

# A New Fluorescent Sensor for Arsenic(III) Determination in Aqueous Media

Soner ÇUBUK,<sup>†</sup> Mustafa Can TAŞKAN, Ece KÖK YETİMOĞLU,<sup>†</sup> and M. Vezir KAHRAMAN

*Marmara University, Faculty of Arts and Sciences, Chemistry Department, Goztepe, 34722 Istanbul, Turkey*

A novel polymeric membrane sensor was developed by using 2-hydroxyethyl acrylate, trimethylolpropane triacrylate, (3-mercaptopropyl)trimethoxysilane, and poly(ethylene glycol)diacrylate for As(III) determination. Various parameters, like the pH, response time, the foreign ions, and concentration effects were investigated for deciding the optimum working conditions of the polymeric sensor. As a result of this investigation, the optimum pH was found to be 2, and the response time was found to be 30 s. The linear range of the sensor was  $6.65 \times 10^{-9} - 3.99 \times 10^{-8} \text{ mol L}^{-1}$  ( $0.50 - 2.99 \mu\text{g L}^{-1}$ ) with a detection limit of  $2.33 \times 10^{-9} \text{ mol L}^{-1}$  ( $0.18 \mu\text{g L}^{-1}$ ). Soy flour and well-water samples were successfully analyzed with the developed sensor. The sensor can be used at least 100 times after regeneration. It could be reused by washing with purified water and showed good stability for 6 months.

**Keywords** As(III), polymeric membrane, sensor, fluorimetry

(Received November 2, 2019; Accepted December 25, 2019; Advance Publication Released Online by J-STAGE January 3, 2020)

## Introduction

For thousands of years, arsenic has affected people more than other toxic elements and compounds. For this reason, it is known as “the king of poisons”. Today, a lot of people are exposed to chronic high levels of arsenic through water, air, soil, food. Toxic effects of arsenic can be seen both in the industrialized and developing countries. The increase in contamination of arsenic through air, water and soil increases the anxiety about arsenic poisoning. Arsenic can be observed as many different inorganic and organic structures, and its toxicity is related to its form and oxidation states. Arsenic can be found in oxidation states of -III, 0, III and V and inorganic oxyanion arsenite ( $\text{As}^{3+}$ ) is the most toxic structure.

The main ways that humanity is exposed to arsenic are in water, nutrition and inhalation. Other than those, people who are working with wood preservatives, chemical weapons, pigments, pharmaceuticals and arsenic-based pesticide industries are exposed to arsenic due to occupational reasons.<sup>1-3</sup>

Prolonged exposure to arsenic causes skin diseases as wells as nervous system, respiratory system and reproductive disorders. Also, exposure to arsenic leads to diseases such as cancer, necrosis, diabetes, and high blood pressure.<sup>4-7</sup> The quantitative monitoring of arsenic is very important because of its toxicity. The maximum amount of arsenic allowed in drinking water was reduced from 50 to 10  $\mu\text{g/L}$  by the United States Environmental Protection Agency (US EPA) due to an increase in arsenic-induced diseases.<sup>8</sup>

There are many methods used for the determination of arsenic, such as graphite furnace atomic absorption spectroscopy

(GF-AAS),<sup>9</sup> cathodic stripping voltammetry (CSV),<sup>10</sup> and anodic stripping voltammetry (ASV),<sup>11</sup> as well as flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS),<sup>12</sup> liquid chromatography-inductively coupled plasma mass spectrometry (LC-ICP-MS),<sup>13</sup> and capillary zone electrophoresis (CZE).<sup>14</sup> Although these methods have high precision and accuracy for the determination of low arsenic levels, they require expensive instrument, qualified personnel, and a laborious sample-preparation procedure.<sup>15-17</sup>

In this work, the preparation of a new sensitive and selective polymer-based fluorescent sensor for As(III) determination was reported. The parameters, such as the pH effect, linear range, detection limit, reusability, and selectivity, were systematically examined.

