Turkish Journal of Chemistry

http://journals.tubitak.gov.tr/chem/

Research Article

Turk J Chem
(2019) 43: 239 – 250
© TÜBİTAK
doi:10.3906/kim-1805-3

Rapid and on-site electrochemical detection of bisphenol A and arsenic in drinking water using a novel electrode array

Yıldız ULUDAĞ[1,*], **Zehra ÖLÇER**[1,2], **Canan DOĞAN**[3], **Turghun MUHAMMAD**[1,4], **Zeynep ALTINTAŞ**[1,5]

[1]Bioelectronic Devices and Systems Group, UEKAE-BİLGEM, Scientific and Technological Research Council of Turkey (TÜBİTAK), Kocaeli, Turkey
[2]Department of Chemistry, Gebze Institute of Technology, Kocaeli, Turkey
[3]Food Institute, TÜBİTAK Marmara Research Center, Kocaeli, Turkey
[4]Xinjiang Key Laboratory of Oil and Gas Fine Chemicals, College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi, P.R. China
[5]Technical University of Berlin, Berlin, Germany

Received: 03.05.2018 • **Accepted/Published Online:** 23.11.2018 • **Final Version:** 05.02.2019

Abstract: The paper describes a novel dip-and-gauge hand-held sensor device for the rapid, cost-effective, and on-site detection of bisphenol A and arsenic in drinking water samples. Different working electrode diameters ranging from 1.5 mm to 4 mm were designed and fabricated to construct a new electrochemical biosensor. The sensor was employed for the chronoamperometric detection of bisphenol A and voltammetric determination of arsenic in drinking water samples. Bisphenol A measurements resulted in a detection limit of 10 ng mL^{-1} with a linear range of 0–4000 ng mL^{-1}. Baby products and bottles have to be completely free of bisphenol and hence a liquid-phase microextraction method has been developed to reduce the detection limit further to 0.6 ng mL^{-1}. Arsenic detection was investigated in the concentration range of 0.4–250 ng mL^{-1} with a detection limit of 1.9 ng mL^{-1}. The current study showed that the designed electrode array allows low detection limits (below threshold levels), although a bare gold surface is used for the study. Hence, together with a hand-held sensor device that works by simply dipping the sensor chip into a water container, this cost effective system has the potential to be used either by household consumers or for on-site inspection purposes.

Key words: Electrode array, bisphenol, arsenic, amperometry, voltammetry, hand-held sensor

1. Introduction

Bisphenol A is used for production of polycarbonate plastics, epoxy, and polysulfone resins, which are widely utilized as inner surface coatings of food containers, water bottles, baby bottles, and beverage cans. Bisphenol A can be released from the packages and migrate into the food or water inside, which is promoted by high temperature or acidity of the food stored.[1,2] Bisphenol A and its derivatives are harmful to living organisms as typical endocrine disruptors; hence, the migration of bisphenol A from the packaging to the food or beverage and further consumption by humans is considered as a risk, and the maximum allowed concentration of bisphenol A in drinking water is 500 ng mL^{-1} according to EU regulations.[3] However, baby products and bottles should be completely free of this toxic compound. Therefore, bisphenol A detection is important and various techniques have been developed for the determination of bisphenol A, such as gas chromatography-mass spectrometry,[4]

*Correspondence: yildiz.uludag@tubitak.gov.tr

high-performance liquid chromatography (HPLC),[5–7] and fluorescence detectors,[1] but all of these methods require time-consuming pretreatment process, expensive consumables, and skilled personnel.

Another important water contaminant, arsenic, is a vastly toxic element that leads to poisoning of a noteworthy amount of people, particularly in many developing countries. Long-term exposure to arsenic causes a variety of severe diseases including heart disease, stillbirth, and cancer.[8–10] It exists in water systems mainly in two different forms: arsenate ion and arsenite ions. The second form is 50 times more poisonous than the first because of its interaction with enzymes in the human respiratory system. The threshold level allowed in drinking water is 50 ng mL^{-1}. However, the World Health Organization counsels the acceptable amount as 10 ng mL^{-1}.[11] Inductively coupled plasma mass spectrometry offers a highly sensitive technique for arsenic detection in the nanomolar range and many research groups have been employing this method.[12–15] Nevertheless, it is an expensive tool for field detection. In order to obtain rapid, easy-to-use, and reliable sensors for arsenic detection, recent advances cover the implementations of a variety of natural and artificial ligands as well as signal amplification agents such as gold nanoparticles, magnetic nanomaterials, and carbon nanotubes with the combination of different sensor systems. Among these sensors, electrochemical platforms have dominated due to their ability to detect trace amounts of arsenic and this characteristic makes them have an immense impact to be developed for contaminated water or food products testing.[16] A very interesting study was recently published reporting electrochemical detection of arsenic using Fe_3O_4 microspheres, a room temperature ionic liquid composite, despite the dominancy of noble metals, particularly gold, in the development of electrochemical sensors for arsenic detection. The developed sensing platform was successfully employed for analysis of real samples collected from Inner Mongolia, China.[17]

The producers of bottled water have to send their products to water research centers for testing to make sure that the water is free of these contaminants and wait for the results. Hence, there is a need for a reliable, easy-to-use, and fast measurement tool that can be directly used by the manufacturers, which will reduce the cost and time required for testing. Electrochemical sensors are frequently used for fast and sensitive detection of a variety of compounds.[18,19] In this research we aim to engineer an electrochemical sensor and integrate an on-site detection principle into a hand-held device to compensate this need for sensitive detection of toxic compounds found in bottled water. The tests involve the dipping of the sensor chip into the water container and then measurement of the contaminant amount with electrochemical methods, hence called a dip-and-gauge sensor. Arsenic and bisphenol A were selected as the targets to show the compatibility of the developed dip-and-gauge sensor for the detection of a variety of similar contaminants. The arsenic and bisphenol samples were initially investigated in a buffer for the development of a sensor test and the methodology was then transferred to be used for real samples including tap water, drinking water, and mineral water.

