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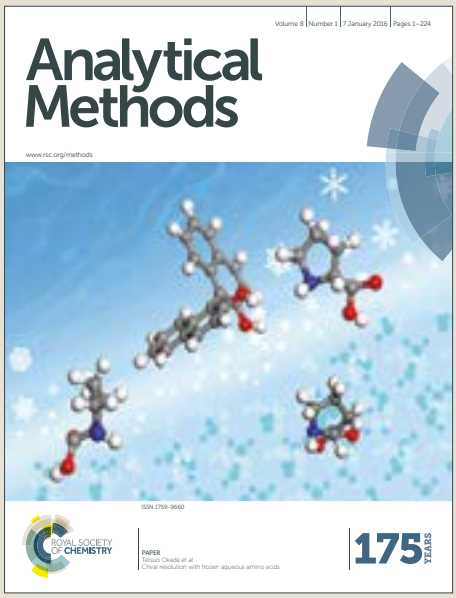

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ARTICLE

A paper-based potentiometric sensing platform based on molecularly imprinted nanobeads for determination of bisphenol A

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Currently, the electrode substrates of solid-contact potentiometric sensors for bisphenol A (BPA) are usually expensive glassy carbon, gold or platinum. This poses serious limits to the wide use of these sensors, especially in less developed countries. Herein, we present here for the first time a simple and ultra-low-cost, disposable paper-based potentiometric sensor for determination of neutral BPA. Uniform-sized molecularly imprinted nanobeads are utilized as a recognition receptor to provide a higher affinity for BPA since they have larger binding capability and can be well dispersed in the polymeric membrane potentiometric sensor. Commercially available chromatography paper is used as the electrode substrate to build up the sensor. It has been found that the proposed paper sensor exhibits similar analytical performance with the classical glassy carbon-based sensor. The present sensor shows a linear anionic potential response over the concentration range from 0.5 to 13 μM with a detection limit of 0.15 μM and exhibits good selectivity over other phenols. The proposed sensing platform has been successfully applied to determination of BPA released from real plastic samples.

Introduction

In recent years, bisphenol A (BPA) has received considerable attention due to its high production, extensive usage and prevalence in the environment.[1,2] Additionally, research has demonstrated that BPA has been shown to possess estrogenic properties and act as an agonist for the estrogen receptors. Currently, many approaches have been developed for the determination of BPA in environment, such as fluorometry,[3,4] high-performance liquid chromatography (HPLC) [5,6] and HPLC coupled with mass spectrometry.[7] Nevertheless, these well-established approaches have some obvious drawbacks such as complicated instruments, intensive labor and tedious procedures. Especially, these measurements cannot easily be carried out in rural areas as well as urban areas in less developed countries because of their high cost.

Currently, electrochemical sensors are exhibiting a great potential to change this situation owing to their intrinsic advantages including favorable portability, short analysis time and inexpensive equipment.[8] As one of generic and highly successful electrochemical sensors, polymeric membrane potentiometric sensor is considered as a promising alternative for BPA analysis since it is resistant to color and turbid interferences which are usually encountered for real-sample analysis.[9,10] Although several potentiometric biosensors have been reported for measurements of BPA, these methods involve the complicated screening processes of antibodies or aptamers for BPA.[11,12] Recently, we developed a potentiometric sensor to detect BPA.[13] However, in that work, a conventional liquid-contact ion-selective electrode (ISE) which contains an inner filling solution was applied as the sensor. Such conventional electrode suffers from problems of big volume, trivial maintenance and hard portability, thus restricting its wide applications.

Solid-contact ISEs which eliminate the internal solution and are easily miniaturized have been recognized as the means by which the next ISE generation will be

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constructed.[14,15] It has been well known that the electrode substrates for these electrodes are usually glassy carbon, gold or platinum. It is clear that these substrates are very expensive. This poses serious limits to their wide use, especially in less developed countries. To reduce cost, simplify instrumentation, and incorporate functionality, paper has become a simple, flexible and reliable platform for analytical devices.[16-19] Thus, paper would be a particularly attractive substrate for low-cost potentiometric sensor.[20]

Herein, we present a novel and low-cost paper-based potentiometric sensor for determination of BPA. It is based on a molecularly imprinted polymer (MIP) as a receptor. Compared to the natural receptors such as antibodies and aptamers, MIPs are cheaper, more robust, and easier to produce.[21] Above all, they can selectively bind a wide range of analytes with similar affinities and selectivities to their biological counterparts.[22] The printed Whatman chromatography paper is used as the electrode substrate. The uniform-sized MIP nanobeads for BPA are synthesized and incorporated into the sensing membrane for the selective recognition of BPA. It will be shown that the MIP nanobeads-based polymeric membrane paper sensor could be effectively employed as the sensing platform for potentiometric detection of BPA. To the best of our knowledge, this work reports the first MIP-based potentiometric paper sensor.

