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Molecularly Imprinted Solid-Phase Extraction for Selective Extraction of Bisphenol Analogues in Beverages and Canned Food

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Supporting Information

ABSTRACT: This study aimed to develop a selective analytical method for the simultaneous determination of seven bisphenol analogues in beverage and canned food samples by using a new molecularly imprinted polymer (MIP) as a sorbent for solid-phase extraction (SPE). Liquid chromatography coupled to triple-quadruple tandem mass spectrometry (LC−MS/MS) was used to identify and quantify the target analytes. The MIP-SPE method exhibited a higher level of selectivity and purification than the traditional SPE method. The developed procedures were further validated in terms of accuracy, precision, and sensitivity. The obtained recoveries varied from 50% to 103% at three fortification levels and yielded a relative standard deviation (RSD, %) of less than 15% for all of the analytes. The limits of quantification (LOQ) for the seven analytes varied from 0.002 to 0.15 ng/mL for beverage samples and from 0.03 to 1.5 ng/g for canned food samples. This method was used to analyze real samples that were collected from a supermarket in Beijing. Overall, the results revealed that bisphenol A and bisphenol F were the most frequently detected bisphenols in the beverage and canned food samples and that their concentrations were closely associated with the type of packaging material. This study provides an alternative method of traditional SPE extraction for screening bisphenol analogues in food matrices.

KEYWORDS: *bisphenols, molecularly imprinted polymer, solid-phase extraction, beverage, canned food*

INTRODUCTION

Bisphenols (BPs) are a group of anthropogenic chemicals that consist of two phenolic rings that are joined through a bridging carbon or other chemical structure.[1] BPs are commonly used in the plastics industry as additives or intermediates to impart properties such as stability, hot tear strength, flame resistance, and softness. Bisphenol A (BPA) is the most common BP and is mainly used in the manufacturing process of polycarbonate plastics and epoxy resins, of which approximately 8 billion pounds are produced annually.[2,3] Increasing concerns over the health risks of BPA began because of its endocrine disruption effects in humans and its wide use in food and beverage containers and packaging. Due to regulatory pressure regarding the production and consumption of BPA, other BP analogues, including bisphenol S (BPS), bisphenol F (BPF), and bisphenol B (BPB), have been developed as alternatives for BPA in industrial applications.[4−6]

However, these chemicals seem not to be safer than BPA. Recently published studies have provided evidence that bisphenol AF (BPAF) can function as an endocrine disruptor by acting as agonists or antagonists for estrogen receptor α or estrogen receptor β.[7,8] By using standardized transactivation assays, Grignard et al.[9] demonstrated that the estrogenic activities of BPA and BPS are of comparable potency. Beside BPAF and BPS, BPF has also shown endocrine disruption activity, and the halogenated derivatives tetrachlorobisphenol A (TCBPA) and tetrabromobisphenol A (TBBPA) have been found to disrupt thyroid hormone receptor signaling.[10,11]

Due to the possible adverse effects on human health, these chemicals in food are of special concern because contamination of food with BPA is usually caused by contact with food packaging materials containing epoxy resins and polycarbonate.[12] In fact, some other bisphenols have been reported to contaminate foodstuffs. Viñas et al.[13] determined that the concentrations of BPS that were migrating from food cans varied from not detectable (ND) to 175 ng/mL in supernatant liquid and from ND to 36 ng/g in food. BPF was detected in soft drinks at concentrations of tens to hundreds of nanograms per liter and in the filling liquids of canned vegetables at higher concentrations.[14] Cunha et al.[15] detected BPB in 50% of the canned beverages tested, with levels ranging from ND to 0.16 ng/mL. TBBPA occurred in approximately 70% of the total diets of the studied samples, with levels ranging from ND to 0.2 ng/g lipid weight.[16] More recently, several studies have attempted to determine the occurrence of a group of BP analogues in foodstuffs from the United States and China, which has revealed widespread contamination of BPs in the food supply.[6,17] To control the migration of BPs to food, specific migration limits have been set for BPA (0.6 mg/kg of food, except for baby bottles, for which BPA was banned by the European Union in 2011) and BPS (0.05 mg/kg of food). In addition, BPF is not allowed in plastic materials that are intended to contact food, according to European law.[12]

Solid-phase extraction (SPE) is by far the most popular technique for extracting BPA at trace levels from liquid foods or for purifying extracts that result from the treatment of complex food matrices.[18] In particular, there has been an increase in the

