Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

*J. Serb. Chem. Soc.* *82* (3) 317–328 (2017)
*JSCS–4968*

UDC 681.586.5:546.492–71+54–145.2:678.743+543.42
*Original scientific paper*

# New optical sensor based on the immobilization of a triazene ligand in PVC membrane for Hg(II) ion

HOMA SHAFIEKHANI[1]*, FAHIMEH NEZAM[2] and SHAHRIYAR BAHAR[1]

[1]*Department of Chemistry, Payame Noor University (PNU), P. O. Box 19395-4697 Tehran, Iran and* [2]*Department of Chemistry, Lamerd Branch, Islamic Azad University, Lamerd, Iran*

(Received 20 May, revised 10 August, accepted 3 October 2016)

*Abstract*: This paper describes the development and creation of a new sensitive optical sensor that is quite selective to Hg(II) ions in aqueous solution. The sensing element, the newly synthesized methyl 2-[3-(3-methylphenyl)-2-triazen-1-yl]benzoate, incorporated into a plasticized poly(vinyl chloride) membrane, is able to determine Hg(II) ion with a high selectivity over a wide dynamic range from 5.0–115.1 μg $L^{-1}$ at pH 7.5 with a lower detection limit of 0.67 μg $L^{-1}$. The response of the optode membrane to Hg(II) was fully reversible and revealed a very good selectivity towards Hg(II) ion from a wide variety of other metal ions in solution. The overall performance characteristics of the sensor were evaluated and good reversibility, wide dynamic range, long life span, long-term response stability and high reproducibility were found. The proposed optical sensor gives proper results in applications including direct determination of the Hg(II) ion in real environmental samples.

*Keywords*: spectrometry; optode, heavy metal; mercury; poly(vinyl chloride); triazenes.

## INTRODUCTION

Mercury is one of the most widely recognized toxic heavy metals. Natural phenomena and human activities, including volcanic eruptions, wind erosion, water erosion, solid waste incineration and industrial production, can result in mercury pollution of the environment. Natural processes in aquatic systems convert the less toxic element and inorganic compounds of mercury into much more toxic methylmercury. Methylmercury is concentrated and collected in the food chain, leading to excessive concentrations in a few species of seafood and fish, which many humans consume. Wide application of mercury in the production of chemical substances, its electric power and electronic usages and industrial ext-

---

* Corresponding author. E-mail: shafieehoma@yahoo.com

doi: 10.2298/JSC160520093S

racts mean that its determination is crucial.[1–6] Concern over the distinct toxicity of mercury has stimulated explorations aimed at developing price-favorable, fast, and facile methods to monitor mercury in biological, industrial and food samples.[7–9] In comparison to conventional techniques,[10–19] such as differential spectroscopy and electrochemical techniques: atomic absorption / emission spectroscopy, inductively coupled plasma mass spectrometry (ICP-MS), selective cold vapor atomic fluorescence spectrometry, X-ray microanalysis and a variety of potentiometric ion-selective electrodes, chemical sensors based on measurements of optical signals are considered as advanced techniques due to their simplicity, reasonable selectivity, improved sensitivity, low detection limit and fieldwork applicability. As such, there is a developing need or desire for constructing optical chemical sensors (optodes) for fast and economical monitoring of the mercuric ion in real time. Hitherto, numerous excellent optodes with different mechanisms have been reported for the detection of Hg(II).[20–28] These optodes differ in performance characteristics but none of them met all the necessities required concurrently for a good optical sensor. In this work, a novel photometric sensor based on a newly synthesized ligand is introduced. The senor showed a significant absorbance signal change on exposure to an aqueous solution containing mercury(II) ion, high selectivity, and showed the theoretically predicted absorbance response to the concentration of mercury(II) ion. Therefore, the selectivity, response time, reproducibility, reversibility, and lifetime of the proposed optode membrane will be discussed in details. The current paper encompasses the fabrication of an optode that utilizes a triazene ligand as the sensing reagent for the determination of low levels of mercury.

Triazenes are a diverse class of compounds that have been extensively studied for their anticancer capacity. These compounds consist of an amine directly bonded to an azo group, as shown in Fig. 1. The functional group is also known as the diazo amino group from older literature,[29] and usually adopts a *trans*-configuration in the ground state.[30] Triazenes can bind to metals in both monodentate and bidentate manners. The products of the reaction of triazene and metal are air and moisture stable and are easily prepared.[31] In the present study, the suitability of methyl 2-[3-(3-methylphenyl)-2-triazen-1-yl]benzoate as a mercury colorimetric agent for the preparation of Hg(II) selective PVC optical membrane sensor was investigated and applied for the determination of the concentration of Hg(II) ions in some water samples with satisfactory results.