Experimental

Apparatus

All electromotive force (EMF) measurements were carried out at ambient temperature using a CHI660C electrochemical workstation (Shanghai Chenhua Apparatus) with Ag/AgCl (3 M KCl) as reference electrode in the galvanic cell: Ag/AgCl (3M KCl)/sample solution/ ISE membrane/solid contact. A glassy carbon rod (3 mm Ø) was used as the electrode substrate for a classical solid-contact potentiometric ion sensor. Scanning electron microscopy (SEM) images were taken using a S-4800 scanning electron microscope (HITACHI Ltd., Japan). A XEROX Phaser 8560DN wax inkjet printer purchased from Fuji XEROX Company was utilized to pattern wax-based solid ink on the Whatman chromatography paper (Whatman chromatography No.1 paper, GE) with the highest resolution of 2400 dpi.

Chemicals and materials

All chemicals were commercially available as analytical reagent. Bisphenol A (BPA), acetonitrile (ACN), methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), methanol, high molecular weight poly (vinyl chloride) (PVC), dioctylphthalate (DOP), tridodecylmethylammonium chloride (TDMAC), tetradodecylammonium tetrakis (4-chlorophenyl) borate (ETH 500) were purchased from Sigma-Aldrich. 2,2-azobisisobutyronitrile (AIBN) and tetrahydrofuran (THF) were obtained from Sinopharm Chemical Reagent Co., Ltd (China). Conductive carbon ink was purchased from Bohui New Materials Tech. Co. Ltd (Jiangsu, China), which is composed of conductive carbon black and metal powder, resin and solvent. All other reagents were of analytical grade and used as received. Aqueous solutions were prepared by dissolving the appropriate salts in deionized water (18.2 MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system.

Synthesis of BPA-imprinted nanobeads

BPA-imprinted nanobeads were synthesized by using the classical precipitation polymerization method.[23] 0.5 mmol of BPA template and 3.0 mmol of MAA were dissolved in 15 mL of acetonitrile in a 25 mL screw-capped thick-walled glass tube. The mixture was sonicated, and placed for 1 h for pre-complex formation between template and monomer molecules. 3.0 mmol of EGDMA and 80 mg of AIBN were added into the mixture. The resulting mixture was de-oxygenated by purging with N_2 gas for 10 min and then polymerized at 70 C^o in oil bath for 18 h. After polymerization, the polymer obtained was collected by vacuum filtration, grinded, and washed circularly with 150 mL methanol/acetic acid (1:1) to remove the un-reacted species. After that, the polymer particles were added to a mixture of methanol/1 M NaOH (75:25 v/v), and heated in a reflux for 20 h to remove the template. The resulting polymer was then dried overnight at room temperature. The corresponding non-imprinted polymers (NIP) were prepared similarly using the previous protocol but in the absence of the template molecule.

Fabrication of paper-based sensors

Firstly, the printed Whatman chromatography paper was kept in an oven at 150 °C for 2 min till the wax was penetrated completely into the paper to form hydrophobic wax barriers and then cooled to room temperature. On a 6.5 cm × 5.5 cm piece of the paper, the carbon ink was then coated using a conventional paintbrush. The paper was then dried at room temperature for 5 min and then in an oven at 70 °C for 10 min. The conductivity of the obtained carbon

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ink-based paper was measured by using a source-measurement unit. These steps were repeated several times until the impedance of the dried paper reaches a stable value, which is usually around 300 Ω/cm^2.

The conductive paper was cut into small strips (0.5 cm × 2 cm) and coated with an adhesive plastic film mask to avoid the connection of carbon ink with the solution. Then, a well defined circular orifice (ø = 3 mm) which can limit the sensing area of the membrane was punched from the plastic mask. A volume of 20 µL of the corresponding membrane cocktail was drop-casted onto this orifice to obtain the desired ISE sensing membrane. These procedures were found to give optimum results (mechanical stability, reproducibility and good calibration parameters, etc.). Other uncovered parts on the other side of the conductive paper was used to connect with the potentiometer. Details of the electrode design and construction are shown in Fig. 1.

