Preparation of dummy template imprinted polymers at surface of silica microparticles for the selective extraction of trace bisphenol A from water samples

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ABSTRACT

Molecularly imprinted polymers for bisphenol A (BPA) were prepared by using surface molecular imprinting technique. Analogues of BPA, namely 4,4′-dihydroxybiphenyl and 3,3′,5,5′-tetrabromobisphenol A, were used as the dummy templates instead of BPA, to avoid the leakage of a trace amount of the target analyte (BPA). The resulting dummy molecularly imprinted polymers (DMIPs) showed the large sorption capacity, high recognition ability and fast binding kinetics for BPA. The maximal sorption capacity was up to $958\,\mu mol\,g^{-1}$, and it only took 40 min for DMIPs to achieve the sorption equilibrium. The DMIPs were successfully applied to the solid-phase extraction coupled with HPLC/UV for the determination of BPA in water samples. The calibration graph of the analytical method was linear with a correlation coefficient more than 0.999 in the concentration range of $0.0760–0.912\,ng\,mL^{-1}$ of BPA. The limit of detection was $15.2\,pg\,mL^{-1}$ (S/N = 3). Recoveries were in the range of 92.9–102% with relative standard deviation (RSD) less than 11%. The trace amounts of BPA in tap water, drinking water, rain and leachate of one-off tableware were determined by the method built, and the satisfactory results were obtained.

1. Introduction

Bisphenol A (BPA) is widely used in the production of polycarbonate plastics, epoxy resins. Therefore, it is usually found in many plastic consumer products including water pipes, drinking containers and tableware [1]. Many evidences have shown that BPA has toxic properties, inducing estrogenic endocrine disruption and promotion of tumorigenic progression [2]. Recent study has indicated that BPA even at extremely low concentration ($0.23\,pg\,mL^{-1}$) would initiate the derangement of corpuscular functions to make the disorder of estrogenic hormone secretion [3]. Because of the wide availability of BPA in the environment, and human being at the top of food chain in the natural world, the potential adverse effects of BPA on human health have generated a great concern. Therefore, it is very necessary to monitor trace BPA in environmental water samples.

The trace analysis of environmental water samples generally needs a pretreatment step in order to reduce the matrix interference and enrich the analyte. Solid-phase extraction (SPE) is the currently leading technique for the extraction of pollutants from environmental liquid samples [4], and the development of new sorbent materials in this field is highlighted. In particular, increasing the selectivity of sorbent in the extraction of analytes from large sample volume is highly desirable for monitoring trace analytes in complex samples [5]. Molecularly imprinted polymers (MIPs) as SPE sorbents have attracted considerable attention for being easy to prepare and being able to adsorb the template molecules selectively from a mixture of chemical species.

There are some reports that MIPs for BPA have been used as SPE sorbents [6–13] and seem to become the promising development to circumvent the drawbacks of traditional SPE sorbents [14–17]. However, most previous MIPs for BPA were prepared by bulk polymerization or precipitation polymerization. As we know, these kinds of MIPs exhibit high selectivity but serious templates leakage and poor site accessibility. This is because the imprinted polymatrices are usually thick, the residual template molecules and the recognition sites are embedded in the matrices deeply.

To avoid the leakage of the residual BPA template molecules, the structural analogues of BPA, such as p-t-octylphenol (OP), p-tert-butylphenol (BP) and 4,4-methylenebisphenol (MBP), were used as templates [18–21], and corresponding MIPs are so-called "dummy

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molecularly imprinted polymer" (DMIP). DMIP can effectively prevent the inaccurate determination of the trace target compound.

Recently, nanostructured, surface imprinted materials have attracted considerable research interest [22–24]. The supports of the surface imprinted materials are silica nanoparticles which are mechanical/chemical stability, low cost, and ease of preparation. Most recognition sites are situated at the surface of the materials or in the proximity of the surface, and this makes target molecules faster to rebind and easier to remove [25]. The nanoparticles have a small dimension with high surface-to-volume ratio and contain more recognition sites. In our previous study, we prepared BPA-imprinted polymers at the surface of 400 nm-sized silica microparticles [26]. The BPA-imprinted polymers we prepared had the characteristics of high sorption capacity and fast and selective binding for BPA, and were successfully used as SPE sorbents to determine BPA in chemical cleansing and cosmetics samples.

In this study, we prepared DMIPs for BPA at the surface of 400 nm-sized silica microparticles by using 4,4′-dihydroxybisphenyl (DDBP) and 3,3′,5,5′-tetrabromobisphenylas (TBBPA) as dummy templates for the first time. The efficacy of the prepared DMIPs was evaluated by dynamic sorption and static sorption tests. Comparison between the DMIPs and C18 was also made. Finally, the DMIP was successfully applied to solid-phase extraction coupled with HPLC/UV to determine the trace BPA in real water samples. Encouraging results were obtained.