2. Results and discussion

In the current study, the amounts of bisphenol A and arsenic were determined electrochemically with the use of newly designed sensor chips. A new electrode array was designed that has a small imprint, but not small enough to be fabricated by time-consuming and expensive photolithography processes. Three main parameters have been considered when designing new arrays: one was the use of gold as a quasi-reference electrode instead of conventional Ag/AgCl electrodes (to simplify the fabrication process), the second was the use of shared reference and counter electrodes (to produce smaller sensors), and third, in order to obtain the best electrochemical signals, the distances between the two working electrodes and shared reference and counter electrodes had to be kept equal. These parameters were investigated to find the best array geometry for electrochemical detection. An

electrode of 2.5 mm in diameter was selected based on the optimization studies by considering the current density per area on the electrode surface and the entire research was conducted by employing this sensor with two electrodes.

2.1. Characterization of the fabricated sensor chips

Cyclic voltammetry characterization of different sensor chips was performed using 1 mM potassium ferricyanide solution in 1 M KCl to be sure that the fabricated sensors resulted in consistent electrochemical responses. Five different sensor chips were employed for the characterization studies and they produced very similar oxidation-reduction peaks in the scan range of –0.5 to 0.2 V (Figures 1a–1c). Therefore, the quality and reliability of the sensor chips to be used for the assays were determined.

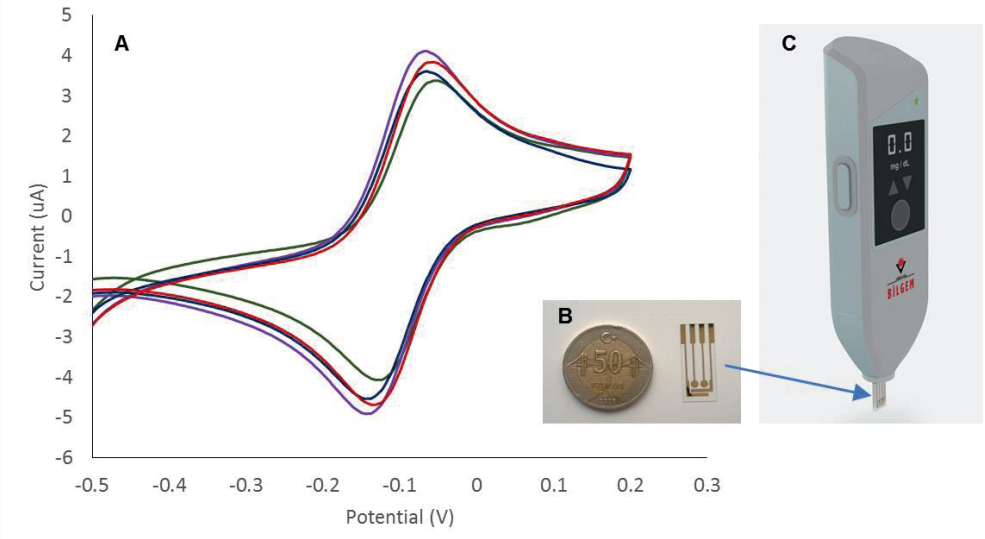
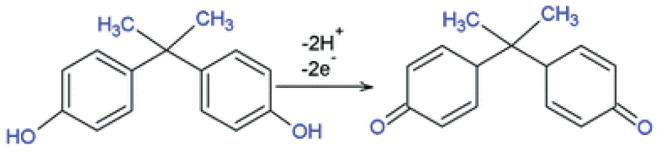


Figure 1. A) Cyclic voltammetry characterization of five separate electrode arrays to determine the quality and reliability of the sensor system using 1 mM $K_4[Fe(CN)_6]$/KCl. B) Designed and fabricated electrode array. C) Dip-and-gauge hand-held biosensor incorporating the electrode array designed for the detection of bisphenol A and arsenic in water samples.

2.2. Bisphenol A detection assay

As an electroactive material, bisphenol A shows an oxidation peak between 0.4 and 0.6 V in phosphate buffer.[20,21] (Scheme). Hence, the amperometric response of bisphenol A at 0.5 V was investigated initially by means of a screen-printed gold electrode (d = 4 mm) and gold-coated glass slides consisting of different electrode sizes (d = 1.5, 2, 3, 4 mm).



Scheme. The electrochemical oxidation mechanism of bisphenol A at the electrode surface.[22]

As the diameter of the electrodes decreases, the current density increases; however, this also means that the magnitude of the sensor responses decreases. While very small electrodes may result in high current density, at very low analyte concentrations the sensor may result in no response at all. Therefore, an optimum electrode size needs to be chosen that results in high current density together with reasonable sensitivity and detection limit. With this fact in mind, although the current density of the 1.5 mm diameter gold electrodes was 34% higher than that of the 2 mm electrodes, to obtain high signals from the lowest concentration of bisphenol A, 2.5 mm was chosen as the optimum electrode size. Hence, a new electrode array with two working electrodes, a shared reference, and counter electrodes was designed and fabricated for the studies.