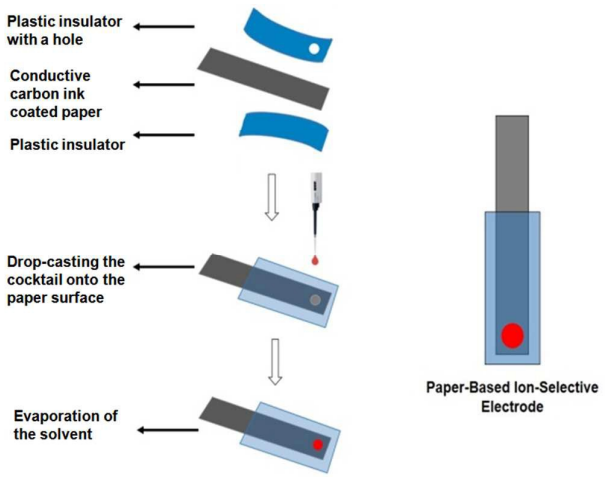

Fig. 1 Schematic illustration for fabrication of the potentiometric paper-based sensor.

Membrane preparation and EMF measurements

The BPA-selective membrane was prepared by dissolving 200 mg of membrane components in 2 mL THF. The membrane composition contained (in wt%) 6.0 % MIP (NIP), 1.0 % TDMAC, 2.0 % ETH 500, 36.4 % PVC and 54.6 % DOP; for comparison, the blank membrane contained 1.0 % TDMAC, 2.0 % ETH 500, 38.8 % PVC and 58.2 % DOP.

As a comparison, glassy carbon electrodes (GCEs) were used as conducting substrates for the conventional electrode. Before use, these electrodes were polished with 0.3 µM Al_2O_3 slurries, rinsed with water, ultrasonicated for 10 min in water, washed with ethanol, and left to dry. Finally, the resulting GCE was inserted into a piece of matched PVC tubing at the distal end. 100 µL of the membrane cocktail was drop-cast onto the transducer layer and allowed to dry for 2 h. Before measurements, all the electrodes were conditioned in 33 mM phosphate buffer solution (PBS) of pH 7.5 for 2 h.

Results and discussion

Characterization of MIPs

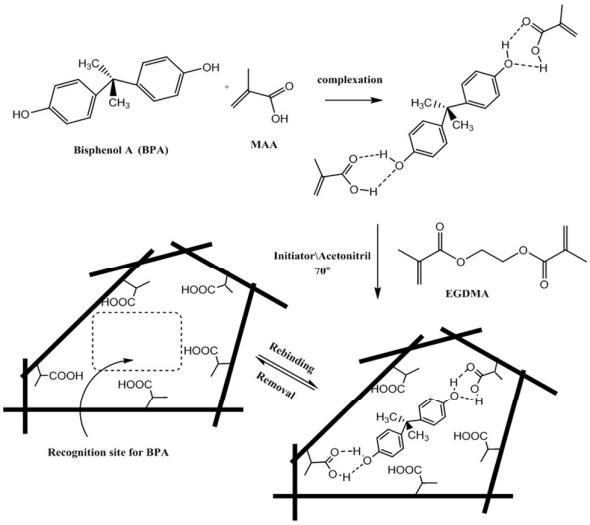

Fig. 2 Representation of the synthesis of MIP nanobeads for BPA.

For selective recognition of BPA, the non-covalent molecular imprinting approach was employed using MAA as the functional monomer, and EGDMA as the cross-linker. A schematic representation for the imprinting process is shown in Fig. 2. In this process, the -OH group of BPA can form strong hydrogen bonding with the -COOH group of the functional monomer, thus improving the binding affinity and specificity of the MIP. The micrographs of the obtained imprinted nanobeads were investigated by SEM. As shown in Fig. 3a, the BPA imprinted nanobeads are uniform-sized spherical with a diameter distribution of 200~300 nm. It can be expected that these nanobeads not only can be well dispersed in the polymeric ISE membrane but also have a higher binding capability than the traditional microbeads. These will lead to more available binding sites in the sensing membrane and thus result in better response performance.[24,25] In addition, it should be noted that the NIP nanobeads prepared with the same recipe except for omission of the template are slightly rougher and more irregular than the MIP beads (Figure 3b). This is due to the fact that the template could influence the polymer formation. Indeed, it has been