## Experimental

### Reagents and chemicals

Commercial chemicals (poly(ethylene glycol) diacrylate (PEGDA), 2-hydroxyethyl acrylate (HEA), trimethylolpropane triacrylate (TMPTA), (3-mercaptopropyl)trimethoxysilane (MPTS) and the photoinitiator) were bought from Sigma-Aldrich. A 1000  $\text{mg L}^{-1}$  As(III) standard solution was purchased from Sigma. Standard solutions of As(III) were diluted with distilled water to prepare working stock solutions. Ultra-pure water was used in all experiments, and a Milli-Q water purification system was used for this purpose. The obtained purified water had a resistivity of 18.2  $\text{M}\Omega \text{ cm}$ .

### Fluorescence sensor preparation

A polymeric sensor was prepared by the UV-curing technique. PEGDA was the main polymeric substance. MPTS and HEA were used as a reactive monomers and TMPT was used for a crosslinker. 2-Hydroxy-2-methylpropiophenone was used as a

<sup>†</sup> To whom correspondence should be addressed.

E-mail: sonercubuk@marmara.edu.tr (S. C.); ecekok@marmara.edu.tr (E. K. Y.)

photo initiator, 40% PEGDA, 25% HEA, 30% TMPTA, and 5% MPTS mixed in a beaker and photo initiator was added at 3% with respect to the total amount of the formulation. The mixture was stirred until reacting homogeneity. The mixture was then poured into Teflon® molds (W, 12 mm; L, 50 mm; D, 1 mm) and cured under a UV lamp (OSRAM 300 W;  $\lambda_{\max}$ , 365 nm) for 150 s. After curing, the membranes were taken from the mold and put into purified water to remove any unreacted chemicals and the photoinitiator. After that, films were taken out and dried in a lyophilizer for 24 h.

#### Characterization

FTIR spectra obtained from a Perkin Elmer Spectrum 100 ATR-FTIR spectrophotometer and SEM images obtained from a Philips XL30 ESEM-FEG/EDAX were used to determine the functional groups contained in the prepared membrane, as well as its surface morphology, respectively.

## Results and Discussion

#### Characterization of the membrane sensor

FTIR spectroscopy work to identify functional groups on the prepared polymeric membrane, the FTIR spectrum was recorded. As can be seen from Fig. 1, the -OH group of HEA is observed at  $3451\text{ cm}^{-1}$  and aliphatic -CH stretching appeared at  $2927\text{ cm}^{-1}$ . The peak from the Si-O bond was recorded at  $1071\text{ cm}^{-1}$  and the peak of the stretching vibrations of the carbonyl group can be seen at  $1722\text{ cm}^{-1}$ .

SEM imaging the prepared membranes surface morphology is

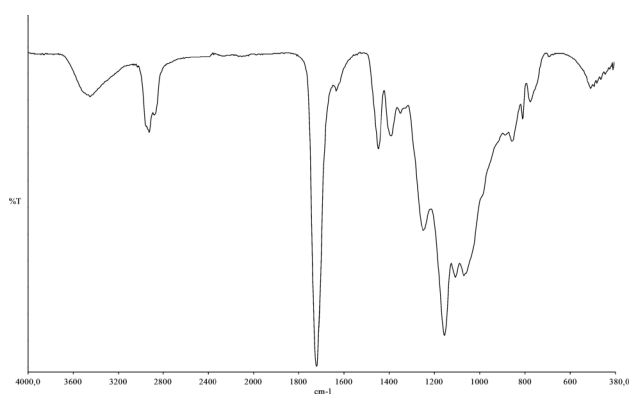


Fig. 1 FTIR spectrum of the prepared P (PEGDA/TMPTA/HEA/MPTS) membrane.

a crucial factor concerning an influential fluorescent sensor. The SEM images given in Fig. 2 were recorded using different magnification factors to determine the surface morphology of the prepared membrane. As can be seen, the surface of the membrane is as expected without cracks, and being homogeneous and non-porous.