2. Experimental

2.1. Materials and chemicals

4,4′-Dihydroxybiphenyl (DDBP), 3,3′,5,5′-tetrabromobisphenol A (TBBPA), 4-vinylpyridine (4-VPY), vinyltrimethoxysilane (VTTS), and ethylene glycol dimethacrylate (EGDMA) were all purchased from Sigma-Aldrich (USA). Bisphenol A (BPA), p-tert-butylphenol (BP), and tetraethylorthosilicate (TEOS) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Azo-bis-isobutyronitrile (AIBN) was purchased from Shanghai Jingchun Chemical Reagent Co., Ltd. (China) and purified through recrystallization in ethanol before use. Ultra pure water was obtained from a PURELAB Classic water purification system (PALL, USA). Methanol was of HPLC-reagent grade and all other chemicals used were of analytical grade.

2.2. Instrumentation

The chromatographic system consisted of a Waters 515 HPLC pump and a Waters 2487 Dual λ absorbance detector (Waters, USA). All separations were carried out on a Diamonsil C18 column (250 mm × 4.6 mm I.D., 5 μm packing) with a flow rate of 1.0 mL min^{-1} at 33 °C. The UV detector was operated at 278 nm for BPA, DDBP and BP, and 292 nm for TBBPA, respectively. Analytical sample injector was equipped with 20 μL sample loop. The mobile phase was composed of methanol and ultra pure water (80:20). FT-IR spectra were recorded on a TENSOR 27 spectrometer (Bruker, Germany). The concentrations of the BPA before and after the sorption were recorded by a UV2450 spectrophotometer (Shimadzu, Japan).

The DMIP–SPE study was carried out in an off-line mode using a solid-phase extraction cartridge supplied by Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

2.3. Preparation of dummy molecularly imprinted polymer

2.3.1. Preparation of uniform silica particles

Uniform silica microparticles were synthesized by the hydrolysis of TEOS according to the reported Stöber method [27] and

Table 1
Preparation of DMIPs with different templates.

	Template	Functional monomer	Cross-linker
DMIP1	DDBP 1 mmol	4-VPY 4 mmol	EGDMA 5.5 mmol
DMIP2	TBBPA 1 mmol		

purified by a centrifugation method. The size of the silica microparticles was around 400 nm in diameter with excellent size mono disperse.

2.3.2. Chemical modification on the surface of silica particles

0.5 mL of VTTS was added to a suspension of 400 nm-sized silica microparticles (100 mg) in 20 mL of toluene. The above solution was stirred for 5 min, and then appropriate aqueous ammonia was added. The mixture was stirred over night at room temperature. The product was collected by centrifugation and then washed with toluene.

2.3.3. Imprinting at the surface of modified silica microparticles

Modified silica microparticles obtained above were dispersed in 20 mL of toluene by ultrasonic vibration. DDBP or TBBPA as a template, 4-VPY as a functional monomer, EGDMA as a cross-linker and AIBN (80 mg) as an initiator were all dissolved in the above solution. The preparation of DMIPs with different templates is shown in Table 1. The polymerization reaction was carried out at 65–70 °C under nitrogen for 24 h. The non-imprinted polymer (NIP) was prepared identically except for the addition of template molecules.

The polymers were separated by centrifugation, washed with a mixture of methanol and acetic acid (9:1, v/v) to remove the templates. A UV spectrometer was then employed to confirm that washout of template molecules was complete, as determined by absorbencies of template molecules (278 nm for DDBP and 292 nm for TBBPA). Finally, the polymers were washed with methanol to neutral. The resulting particles were dried at 60 °C for 12 h.

2.4. Evaluation of sorption characteristic of DMIPs

Dynamic and static sorption tests of the imprinted and non-imprinted silica microparticles were carried out according to the reported methods [28]. The concentrations of the BPA were monitored by a UV spectrophotometer.

2.5. Evaluation of DMIPs as SPE sorbents

2.5.1. Comparison between DMIP–SPE and C18–SPE

DMIPs, C18 and NIPs, each weighing 100 mg, were packed into empty 3 mL polypropylene SPE cartridge, respectively. After the columns were accordingly preconditioned with 5.0 mL of methanol and 5.0 mL of ultra pure water, a serial of ultra pure water (10 mL, 50 mL and 100 mL), each spiked with 228 ng of BPA, were loaded onto the SPE columns at the speed of 0.5 mL min^{-1}, respectively. Each column was washed with 5.0 mL of 0.1% triethylamine aqueous solution before being eluted with 3.0 mL of methanol. The elution was dried under a stream of nitrogen and the residue was redissolved with 1.0 mL of MeOH/H$_2$O solution (80:20, v/v), and then analyzed by HPLC via UV detection.