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found that the template-monomer complex can change the solubility of the growing polymer, thus altering the polymer morphology.[26,27]

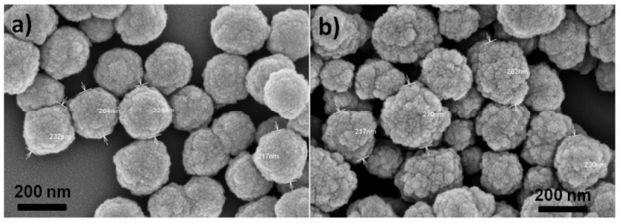

Fig. 3 SEM images for (a) the MIP and (b) the NIP nanobeads.

Paper substrate and conductivity

Paper is inherently nonconductive, but the painting of the conductive substance onto the porous nonconductive paper can produce large active electrode areas. In this work, conductive carbon ink was selected as the conductive material for fabrication of potentiometric paper sensor because it can be easily adsorbed onto the fibres of the paper and the resultant paper exhibits excellent conductivity. Fig. 4 shows the result for the conversion of a conventional paper into a conductive paper through the successive painting of carbon ink. Before coating the carbon ink, the resistance of the paper was extremely high, but it quickly decayed after painting several layers of the carbon Ink. Typically, values close to 300 Ω/sq were reached after application of two layers of the ink. It has been well known that the ability to resist bending, twisting or any other mechanical stress, is an attractive feature for the robust and flexible sensors. In this work, no significant changes in both electrical resistance and mechanical properties were observed after bending and folding the conductive paper for many times.

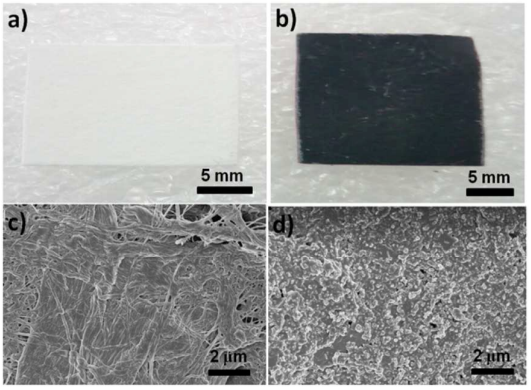

Fig. 4 Conversion of a chromatographic filter paper into a conductive paper. (a) Photographic images for the filter papers before (a) and after (b) the painting of carbon ink. SEM images for the surfaces of the papers before (c) and after (d) the painting of carbon ink.

In order to illustrate the conductive conversion process clearly, the macro- and micro-structures were characterized, respectively. Fig. 4a and 4b show the photographic macro-images of the paper before (a) and after (b) the painting of carbon ink. As can be seen, after the painting a dark and porous paper surface can be obtained. SEM images was further employed to characterize the micro-structure of the paper before (Fig. 4c) and after (Fig. 4d) the painting. It can be seen that after painting the cellulose fibres of the nonconductive paper are covered by a widespread randomly interconnected network of carbon ink. The excellent stabilization of carbon ink on the cellulose fibres can hinder the drop from the fibre surface upon rinsing the paper with water. Additionally, the microstructural changes of the sensing platform were also investigated by using SEM before and after measurement. As illustrated (Fig. S1 in the Supporting Information), no obvious microstructural changes can be observed for both sides of the sensing platform before and after detection. This is probably due to the excellent lipophilicity of polymeric sensing membrane and the high hydrophobicity of the carbon ink.

Potentiometric detection of BPA

For a traditional ISE, the sensing membrane is usually conditioned with the primary ion and the electrodes are measured under classical equilibrium conditions for the Nernstian sensor response. In our previous work, it has been found that classical potentiometric sensors usually exhibit rather poor responses to ionic bisphenols,[13,28] while electrically neutral phenols and their derivatives could generate strong anionic potential responses on quaternary ammonium salt-doped polymeric membrane potentiometric sensors under near-neutral pH conditions. These unexpected anionic responses can be explained by the net movement of hydrogen ions from the membrane phase to the aqueous phase stimulated by neutral phenols.[29] Inspired by these findings, we explored the application of the nonclassical response in the BPA detection. In order to guarantee that BPA exists mostly in its neutral form, 30 mM PBS with a pH of 7.5 was used as the background solution. To achieve sensitive detection of neutral BPA, experiments were further carried out to optimize the experimental parameters. It has been well established that the plasticizer, the membrane solvent, not only dissolves ionophore and ion-exchanger and gives a homogeneous organic phase but also influences the dielectric constant (εr) of the membrane phase and the mobility of the

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ligands and their complexes. Hence, the influence of the plasticizer on the potential response of the sensing membrane was investigated and the results are shown in Fig. S2 in the Supporting Information. It can been seen that better response behavior can be obtained by using nonpolar plasticizer DOP which shows the best performance in sensitivity. This is probably due to the fact that BPA can be favorably extracted into the polymeric sensing membrane with DOP as solvent.