Electrochemical detection of bisphenol A was successfully achieved by amperometry in the concentration range of 0–2000 ng mL^{-1} using both a screen-printed electrode (d = 4 mm) and 2.5 mm gold electrode array and a detection limit of 100 ng mL^{-1} and 10 ng mL^{-1} was obtained, respectively. Overall results were subjected to logarithmic regression analysis, revealing very good correlation of data with an R^2 value of 0.98 (Figures 2a and 2b). The detection of bisphenol A in different water sources was also investigated and the results were compared with standards prepared in PBS buffer. A 10 ng mL^{-1} concentration of bisphenol A spiked in water samples was tested (n = 6) and similar results were recorded for PBS and tap water, whereas mineral water and natural spring water produced slightly lower sensor responses. The data can be normalized according to different water sources for accurate detection (Figure 3).

Although EU regulations determine the threshold level of bisphenol A for drinking water as 500 ng mL^{-1}, baby products and bottles have to be completely free of bisphenol. Nevertheless, baby bottles release bisphenol A into the water with time. Due to this fact, there is a need to find a solution for the measurement of trace bisphenol A concentrations. With this aim, we developed a method to concentrate the bisphenol A in a solution and hence increase the signal of the sensor. Liquid-phase microextraction of bisphenol A using a hollow fiber system allowed us to achieve this in the current study and it led to 93.43% increase in the sensor signal with a minimal standard error (<1.8%) for 500 ng mL^{-1} of bisphenol A. The reason to select this concentration was to see the significance of the hollow fiber method with a well-established concentration. Thus, the current limit of detection (LOD) of bisphenol A assay using this approach could be decreased from 10 ng mL^{-1} to 0.6 ng mL^{-1}.

In recent years, novel methods have been developed for the detection of phenolic compounds using biosensor technology.[23–29] Nanomaterial applications and electrochemical sensors have been particularly employed to enhance bisphenol A detection systems, although they all require very complex methodologies that cannot be widely used. Comparative investigations using nickel, iron oxide, and gold nanoparticles were implemented with an electrochemical biosensor for bisphenol A detection and the detection limits were obtained as 1.62 ng mL^{-1}, 1.89 ng mL^{-1}, and 2.28 ng mL^{-1}, respectively. The proposed method allowed to detect bisphenol A in buffer with a response time of less than 30 s based on amperometry.[30] Amperometric detection of bisphenol A was also investigated in milk by utilizing PAMAM-Fe_3O_4 modified glassy carbon electrode and a detection limit of 1.14 ng mL^{-1} was achieved.[3]

A nanographene-based tyrosinase sensor was constructed for bisphenol A detection to be compared with multiwall carbon nanotubes (MWNTs) modified tyrosinase biosensor and it offered superiority over the MWNT-based platform in terms of sensor signal, repeatability, and LOD. The sensor was able to measure bisphenol A up to 33 nmol L^{-1} (7.53 ng mL^{-1}) with a linear range of 100–2000 nmol L^{-1} in buffer, whereas it could detect 0.66 µg mL^{-1} and 1.42 µg mL^{-1} bisphenol A for water samples in feeding bottles and drinking bottles,

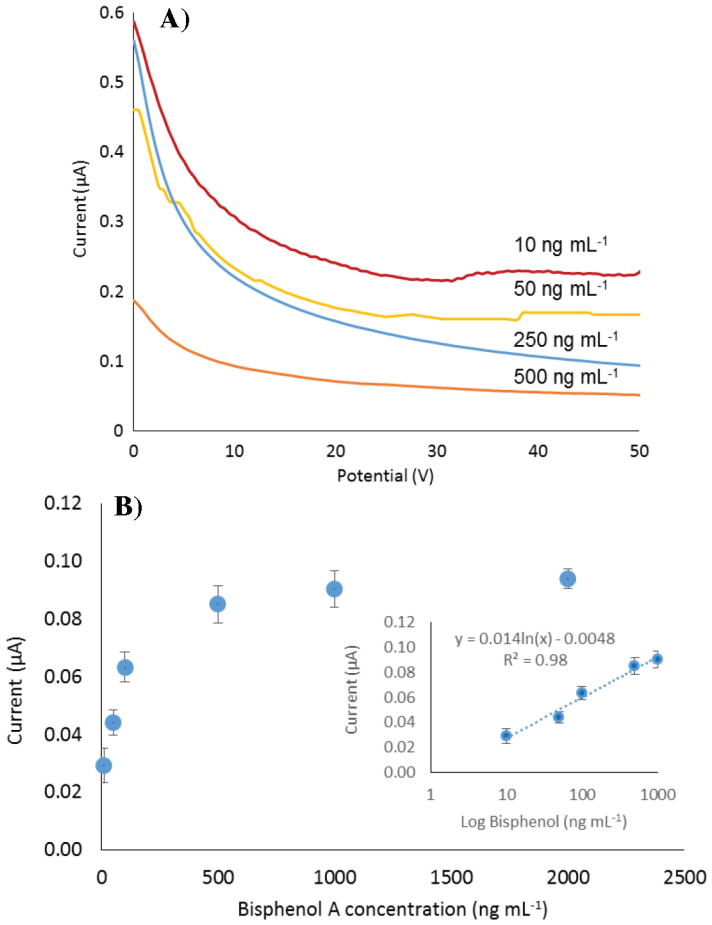


Figure 2. Real-time sensor profiling of bisphenol A detection in the concentration range of 10–500 ng mL^{-1} in drinking water (A) and overall results of bisphenol A detection between 10 and 2000 ng mL^{-1} with logarithmic regression analysis (B).