## EXPERIMENTAL

### *Material and instruments*

All chemicals were of analytical reagent grade (Merck, Darmstadt, Germany). Doubly distilled water (Almas, Larestan, Iran) was utilized throughout the experiments. A 1 mg mL$^{-1}$ Hg(II) stock solution was prepared by dissolving of 0.1708 g $Hg(NO_3)_2 \cdot H_2O$ in doubly distilled water and 0.5 mL of (1 mol L$^{-1}$) $HNO_3$ and diluted to 100 mL in a volumetric flask.

Then, sample solutions were prepared by appropriate dilution. The triazene ligand was synthesized and its structure has been confirmed. Buffer solutions were prepared from boric acid/ /acetic acid/phosphoric acid (0.04 mol $L^{-1}$ each), and the pH adjustments were made by the addition of (1 mol $L^{-1}$) sodium hydroxide solution and (1 mol $L^{-1}$) hydrochloric acid. A PG T80 PC UV–Vis spectrophotometer (Leicestershire LE17 5BH, UK) with 1 cm quartz cell was used for recording all spectra and absorbance measurements. A Metrohm 827 pH-meter (Greifensee, Switzerland) with a combined glass electrode was used after calibration against standard Merck buffers for pH adjustment. Di-butyl phthalate (DBP) as a plasticizer, tetrahydrofuran (THF), and high relative molecular weight poly(vinyl chloride) (PVC) were used for membrane preparation.

*Preparation of methyl 2-[3-(3-methylphenyl)-2-triazen-1-yl]benzoate*

Methyl 2-[3-(3-methylphenyl)-2-triazen-1-yl]benzoate, was prepared as below: 10 g of ice and 150 mL of water were poured in a 250 mL flask and then the flask was cooled to 0 °C in an ice bath. Then, 3.2 mL (0.023 mol) methyl 2-aminobenzoate and 10 mL (0.12 mol $L^{-1}$) of hydrochloric acid (37 %) were added to the flask. Then, a solution containing $NaNO_2$ 1.72 g (0.025 mol) in 10 mL of water was added slowly to the resulting solution over 15 min. The pH of the solution was then adjusted at 6 by addition of a solution containing 1 g of sodium acetate in 10 mL of water. After mixing for 15 min, the obtained solution was added to a mixture of 3 mL of *m*-toluidine in methanol (0.023 mol), 5 mL of methanol, and 4 mL of water. After mixing for 24 h, the yellow precipitate was filtered off and dried. After recrystalization from hexane, suitable crystals of the compound were obtained by slow evaporation of the solvent.[32] The starting materials and the reaction procedure are presented in Fig. 1.

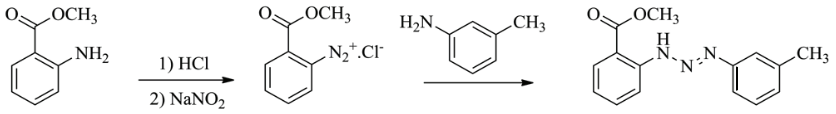

Fig. 1. General procedure for the preparation of methyl 2-[3-(3-methylphenyl)-2-triazen-1-yl]benzoate.

*Membrane preparation*

Microscope slides were cut into 9 mm×50 mm dimensions to prepare glass slides to fit easily into a standard spectrophotometer glass cells (10 mm×10 mm×50 mm). Membrane solutions have been prepared by dissolving 32 mg PVC, 64 µL DBP and 8 mg ligand in 2.0 mL THF. The solution was stirred with a magnetic stirrer to acquire a homogeneous mixture. To enhance the adhesion of the membrane, the glass slides had been wiped clean with THF, sulfuric acid and sodium hydroxide solutions and then thoroughly rinsed with distilled water and finally dried in an oven at 110 °C.[33] The membranes were cast by placing 25 µL of the homogenized membrane solution onto a glass slide, and spread quickly using a spin-on device (1650 rpm rotation frequency). The prepared membranes were dried in ambient air for 15 min and then kept in a clean and dark place for 2 h to evaporate absolutely the solvent. Blank (reference) membranes were prepared in a similar manner excluding the ligand from the membrane solution. All measurements were executed at room temperature.