Under the optimized conditions, the potential response of paper-based sensor to neutral BPA is shown in Fig. 5. Here, the potential difference between the baseline potential values and those measured at a fixed time (i.e., 100 s) after BPA addition is used for quantification. As expected, the higher concentrations can induce stronger anionic responses. These stronger responses for the neutral BPA at high concentrations can be attributed to the more net movements of cationic species (H^+) from the membrane to the aqueous phase.[29] Detailed analysis of the experimental results indicates that the potential response is proportional to the concentration of neutral BPA in the range of 0.5 to 13 μM with a detection limit of 0.15 μM (3σ). In addition, as a comparison, the same membrane composition was built on glassy carbon to compare the performance of the paper sensors with these conventional electrodes under similar conditions. As illustrated (Fig. S3 in the Supporting Information), the response performance of the paper-based sensor is comparable to that of the classical electrode, although its response speed and stability is slightly inferior to the classical one. This can confirm that the low-cost paper is an effective alternative to expensive noble metal electrode substrate.

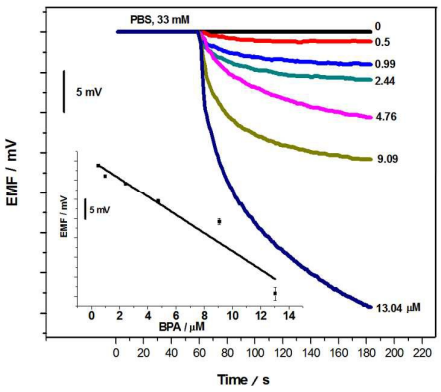

Fig. 5 Typical dynamic potentiometric responses of paper-based sensor to different concentrations of neutral BPA in 33 mM PBS at pH 7.5. The inset shows the calibration curve for BPA. Each error bar represents one standard deviation for three measurements.

As a comparison, the responses of NIP-based and blank membrane-based sensors were measured. As shown in Fig. 6, the MIP-based membrane sensor exhibits a much higher anionic response towards the same concentration of BPA than the blank and NIP membrane-based sensors. This suggests the successful imprinting and the specific interaction between MIP sites and BPA in the polymeric membrane.

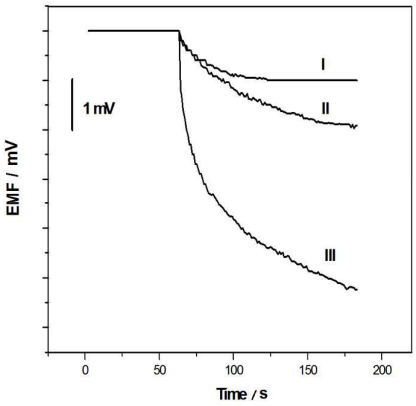

Fig. 6 Dynamic potential responses to 2.44 μM neutral BPA using the blank (I), NIP (II) and MIP (III) membrane-based paper sensors. Membrane ingredients: MIP membrane, 36.4 wt% PVC, 54.6 wt% DOP, 1.0 wt% TDMAC, 2.0 wt% ETH 500 and 6.0 wt% MIP; NIP membrane, 36.4 wt% PVC, 54.6 wt% DOP, 1.0 wt% TDMAC, 2.0 wt% ETH 500 and 6.0 wt% NIP; blank membrane, 38.8 wt% PVC, 58.2 wt% DOP, 1.0 wt% TDMAC and 2.0 wt% ETH 500.

Selectivity measurements

The selectivity test of the proposed sensors over other phenols such as bisphenol S (BPS), tetrabromo bisphenol A (TBBP), 1-naphthol, 2-nitrophenol, 3-nitrophenol, 2,6-dimethylphenol (DMP) and 4,4'-dihydroxybiphenyl (DHBP), respectively, is shown in Fig. 7. The potential responses towards BPA were recorded in the concentration range of 0.5-13 μM. Since all of the phenolic compounds used in selectivity measurements have p*K*a range of 7.8-10.5, they occur mainly or almost exclusively in their undissociated forms at pH 7.5.