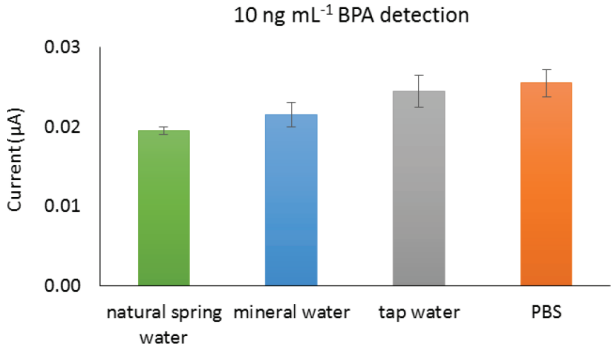


Figure 3. Comparison of sensor results for a variety of water samples and PBS buffer contaminated with 10 ng mL^{-1} of bisphenol A.

respectively.[31] A similar method has been reported for direct and fast detection of bisphenol A using a graphene-gold nanoparticle composite-based electrochemical tyrosinase biosensor, and a detection limit of 1 nM was obtained in buffer with reproducible sensor response.[17]

Optical-based surface plasmon resonance biosensors were also successfully employed for bisphenol A detection and their efficiency to be used for real sample analysis was shown with wastewater. Although typical detection limits of SPR biosensors for bisphenol A are around 1 ng mL^{-1},[32,33] the researchers estimated the LOD as 0.08 and 0.14 ng mL^{-1} in PBS and wastewater, respectively, using antibody-based affinity arrays that require covalent immobilization of the receptors onto the surface as well as surface modification.[34] Other biosensing platforms based on the application of aptamers with fluorescent biosensors have been recently reported with their detection limits reaching very low ng mL^{-1} levels.[16,35] However, all of these methods require dealing with very advanced experimental procedures and are quite far from being easily applied by manufacturers or governmental bodies for water or food testing of bisphenol A. The dip-and-gauge sensor and sensor chip developed in this study enable out-of-the-laboratory, on-site detection of bisphenol A in a minute without expensive and time-consuming sensor chip fabrication and is suitable to be used for bisphenol A measurements in drinking water samples. Hence, this system has great potential to be used by bottled water consumers, by bottled water producing companies, or by testing laboratories.

2.3. Arsenic detection assay

Being a highly toxic compound for human body in high quantities, it is vital to be sure that both water sources and foods are not contaminated with arsenic. Offering an easy-to-use hand-held device for arsenic detection therefore has momentous impact. Taking this into consideration, a two-electrode sensor system has provided a measurement method that can be used by individuals or manufacturers by simply dipping the sensor electrodes into water sources and taking the measurements based on the cyclic voltammetry method. Cyclic voltammetry tests have been performed on arsenic-containing samples and the redox peak responses obtained have been used as the sensor signal responses. In this study, arsenic detection was investigated both in buffer and different water sources including tap and drinking water. The analyte was successfully detected in the concentration range of 0.4–250 ng mL^{-1} with a detection limit of 1.9 ng mL^{-1} based on electrochemical interaction of the analyte on the electrodes avoiding surface chemistry and complex assay methodology (Figure 4). The overall results were evaluated and very good reproducibility was achieved with a correlation coefficient of 0.98 at around 0.25 V.

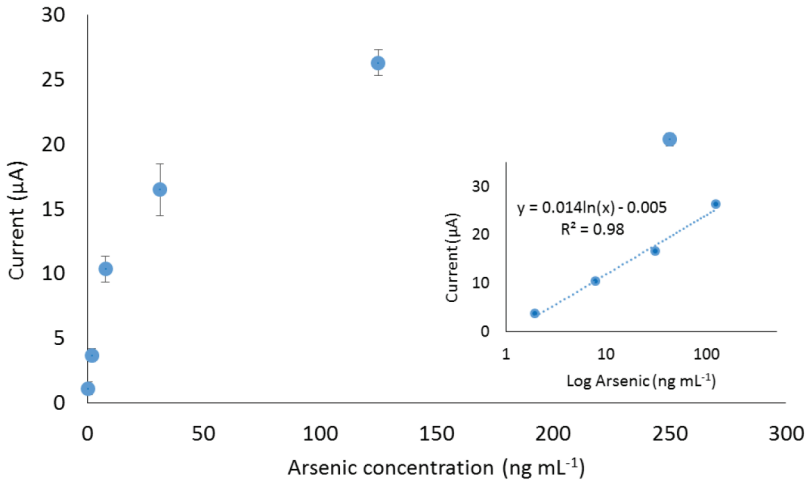


Figure 4. Cyclic voltammetry tests were performed on arsenic-spiked samples and the redox responses obtained were used as the sensor signal responses. The figure shows the overall results of the arsenic detection signal with standard errors and logarithmic regression of data with R^2 value of 0.98 at 0.25 V.

To show the clear difference of arsenic cyclic voltammetry response with respect to the bare gold chip and water, cyclic voltammetry characterization was also conducted. Bare gold sensor produced an expected cyclic voltammetry curve with oxidation-reduction peaks using the potassium ferricyanide solution in KCl, whereas normal and 125 ng mL^{-1} arsenic-contaminated water samples resulted in completely different cyclic voltammetry profiles, as shown in Figure 5.

