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

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Abstract

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

Keywords: As(III), polymeric membrane, sensor, fluorimetry
Introduction

For thousands of years, arsenic has affected the 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 effect of arsenic can be seen both in the developed and developing countries. The increase in contamination of the 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 (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 in wood preservative, chemical weapon, pigment, pharmaceutical and arsenic based pesticide industries are exposed to arsenic due to occupational reasons$^{1-3}$.

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

There are many methods used for determination of arsenic such as graphite furnace atomic absorption spectroscopy (GF-AAS)$^9$, cathodic stripping voltammetry (CSV)$^{10}$, and anodic stripping voltammetry (ASV)$^{11}$, flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS)$^{12}$, liquid chromatography-inductively coupled plasma mass spectrometry (LC-ICP-MS)$^{13}$, capillary zone electrophoresis (CZE)$^{14}$. Although these methods have high precision and accuracy for the determination of low arsenic levels, they require expensive instruments, qualified
personnel, and a laborious sample preparation procedure\textsuperscript{15-17}.

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

**Experimental**

**Reagents and chemicals**

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

**Fluorescence sensor preparation**

The polymeric sensor was prepared by UV-curing technique. PEGDA was main polymeric substance. MPTS and HEA were used as a for reactive monomer and TMPT was used for crosslinker. 2-hydroxy-2-methylpropiophenone was used as a photo initiator. 40% PEGDA, 25%HEA, 30%TMPTA, 5% MPTS mixed in a beaker and photo initiator was added at a 3% with respect to total amount of formulation. The mixture was stirred until homogeneity. Then, the mixture was poured into Teflon\textsuperscript{®} molds (W: 12 mm, L: 50 mm, D: 1 mm) and cured under UV lamp (OSRAM 300 W, λ\textsubscript{max} = 365 nm) for 150 seconds. After curing, the membranes were taken from mold and put into purified water to remove the unreacted chemicals and photoinitiator. After that films were taken out and dried in lyophilizator for 24 hours.
Characterization

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

Results and Discussion

Characterization of the membrane sensor

FTIR spectroscopy work

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

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

The prepared membranes surface morphology is a crucial factor for an influential fluorescent sensor. The SEM images given in Figure 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, homogeneous and non-porous.

![SEM images](image)

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

**Spectral characterization**

For this purpose; excitation and emission spectra were recorded using different slit ranges and photo-multiplier tube (PMT) voltage of the solutions in which As(III) ions were present at a concentration of 1.33x10^4 mol L\(^{-1}\) (1.00 µg L\(^{-1}\)) and no As(III) containing solutions, respectively (Fig.3).
Fig. 3. Excitation ($\lambda_{\text{ex}}$=376 nm) and emission ($\lambda_{\text{em}}$=422 nm) spectra of the polymeric membrane, (a) absence of As(III) ions, (b) presence of $1.33 \times 10^{-8}$ mol L$^{-1}$ As(III) ions.

**Influence of pH**

The effect of pH on the fluorescence intensity of the membrane was examined by using 8 solutions prepared from pH:1 to pH:8 containing As(III) ions at a concentration of $1.33 \times 10^{-8}$ mol L$^{-1}$ (1.00 µg L$^{-1}$). The 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 pH: 2, and this pH was used for further studies.
Fig. 4. pH effect on the polymeric As(III) sensor (t:30 sec., n=6)

Response time

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

Fig. 5. The influence of response time on fluorescence intensity of the As(III) sensor.
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 $6.65 \times 10^{-9} \text{ mol L}^{-1}$ - $3.99 \times 10^{-8} \text{ mol L}^{-1}$. In order to determine the limit of detection value (LOD) of the developed method, measurements were made with 7 different blank solutions. The LOD was calculated as 3 times (3ss) of the standard deviation value obtained from these measurement results, and this limit were obtained as $2.33 \times 10^{-9} \text{ mol L}^{-1}$.

Fig. 6. Fluorescence emission spectra of the sensing membrane in the presence of different concentration 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) $3.99 \times 10^{-8} \text{ mol L}^{-1}$ ($\lambda_{ex} = 376 \text{ nm}$). The inset shows the calibration curve of the sensor ($\lambda_{ex/em}=376 \text{ nm}/422 \text{ nm}$); (I₀-I, where I₀ and I absence and presence of the As(III) ions, respectively) (n=6).
**Regeneration and reusability of the As(III) sensor**

For the regeneration of the sensor, washing with pure water for 2 minutes after total washing with pH: 2 buffer solution was found to be sufficient. For this process, the change in the fluorescence intensity of the membrane in the presence of a solution containing 1.33x10^{-8} 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 has been found that the same sensor can be used for measurements up to 100 times after the required washing.

**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 As (III) ion determination. These studies were performed by adding metal ions in a certain amount to solutions containing 1.33x10^{-8} mol L^{-1} As(III) ions, and the concentrations of foreign ions at which these changes were at most ± 5% were considered acceptable limits. The limit values for the study were given in Table 1.