2.5.2. Selective extraction of BPA from BPA and its analogues on DMIP1–SPE column

The selective extraction of BPA from BPA and its analogues (TBBPA, DDBP and BP) were investigated on the DMIP1–SPE column. The chemical structures of BPA and its analogues are shown in Fig. 1. The loading solutions were a serial of 10 mL of ultra pure water containing 10 nmol of BPA and different amounts of TBBPA, DDBP and BP. The molar ratios of BPA to its analogues in the loading
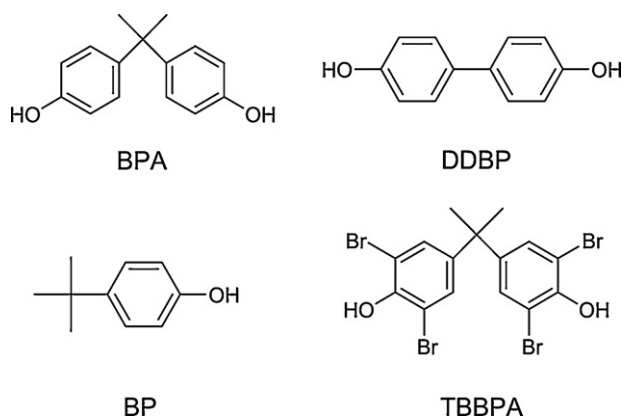
Fig. 1. The molecular structures of BPA, DDBP, TBBPA and BP.

solution were 1:1, 1:2, 1:3, 1:4 and 1:5, respectively. After the same washing and elution procedures described above, the compounds in elution fractions were analyzed by HPLC via UV detection.

In order to find out the maximum loading volume that could be sustained by the DMIP1–SPE without leakage of the analyte, 10 mL, 50 mL, 100 mL, 250 mL, 500 mL and 1000 mL of ultra pure water, each containing 228 ng of BPA, were loaded on the DMIP1–SPE column, respectively.

2.6. Method validation and application to real samples

DMIP1–SPE coupled to HPLC–UV was developed to determine the trace BPA in real samples. The linearity of the analytical method was evaluated by a calibration curve in the range of 0.0760–0.912 ng mL^{-1} of BPA ($n = 5$). The ultra pure water was spiked with BPA to achieve final concentrations of 0.0760, 0.152, 0.304, 0.608, and 0.912 ng mL^{-1}. The limit of detection (LOD) was defined as three times ratio of signal to noise. The loading volume of aqueous BPA standard solution was 150 mL.

For the assessment of the accuracy and the precision, real samples spiked with BPA were tested by the method built.

The containers used to collect water samples were all made of dry and clear glass bottles to prevent BPA contamination. After being filtered through a 0.22 μm filter, the collected water samples were stored in dark at 4 °C and the further SPE procedure was accomplished within 24 h to avoid any microbial degradation of analytes.

The tap water was collected from the laboratory. The drinking water was the boiled purified water from a plastic barrel installed in water dispenser. The rain was collected at Gulou District (Nanjing, China) in June; 2009. The leachate of the plastic cup and food box was collected from the containers steeped with 150 mL of ultra pure water at 80 °C for 1 h [29]. The loading volume of each sample was 150 mL.

3. Results and discussions

3.1. Preparation of dummy molecularly imprinted polymers

Fig. 2 showed the possible preparation process of molecular imprinting at the surface of 400 nm-sized silica microparticles. It illustrated the two major steps involved in the imprinting synthesis. First, the silica microparticles were chemically modified with VTTS. Ethylenic linkages were coated on the surface of the microparticles. Secondly, the template (DDBP or TBBPA), the functional monomer (4-VPY) and the cross-linker (EGDMA) copolymerized on the surface of the modified silica microparticles. After the residues of the reactants and the template were removed, a large number of tailor-made cavities on the surface of silica microparticles were formed, and the DMIPs were finally obtained.

Herein, DMIPs were synthesized by noncovalent imprinting method. Since all non-covalent forces are significantly influenced by the properties of solvent [30], five kinds of solvents including methanol, acetonitrile, tetrahydrofuran, chloroform and toluene were investigated. The experimental results showed that the DMIPs prepared in toluene obtained the highest molecular recognition ability. The probable reasons are those, first, the polarity of toluene is the lowest among the above solvents, which do not weaken the strength of hydrogen bond between the template molecule and functional monomer. Secondly, reactants dissolve more easily in toluene. Thirdly, toluene can produce suitable pore size [31]. Therefore, toluene was chosen as the solvent in the process of imprinting at the surface of modified silica microparticles.

3.2. Characteristic of the FT-IR spectra

To confirm the successful modification on the surface of silica microparticles and preparation of DMIPs and NIPs, FT-IR spec-
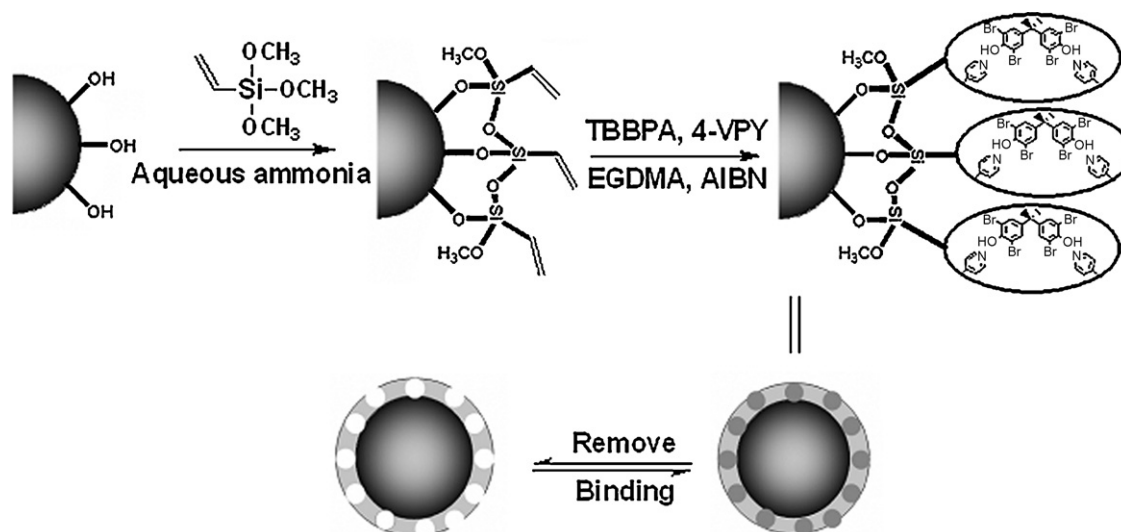