*Absorbance measurement*

The prepared membrane was placed in a buffer solution at pH 7.5 for 2 min to attain equilibrium. Then, the membrane was placed in a quartz cell containing 2.0 mL of universal buffer (pH 7.5) in the sample path of the spectrophotometer. The quartz cell in the reference path of the spectrophotometer consisted of a blank film. The baseline was corrected in the intended area. Then a sample solution containing an appropriative amount of Hg(II) ions was injected into the cell with a micro-syringe. After 8 min, the absorbance was measured at 362 nm.

## RESULTS AND DISCUSSION

### *Spectrophotometric study of the solution*

In order to determine the stoichiometry and stability of the resulting metal–ligand complexes, in a typical procedure, 2.0 mL of a $5.0\times10^{-5}$ mol $L^{-1}$ ligand solution in dimethylformamide (DMF) was located inside the spectrophotometer cell and the absorbance of the solution was measured in the wavelength range 300–450 nm. Then, a known amount of a concentrated solution of Hg(II) in DMF ($1.3\times10^{-4}$ mol $L^{-1}$) was added in a stepwise manner using an 10 μL Hamilton syringe. The absorbance spectrum of the solution was recorded after each addition. The absorbance curves are shown in Fig. 2.

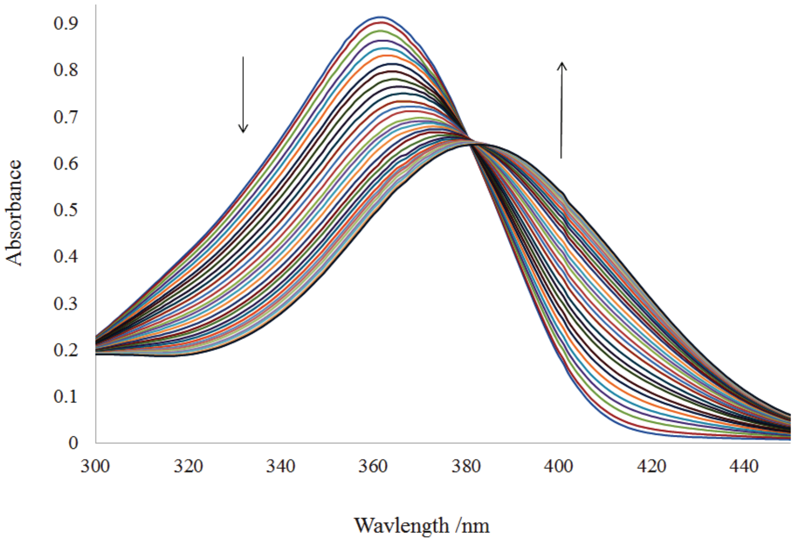

Fig. 2. Absorbance spectra of the ligand solution ($5\times10^{-5}$ mol $L^{-1}$) in DMF and increasing amounts of Hg(II) ion solution ($1.30\times10^{-4}$ mol $L^{-1}$). The arrows show the direction of absorbance with increasing the concentration of Hg(II) ions.

On addition of Hg(II) ions, a decrease in the absorbance at 362 nm was observed. With decreasing absorbance at 362 nm, a new peak at approximately 392 nm formed, which corresponded to the formation of an Hg(II)–ligand complex. The resulting plots of the absorbance at 392 nm against metal ion/ligand mole ratios are shown in Fig. 3. From the sharp inflection point observed for Hg(II) at a mole ratio of 2, it could be concluded that a 2:1 complex of [$L_2$–Hg] was formed in DMF solution. The formation constants of the resulting complexes were evaluated by computer fitting of the corresponding mole ratio data to proper mass balance equations[34] using a non-linear curve-fitting program, KINFIT.[35] The program is based on the iterative adjustment of calculated values of absorbance intensity to the observed values using the Newton–Raphson procedure. The output of the program comprises the refined parameters, the sum-of-squares, and the standard deviations of the data. The resulting formation constants value, $k\beta$, is 7.1.