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

| Foreign ions | Tolerance level\(^a\) |
|--------------|-----------------------|
| Hg^{2+}      | 4.98x10^{-7}          |
| Cu^{2+}      | 3.93x10^{-5}          |
| Fe^{3+}      | 4.48x10^{-5}          |
| Mn^{2+}      | 4.55x10^{-5}          |
| Mg^{2+}      | 2.06x10^{-4}          |
| Ni^{2+}      | 1.70x10^{-5}          |
| Pb^{2+}      | 1.21x10^{-6}          |
| Zn^{2+}      | 1.53x10^{-6}          |
| As^{5+}      | 1.33x10^{-5}          |

\(^a\) Less than ± 5% relative error.
Analytical application of As(III) sensing membrane

Soya flour and well water were used as a real samples to investigate the applicability of the prepared membrane sensor to real samples. The samples were prepared according to international standard NMKL 186 method. The amounts of As(III) contained in these samples were previously determined by the ICP-MS method and summarized in Table 2.

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

| Sample Name   | Proposed method (mol L⁻¹) | ICP-MS (mol L⁻¹) | RSD (%) |
|---------------|----------------------------|------------------|---------|
| Soya flour    | (1.40±0.14)x10⁻⁸           | (1.43±0.09)x10⁻⁸ | 2.38    |
| Well water    | (1.08±0.03)x10⁻⁸           | (1.04±0.02)x10⁻⁸ | 2.95    |

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 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 with 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 with high salt concentrations. Furthermore, because the MS detector is complex and expensive, it limits the use of ICP, 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, poor accuracy make this method disadvantageous for
routine analysis. Although these methods are considered sufficient as a linear range; because of
the difficulty of sample preparation procedures, expensive equipment, the need for well-trained
personnel, careful control of test conditions of these methods; a faster, economical and practical
method has to be developed instead of these methods. As can be seen from Table 3, it is obvious
that the method we developed is superior to the current As(III) determination methods in terms of
many parameters.

Table 3. Comparison with literature methods.

| Method          | Time (s) | LOD (mol L$^{-1}$) | Linear Range (mol L$^{-1}$) | pH  | Ref. |
|-----------------|---------|--------------------|-----------------------------|-----|------|
| HGAAS           | 70 sec. | 1.06x10$^{-10}$    | 4.00x10$^{-10}$-5.34x10$^{-8}$ | 10  | 5    |
| GFAAS           | 3 min   | 3.47x10$^{-9}$     | 3.47x10$^{-9}$-1.34x10$^{-7}$ | Acidic | 9    |
| DPCSV           | 6 min.  | 4.00x10$^{-9}$     | 3.34x10$^{-8}$-2.54x10$^{-6}$ | Acidic | 10   |
| ASV             | 4 min   | 2.54x10$^{-9}$     | 1.34x10$^{-8}$-1.00x10$^{-5}$ | 3.50 | 11   |
| FI-HG-AAS       | 30 sec. | 4.00x10$^{-9}$     | 1.34x10$^{-7}$-1.34x10$^{-6}$ | <2  | 12   |
| LC-ICP-MS       | 10 min. | 2.67x10$^{-9}$     | 2.67x10$^{-8}$-1.34x10$^{-6}$ | 6   | 13   |
| CZE             | 5 min.  | 3.47x10$^{-7}$     | 6.67x10$^{-7}$-6.67x10$^{-5}$ | 9.28 | 14   |
| Spectrophotometric | 300     | 1.87x10$^{-7}$     | 1.34x10$^{-6}$-2.67x10$^{-5}$ | 4.75 | 18   |
| Colorimetric    | NM      | 7.47x10$^{-8}$     | 2.00x10$^{-3}$-4.00x10$^{-3}$ | NM  | 19   |
| Spectrofluorimetric | NM     | 5.34x10$^{-6}$    | 5.34x10$^{-6}$-1.16x10$^{-4}$ | 6   | 20   |
| Square wave (SW)-ASV | 150 sec. | 1.30x10$^{-8}$     | 6.67x10$^{-9}$-2.00x10$^{-7}$ | 8   | 21   |
| ASV             | 300 sec.| 2.00x10$^{-9}$     | 2.67x10$^{-9}$-3.34x10$^{-6}$ | 2   | 22   |
| HPLC/HGAFS      | 5 min.  | 8.41x10$^{-10}$    | 2.67x10$^{-7}$-1.34x10$^{-6}$ | 6.8 | 23   |
| HG-GFAAS        | 30 sec. | 8.54x10$^{-11}$    | 5.34x10$^{-10}$-5.33x10$^{-9}$ | NM  | 24   |
| ETAAS           | 9 min.  | 5.34x10$^{-10}$    | 1.33x10$^{-9}$-2.64x10$^{-7}$ | 4.2 | 25   |
| GFAAS           | NM      | 4.00x10$^{-10}$    | 2.67x10$^{-9}$-2.67x10$^{-7}$ | 2   | 26   |
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 distilled water and buffer solution and can be used at least 100 times. The experiments were carried out at pH 4.0. Our result is consistent with 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 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\textsuperscript{30-31}. 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 as low as 2.30x10\textsuperscript{-9} mol L\textsuperscript{-1}. 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.

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**Figure Captions**

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