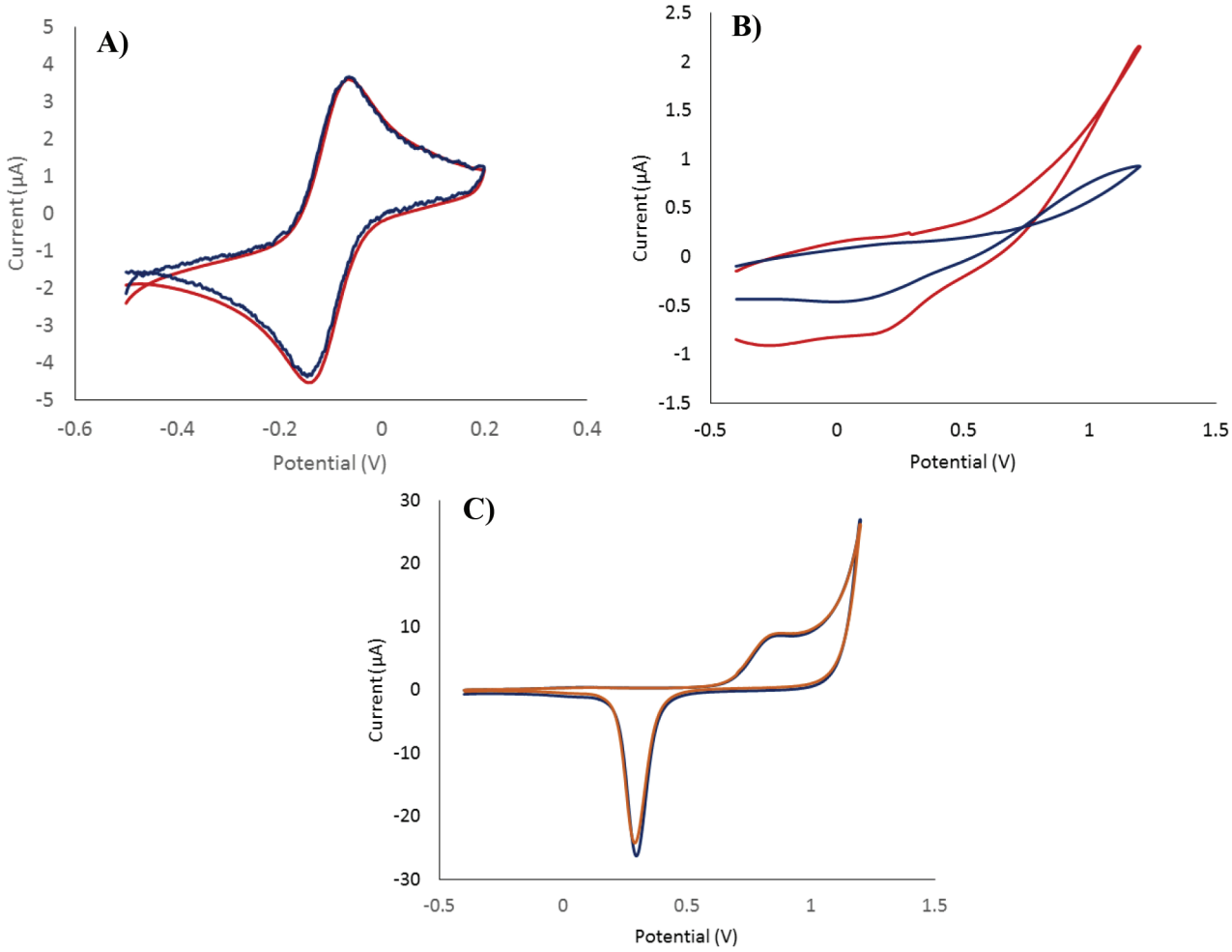


Figure 5. Cyclic voltammetry CV characterization of potassium ferricyanide solution in KCl (A), tap water (B), and arsenic-spiked water (C) using dip-and-gauge sensor system and consistency of the results between two separate sensor chips.

The stability of sensor response and reproducibility of the results have a great impact on obtaining a reliable and sensitive system. Therefore, the variation of the sensor signal between subsequent arsenic detection experiments was also investigated to show the efficiency of the novel dip-and-gauge sensor. For this, a certain amount of arsenic (125 ng mL^{-1}) was spiked in tap water and 4 separate experiments were conducted, which also indicated the reusability of the same sensor chip for subsequent testing (Figure 6).

To compare the results of different water samples contaminated with arsenic using the dip-and-gauge sensor, a comparative study was also performed. A concentration of 31 ng mL^{-1} of arsenic gave an average signal of 12.0 ± 0 .60 µA (n = 3) and 13.77 ± 1.18 µA (n = 3) for drinking and tap water, respectively, with a clear difference with respect to the controls (Figure 7).

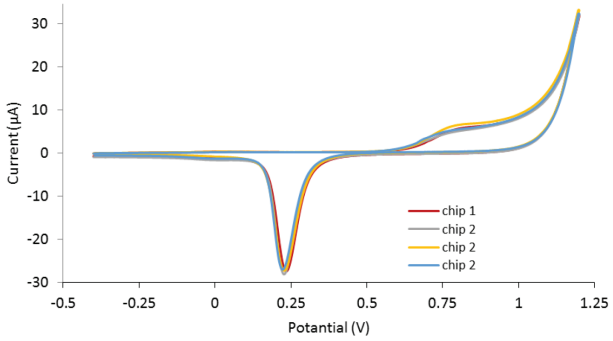


Figure 6. Reproducibility of the redox response results on the same sensor chip using 125 ng mL^{-1} arsenic-spiked tap water for four separate experiments.

