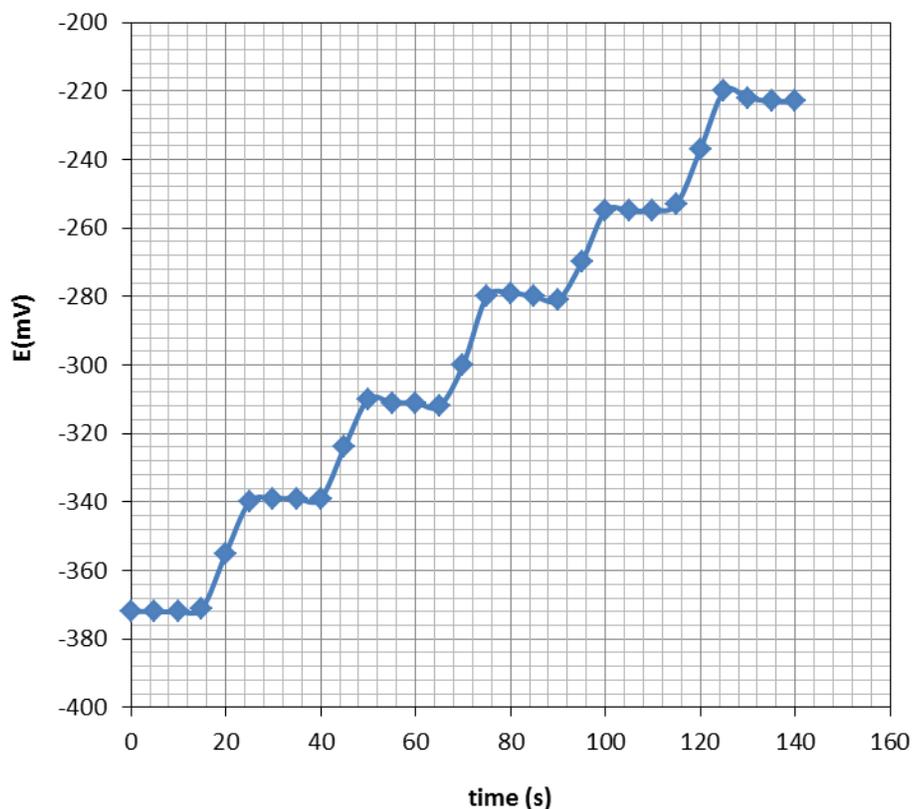


Fig. 2. Dynamic response time of the Hg ASS PVC membrane sensor

Table 3. Results of mercury analysis in waste water samples

Sample	Found by the sensor* (mol/L)	Found by ICP-OES(mol/L)
Sample 1	$5.73 \pm 0.67 \times 10^{-6}$	$5.68 \pm 0.32 \times 10^{-6}$
Sample 2	$4.26 \pm 0.43 \times 10^{-6}$	$4.14 \pm 0.28 \times 10^{-6}$
Sample 3	$5.44 \pm 0.52 \times 10^{-6}$	$5.27 \pm 0.33 \times 10^{-6}$

\* The results are based on five replicate measurements.

method. The RSD values by ASS PVC membrane were 2.55, 2.70 and 3.10%. The RSD values for the intra- and inter-day assays in the cited formulations performed in the same laboratory by the two analysts did not exceed 4.0%.

To assess the applicability of the proposed sensor to real samples,  $\text{Hg}^{2+}$  amounts of some industrial wastewater samples were analyzed. The samples were collected and acidify with  $\text{HNO}_3$ . Each sample was analyzed three times using the proposed mercury sensor by calibration method. The samples also analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) as a reference method. The results are given in Table 3, which shows that the amount of mercury recovered with the help of the sensor are in good agreement with reference method.

## CONCLUSION

All-solid-state potentiometric PVC membrane sensor was constructed for fast and simple determination of mercury ions in waste water samples. The solid contact as an effective transducer was made based on graphite, reduced graphene oxide, epoxy resin on a copper wire. A thin layer PVC membrane coated on the surface of the transducer composed of 30% PVC, 62% NPOE, 3% ionic liquid, and 5%  $\text{Hg}^{2+}$  ion imprinted polymer. Hg ion imprinted polymer was used as sensing element. The sensor showed dynamic linear range of the sensor is  $1.0 \times 10^{-8}$ - $1.0 \times 10^{-3}$  mol/L of the mercury concentration and detection limit of  $3.2 \times 10^{-9}$  mol/L. The proposed sensor was successfully applied in determination of mercury ions in some water samples.

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