#### Spectral characterization

For this purpose, excitation and emission spectra were recorded using different slit ranges and photo-multiplier tube (PMT) voltages of the solutions in which As(III) ions were present at a concentration of  $1.33 \times 10^{-8}\text{ mol L}^{-1}$  ( $1.00\text{ }\mu\text{g L}^{-1}$ ) and no As(III) containing solutions, respectively (Fig. 3).

#### Influence of the pH

The effect of the pH on the fluorescence intensity of the membrane was examined by using 8 solutions prepared from pH values from 1 to 8, and containing As(III) ions at a concentration of  $1.33 \times 10^{-8}\text{ mol L}^{-1}$  ( $1.00\text{ }\mu\text{g L}^{-1}$ ). A graph obtained from the study is given in Fig. 4. As can be seen from the related graph, the maximum fluorescence intensity was reached at a pH of 2; this pH was used for further studies.

#### Response time

The change in the fluorescence intensity of a solution containing As(III) ions at a concentration of  $1.33 \times 10^{-8}\text{ mol L}^{-1}$  was investigated at a pH of 2 at 10 s time intervals for a period of 300 s. As can be seen from Fig. 5, the fluorescence intensity increased from the start to 30 s and remained constant until the 90 s, and then began to decrease. Therefore, 30 s, the minimum time at which the maximum fluorescence intensity was reached, was used as the optimal time to measure the arsenic concentration. This time period (30 s) was used in other parts of the study.

#### Measuring range and detection limit

As a result of the study to determine the linear range of the method developed for the determination of As(III), the calibration graph (Fig. 6) was found to be linear in the range of  $6.65 \times 10^{-9} - 3.99 \times 10^{-8}\text{ mol L}^{-1}$ . In order to determine the limit of detection (LOD) value of the developed method, measurements were made with 7 different blank solutions. The LOD was calculated as 3-times (3 $\sigma$ ) the standard-deviation value obtained from these measurement results, and this limit was obtained as  $2.33 \times 10^{-9}\text{ mol L}^{-1}$ .

#### Regeneration and reusability of the As(III) sensor

For regeneration of the sensor, the washing with pure water for 2 min after total washing with a pH 2 buffer solution was

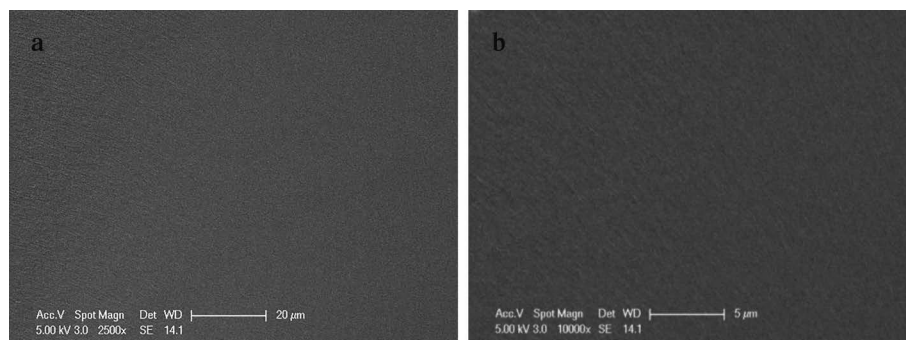


Fig. 2 SEM images of the polymeric membrane at (a) 2500 $\times$  and at (b) 10000 $\times$  magnifications.