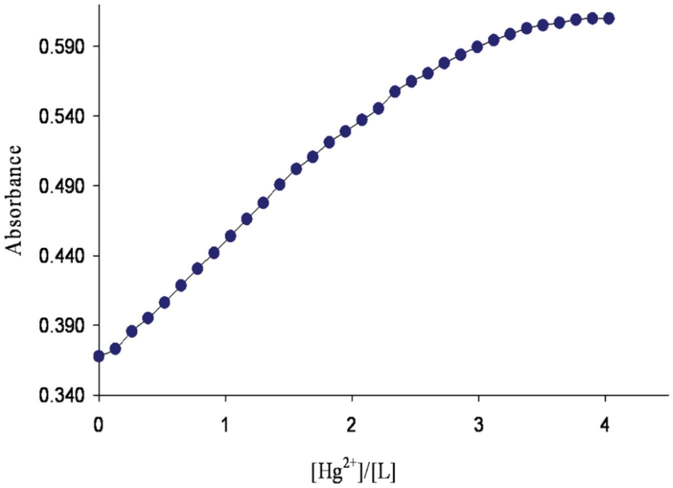

Fig. 3. The absorbance measured in DMF solution at 392 nm *vs*. [Hg(II)]/[L] mole ratio plot.

*Effect of the pH of test solution on the sensor response*

The pH of the sample solution influences the sensor selectivity and the linear dynamic range.[36] The influence of the pH of the test solution on the response of the proposed Hg(II) ion-selective optical sensor is illustrated in Fig. 4. To optimize the pH, the absorbance for 50 μg $L^{-1}$ Hg(II) ions in universal buffer was measured at 362 nm in the pH range 2.0–10.0, Fig. 4, It could be seen that the absorbance increased rapidly on changing the pH from 2.0 to 7.5, while it decreased at pH values higher than 7.5. This phenomenon might be because of the weak complexation at lower pH values (pH < 3.0). On the other hand, the reduced optical response of the proposed sensor at pH > 7.5 could be due to a possible formation of the hydroxide of Hg(II) ions. Thus, pH 7.5 was selected as the working pH for all subsequent experiments.

*Dynamic range*

A calibration curve was obtained by plotting the defined signal *vs*. the Hg(II) concentration. The changes in the absorbance signals of the optode film with respect to various concentrations of Hg(II) ions in the range 5.0–115.1 μg $L^{-1}$ at pH 7.5 are shown in Fig. 5 and 115.1 μg $L^{-1}$ was found as the concentration of Hg(II) ions that saturates the film. The regression equation was:

$$\Delta A = 0.0027c - 0.0051$$

with a correlation coefficient of 0.9980, where $\Delta A$ is the increase in absorbance of the film at 362 nm for a fixed time of 8 min, and $c$ is the concentration of Hg(II) in µg $L^{-1}$. The detection limit, which was estimated as the concentration of analyte producing an analytical signal equal to three times the standard deviation of the blank signal, was found to be 0.67 µg $L^{-1}$.

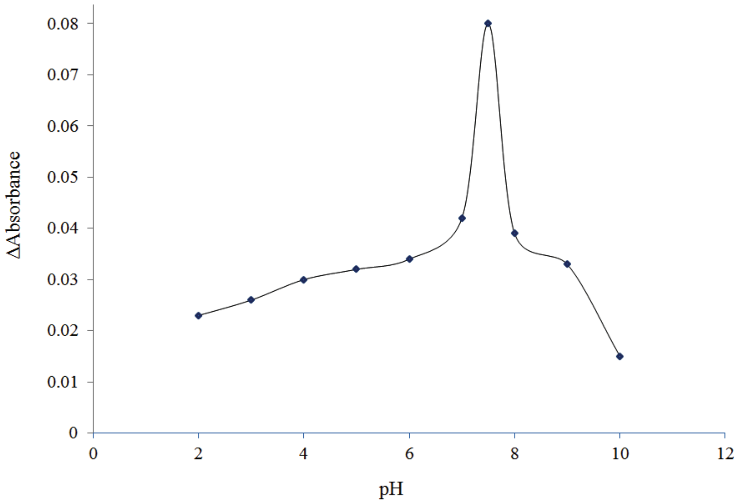

Fig. 4. Effect of pH on the response of membrane at 362 nm when the film was exposed to 50 µg $L^{-1}$ Hg(II) ion.