Experiments show that the selectivity order for paper-based MIP membrane sensor is: BPA> DHBP～BPS> 1-naphthol> 3-nitrophenol >2-nitrophenol >> DMP>TBBP. It has been well established that the selectivity order for neutral phenols usually reflects the acidity and lipophilicity of these phenolic compounds.[30] The general trend is that a phenol derivative with a stronger acidity and higher lipophilicity induces a stronger anionic response. However, the acid dissociation constant and partition coefficient of TBBP are 8.5 and 5.9,

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respectively, TBBP does not show interfering effect on the response towards BPA. This can be attributed to the specific binding recognition of BPA by MIP beads as the sensory element.

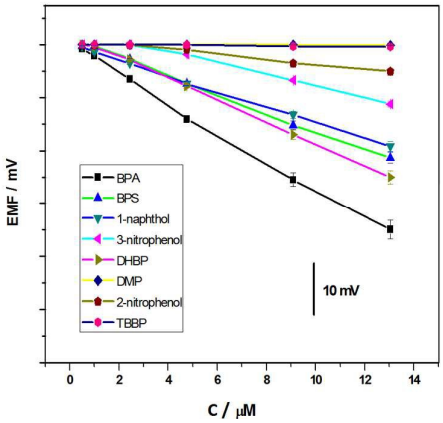

Fig. 7 Potentiometric selectivity of MIP membrane-based sensors towards bisphenol S (BPS), tetrabromo bisphenol A (TBBP), 1-naphthol; 2-nitrophenol, 3-nitrophenol, 4,4'-dihydroxybiphenyl (DHBP) and 2,6 dimethylphenol (DMP).

As a control, the potential response of the NIP-based sensor was also evaluated and presented in Fig. S4 in the Supporting Information. Smaller changes in the potential responses can be observed as compared to the MIP-based sensor. This can further confirm that the potential response is mainly induced by the specific interactions between the MIP sites in the polymeric membrane and BPA.

Analytical applications

To evaluate the feasibility of the proposed paper-based sensor in real sample analysis, the proposed sensors were introduced for determination of BPA released from some optical disc storage devices (e.g. CD and DVD) and commercial polycarbonate (PC) baby bottles collected from the local market. The samples were washed with deionized water and cut into small pieces and then mixed with 50 mL deionized water. The samples were heated in the oven at 90 ^{o}C for 6 h and left overnight in contact with its container to cool. After cooling, the samples were analyzed by the proposed sensors and HPLC method as a reference method. The results are shown in Table 1. It can be seen that the recoveries vary from 93% to 102.5%, and the data obtained by the polymeric membrane sensor agree well with those obtained by the HPLC method. These results indicate that the proposed sensor has promising feasibility for rapid determination of melamine in complex samples.

Table 1 Application of the proposed paper sensor to determination of BPA in real samples

Sample	BPA, μM	
	Paper-based sensor [a]	HPLC [a]
Optical disc storage device		
1	33.2 ± 0.4	30.1 ± 0.3
2	24.1 ± 0.2	22.4 ± 0.5
3	13.8 ± 0.8	11.1 ± 0.3
4	22.4 ± 0.3	19.5 ± 0.4
PC drinking bottle	0.39 ± 0.06	0.23 ± 0.04

[a] Average value of three determinations ± standard deviation

Conclusions

A simple, low-cost disposable paper-based platform based on uniform-sized MIP nanobeads for potentiometric sensing of BPA has been demonstrated for the first time. Compared with other paper-based electrochemical sensing platforms based on MIP,[31] the proposed paper-based potentiometric sensing platform possesses several unique features. First, potentiometric measurements are simple, independent of sample volume and only minimally perturb the samples. Second, the fabrication of the platform is fast, easy and inexpensive. In addition, the proposed sensing platform offers the advantages of fast response, good selectivity, excellent accuracy. Since many MIPs have been extensively exploited in analytical chemistry, this methodology is promising to develop MIP based potentiometric paper sensors for measurements of various organic pollutants.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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For the first time, A simple, low-cost paper-based platform based on uniform-sized MIP nanobeads for potentiometric sensing of bisphenol A is reported.