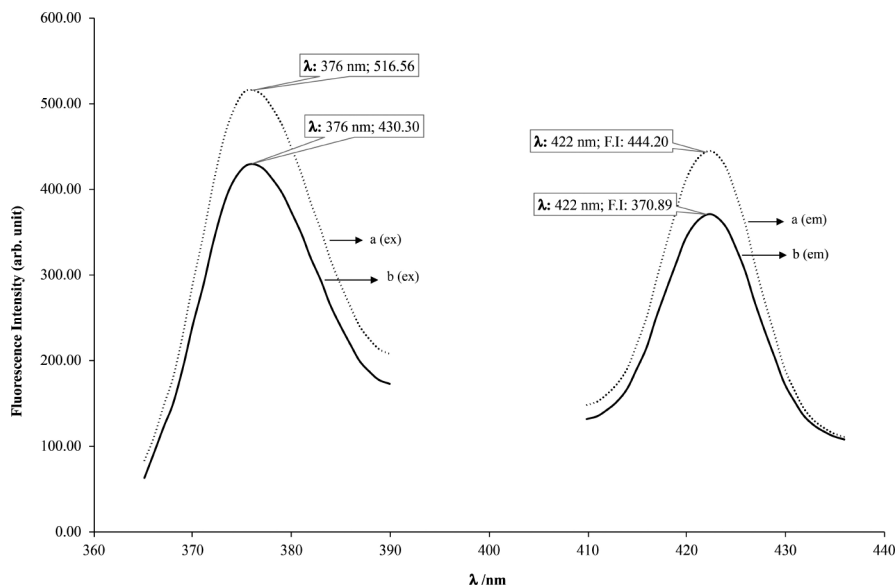


Fig. 3 Excitation ( $\lambda_{\text{ex}} = 376 \text{ nm}$ ) and emission ( $\lambda_{\text{em}} = 422 \text{ nm}$ ) spectra of the polymeric membrane. (a) Absence of As(III) ions; (b) presence of  $1.33 \times 10^{-8} \text{ mol L}^{-1}$  As(III) ions.

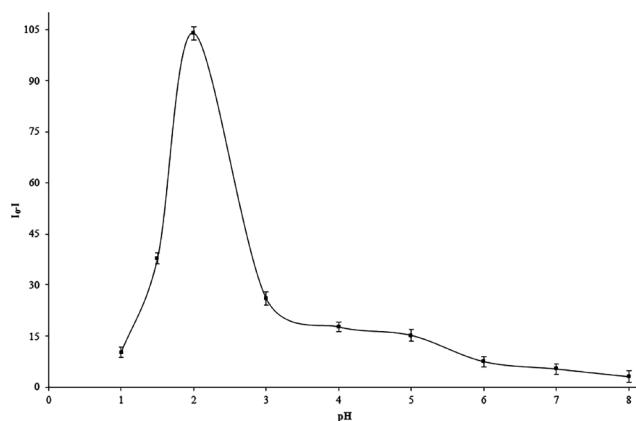


Fig. 4 pH effect on the polymeric As(III) sensor ( $t: 30 \text{ s}$ ,  $n = 6$ ).

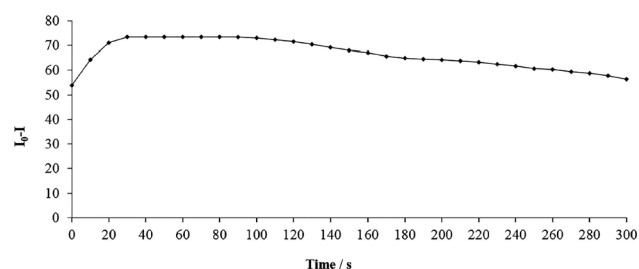


Fig. 5 Influence of the response time on the fluorescence intensity of the As(III) sensor.

found to be sufficient. For this process, the change in the fluorescence intensity of the membrane in the presence of a solution containing  $1.33 \times 10^{-8} \text{ mol L}^{-1}$  As(III) was investigated. After washing, it was determined that the membrane could reach the fluorescence intensity at the beginning. Moreover, it was found that the same sensor could be used for measurements up to 100 times after the required washing.