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number of studies using SPE pretreatment in cooperation with liquid chromatography coupled to triple-quadruple tandem mass spectrometry (LC−MS/MS) to quantify BPs in foodstuffs because this method is highly sensitive, has a wide range of applicability, and consumes less solvent. However, the traditional SPE sorbents generally retain analytes by nonselective hydrophobic or polar interactions that lead to partial coextraction of interferences, resulting in suppression of the analyte signal.[19,20] In order to enhance the selectivity of the extraction, molecularly imprinted polymers (MIPs), based on specific recognition of the template molecule, allowing a selective extraction of a target molecule or its structural analogues, were developed.[21−23] In the past few years, MIPs were widely used as a new selective sorbent for cleaning up SPE and for extracting trace levels of compounds from complex matrices.[24−26] Several approaches have been used to prepare BPA imprinted polymers and have been applied to analyze foodstuffs.[27,28] However, the application of MIP for the determination of structurally related BP analogues in foodstuffs has been limited to date.

In this study, we aim to develop a method for the group-selective extraction of seven BPs (BPS, BPF, BPA, BPB, BPAF, TCBPA, and TBBPA) in beverage and canned food samples based on MIP-SPE with LC−MS/MS analysis. The high selectivity of MIP-SPE was compared with the selectivity of the traditional HLB SPE cartridge. In addition, the validated method was used to determine the target compound concentrations in beverage and canned food samples that were collected from a supermarket in Beijing. To our knowledge, this is the first study in which seven bisphenols were included together as target compounds in the development of an analytical method based on MIP-SPE for analyzing foodstuffs.

MATERIALS AND METHODS

Reagents and Chemicals. For this experiment, BPS (purity >98%), BPF (purity >99%), BPA (purity 98.5%), BPA-d_4 (purity >97.8%), BPB (purity >98%), and BPAF (purity 98%) were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). BPF-d_{10} and BPS-$^{13}C_{12}$ (purity >99%) were purchased from Toronto Research Chemical Inc. (Ontario, Canada), and BPAF-d_4 was purchased from CDN Isotopes Inc. (Quebec, Canada). TCBPA (purity >99%), TCBPA-$^{13}C_{12}$ (purity >99%), TBBPA (purity >99%), and TBBPA-$^{13}C_{12}$ (purity >99%) were obtained from Cambridge Isotope Laboratories Inc. (Andover, MA). In addition, water, acetonitrile (MeCN, water <0.01%), and methanol (MeOH, water <0.01%) were purchased from Sigma−Aldrich (LC−MS-grade, St. Louis, MO). Furthermore, the formic acid and ammonium hydroxide for analysis (28−30 wt % solution of NH_3 in water) were supplied by Acros Organics (Morris Plains, NJ). The molecularly imprinted polymers (product code AFFINIMIP SPE bisphenol A cartridges) were provided by Polyintell (Val de Reuil, France). Oasis HLB cartridges (200 mg, 6 mL) were purchased from Waters (Milford, MA), and the stock standard solutions (1000 mg/L) were individually prepared by dissolving in MeOH and were stored at −20 °C. Working solutions were prepared by serial dilution of stock solutions with MeOH/water (50:50 v/v).

Sample Collection. Fourteen beverage samples [7 pairs; in each pair one is packed in cans and another in poly(ethylene terephthalate) (PET) or Tetra Pak] and four canned foods from different brands, commonly consumed by the local population, were purchased from a supermarket in Beijing, China. They contained soda, tea drink, juice, vegetable, and meat. Purchasing of the samples was carried out in February 2014. All samples were stored at room temperature and opened only at the moment of analysis.

Sample Preparation and Solid-Phase Extraction Procedure. After the samples had been opened, the carbonated beverage samples were degassed by sonication for 30 min to form the loading solution for SPE procedures. Juice and milk samples were centrifuged at 9000g for 5 min to avoid blocking of the cartridges. Regarding the canned food, a total of 1 g of each homogenized sample was added to 5 mL of MeCN for extraction. Following sonication for 20 min, the mixtures were centrifuged at 9000g for 5 min, and the supernatants were collected. Subsequently, 5 mL of hexane was added to remove the fat by liquid−liquid extraction. The MeCN layer was collected and evaporated to 1 mL under a gentle nitrogen stream, which was diluted to 10 mL with LC−MS-grade water to form the loading solution.