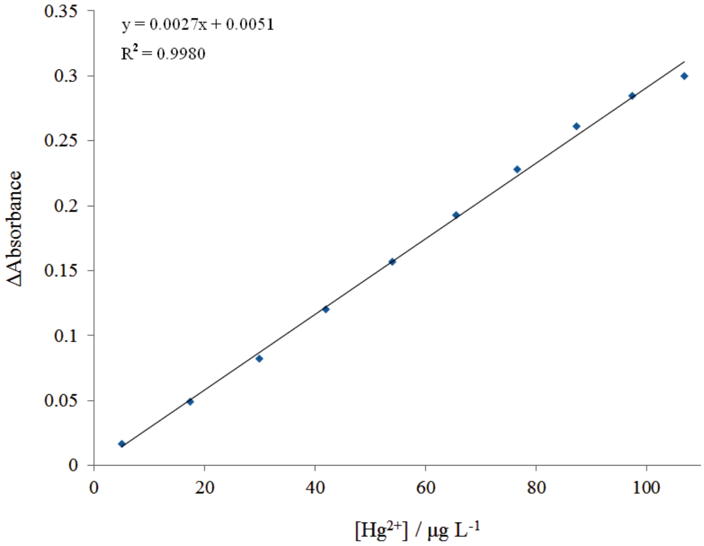

Fig. 5. Calibration curve of the membrane at 362 nm in the range 5.0–115.1 µg $L^{-1}$ at pH 7.5.

*Response time*

As is known, the response time ($t_{95\ \%}$) of a sensor, *i.e.*, the time required for the response of the sensor towards a certain concentration of the measured ion to reach 95 % of its final value (steady state),[37] is one of the predominant parameters that must be determined experimentally. The time-dependent response characteristics of the optical film when immersed in a buffer solution containing 50 μg $L^{-1}$ Hg(II) ions is presented in Fig. 6.

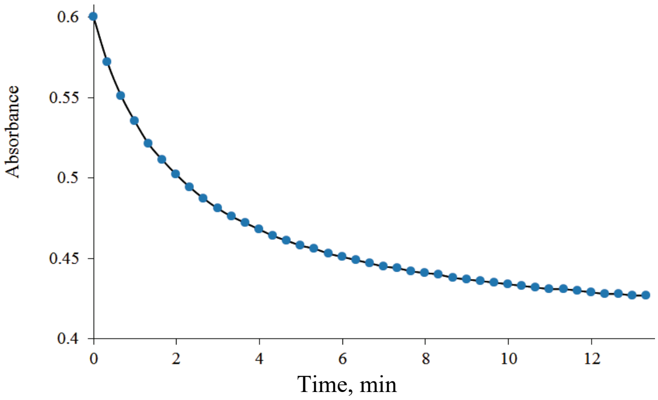

Fig. 6. Typical response curve of the optode film at 362 nm as a function of the time of film exposure to 50 μg $L^{-1}$ Hg(II) at pH 7.5.

Figure 6 indicates that the shortest response time of the film is about 8 min in which the sensor is able to monitor reversibly and reproducibly Hg(II) ions.

*Regeneration of the optode membrane*

The optical membrane should be regenerated using a suitable stripping reagent after its contacts with an Hg(II) solution and gets ready for the following measurements. Some reagents, such as HCl, NaOH, $H_2SO_4$, $HNO_3$ and EDTA, were studied as regenerating reagents. It was found that the best results were obtained by application of EDTA, which gave short membrane regeneration times, 40–50 s. After this regeneration and before the next measurement of the mercury concentration, the optode required positioning in buffer pH 7.5 for 10 min.

*Reproducibility and reversibility*

The reproducibility and reversibility are vital traits of an optical sensor. These traits were tested *via* absorbance intensity measurements of the same membrane sensor when it was exposed to 50 μg $L^{-1}$ Hg(II) ion in a universal buffer solution of pH 7.5 and then to a 0.01 mol $L^{-1}$ EDTA solution, as proven in Fig. 7. The mean absorbance values ($n = 5$) were 0.795±0.006 and 0.836±0.009 in the presence of Hg(II) ions and the EDTA solution, respectively. The mean difference in the absorbance was approximately 0.041±0.0011. For this reason, it could be concluded that the system is highly reversible.

The between membrane reproducibility was also acquired by preparing five membranes using the same membrane solution. The ensuing coefficient of variation for these membranes was observed to be 3.5 %, and the test results confirmed no significant difference between the produced membranes.

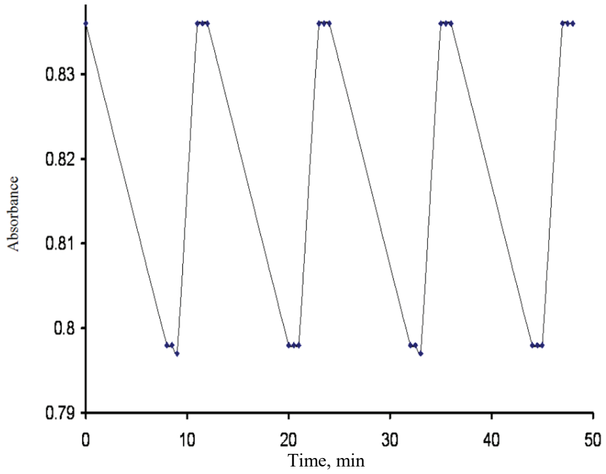

Fig. 7. Variation of the absorbance of the membrane at 362 nm for repetitive exposure to a 50 µg $L^{-1}$ solution of Hg(II) ions and a 0.01 mol $L^{-1}$ solution of EDTA at pH 7.5.