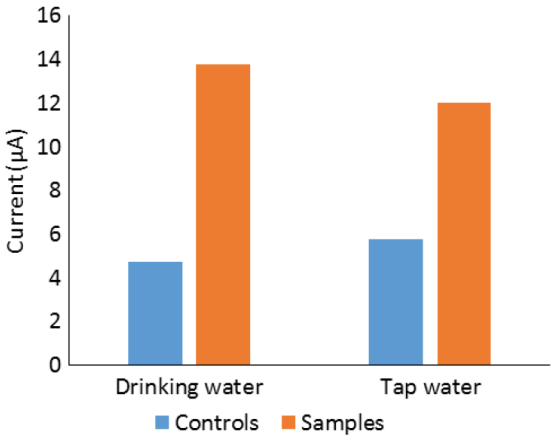


Figure 7. Comparative study of controls and arsenic-spiked drinking and tap water using dip-and-gauge biosensor. The sensor signal represents the redox peaks obtained from the CV tests.

Wu et al. reported an ultrasensitive aptamer sensor based on surfactant-induced aggregation of gold nanomaterials for the detection of arsenic in aqueous solution. The colorimetric and resonance scattering-based biosensor provided a detection limit of 40 ng mL^{-1} in the investigation range of 1–1500 ng mL^{-1},[36] whereas LOD was achieved as 1.9 ng mL^{-1} in our work using the dip-and-gauge system in the concentration range of 0.4–250 ng mL^{-1}. A recent study described a biosensor for arsenic detection in contaminated water based on a carbon paste electrode, which was modified with *Porphyridium cruentum* biomass, and the sensor achieved a detection limit of 2.5 ng mL^{-1} with differential pulse anodic stripping voltametric technique.[37]

Many investigations on arsenic detection using sensors can be found in the current literature;.[38–41] however, to best of our knowledge there is no alternative system to our dip-and-gauge sensor, which offers the most rapid and easy-to-use tool to be employed by bottled water producers and governmental bodies working on water quality assessments out of laboratory without a need for experienced personnel.

2.4. Advantages of the designed electrode

The smaller electrode area of the designed sensor chip enables a compact design together with two working electrodes and a shared reference and counter electrodes. Hence, by just placing a sensor chip to the dip-and-gauge biosensor, two consecutive bisphenol A measurements can be performed. As the sensors for arsenic can be used multiple times, the measurement number per sensor will be higher. More importantly, the current design enables much smaller concentrations of the analyte to be detected with respect to the screen-printed electrodes (for bisphenol A, 10 times lower detection limit was achieved) with just clean, bare Au surfaces. Therefore, there is no need to modify the sensor surface with self-assembled monolayers or polymeric/composite surfaces that not only elongate the sensor fabrication but also increase the cost. In short, the advantages of the designed sensor with respect to conventional screen-printed electrodes can be summarized as high sensitivity, multiplex measurements, ease of fabrication, and a small footprint.

2.5. Conclusions

In this work, we have reported a newly designed electrode array that provides a convenient tool for rapid and accurate detection of bisphenol A and arsenic in water samples and has potential for commercial use.

The advantages of the proposed detection platform with respect to existing technologies are its ease of use, sensitivity, reliability, and cost-effectiveness. Over the last two decades, there has been an explosive development of miniaturized analytical systems and related techniques based on electrochemical sensors. The novel sensor system provides a convenient tool for fast, sensitive, low-cost, and automated sensing of bisphenol A and arsenic with LOD of 0.6 ng mL^{-1} and 1.9 ng mL^{-1}, respectively, in wide investigation ranges, and the achieved detection limits are much lower than the threshold levels of both toxic compounds allowed in drinking water (500 ng mL^{-1} for bisphenol A and 10 ng mL^{-1} for arsenic). Together with a hand-held sensor device that works by simply dipping the sensor chip into a water container (Figure 1c), this cost-effective system has the potential to be used either by household consumers or for on-site inspection purposes. The implementations of the developed sensor system can be extended to the detection of similar toxic compounds found in water and food sources.

3. Experimental

3.1. Materials

Phosphate buffered saline tablets (PBS, 0.01 M phosphate buffer, 0.0027 M potassium chloride, and 0.137 M sodium chloride, pH 7.4), spectrophotometric grade ethanol, bisphenol, HPLC grade acetonitrile, toluene, octanol, and potassium ferricyanide were purchased from Sigma-Aldrich (Poole, UK). Potassium chloride (KCl) was purchased from Fisher Scientific (Loughborough, UK). Oxygen-free argon was purchased from Habaş (İstanbul, Turkey). Ultrapure water (18 MΩ cm^{-1}) was obtained from a Milli-Q water system (Millipore Corp., Tokyo, Japan). Arsenic was obtained from the Food Institute (TÜBİTAK, Kocaeli, Turkey).

3.2. Safety awareness

Due to the toxic properties of bisphenol A and arsenic, safety precautions were applied, such as wearing gloves, protection glasses, and lab coats at all times and facial masks when handling powdered bisphenol A and arsenic. The compounds were stored in a locked fridge specified for toxic reagents according to safety instructions.

3.3. Transducer fabrication

A sensor chip was designed and fabricated on glass slides that consisted of working electrodes in diameters of 1.5, 2, 2.5, 3, and 4 mm; each sensor consisted of 2 working electrodes with shared Au counter and quasi-reference electrodes. The design of the electrodes was formed on the glass slides by means of a fine metal mask made of a laser-cut patterned stainless steel, and Au metal was deposited on the wafer using an electron beam evaporator (Figure 1b). Before the application of Au (200 nm), a 20 nm Ti layer was applied to the glass slides as an intermediary adhesive layer to increase the adhesion between the Au and glass. After metal evaporation, the glass slide was fixed onto a plastic substrate for ease of use.