Fig. 2. Schematic representation of the possible process of molecular imprinting at the surface of silica microparticles.
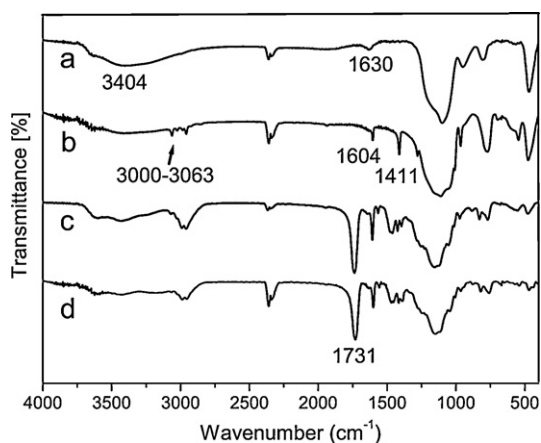
Fig. 3. FT-IR spectra of (a) pure silica microparticles; (b) modified silica microparticles; (c) DMIPs; (d) NIPs.

Fig. 5. Sorption kinetics of the DMIPs and NIPs for BPA (0.25 mmol L^{-1}).

tra were obtained for pure silica microparticles, modified silica microparticles, DMIPs and NIPs. In Fig. 3a, the adsorption observed at 3404 cm^{-1} attributed to the hydroxyl group on the surface of the pure silica microparticles. In Fig. 3b, the above adsorption disappeared. The adsorption observed around 3000–3063, 1604 and 1411 cm^{-1} indicated the existence of C=C–H group in the modified silica microparticles. The characteristic peaks of pyridine ring were overlaid with those of C=C–H group. Therefore, the peaks of pyridine ring in DMIPs and NIPs were not obvious in Fig. 3c and 3d, respectively. But, a strong adsorption at 1731 cm^{-1} indicated the existence of the C=O group in DMIPs and NIPs.

3.3. Evaluation of the sorption characteristic of DMIPs

The sorption capacities Q (μmol g^{-1}) were calculated by the following equation: $Q = (C_0 - C)V/W$, where C_0 and C were the template concentrations (μmol L^{-1}) in the solutions which were measured initially and after sorption, respectively; V (L) was the volume of the bulk solution and W (g) was the weight of the particles. The binding isotherm of BPA onto DMIPs and NIPs is showed in Fig. 4. The sorption capacity of DMIP1, DMIP2 were 918, 958 μmol g^{-1}, respectively, which were about three times that of the corresponding NIP. The sorption capacities of the DMIPs prepared were superior to those of most MIPs using BPA as a template reported in the literature [7,32–34]. The largest sorption capacity of MIPs for BPA in the literature was 298 μmol g^{-1}, which was only one-third of ours. The reason may be that the present DMIPs contained more recognition sites for being prepared at the surface of
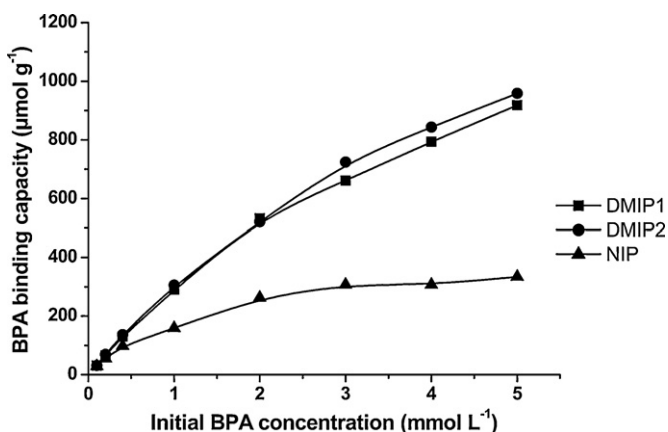
smaller size silica microparticles and owning greater surface-to-volume ratio.

Previously, BP and OP were used as templates to synthesize DMIPs for BPA. Since they occupied only one interaction site when rebinding with BPA, the DMIPs reported had much poorer ability to recognize BPA when compared with the MIPs using BPA as a template [19–21]. The dummy templates we chose were DDBP and TBBPA, which have two interaction sites, and more structurally similar to BPA than BP and OP. So, the DMIPs in our study had stronger sorption capacity and higher selectivity to bind BPA.