A diagram of the MIP-SPE procedure is shown in Figure 1. Briefly, the pretreated loading solutions were loaded onto the MIP-SPE

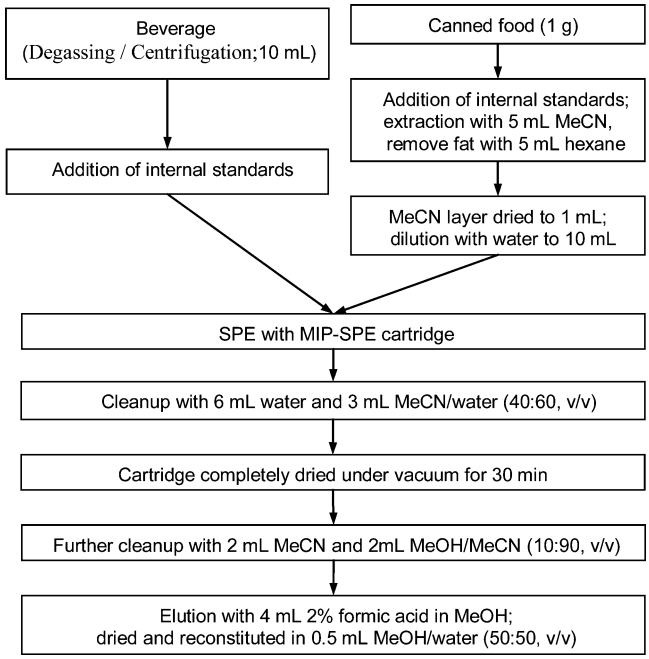

Figure 1. Diagram of MIP-SPE procedure for analysis of target BPs in beverage and canned food.

cartridges at a flow rate of 1 mL/min. The MIP-SPE cartridges had been previously conditioned with 3 mL of MeOH, 3 mL of MeCN, and 3 mL of water. After the loading step, the sorbents were cleaned up with water and MeCN/water (40:60 v/v). Next, the sorbents were completely dried and further washed with MeCN and MeOH/MeCN (10:90 v/v). After elution, the eluates were evaporated to dryness and the residues were reconstructed in 500 μL of a MeOH/water (50:50 v/v) solution for LC−MS analysis.

The protocol for HLB cartridges was conducted according to our previous report.[29] Briefly, the HLB cartridges were conditioned with 6 mL of MeOH and 6 mL of water. After loading of the samples, the cartridges were washed with 6 mL of MeOH/water (50:50 v/v) to remove interference. In addition, the extracts were eluted with 6 mL of 2% ammonia in 100% MeOH. The eluates were evaporated and reconstructed in 500 μL of a MeOH/water (50:50 v/v) mixture before LC−MS analysis.

LC−MS Analysis. The target analytes were separated with an Acquity ultraperformance liquid chromatography system (Waters, Milford, MA). The analytical column was an Acquity ethylene bridged hybrid (BEH) C18 column (2.1 mm × 100 mm; 1.7 μm; Waters). The mobile phase consisted of a MeOH−water isocratic mixture (40:60 v/v), which was held for 1 min, and a linear gradient from 40% to 80% MeOH that was held for 5 min. The MeOH content was increased to 100% at 6.1 min, held for 2.0 min, and returned to the initial conditions for equilibration. The flow rate was 0.3 mL/min and the injection volume was 5 μL.

A Xevo TQ-S triple-quadrupole mass spectrometer (Waters, Milford, MA) was used to determine the analyte concentrations. The MS/MS acquisition was operated in negative-ion mode with multiple reaction monitoring (MRM). The source operating conditions were as follows: a capillary voltage of 2.9 kV; source and desolvation temperatures of 150 and 400 °C, respectively; and a desolvation gas flow rate of 1000 L/h. For each analyte, identification was based on the retention time of the quantification and conformation ions. The corresponding cone voltage and collision energies were optimized for maximum intensity (see Supporting Information for optimized MS/MS parameters).

Method Validation. Three types of foodstuffs (orange juice, red wine, and canned fish) were used to evaluate the analytical characteristics of the procedure based on the use of MIP-SPE as a selective sorbent prior to chromatographic analysis. This method was evaluated in terms of linearity, accuracy, precision, and sensitivity. In the present study, isotopic internal standards were employed to compensate for the matrix effects and the loss during analysis. Calibration curves were constructed by plotting the peak area ratios of the pure analytes to the internal standards against the analyte concentrations (linearity ranges for BPF, BPB, and TBBPA were 0.2, 0.5, 1, 2, 5, 10, and 20 ng/mL; for BPA and TCBPA, 0.1, 0.25, 0.5, 1, 2.5, 5, and 10 ng/mL; and for BPS and BPAF, 0.02, 0.05, 0.1, 0.2, 0.5, 1, and 2 ng/mL). BPA-d_4 was selected as an internal standard for BPB because no commercially labeled standards are available. For assessment of accuracy and precision, the whole MIP-SPE procedures were applied to orange juice, red wine, and canned fish samples spiked with seven BPs at three fortification levels. Analyses of six replicates were conducted to evaluate the precision of the method (expressed as the relative standard deviation, RSD %) and to evaluate the accuracy (expressed as absolute recovery).