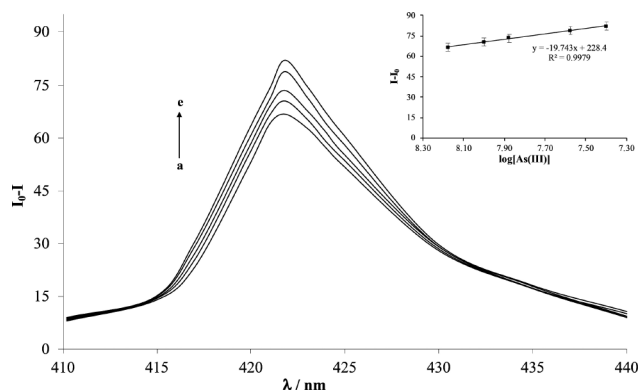


Fig. 6 Fluorescence emission spectra of the sensing membrane in the presence of different concentrations of As(III) at pH 2.0. (a)  $6.65 \times 10^{-9} \text{ mol L}^{-1}$ , (b)  $9.97 \times 10^{-9} \text{ mol L}^{-1}$ , (c)  $1.33 \times 10^{-8} \text{ mol L}^{-1}$ , (d)  $2.66 \times 10^{-8} \text{ mol L}^{-1}$ , (e)  $3.99 \times 10^{-8} \text{ mol L}^{-1}$  ( $\lambda_{\text{ex}} = 376 \text{ nm}$ ). The inset shows the calibration curve of the sensor ( $\lambda_{\text{ex/em}} = 376/422 \text{ nm}$ ); ( $I_0 - I$ , where  $I_0$  and  $I$  indicate the absence and presence of the As(III) ions, respectively) ( $n = 6$ ).

#### Interference of the coexisting foreign ions

In this study, changes in the fluorescence intensity of the polymer-based membrane prepared were measured to investigate the effect of possible foreign ions, which could limit the As(III) ion determination. These studies were performed by adding metal ions in a certain amount to solutions containing  $1.33 \times 10^{-8} \text{ mol L}^{-1}$  As(III) ions; and the concentrations of foreign ions at which these changes were at most  $\pm 5\%$  were considered acceptable limits. The limit values for the study are given in Table 1.

#### Analytical application of As(III) sensing membrane

Soya flour and well-water were used as real samples to investigate the applicability of the prepared membrane sensor to real samples. The samples were prepared according to the international standard NMKL 186 method. The amounts of

As(III) contained in these samples were previously determined by the ICP-MS method, and are summarized in Table 2.

#### Comparison with literature methods

A comparison of the developed method with literature methods is given in Table 3. The methods based on hydride generation are limited to the materials that make up the volatile arsines, and require precise control of the reaction conditions. Some interfering elements reduce the effectiveness of the method. Furthermore, the method is laborious and allows for the detection of a single element. Most of the GFAAS-based methods for arsenic determination require preconcentration or

pre-separation in order to be able to determine the ppb range. This combined technique is not only time consuming, but also expensive. Although the ICP-MS method is frequently used for arsenic analysis in environmental samples, it is difficult to work with samples having high salt concentrations. In addition, the MS detector limits the use of ICP because it is complex and expensive. Although the ICP-MS method is frequently used for arsenic analysis in environmental samples, it is difficult to work with samples having high salt concentrations. Furthermore, because the MS detector is complex and expensive, use of ICP is limited, especially for routine analysis and quality control studies. Anodic stripping voltammetry-based methods have also been used recently for arsenic determination. However, As(V) related memory effects in solid electrodes, low sensitivity, and poor accuracy make this method disadvantageous for routine analysis. Although these methods are considered to be sufficient for a linear range, because of the difficulty of sample-preparation procedures, expensive equipment, the need for well-trained personnel, and careful control of the test conditions of these methods, a faster, economical and practical method must be developed instead of these methods. As can be seen from Table 3, it is obvious that the method that we developed is superior to the current As(III) determination methods in terms of many parameters.