Binding studies were also carried out at different time intervals. As shown in Fig. 5, it only took 40 min for DMIP1, DMIP2 and NIP to achieve the equilibrium. The DMIPs had a faster sorption kinetics feature than the BPA-imprinted polymers in the previous reports [33–35], which spent at least 4 h to reach the equilibrium. Since the recognition sites of BPA-imprinted polymers in the literature existed not only at the surface but also in the deep polymer matrix, it took a longer time for target to access the binding sites in the deep polymer. The binding sites of the DMIPs prepared were at the surface or in the proximity of the surface. So it is an easy diffusion for target to access the recognition sites. This merit is especially favorable for SPE.

3.4. Evaluation of DMIPs as SPE sorbents

3.4.1. Comparison between DMIP–SPE and C18–SPE

Fig. 6 showed that BPA was retained on the DMIP–SPE columns with recoveries in the range of 83.9–106%. However, only about 75% of BPA was recovered for NIP and C18 SPE columns. It was
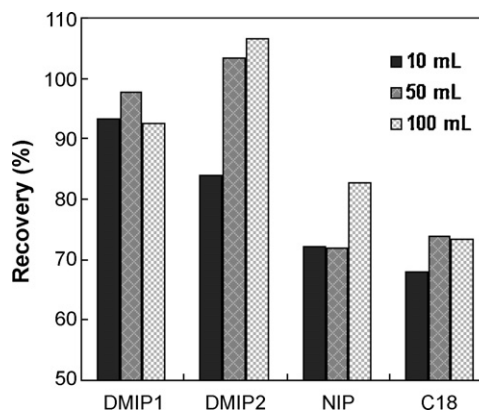

Fig. 4. Sorption isotherms of the DMIP and NIP sorbents for BPA.

Fig. 6. Recoveries of BPA after loading of 10 mL, 50 mL and 100 mL aqueous solution of BPA onto the DMIPs, NIPs and C18 columns, respectively.
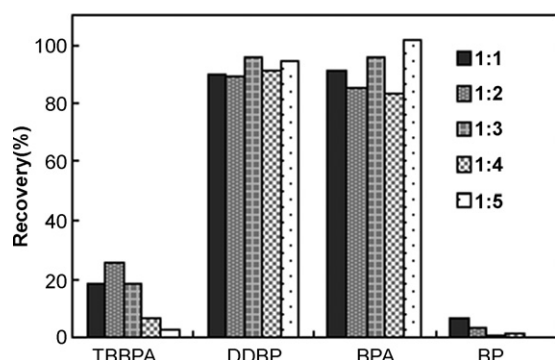
Fig. 7. Recoveries of BPA, TBBPA, DDBP and BP on the DMIP1–SPE columns with different molar ratios of BPA to its analogues.

obvious that DMIP–SPE columns were superior to the C18 and NIP SPE columns.

3.4.2. Evaluation of DMIP1 as SPE sorbents

The selective extraction of BPA among BPA and its structural analogues (TBBPA, DDBP and BP) was studied on the DMIP1 column. From Fig. 7, we could find that only DDBP and BPA were selectively retained on the column. DDBP had high recoveries of 89.1%–95.9% because it was used as the template in the preparation of DMIP1. The recoveries of BPA were around 90% in different situations even if the concentrations of BPA analogues were five times that of BPA. TBBPA and BP were poorly retained, and their recoveries were less than 30%. Therefore, the DMIP1–SPE column had not only high selectivity, but also an adequate ability of anti-interferences.

Breakthrough volume is an important factor which indicates the enrichment ability of a SPE column for the target analyte at a very low concentration. As shown in Table 2, there is no BPA loss (analyte breakthrough) even if 1 L of BPA standard solution was loaded. The breakthrough volume of the DMIP–SPE column was twice as much as that reported in Alexiadou's paper [6]. It indicated that DMIPs in our study could be used as SPE sorbents for extracting trace BPA from environmental samples where high volumes of water are usually loaded.

Moreover, the present DMIPs had two advantages over the previous BPA-imprinted polymers we prepared [26]. One was that the present DMIPs could bind BPA in water while the later could only bind BPA in organic solvents. The reason may be that the DMIPs contained pyridine ring and this made their polarity increased. The other was that the DMIPs as SPE sorbents could avoid the leakage of a trace amount of the target analyte (BPA).

3.5. Method validation and application to real samples

Under the optimized conditions of HPLC–UV coupled to DMIP1–SPE, the calibration graph was linear with a correlation coefficient of >0.999 in the concentration range of 0.0760–0.912 ng mL^{-1}. The regression equation was $A = 3015C + 137.83$, where C is the concentration of BPA, and A is the peak area. The LOD was 0.0506 ng mL^{-1}, and the rel-

Table 2
Recoveries of the different volumes of BPA loaded on the DMIP1–SPE.