The limits of quantification (LOQ) and the limits of detection (LOD), through the proposed method, were determined on the basis of the signal-to-noise (S/N) ratio of the actual analyte peak and the baseline close to the peak. This procedure was performed by successive analyses of spiked noncontaminated samples with decreasing amounts of the analytes until an S/N ratio of 10:1 (LOQ) or 3:1 (LOD) was reached.[13,15] LOQ of BPA in canned food could not be measured because of high background levels in all of these samples, and the corresponding LOQ was estimated by BPA-d_4 in the present study.

Quality Assurance and Quality Control (QA/QC). Different authors have reviewed the challenge of accurately detecting BPA at ultralow concentrations.[18,30] Background contamination can easily occur at trace levels because the target analytes are inherently ubiquitous in the laboratory environment. In this study, heat-treated glassware, LC−MS-grade solvents, and solvent-washed materials were used to prevent background contamination. In addition, one key problem associated with the development of an MIP-SPE method occurs because the residual template is not completely removed from the polymeric matrix and leaking occurs during the SPE procedure, which results in a false-positive result when the same molecule is used as the template. The template of the MIP sorbent that was used in this experiment is a dummy template that was synthesized commercially and contains two aromatic rings that are similar to BPA, one of which is a phenol. The template is removed by thoroughly washing and does not interfere with the target analytes. Furthermore, a procedural blank containing LC−MS water in place of the foodstuff samples was subjected to the same extraction protocol as the actual samples and was analyzed to evaluate the contamination levels for the entire procedure. Only trace levels of BPA (S/N < 5) and BPS (S/N < 2) were found in the procedural blank (see Supporting Information). The corresponding peak areas were deducted from the analysis results. Quantification was based on the internal calibration curves constructed by injection of seven calibration standards. A midpoint calibration standard was injected to check instrumental drift in sensitivity, and pure MeOH was injected to monitor sample carryover after every 10th sample analysis.

RESULTS AND DISCUSSION

Development of the Molecularly Imprinted Polymer Solid-Phase Extraction Procedure. In this study, the MIP-SPE procedure was optimized on the basis of the manufacturer's instructions (AFFINIMIP SPE bisphenol A cartridges) to develop an MIP-SPE method that was suitable for simultaneous extraction of related BP analogues in beverage and canned food samples. First, the loading solutions were kept in an aqueous environment with less than 10% organic solvent, which resulted in complete retention of the analytes on the MIP-SPE through nonspecific interactions, such as hydrophobic or ion-exchange interactions. For the washing step, 6 mL of pure water was used to eliminate salts and hydrophilic interference. Next, 3 mL aliquots of the different MeCN/water solvent compositions (40:60, 50:50, and 60:40 v/v) were assessed to select a suitable solvent for removing the nonselectively bound polar matrix interference. A washing solvent consisting of 3 mL of MeCN/water (40:60 v/v) was optimal for cleaning and did not compromise recovery of the analytes.

To enable the polymer to selectively interact with the analytes, a complete drying step was necessary for the sorbents to shift from the aqueous to the nonaqueous washing step. After the drying step, 2 mL of MeCN (a polar nonprotic solvent) was used to induce the formation of specific interactions through hydrogen bonds between the analytes and the MIP monomers. Next, 2 mL of a MeOH/MeCN (10:90 v/v) mixture was applied to the cartridges to elute nonspecifically bound apolar matrix interference. As shown in Figure 2, recovery was closely associated with MeOH content

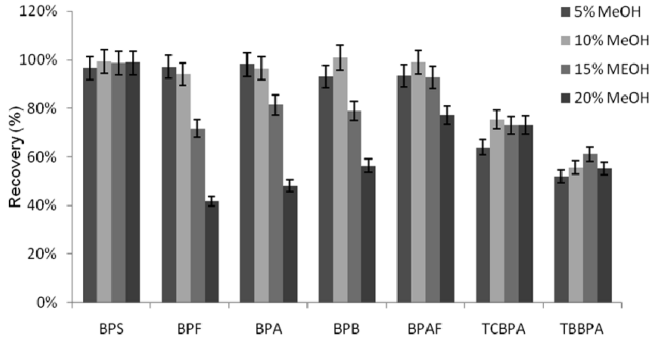

Figure 2. Comparison of analyte recoveries for use of different MeOH concentrations in MeCN during the washing step (n = 3).

in the MeCN that was used in the washing step, and more than 10% MeOH in the MeCN resulted in significant losses of BPF, BPA, and BPB but not the other BPs. The presence of a higher portion of protic solvent, such as MeOH, would break the specific interactions, and these compounds with lower affinities for MIP were more easily removed during the washing step. When optimizing the elution conditions, we found that TCBPA and TBBPA were difficult to elute from the cartridge when 100% MeOH was used as the solvent. The desorption of these two compounds was achieved by percolating 100% MeOH with the addition of 2% formic acid, which was effective for disrupting the interactions between analytes and sorbents and for obtaining satisfactory recoveries.