The sensor chips were cleaned using argon plasma prior to use. The chips were attached to a clamp for cyclic voltammetry and amperometric measurements. The reuse of sensor chips was accomplished by plasma cleaning the arrays twice. Cyclic voltammetry and amperometric measurements were performed with a MicroStat 8000 Electrochemical Analyzer with the general purpose electrochemical software Dropview 1.4 (Dropsens, Asturias, Spain). Cyclic voltammetry tests were performed for electrode characterization using 1 mM potassium ferricyanide solution in 1 M KCl. Amperometry was employed for bisphenol detection, whereas cyclic voltammetry was utilized in arsenic assays.

3.4. Electrochemical measurement of bisphenol A and arsenic

The tests involved the dipping of the sensor chip into the standard solution/water sample and then measuring the contaminant amount with electrochemical methods, hence called a dip-and-gauge sensor. The sensor chip was dipped into a bisphenol A solution (in PBS) with different concentrations (0–2000 ng mL^{-1}). The amperometric measurement was carried out at 0.5 V for 60 s. For arsenic determination tests, cyclic voltammetry was performed in the range of –0.2 to 1.2 V using 0.4 to 250 ng mL^{-1} arsenic solutions. The sensor chips can be used multiple times since arsenic does not cause any residual on the electrode surface, whereas it is not possible to use the same chip for subsequent measurement of bisphenol A unless it is plasma-cleaned.

3.5. Testing in real samples

To validate the compatibility of the dip-and-gauge sensor for the detection of bisphenol A and arsenic, these toxic compounds were prepared and measured in a variety of water sources including tap water, drinking water, and mineral water. A 10 ng mL^{-1} concentration of bisphenol A was diluted and detected in these water systems and the results were compared. For arsenic detection, 31.25 ng mL^{-1} was prepared and determined in the cyclic voltammetry working range of –0.2 to 125 V.

3.6. Liquid-phase microextraction of bisphenol A

This protocol was developed to concentrate the bisphenol A in a solution. Therefore, the sensor capacity was increased to enable measuring at much lower concentrations. The Accurel Q3/2 polypropylene hollow fiber used for liquid-phase microextraction was purchased from Membrana GmbH (Wuppertal, Germany). The inner diameter, pore size, and thickness of the wall were 600 µm, 0.2 µm, and 200 µm, respectively. Before use, the hollow fiber was cut manually into segments of 8 cm long. Each segment was ultrasonically cleaned in acetone for 5 min in order to remove any contaminants prior to drying. Extractions were performed according to the following procedure: 6 mL of water sample including 500 ng mL^{-1} of bisphenol A was add to an 8 mL vial, and then the pH of the solution was adjusted to 4.0 with 2 M HCl and finally water was added to a total volume of 8.0 mL. The hollow fiber was dipped in toluene for 5 s to ensure that the pores of the hollow fiber were impregnated with the extracting solvent. After solvent impregnation, the fiber was dipped in water for 10 s to remove excess solvent. Subsequently, 90 mM NaOH (acceptor phase) was injected into the lumen. The impregnated and filled fiber was then placed in the sample vial for immediate extraction. Both open ends of the medical syringe needles were closed to prevent solvent volatilization during extraction. During the extraction, the sample solution was continuously stirred at room temperature with a magnetic stirrer at 900 rpm for 40 min. Finally, the extract was tested using the developed sensor.

Acknowledgment

This project was supported by BİLGEM - TÜBİTAK (the Scientific and Technological Research Council of Turkey) (Grant Nos. S569000 & 100121), a Republic of Turkey Ministry of Development Infrastructure Grant (No: 2011K120020), and TÜBİTAK BİDEB 2221.

References

1. Braunrath, R.; Podlipna, D.; Padlesak, S.; Cichna-Markl, M. *J. Agr. Food Chem.* **2005**, *53*, 8911-8917.
2. Huang, H.; Li, Y.; Liu, J.; Tong, J.; Su, X. *Food Chem.* **2015**, *185*, 233-238.