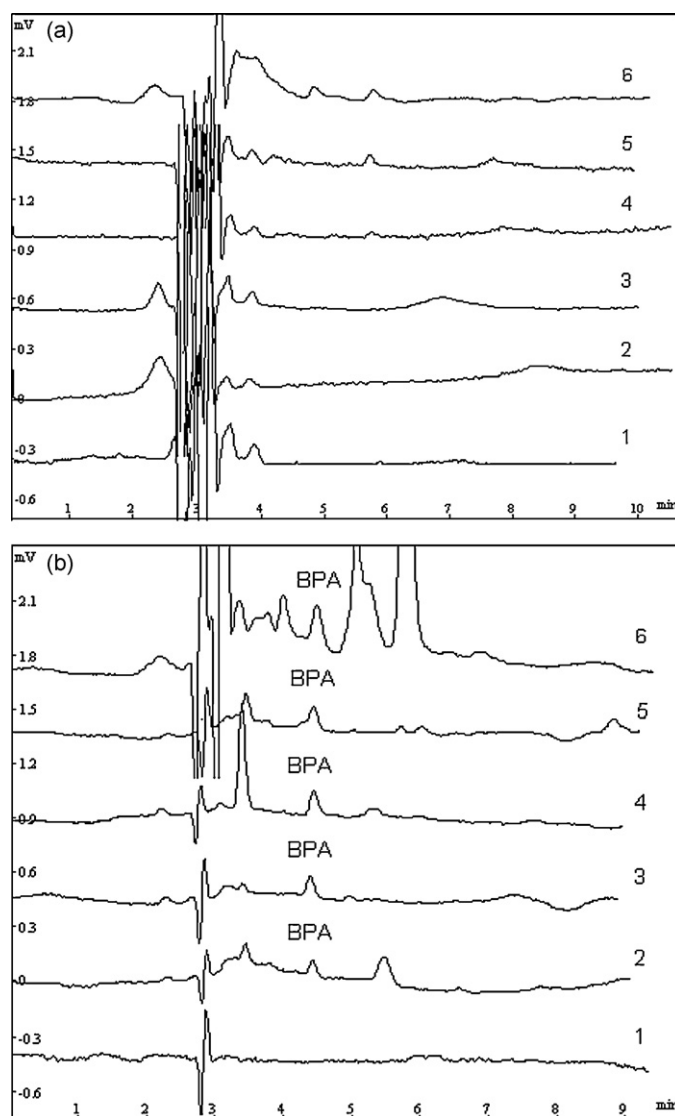| Sample volume (mL)	Spiked level (ng mL^{-1})	Recovery (%)
10	22.8	93.2
50	4.56	97.7
100	2.28	92.5
250	0.912	94.8
500	0.456	89.2
1000	0.228	110

Fig. 8. Chromatograms of water samples (a) without SPE, (b) with DMIP1–SPE: (1) the ultra pure water; (2) The tap water; (3) The drinking water; (4) Leachate of plastic cup; (5) Leachate of food box; (6) The rain.

ative standard deviation (RSD) was 5.7% at a concentration of 0.304 ng mL^{-1} ($n = 5$).

To demonstrate the application of the method, real environmental samples, i.e. tap water, drinking water, rain and leachate of one-off dishware were analyzed. The chromatograms are represented in Fig. 8. As shown in Fig. 8a, BPA in all the samples could not be detected by HPLC via UV detection without enrichment. After 150 times enriched by DMIP1–SPE, BPA could be detected and the resulting chromatograms are shown in Fig. 8b. From Fig. 8a and 8b, we also found that there was no BPA detected in ultra pure water before and after SPE. So, ultra pure water did not affect the experimental results when it was used as solvent to prepare BPA standard solutions and leachate of one-off dishware.

The contents of trace BPA in all samples were displayed in Table 3. The amount of BPA in the purified water (drinking water), which is commonly used in Chinese families, was more than that in the tap water. The possible reason was that some components made by resin were used in the water purification system. The concentrations of BPA in the leachate of plastic cup and food box were 0.164 ng mL^{-1} and 0.207 ng mL^{-1}, respectively. By the way, we also tested BPA in paper cup, and found that the concentration of BPA in

Table 3
Determination of BPA in environmental samples ($n = 5$).

Sample	Concentration (ng mL^{-1})	RSD (%)	BPA spiked (ng mL^{-1})	Recovery (%)	RSD (%)
Tap water	0.0855	8.9	0.0912	102	8.2
Drinking water	0.122	13.7	0.152	101	10.9
Leachate of plastic cup	0.164	8.0	0.152	92.9	6.9
Leachate of food box	0.207	9.8	0.152	95.8	8.8
Rain	0.590	11.8	–*	–	–

* Due to high content of BPA, no BPA was added to the rain sample.

the leachate of paper cup was very high and could be easily assayed without enrichment. So, it suggested that people minimize the use of one-off tableware. This is of benefit to both human health and environmental protection. The concentration of BPA in the rain was 0.590 ng mL^{-1}, which was highest in all water samples. Because large amounts of BPA are produced annually, BPA enters air particles during production at plastics manufacturing plants. Moreover, the standard BPA solutions were added to the all samples except rain sample to obtain the recovery (shown in Table 3). BPA in the samples were assayed with good recovery and precision. The average recoveries were in the range of 92.9–102%, and the RSDs were less than 10.9%. It indicated that the method was accurate, selective and practical for the determination of trace BPA in environmental water samples.