*Short-term stability, repeatability and lifetime*

To examine the short-term stability of the sensor, its response in contact with 50 µg $L^{-1}$ of Hg(II) ions in a buffer of pH 7.5 was recorded over a period of 2 h with an interval of 5 min. From the relative standard deviation of the absorbance was 5.8 % ($n$ = 25) and hence, no leakage of ligand from the membrane during this period was evidenced. This suggests the optode membrane has good short-term stability and repeatability. The optode was stable over a period of one month when it was not in use (the membrane was kept in air) and the signal value of the membrane did not change.

*Selectivity*

Obviously, selectivity is one of the most critical properties of a sensor and indicates its relative response to the analyte ion and to the other ions present in solution. In order to study the effect of the different cations on the determination of Hg(II) ions using the proposed membrane, its absorbance at $\lambda$ = 362 nm under the optimum conditions was measured for a solution of 50 µg $L^{-1}$ Hg(II). Then, the response of the optical sensor was measured in a solution containing some other metal ions, including $K^+$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Co^{2+}$, $Pb^{2+}$, $Zn^{2+}$,

$Ni^{2+}$, $Fe^{2+}$ and $Fe^{3+}$, the concentration of which was 100 times greater than the primary ion. The species were considered as interference if they caused an analytical variation of 5 % or more as compared to the analytical signal obtained in the absence of the interfering species ($A_0$). The resulting relative error is defined as $RE = 100((A_0–A)/A_0)$. The results in demonstrated that the only cation having a relative error grater than 5 % was $Cd^{2+}$ (Table I).

TABLE I. The selectivity of the sensor towards Hg(II) ion over interfering ions

| Interfering ion | *RE* / % | Interfering ion | *RE* / % |
|---|---|---|---|
| $K^+$ | 0.48 | $Co^{2+}$ | 2.75 |
| $Na^+$ | 0.53 | $Pb^{2+}$ | 3.68 |
| $Mg^{2+}$ | 0.73 | $Zn^{2+}$ | 3.12 |
| $Ca^{2+}$ | 2.21 | $Ni^{2+}$ | 4.21 |
| $Cu^{2+}$ | 2.37 | $Fe^{2+}$ | 2.59 |
| $Cd^{2+}$ | 6.26 | $Fe^{3+}$ | 3.51 |

### *Comparison with other methods*

The overall performance of the proposed optical sensor is compared in Table II with a number of previous mercury optodes. The proposed optical sensor gives the advantage of short response time and low detection limit. The sensor exhibits Hg(II) selectivity against other heavy metal ions. In comparison with other reported Hg(II) selective optical sensors, the proposed sensor has the lowest detection limit.

TABLE II. Resent Hg(II) optodes based on various organic ionophores; TAC: triacetylcellulose

| Ionophore | Membrane | Linear range, mol $L^{-1}$ | Detection limit, mol $L^{-1}$ | Response time, min | Ref. |
|---|---|---|---|---|---|
| 2-[1-[(2-sulfanylphenyl) imino]ethyl]phenol | Sol–gel | $1.0\times10^{-2}$ – – $1.0\times10^{-5}$ | $1.0\times10^{-6}$ | 3 | 38 |
| Indigo carmine; *N*-cetylpyridinium chloride | TAC | $2.4\times10^{-5}$– – $4.7\times10^{-4}$ | $7.2\times10^{-6}$ | 8-10 | 39 |
| (*E*)-1-(2-ethoxyphenyl)-3-(4-nitrophenyl)-1-triazene | TAC | $3.5\times10^{-5}$ – – $4.5\times10^{-4}$ | $3.1\times10^{-7}$ | 15 | 31 |
| Rhodamine 6G-P | TAC | $4.9\times10^{-8}$ – – $2.5\times10^{-5}$ | $6.5\times10^{-9}$ | 20 | 40 |
| Methyl 2-[3-(3-methylphenyl)-2-triazen-1-yl]benzoate | PVC | $2.5\times10^{-8}$ – – $5.7\times10^{-7}$ | $3.3\times10^{-10}$ | 8 | This work |

### *Determination of mercury in water samples*

The proposed optical sensor was found to function well under laboratory conditions. In order to test the practical application of the present sensor, tap water samples spiked with different amounts of Hg(II) ions were measured by the proposed optode. The Hg(II) content of water samples was analyzed by standard addition method and then determined by the proposed optode (Table III). Each sample with the proposed sensor was analyzed in five replicates. The results display that the sensor is appropriate for the determination of Hg(II) concentrations in such samples with good precision and accuracy.