3. Yin, H.; Cui, L.; Chen, Q.; Shi, W.; Ai, S.; Zhu, L.; Lu, L. *Food Chem.* **2011**, *125*, 1097-1103.
4. Shin, H. S.; Park, C. H.; Park, S. J.; Pyo, H. *J. Chromatogr. A* **2001**, *912*, 119-125.
5. Yoon, Y. M.; Westerhoff, P.; Snyder, S. A.; Esparza, M. *Water Res.* **2003**, *37*, 3530-3537.
6. Rezaee, M.; Yamini, Y.; Shariati, S.; Esrafili, A.; Shamsipur, M. *J. Chromatogr. A* **2009**, *1216*, 1511-1514.
7. Cunha, S. C.; Fernandes, J. O. *Food Control* **2013**, *33*, 549-555.
8. Smith, A. H.; Lingas, E. O.; Rahman, M. *Bull. World Health Org.* **2000**, *78*, 1093-1103.
9. Bond, G. R. *Clin. Tox.* **2009**, *47*, 469-469.
10. Sarker, M. M. R. *Int. J. Environ. Res. Pub. Health.* **2010**, *7*, 3644-3656.
11. Mulvihill, M.; Tao, A.; Benjauthrit, K.; Arnold, J.; Yang, P. *Angew. Chem. Int. Edit.* **2008**, *47*, 6456-6460.
12. Richardson, S. D.; Ternes, T. A. *Anal. Chem.* **2005**, *77*, 3807-3838.
13. Melamed, D. *Anal. Chim. Acta* **2005**, *532*, 1-13.
14. Klaue, B.; Blum, J. D. *Anal. Chem.* **1999**, *71*, 1408-1414.
15. Leermakers, M.; Baeyens, W.; De Gieter, M.; Smedts, B.; Meert, C.; De Bisschop, H. C.; Morabito, R.; Quevauviller, P. *TRAC-Trends Anal. Chem.* **2006**, *25*, 1-10.
16. Merulla, D.; Buffi, N.; Beggah, S.; Truffer, F.; Geiser, M.; Renaud, P.; van der Meer, J. R. *Curr. Opin. Biotech.* **2013**, *24*, 534-541.
17. Gao, C.; Yu, X. Y.; Xiong, S. Q.; Liu, J. H.; Huang, X. J. *Anal. Chem.* **2013**, *85*, 2673-2680.
18. Altuntaş, D. B.; Akgül, G.; Yanık, J.; Anık, Ü. *Turk. J. Chem.* **2017**, *41*, 455-465.
19. Çolak, O.; Arslan, F. *Turk. J. Chem.* **2015**, *39*, 84-95.
20. Ndlovu, T.; Arotiba, O. A.; Sampath, S.; Krause, R. W.; Mamba, B. B. *Sensors* **2012**, *12*, 11601-11611.
21. Fan, H.; Li, Y.; Wu, D.; Ma, H.; Mao, K.; Fan, D.; Du, B.; Li, H.; Wei, Q. *Anal. Chim. Acta* **2012**, *711*, 24-28.
22. Yasri, N. G.; Sundramoorthy, A. K.; Gunasekaran, S. *RSC Adv.* **2015**, *5*, 87295-87305.
23. Portaccio, M.; Di Tuoro, D.; Arduini, F.; Lepore, M.; Mita, D. G.; Diano, N.; Mita, L.; Moscone, D. *Biosens. Bioelectron.* **2010**, *25*, 2003-2008.
24. Portaccio, M.; Di Tuoro, D.; Arduini, F.; Moscone, D.; Cammarota, M.; Mita, D. G.; Lepore, M. *Electro. Acta* **2013**, *109*, 340-347.
25. Zehani, N.; Fortgang, P.; Lachgar, M. S.; Baraket, A.; Arab, M.; Dzyadevych, S. V.; Kherrat, R.; Jaffrezic-Renault, N. *Biosens. Bioelectron.* **2015**, *74*, 830-835.
26. Ragavan, K. V.; Rastogi, N. K.; Thakur, M. S. *TRAC-Trends Anal. Chem.* **2013**, *52*, 248-260.
27. Ragavan, K. V.; Selvakumar, L. S.; Thakur, M. S. *Chem. Comm.* **2013**, *49*, 5960-5962.
28. Mei, Z.; Chu, H.; Chen, W.; Xue, F.; Liu, J.; Xu, H.; Zhang, R.; Zheng, L. *Biosens. Bioelectron.* **2013**, *39*, 26-30..
29. Huang, J.; Zhang, X.; Lin, Q.; He, X.; Xing, X.; Huai, H.; Lian, W.; Zhu, H. *Food Control* **2011**, *22*, 786-791.
30. Alkasir, R. S. J.; Ganesana, M.; Won, Y.-H.; Stanciu, L.; Andreescu, S. *Biosens. Bioelectron.* **2010**, *26*, 43-49.
31. Wu, L.; Deng, D.; Jin, J.; Lu, X.; Chen, J. *Biosens. Bioelectron.* **2012**, *35*, 193-199.
32. Soh, N.; Watanabe, T.; Asano, Y.; Imato, T., *Sens. Material.* **2003**, *15*, 423-438.
33. Matsumoto, K.; Sakai, T.; Torimaru, A.; Ishitobi, S. *J. Fac. Agr. Kyushu Univ.* **2005**, *50*, 625-634.
34. Hegnerova, K.; Piliarik, M.; Steinbachova, M.; Flegelova, Z.; Cernohorska, H.; Homola, J. *Anal. Bioanal. Chem.* **2010**, *398*, 1963-1966.
35. Zhu, Y.; Cai, Y.; Xu, L.; Zheng, L.; Wang, L.; Qi, B.; Xu, C. *ACS Appl. Mater. Inter.* **2015**, *7*, 7492-7496.
36. Wu, Y.; Liu, L.; Zhan, S.; Wang, F.; Zhou, P. *Analyst.* **2012**, *137*, 4171-4178.

37. Zaib, M.; Saeed, A.; Hussain, I.; Athar, M. M.; Iqbal, M. *Biosens. Bioelectron.* **2014**, *62*, 242-248.

38. Huang, C. W.; Wei, C. C.; Liao, V. H. C. *Chemosphere.* **2015**, *141*, 44-49.

39. Li, L.; Liang, J.; Hong, W.; Zhao, Y.; Sun, S.; Yang, X.; Xu, A.; Hang, H.; Wu, L.; Chen, S. *Environ. Sci. Tech.* **2015**, *49*, 6149-6155.

40. Kaur, H.; Kumar, R.; Babu, J. N.; Mittal, S. *Biosens. Bioelectron.* **2015**, *63*, 533-545.

41. Webster, D. P.; TerAvest, M. A.; Doud, D. F. R.; Chakravorty, A.; Holmes, E. C.; Radens, C. M.; Sureka, S.; Gralnick, J. A.; Angenent, L. T. *Biosens. Bioelectron.* **2014**, *62*, 320-324.