4. Conclusions

We prepared DMIPs for BPA by using surface molecular imprinting technique. The analogues of BPA, i.e. DDBP and TBBPA, were used as the dummy templates instead of BPA, to prevent inaccurate determination of trace BPA in water samples in case of the leakage of BPA remaining in the MIPs. The resulting DMIPs showed the large sorption capacity and fast binding kinetics for BPA. DMIP1 as solid-phase extraction sorbent was successfully coupled with HPLC/UV to determine the trace amounts of BPA in tap water, drinking water, rain and leachate of one-off dishware.

It is believed that an ultra trace level of BPA will be obtained if the DMIP–SPE is coupled with more sensitive detectors, such as fluorescence detector and mass spectrum detector, etc, or when the loading volume of samples is increased.

References

[1] L.N. Vandenberg, R. Hauser, M. Marcus, N. Olea, W.V. Welshons, Human exposure to bisphenol A (BPA), Reprod. Toxicol. 24 (2007) 139–177.
[2] R.A. Keri, S.M. Ho, P.A. Hunt, K.E. Knudsen, A.M. Soto, G.S. Prins, An evaluation of evidence for the carcinogenic activity of bisphenol A, Reprod. Toxicol. 24 (2007) 240–252.
[3] W.V. Welshons, S.C. Nagel, F.S. vom Saal, Large effects from small exposures. III. Endocrine mechanisms mediating effects of bisphenol A at levels of human exposure, Endocrinology 147 (2006) 56–69.
[4] S. Rubio, D. Pérez-Bendito, Recent advances in environmental analysis, Anal. Chem. 81 (2009) 4601–4622.
[5] Q.Z. Zhu, P. Degelmann, R. Niessner, D. Knopp, Selective trace analysis of sulfonylurea herbicides in water and soil samples based on solid-phase extraction using a molecularly imprinted polymer, Environ. Sci. Technol. 36 (2002) 5411–5420.
[6] D.K. Alexiadou, N.C. Maragou, N.S. Thomaidis, G.A. Theodoridis, M.A. Koupparis, Molecularly imprinted polymers for bisphenol A for HPLC and SPE from water and milk, J. Sep. Sci. 31 (2008) 2272–2282.
[7] X.M. Jiang, W. Tian, C.D. Zhao, H.X. Zhang, M.C. Liu, A novel sol–gel-material prepared by a surface imprinting technique for the selective solid-phase extraction of bisphenol A, Talanta 72 (2007) 119–125.
[8] Y. Lin, Y. Shi, M. Jiang, Y. Jin, Y. Peng, B. Lu, K. Dai, Removal of phenolic estrogen pollutants from different sources of water using molecularly imprinted polymeric microspheres, Environ. Pollut. 153 (2008) 483–491.
[9] Y. Jin, M. Jiang, Y. Shi, Y. Lin, Y. Peng, K. Dai, B. Lu, Narrowly dispersed molecularly imprinted microspheres prepared by a modified precipitation polymerization method, Anal. Chim. Acta 612 (2008) 105–113.
[10] V. Pichon, Selective sample treatment using molecularly imprinted polymers, J. Chromatogr. A 1152 (2007) 41–53.
[11] B.S. Vicente, F.N. Villoslada, M.C. Moreno-Bondi, Continuous solid-phase extraction and preconcentration of bisphenol A in aqueous samples using molecularly imprinted columns, Anal. Bioanal. Chem. 380 (2004) 115–122.
[12] Y.S. Ji, J.J. Yin, Z.G. Xu, C.D. Zhao, H.Y. Huang, H.X. Zhang, C.M. Wang, Preparation of magnetic molecularly imprinted polymer for rapid determination of bisphenol A in environmental water and milk, Anal. Bioanal. Chem. 395 (2009) 1125–1133.
[13] E. Herrero-Hernández1, R. Carabias-Martínez, E. Rodríguez-Gonzalo, Use of a bisphenol-A imprinted polymer as a selective sorbent for the determination of phenols and phenoxyacids in honey by liquid chromatography with diode array and tandem mass spectrometric detection, Anal. Chim. Acta 650 (2009) 195–201.
[14] T. Shiomi, M. Matsui, F. Mizukami, K. Sakaguchi, A method for the molecular imprinting of hemoglobin on silica surfaces using silanes, Biomaterials 26 (2005) 5564–5571.
[15] C. Baggiani, G. Giraudi, C. Giovannoli, C. Tozzi, L. Anfossi, Adsorption isotherms of a molecular imprinted polymer prepared in the presence of a polymerisable template - Indirect evidence of the formation of template clusters in the binding site, Anal. Chim. Acta 504 (2004) 43–52.
[16] T. Kubo, K. Hosoya, Y. Watabe, T. Ikegami, N. Tanaka, T. Sano, K. Kaya, Polymer-based adsorption medium prepared using a fragment imprinting technique for homologues of chlorinated bisphenol A produced in the environment, J. Chromatogr. A 1029 (2004) 37–41.
[17] R. Say, E. Birlik, A. Ersöz, F. Yılmaz, T. Gedikbey, A. Denizli, Preconcentration of copper on ion-selective imprinted polymer microbeads, Anal. Chim. Acta 480 (2003) 251–258.
[18] T. Kubo, K. Hosoya, Y. Watabe, T. Ikegami, N. Tanaka, T. Sano, K. Kaya, On-column concentration of bisphenol A with one-step removal of humic acids in water, J. Chromatogr. A 987 (2003) 389–394.
[19] H. Sanbe, K. Hosoya, J. Haginaka, Preparation of uniformly sized molecularly imprinted polymers for phenolic compounds and their application to the assay of bisphenol A in river water, Anal. Sci. 19 (2003) 715–719.
[20] M. Kawaguchi, Y. Hayatsu, H. Nakata, Y. Ishii, R. Ito, K. Saito, H. Nakazawa, Molecularly imprinted solid phase extraction using stable isotope labeled compounds as template and liquid chromatography–mass spectrometry for trace analysis of bisphenol A in water sample, Anal. Chim. Acta 539 (2005) 83–89.
[21] Y. Watabea, K. Hosoya, N. Tanaka, T. Kubo, T. Kondo, M. Morita, Novel surface modified molecularly imprinted polymer focused on the removal of interference in environmental water samples for chromatographic determination, J. Chromatogr. A 1073 (2005) 363–370.
[22] D.M. Gao, Z.P. Zhang, M.H. Wu, C.G. Xie, G.J. Guan, D.P. Wang, A Surface Functional Monomer-Directing Strategy for Highly Dense Imprinting of TNT at Surface of Silica Nanoparticles, J. Am. Chem. Soc. 129 (2007) 7859–7866.
[23] C.X. Zhai, Q. Lu, X.M. Chen, Y. Peng, L.N. Chen, S.H. Du, Molecularly imprinted layer-coated silica nanoparticles toward highly selective separation of active diosgenin from Dioscorea nipponica Makino, J. Chromatogr. A 1216 (2009) 2254–2262.
[24] C. Lu, W. Zhou, B. Han, H. Yang, X. Chen, X. Wang, Surface-imprinted core-shell nanoparticles for sorbent assays, Anal. Chem. 79 (2007) 5457–5461.
[25] S. Tokonami, H. Shiigi, T. Nagaoka, Micro- and nanosized molecularly imprinted polymers for high-throughput analytical applications, Anal. Chim. Acta 641 (2009) 7–13.
[26] R. Zhu, W.H. Zhao, M.J. Zhai, F.D. Wei, Z. Cai, N. Sheng, Q. Hu, Molecularly imprinted layer-coated silica nanoparticles for selective solid phase extraction of bisphenol A from chemical cleansing and cosmetics samples, Anal. Chim. Acta 658 (2010) 209–216.
[27] W. Stöber, A. Finker, E.J. Bohn, Controlled growth of mono-disperse silica spheres in the micron size range, Colloid Interf. Sci. 26 (1968) 62–69.
[28] Q.Z. Feng, L.X. Zhao, W. Yan, J.M. Lin, Z.X. Zheng, Molecularly imprinted solid-phase extraction combined with high performance liquid chromatography for analysis of phenolic compounds from environmental water samples, J. Hazard. Mater. 167 (2009) 282–288.
[29] Y.L. Hu, Y.J. Zheng, F. Zhu, G.K. Li, Sol–gel coated polydimethylsiloxane/β-cyclodextrin as novel stationary phase for stir bar sorptive extraction and its