#### Conclusions

The method developed as a result of our study provides a good alternative to other methods in the literature in terms of its ease of preparation, rapid and precise results, repeated use and economic efficiency. The prepared sensor can be regenerated by washing with a distilled water and buffer solution, and can be used for at least 100 times. The experiments were carried out at pH 4.0. Our result is consistent with that of similar literature studies, showing that the mercapto group is generally selective with respect to lower oxidation states of the hydride forming elements. The reaction mechanism can be linked to the formation of chelates between the arsenite ions in the solution

Table 1 Acceptable limit concentrations of foreign ions under the optimum determination conditions

Foreign ion	Tolerance level <sup>a</sup> /mol L <sup>-1</sup>
Hg <sup>2+</sup>	4.98 × 10 <sup>-7</sup>
Cu <sup>2+</sup>	3.93 × 10 <sup>-5</sup>
Fe <sup>3+</sup>	4.48 × 10 <sup>-5</sup>
Mn <sup>2+</sup>	4.55 × 10 <sup>-5</sup>
Mg <sup>2+</sup>	2.06 × 10 <sup>-4</sup>
Ni <sup>2+</sup>	1.70 × 10 <sup>-5</sup>
Pb <sup>2+</sup>	1.21 × 10 <sup>-6</sup>
Zn <sup>2+</sup>	1.53 × 10 <sup>-6</sup>
As <sup>5+</sup>	1.33 × 10 <sup>-5</sup>

a. Less than ±5% relative error.

Table 2 Comparison of our method and the ICP-MS method for the determination of As(III) ions in soy flour and well-water samples

Sample	Proposed method/mol L <sup>-1</sup>	ICP-MS/mol L <sup>-1</sup>	RSD, %
Soya flour	(1.40 ± 0.14) × 10 <sup>-8</sup>	(1.43 ± 0.09) × 10 <sup>-8</sup>	2.38
Well water	(1.08 ± 0.03) × 10 <sup>-8</sup>	(1.04 ± 0.02) × 10 <sup>-8</sup>	2.95

Table 3 Comparison with literature methods

Method	Time/s	LOD/mol L <sup>-1</sup>	Linear range/mol L <sup>-1</sup>	pH	Ref.
HGAAS	70 s	1.06 × 10 <sup>-10</sup>	4.00 × 10 <sup>-10</sup> – 5.34 × 10 <sup>-8</sup>	10	5
GFAAS	3 min	3.47 × 10 <sup>-9</sup>	3.47 × 10 <sup>-9</sup> – 1.34 × 10 <sup>-7</sup>	Acidic	9
DPCSV	6 min	4.00 × 10 <sup>-9</sup>	3.34 × 10 <sup>-8</sup> – 2.54 × 10 <sup>-6</sup>	Acidic	10
ASV	4 min	2.54 × 10 <sup>-9</sup>	1.34 × 10 <sup>-8</sup> – 1.00 × 10 <sup>-5</sup>	3.50	11
FI-HG-AAS	30 s	4.00 × 10 <sup>-9</sup>	1.34 × 10 <sup>-7</sup> – 1.34 × 10 <sup>-6</sup>	<2	12
LC-ICP-MS	10 min	2.67 × 10 <sup>-9</sup>	2.67 × 10 <sup>-8</sup> – 1.34 × 10 <sup>-6</sup>	6	13
CZE	5 min	3.47 × 10 <sup>-7</sup>	6.67 × 10 <sup>-7</sup> – 6.67 × 10 <sup>-5</sup>	9.28	14
Spectrophotometry	300 s	1.87 × 10 <sup>-7</sup>	1.34 × 10 <sup>-6</sup> – 2.67 × 10 <sup>-5</sup>	4.75	18
Colorimetry	NM <sup>a</sup>	7.47 × 10 <sup>-8</sup>	2.00 × 10 <sup>-5</sup> – 4.00 × 10 <sup>-5</sup>	NM <sup>a</sup>	19
Spectrofluorimetry	NM <sup>a</sup>	5.34 × 10 <sup>-6</sup>	5.34 × 10 <sup>-6</sup> – 1.16 × 10 <sup>-4</sup>	6	20
Square wave (SW)-ASV	150 s	1.30 × 10 <sup>-8</sup>	6.67 × 10 <sup>-9</sup> – 2.00 × 10 <sup>-7</sup>	8	21
ASV	300 s	2.00 × 10 <sup>-9</sup>	2.67 × 10 <sup>-9</sup> – 3.34 × 10 <sup>-6</sup>	2	22
HPLC/HGAFS	5 min	8.41 × 10 <sup>-10</sup>	2.67 × 10 <sup>-7</sup> – 1.34 × 10 <sup>-6</sup>	6.8	23
HG-GFAAS	30 s	8.54 × 10 <sup>-11</sup>	5.34 × 10 <sup>-10</sup> – 5.33 × 10 <sup>-9</sup>	NM <sup>a</sup>	24
ETAAS	9 min	5.34 × 10 <sup>-10</sup>	1.33 × 10 <sup>-9</sup> – 2.64 × 10 <sup>-7</sup>	4.2	25
GFAAS	NM <sup>a</sup>	4.00 × 10 <sup>-10</sup>	2.67 × 10 <sup>-9</sup> – 2.67 × 10 <sup>-7</sup>	2	26
ASV	400 s	2.67 × 10 <sup>-9</sup>	1.33 × 10 <sup>-10</sup> – 6.67 × 10 <sup>-8</sup>	7	27
Spectrofluorimetry	40 min	2.00 × 10 <sup>-12</sup>	1 × 10 <sup>-11</sup> – 1.34 × 10 <sup>-6</sup>	7.2	28
X-ray fluorescence spectrometry	40 s	1.33 × 10 <sup>-8</sup>	0 – 6.67 × 10 <sup>-8</sup>	4	29
Our method	30 s	2.30 × 10 <sup>-9</sup>	6.65 × 10 <sup>-9</sup> – 3.99 × 10 <sup>-8</sup>	2	—