During the SPE process, breakthrough potentially occurred due to the large loading sample volume or the high analyte concentration, which would decrease the recovery of the

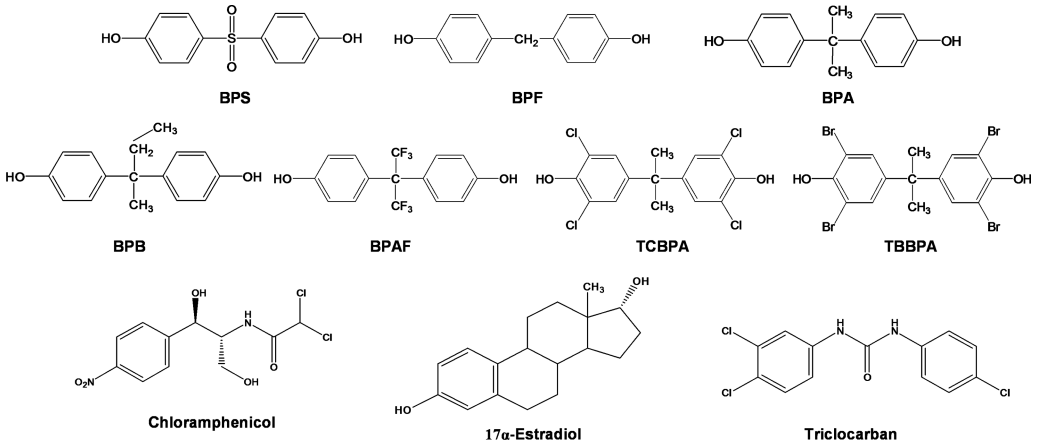

Figure 3. Structures of the seven analytes and the other three compounds used in selectivity binding tests.

method. Therefore, the breakthrough was assessed by extracting spiked orange juice (BPF, BPB, and TBBPA, 0.5 ng/mL; BPA and TCBPA, 0.25 ng/mL; BPS and BPAF, 0.05 ng/mL) with different sample loading volumes (5, 10, 20, 40, and 80 mL). No breakthrough occurred in these tests, and all analytes maintained a stable recovery as the sample volume increased from 5 to 80 mL, which indicated the preconcentration potential of the MIP-SPE. In this study, a 10 mL sample volume was selected because lower preconcentration times were needed, lower matrix interferences were introduced, and the sensitivity was sufficient for routine analysis.

Selectivity of Molecularly Imprinted Polymer Solid-Phase Extraction. To evaluate the selectivity of the MIP-SPE method, a comparison with the hydrophobic−lipophilic balance (Oasis HLB) SPE cartridge, which is one of the most widely employed reverse-phase cartridges for determining BPA concentrations in foodstuffs,[31−33] was conducted. The group-selective potential of the MIP-SPE procedure was tested by spiking the water with analytes and three other compounds (chloramphenicol, 17α-estradiol, and triclocarban) belonging to the same range of polarity as the target analytes (Figure 3). The results obtained by the MIP-SPE procedure were compared with those obtained by the Oasis HLB. As shown in Figure 4, less than 10% of the chloramphenicol was retained by the MIP-SPE cartridge because its chemical structure shared less similarity with the bisphenols and was removed by the washing step. In addition, the lack of retention for triclocarban on the MIP-SPE was observed in the test even if it was a more hydrophobic compound. However, 17α-estradiol was an exception to this behavior; it presented an extraction recovery of approximately 50% on the MIP-SPE cartridge. This recovery is explained by the similar arrangement of phenolic hydroxyl groups to the BP analogues. In contrast, the HLB was expected to be less selective than MIP-SPE because all of the compounds with a wide range of polarities were well retained after the loading and rinsing steps.