TABLE III. Determination of the Hg(II) ions in different water samples (*n*=5).

| Sample | Added, μg $L^{-1}$ | Found, μg $L^{-1}$ | Recovery, % |
|---|---|---|---|
| 1 | – | <DL | – |
| 2 | 17.5 | 17.3 | 98.9 |
| 3 | 42.0 | 42.1 | 100.2 |

## CONCLUSIONS

In this work, a new triazene ligand, methyl 2-[3-(3-methylphenyl)-2-triazen-1-yl]benzoate, was investigated as an appropriate complexing agent for the construction of a PVC optical membrane selective sensor for the detection of low concentrations of mercury(II) ions. Based on the results obtained in this study, the proposed Hg(II) ion–selective optode has many advantages over others, including, ease of preparation, fast response time, outstanding wide dynamic range, very low detection limit, high selectivity, and good reproducibility. This optode was used to determine the concentration of Hg(II) ions in water samples.

*Acknowledgement*. We would like to express our gratitude to the Lamerd Azad University for their assistance and encouragement.

### ИЗВОД

## НОВИ ОПТИЧКИ СЕНЗОР ЗА Hg(II) ЈОНЕ БАЗИРАН НА ИМОБИЛИЗАЦИЈИ ЛИГАНДА ТРИАЗЕНА У ПВЦ МЕМБРАНИ

HOMA SHAFIEKHAN[1], FAHIMEH NEZAM[2] и SHAHRIYAR BAHAR[1]

[1]*Department of Chemistry, Payame Noor University (PNU), P. O. Box 19395-4697 Tehran, Iran и*
[2]*Department of Chemistry, Lamerd Branch, Islamic Azad University, Lamerd, Iran*

У овом раду је описан развој и креирање новог осетљивог оптичког сензора, веома селективног у односу на Hg(II) јоне у воденом раствору. Сензорски елемент, новосинтетисан метил-2-[3-(3-метилфенил)-2-триазен-1-ил]бензоат, инкорпориран у пластификовану поливинил-хлорид мембрану, у могућности је да одреди Hg(II) јон са високом селективношћу у широком динамичком опсегу (5,0–115,1 μg $L^{-1}$) на pH 7,5 са ниском границом детекције од 0,67 μg $L^{-1}$. Одговор мембране оптоде на Hg(II) је потпуно реверзибилан и добија се веома добра селективност према Hg(II) јонима у односу на велики број других металних јона у раствору. Евалуиране су карактеристике сензора, који је показао добру реверзибилност, широк динамички опсег, дуготрајност и стабилност одговора и високу репродуктивност. Предложени оптички сензор може потенцијално да се примени за директно одређивање Hg(II) јона у узорцима из животне средине.

(Примљено 20. маја, ревидирано 10. августа, прихваћено 3. октобра 2016)