a. NM: Not mentioned.

and the mercapto functional groups on the polymer surface. It has been reported that thiols form stable complexes with arsenicals in acidic solutions better than neutral pH.<sup>30,31</sup> In the presence of possible foreign ions, the determination of As(III) can be performed, especially if the As(V) is at a concentration of 1000-times the As(III) ions, the sensor performance is not affected. Furthermore, the developed method has a detection limit of as low as  $2.30 \times 10^{-9}$  mol L<sup>-1</sup>. Our sensor has been successfully applied to soy flour and well-water samples. Due to the limited number of previous studies in the literature, it will guide new studies in this field.

### Acknowledgements

This work was supported by Marmara University, Commission of Scientific Research Project (M.Ü.BAPKO) under grant FEN-A-041213-0455.

### References

1. R. W. Kapp Jr., "Arsenic: Properties and Determination, *Encyclopedia of Food and Health*", **2016**, BioTox, Monroe Township, NJ, USA, 249 - 255.
2. K. S. M. Abdul, S. S. Jayashinghe, E. P. S. Chandana, C. Jayasumana, and P. M. C. S. De Silva, *Environ. Toxicol. Pharmacol.*, **2015**, *40*, 828.
3. D. Sanchez-Rodas, A. M. Sanchez de la Campa, and L. Alsioufi, *Anal. Chim. Acta*, **2015**, *898*, 1.
4. S. Sirawatcharin, A. Saithongdee, A. Chaicham, B. Tomapatanaget, A. Imyim, and N. Praphairaksit, *Anal. Sci.*, **2014**, *30*, 1129.
5. H. İ. Ulusoy, M. Akcay, S. Ulusoy, and R. Gurkan, *Anal. Chim. Acta*, **2011**, *703*, 37.
6. S. Sahinkaya, E. Kalıpcı, and M. Ozturk, *Nevşehir Üniversitesi Fen Bilimleri Enstitüsü Dergisi*, **2013**, *2*, 103.
7. Y. Chen, F. Parvez, M. Gamble, T. Islam, A. Ahmed, M. Argos, J. H. Graziano, and H. Ahsan, *Toxicol. App. Pharmacol.*, **2009**, *239*, 184.
8. S. J. S. Flora, "Arsenic: Chemistry, Occurrence and Exposure, *Handbook of Arsenic Toxicology*", **2015**, Academic Press, London, 1 - 49.
9. J. Michon, V. Deluchat, R. A. Shukry, C. Dagot, and J. C. Bollinger, *Talanta*, **2007**, *71*, 479.
10. Y. He, Y. Zheng, and D. C. Locke, *Microchem. J.*, **2007**, *85*, 265.