On the basis of the comparison above, it was shown that the presence of cavities in the MIP occurred. However, this result was not sufficient for demonstrating the real selectivity of the MIP for its application to real samples. Optimal selectivity necessitates the presence of a cleaner baseline or less matrix suppression for real sample analysis. In this study, two types of matrices (orange juice and canned fish) were spiked at the same concentrations and were passed through the MIP-SPE and HLB cartridges for analysis. After extraction and purification by

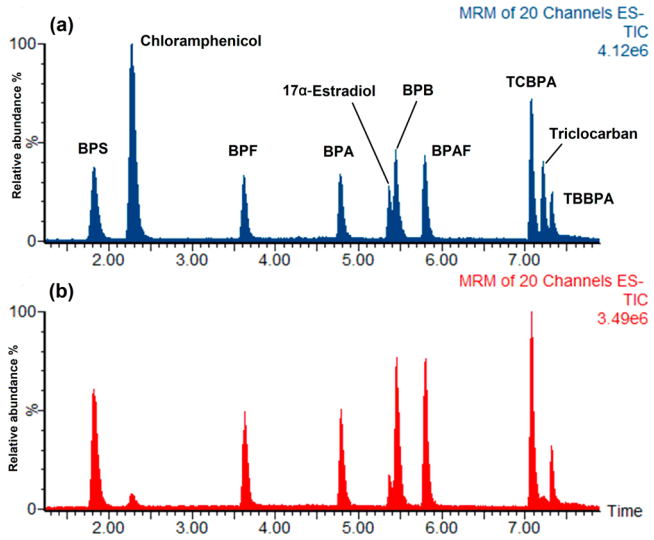

Figure 4. Chromatograms obtained from selectivity tests between (a) Oasis HLB and (b) MIP-SPE. The lack of chloramphenicol, 17α-estradiol, and triclocarban retention on MIP demonstrates the selectivity of the extraction procedure on MIP-SPE.

the MIP-SPE and HLB cartridges, the chromatograms that corresponded to each analyte are shown in Figure 5. Using the MIP-SPE instead of the Oasis HLB for the extraction and purification process resulted in a cleaner baseline and in less matrix suppression for most of the analytes. In addition, another advantage of MIP-SPE is its ability to remove the majority of the pigment from the sample matrix to obtain cleaner extracts (see Supporting Information).

Validation of Molecularly Imprinted Polymer Solid-Phase Extraction Method. The calibration curves were constructed from the peak area ratio of the analyte to the internal standards (BPA-d_4, TCBPA-$^{13}C_{12}$, TBBPA-$^{13}C_{12}$, and BPF-d_{10}, 5 ng/mL; BPS-$^{13}C_{12}$ and BPAF-d_4, 0.5 ng/mL) versus the analyte concentrations and were linear with a correlation coefficient of >0.99 in the concentration ranges evaluated. Table 1 illustrates the recoveries and the RSDs of the analytes in the spiked orange juice, red wine, and canned fish. The results showed that the recoveries were in the 50−103% range, with RSD values of less than 15% for all of the analytes. The LOQ, obtained after the MIP-SPE procedures of 10 mL beverage samples or 1 g canned food samples, varied from 0.002 to 0.15 ng/mL in the beverage samples and from 0.03 to

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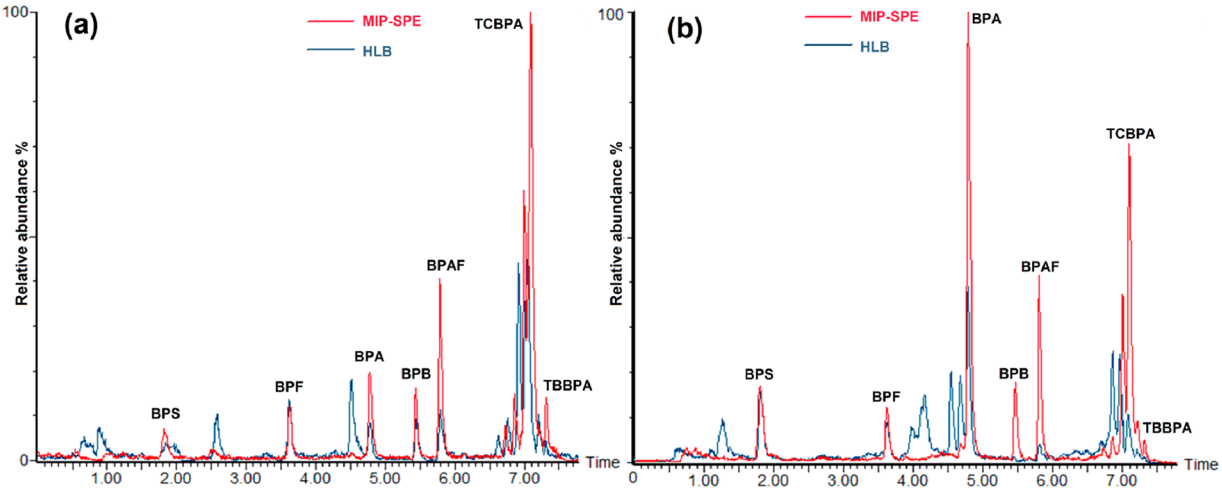

Figure 5. Comparison of purification performance of Oasis HLB and MIP-SPE for (a) spiked orange juice and (b) spiked canned fish samples. Samples were spiked with 2.5 ng of BPF, BPB, and TBBPA; 1.25 ng of BPA and TCBPA; and 0.25 ng of BPS and BPAF.