## REFERENCES

1. A. A. Ensafi, M. Fouladgar, *Sens. Actuators, B* **136** (2009) 326

2. R. Voegborlo, A. El-Methnani, M. Abedin, *Food Chem.* **67** (1999) 341
3. A. Yari, F. Papi, *Sens. Actuators, B* **138** (2009) 467
4. D. W. Boening, *Chemosphere* **40** (2000) 1335
5. H. H. Harris, I. J. Pickering, G. N. George, *Science* **301** (2003) 1203
6. S. A. El-Safty, M. Shenashen, *TrAC, Trends Anal. Chem.* **38** (2012) 98
7. G. K. Darbha, A. Ray, P. C. Ray, *ACS Nano* **1** (2007) 208
8. B. Tang, L. J. Cui, K. H. Xu, L. L. Tong, G. W. Yang, L. G. An, *ChemBioChem* **9** (2008) 1159
9. M. Shamsipur, M. Hosseini, K. Alizadeh, N. Alizadeh, A. Yari, C. Caltagirone, V. Lippolis, *Anal. Chim. Acta* **533** (2005) 17
10. P. Ugo, L. M. Moretto, P. Bertoncello, J. Wang, *Electroanalysis* **10** (1998) 1017
11. J. Capelo, I. Lavilla, C. Bendicho, *Anal. Chem.* **72** (2000) 4979
12. P. E. Koulouridakis, N. G. Kallithrakas-Kontos, *Anal. Chem.* **76** (2004) 4315
13. C. Petisco, B. García-Criado, B. V. de Aldana, I. Zabalgogeazcoa, S. Mediavilla, *Anal. Bioanal. Chem.* **382** (2005) 458
14. F. X. Han, W. D. Patterson, Y. Xia, B. M. Sridhar, Y. Su, *Water Air Soil Pollut.* **170** (2006) 161
15. B. M. W. Fong, T. S. Siu, J. S. K. Lee, S. Tam, *J. Anal. Toxicol.* **31** (2007) 281
16. W. Geng, T. Nakajima, H. Takanashi, A. Ohki, *J. Hazard. Mater.* **154** (2008) 325
17. Y.-L. Yu, Z. Du, J.-H. Wang, *J. Anal. At. Spectrom.* **22** (2007) 650
18. X. Yu, Z. Zhou, Y. Wang, Y. Liu, Q. Xie, D. Xiao, *Sens. Actuators, B* **123** (2007) 352
19. P. Bühlmann, E. Pretsch, E. Bakker, *Chem. Rev.* **98** (1998) 1593
20. C.-Y. Li, X.-B. Zhang, L. Qiao, Y. Zhao, C.-M. He, S.-Y. Huan, L.-M. Lu, L.-X. Jian, G.-L. Shen, R.-Q. Yu, *Anal. Chem.* **81** (2009) 9993
21. J. V. Ros-Lis, M. D. Marcos, R. Mártinez-Máñez, K. Rurack, J. Soto, *Angew. Chem. Int. Ed.* **44** (2005) 4405
22. E. M. Nolan, S. J. Lippard, *Chem. Rev.* **108** (2008) 3443
23. M. H. Lee, S. W. Lee, S. H. Kim, C. Kang, J. S. Kim, *Org. Lett.* **11** (2009) 2101
24. B. Leng, L. Zou, J. Jiang, H. Tian, *Sens. Actuators, B* **140** (2009) 162
25. C. Sanchez-Pedreno, J. Ortuno, M. Albero, M. Garcia, M. Valero, *Anal. Chim. Acta* **414** (2000) 195
26. B. Kuswandi, R. Narayanaswamy, *J. Environ. Monit.* **1** (1999) 109
27. W. H. Chan, R. H. Yang, K. M. Wang, *Anal. Chim. Acta* **444** (2001) 261
28. M. Amini, B. Khezr, A. Firooz, *Sens. Actuators, B* **131** (2008) 470
29. H. Zollinger, *Azo and diazo chemistry: aliphatic and aromatic compounds*, Interscience, New York, 1961
30. N. Chen, M. Barra, I. Lee, N. Chahal, *J. Org. Chem.* **67** (2002) 2271
31. H. Tavallali, H. Shafiekhani, M. K. Rofouei, M. Payehghadr, *J. Braz. Chem. Soc.* **25** (2014) 861
32. V. Ghoulipour, F. Hosseinzadeh, S. Farazi, J. Attar Gharamaleki, B. Notash, M. Rofouei, *J. Coord. Chem.* **67** (2014) 2171
33. L. Ling, Y. Zhao, J. Du, D. Xiao, *Talanta* **91** (2012) 65
34. J. Ghasemi, M. Shamsipur, *J. Coord. Chem.* **36** (1995) 183
35. J. L. Dye, V. A. Nicely, *J. Chem. Educ.* **48** (1971) 443
36. E. Anticó, M. Lerchi, B. Rusterholz, N. Achermann, M. Badertscher, M. Valiente, E. Pretsch, *Anal. Chim. Acta* **388** (1999) 327
37. E. Lindner, K. Tóth, E. Pungor, *Pure Appl. Chem.* **58** (1986) 469

38. K. Alizadeh, R. Parooi, P. Hashemi, B. Rezaei, M. R. Ganjali, *J. Hazard. Mater.* **186** (2011) 1794
39. H. Tavallali, E. Shaabanpur, P. Vahdati, *Spectrochim. Acta, A* **89** (2012) 216
40. N. Thakur, S. A. Kumar, K. A. Kumar, A. K. Pandey, S. D. Kumar, A. Reddy, *Sens. Actuators, B* **211** (2015) 346.