application to analysis of estrogens and bisphenol A, J. Chromatogr. A 1148 (2007) 16–22.

[30] N.W. Turner, E.V. Piletska, K. Karim, M. Whitcombe, M. Malecha, N. Magan, C. Baggiani, S.A. Piletsky, Effect of the solvent on recognition properties of molecularly imprinted polymer specific for ochratoxin A, Biosens. Bioelectron. 20 (2004) 1060–1067.

[31] H.Y. Yan, K.H. Row, Characteristic and synthetic approach of molecularly imprinted polymer, Int. J. Mol. Sci. 7 (2006) 155–178.

[32] T. Ikegami, T. Mukawa, H. Nariai, T. Takeuchi, Bisphenol A-recognition polymers prepared by covalent molecular imprinting, Anal. Chim. Acta 504 (2004) 131–135.

[33] K.G. Yang, Z.B. Liu, M. Mao, X.H. Zhang, C.S. Zhao, N. Nishi, Molecularly imprinted polyethersulfone microspheres for the binding and recognition of bisphenol A, Anal. Chim. Acta 546 (2005) 30–36.

[34] K.G. Yang, B.Q. Li, H. Zhou, J.J. Ma, P.L. Bai, C.S. Zhao, Preparation and selective binding characterization of bisphenol A imprinted polyethersulfone particles, J. Appl. Polym. Sci. 106 (2007) 2791–2799.

[35] B.Y. Yu, X.L. Zhang, J. He, K.G. Yang, C.S. Zhao, Effect of the template molecules and nonsolvent additives on the recognition property of molecular imprinted polyethersulfone particles, J. Appl. Polym. Sci. 108 (2008) 3859–3866.