Table 1. Recoveries, Relative Standard Deviations, and Limits of Quantification of Target Compounds in Food Samples (n = 6)

orange juice				red wine				canned fish			
spike (ng/mL)	recovery (%)	RSD (%)	LOQ (ng/mL)	spike (ng/mL)	recovery (%)	RSD (%)	LOQ (ng/mL)	spike (ng/g)	recovery (%)	RSD (%)	LOQ (ng/g)
Bisphenol S											
0.005	82	9	0.006	0.005	88	13	0.007	0.1	73	3	0.07
0.02	100	6		0.02	78	11		0.2	80	9	
0.05	98	5		0.05	87	8		0.5	82	4	
Bisphenol F											
0.05	82	7	0.054	0.05	78	9	0.029	1	78	10	0.5
0.2	82	8		0.2	96	4		2	74	3	
0.5	82	4		0.5	81	6		5	73	6	
Bisphenol A											
0.025	86	9	0.013	0.025	95	6	0.01	0.5	81	14	0.12
0.1	91	7		0.1	99	5		1	88	6	
0.25	92	4		0.25	99	5		2.5	89	8	
Bisphenol B											
0.05	83	8	0.15	0.05	86	9	0.04	1	79	9	1.5
0.2	93	9		0.2	97	5		2	80	12	
0.5	92	9		0.5	92	5		5	82	3	
Bisphenol AF											
0.005	93	10	0.003	0.005	91	6	0.002	0.1	81	9	0.03
0.02	85	4		0.02	89	5		0.2	79	7	
0.05	103	6		0.05	98	4		0.5	79	3	
Tetrachlorobisphenol A											
0.025	68	8	0.005	0.025	82	11	0.005	0.5	72	15	0.28
0.1	73	5		0.1	72	2		1	74	11	
0.25	84	4		0.25	76	4		2.5	78	9	
Tetrabromobisphenol A											
0.05	50	10	0.012	0.05	60	12	0.032	1	57	14	0.6
0.2	53	5		0.2	65	7		2	61	11	
0.5	61	10		0.5	63	5		5	67	8	

1.5 ng/g in the canned food samples. These results provided lower LOQs for BPA and its analogues relative to the LOQs reported in previously published methods[33−37] (see Supporting Information for comparison with other methods).

Application of the Method. To demonstrate the applicability of the developed method, several beverage samples and canned foods were randomly purchased from local supermarkets in Beijing. Figure 6 shows the typical LC−MS/MS chromatograms that corresponded to canned pork luncheon meat, in which BPS, BPF, and BPA were detected. The analyte concentrations are summarized in Table 2. BPB, TCBPA, and TBBPA were not detected in any of the samples, and the concentrations of the other BPs in the beverage products were generally low. BPA and BPF were the most frequently detected BPs in the beverage samples and varied from ND to 12 ng/mL and from ND to 0.39 ng/mL, respectively. These levels are similar to the levels that were observed in beverages by Geens et al.[33] (BPA, <LOQ−8.1 ng/

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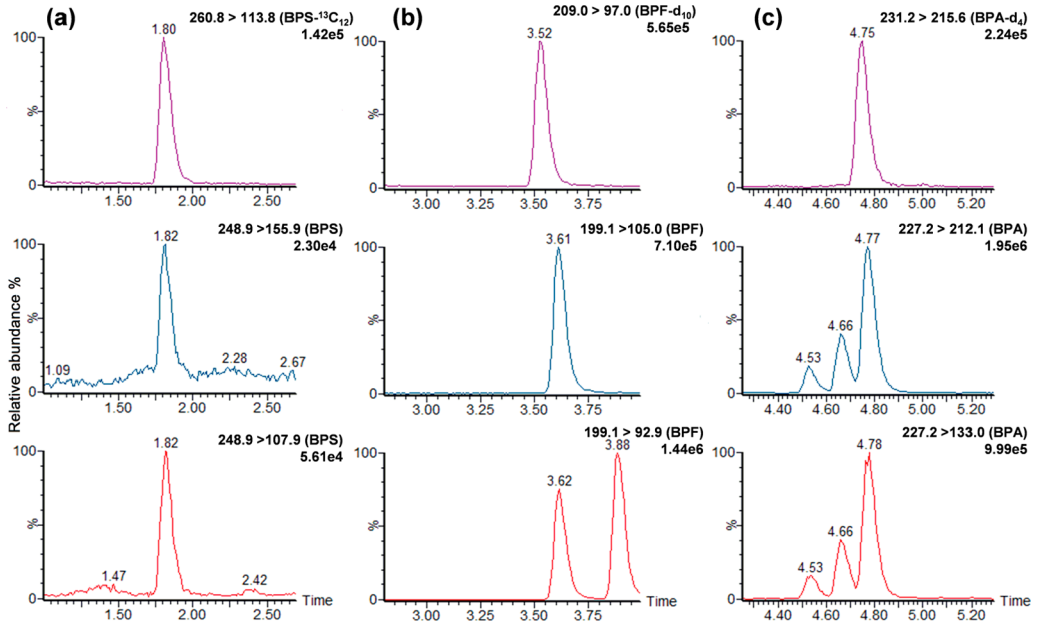