11. Y.-C. Sun, J. Mierzwa, and M.-H. Yang, *Talanta*, **1997**, *44*, 1379.
12. N. M. M. Coelho, A. Cósme da Silva, and C. Moraes da Silva, *Anal. Chim. Acta*, **2002**, *460*, 227.
13. K. Z. Akter, Z. Chen, L. Smith, D. Davey, and R. Naidu, *Talanta*, **2005**, *68*, 406.
14. P. Zhang, G. Xu, J. Xiong, Y. Zheng, Q. Yang, and F. Wei, *Electrophoresis*, **2001**, *22*, 3567.
15. D. Q. Hung, O. Nekrassova, and R. G. Compton, *Talanta*, **2004**, *64*, 269.
16. B. K. Mandal and K. T. Suzuki, *Talanta*, **2002**, *52*, 201.
17. D. E. Mays and A. Hussam, *Anal. Chim. Acta*, **2009**, *646*, 6.
18. S. F. P. Pereira, S. L. C. Ferreira, G. R. Oliveira, D. C. Palheta, and B. C. Barros, *Eclét. Quím.*, **2008**, *33*, 23.
19. Y. Wu, S. Zhan, F. Wang, L. He, W. Zhi, and P. Zhou, *Chem. Commun.*, **2012**, *48*, 4459.
20. P. Chakraborty, P. V. R. Babu, and V. V. Sarma, *Int. J. Environ. Anal. Chem.*, **2012**, *92*, 133.
21. M. Yang, P. H. Li, W. H. Xu, Y. Wei, L. N. Li, Y. Y. Huang, Y. F. Sun, X. Chen, J. H. Liu, and X. J. Huang, *Sens. Actuators B*, **2018**, *255*, 226.
22. M. Kapanica and L. Novonty, *Anal. Chim. Acta*, **1998**, *368*, 211.
23. Z. Xu, H. Y. Hu, D. K. Chen, J. X. Cao, and H. Yao, *Chin. J. Anal. Chem.*, **2015**, *43*, 490.
24. E. M. Becker, M. B. Dessuy, W. Boschetti, M. G. R. Vale, S. L. C. Ferreira, and B. Welz, *Spectrochim. Acta, Part B*, **2012**, *71-72*, 102.
25. A. Tang, G. Ding, and X. Yan, *Talanta*, **2005**, *67*, 942.
26. J. A. Baig, T. G. Kazi, A. Q. Shah, M. B. Arain, H. I. Afridi, G. A. Kandro, and S. Khan, *Anal. Chim. Acta*, **2009**, *651*, 57.
27. Y. Liu, Z. Huang, Q. Xie, L. Sun, T. Gu, Z. Li, L. Bu, S. Yao, X. Tu, X. Luo, and S. Luo, *Sens. Actuators, B*, **2013**, *188*, 894.
28. L. Zeng, D. Zhou, J. Gong, C. Liu, and J. Chen, *Anal. Chem.*, **2019**, *91*, 1724.
29. K. Hagiwara, Y. Koike, M. Aizawa, and T. Nakamura, *Anal. Sci.*, **2018**, *34*, 1309.
30. E. Boyacı, A. Çağır, T. Shahwan, and A. E. Eroğlu, *Talanta*, **2011**, *85*, 1517.
31. L. Dominguez, Z. Yue, J. Economy, and C. L. Mangun, *React. Funct. Polym.*, **2002**, *53*, 205.