Figure 6. Typical LC−MS/MS chromatograms obtained from a canned pork luncheon meat sample: (a) BPS (0.22 ng/g), (b) BPF (35 ng/g), and (c) BPA (30 ng/g) were detected.

Table 2. Concentrations of Bisphenols in Beverage and Canned Food Samples[a]

Beverages					
		concn (ng/mL)			
volume (mL)	packaging type	BPS	BPF	BPA	BPAF
Soda (lemon flavored)					
600	PET	ND	ND	ND	ND
330	can	ND	ND	0.063	ND
Soda (orange flavored)					
600	PET	ND	ND	ND	ND
330	can	ND	<LOQ	<LOQ	ND
Soda (apple flavored)					
600	PET	ND	ND	ND	ND
330	can	ND	<LOQ	0.083	ND
Tea Drinks					
600	PET	ND	ND	0.27	<LOQ
330	can	ND	<LOQ	9.7	ND
Vitamin Drinks					
600	PET	ND	ND	ND	ND
330	can	ND	<LOQ	0.067	ND
Coconut Juice					
245	Tetra Pak	0.036	ND	0.23	0.052
245	can	0.019	0.39	12	0.013
Milk					
125	Tetra Pak	ND	ND	0.019	ND
245	can	ND	0.36	8.8	ND

Canned Foods					
		concn (ng/g)			
sample	weight (g)	BPS	BPF	BPA	BPAF
corn (filling liquid)	425	ND	<LOQ	<LOQ	ND
corn (solid content)		0.26	4.3	6.5	0.070
pork luncheon meat	340	0.22	35	30	ND
fish (tuna)	185	<LOQ	ND	17	ND
fish (fried dace)	227	ND	2.2	58	ND

[a]BPB, TCBPA, and TBBPA were not detected in any of the samples.

mL), Cao et al.[34] (BPA, 0.032−4.5 ng/mL), Cacho et al.[14] (BPF, ND−0.26 ng/mL), and Gallart-Ayala et al.[35] (BPF: ND−0.22 ng/mL). Compared with BPA and BPF, less than 25% of the samples contained BPS and BPAF above the LOQ in the beverages, which indicated their minor use in food contact materials.

Influences of the packaging materials were evaluated by comparing the BP concentrations in seven paired beverage samples. The only difference in each pairs is that one was packed in cans and the other in PET or Tetra Pak. As shown in Table 2, beverages in the packing materials with PET or Tetra Pak had lower BPA and BPF contamination or detection rates relative to the same beverages packed in cans. This result indicated that the BPA and BPF in these types of foods primarily originated from the can's inner coating.

For the canned food samples, BPS, BPA and BPF concentrations were comparable to the BP concentrations that were recently reported for canned food[13,33,36,37](see Supporting Information) and were approximately 1 order of magnitude greater than those in the canned beverages. The higher concentrations in canned food most likely occurred because the chemicals preferred a more lipophilic environment than the aqueous phase or resulted from differences in sterilization conditions and coating types.[33]

In conclusion, the above-mentioned applications proved that this MIP-SPE method is a powerful method to make group-selective extraction and purification in a single step and provide cleaner extracts. The method offers many advantages such as high selectivity, low solvent consumption, and ease of use, which make it possible to replace traditional SPE methods for the analysis of bisphenol analogues in complex matrices.

■ ASSOCIATED CONTENT

Supporting Information

Three tables listing optimized MS/MS parameters, reported method parameters, and reported concentrations of BPs in beverage and canned food samples; two figures showing chromatograms of analytes in the procedural blank and

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comparison of final extracts from MIP-SPE and HLB cartridges. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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