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Direct enrichment and high performance liquid chromatography analysis of ultra-trace Bisphenol A in water samples with narrowly dispersible Bisphenol A imprinted polymeric microspheres column

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Abstract

Direct injection, enrichment and high performance liquid chromatography (HPLC) analysis of ultra-trace Bisphenol A (BPA) in water samples using one narrowly dispersible BPA imprinted polymeric microspheres (MIPM) column in one analysis process was developed. One BPA imprinted MIPM that had the best globular morphology and imprinted efficiency was used as HPLC stationary phase and applied to direct analysis of ultra-trace BPA in water. The optimum direct analysis conditions were: conditioning the MIPM column with water for 10 min, injecting 40 mL water sample directly, eluting with 70% methanol for 13 min and then 100% methanol for 7 min. Under the optimum conditions, the MIPM column can simultaneously extract, enrich, separate and determine ultra-trace BPA in one analysis process with UV detector by injection of large volume water samples (40 mL). The calibration graph was linear with $R^2 > 0.998$ in the ranges from 0.1–100 nmol/L BPA standard solution. The intra- and inter-day RSD are less than 9.5 and 9.6%, respectively. The limit of quantification was 0.1 nmol/L. RSD for spiked tap and lake water was less than 8.9% and the recoveries were 96–101.8%. The enrichment factor for BPA was 10,000 as 40 mL water sample was directly injected and analyzed.

Keywords: Molecularly imprinted polymeric microspheres; Bisphenol A; Direct chromatography analysis; Water samples

1. Introduction

Despite large advancement on highly sensitive analytical instruments for determination of analytes in environmental or biological samples, tedious sample pretreatment procedures are usually required to detect trace analytes. Solid-phase extraction (SPE) has become a routine sample pretreatment method. In order to overcome the low selectivity of routine SPE, immunosorbents (IS), a highly selective separation method using the special molecular recognition between antibody and antigen, is developed. Unfortunately antibody isolation is expensive, time-consuming, and easily denaturized in the presence of organic solvents, which limit the usage of IS on sample pretreatment.

Recently molecularly imprinted polymers (MIPs) have become interesting materials in trace analysis. MIPs are synthetic cross-linked polymers that possess specific cavities designed for a target molecule (template) [1,2]. MIPs can recognize and rebind the target analyte selectively as the antibody does, and present a number of advantages including easy preparation and high thermal and chemical stability [3,4]. Many reviews [5–9] and articles [9–19] about using MIPs as solid-phase extraction sorbents to extract and enrich analytes from different environmental and biological matrices have been reported. Some MIPs also have been used as stationary phase of high performance liquid chromatography (HPLC) to separate template and its structure analogs [16–24,27,28].

In most cases, molecularly imprinted solid-phase extraction (MISPE) is used off-line to chromatographic systems. Few applications [20–24] have been developed thus far as on-line mode. In on-line mode, a MIP column and an analytical column (normally a C18 silica column) connected by a

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column-switching system are coupled to a HPLC system. The MIP column is used as a pretreatment column to extract and enrich analytes from samples, while the analytical column is used to separate and quantify the analytes. Comparing with off-line mode, on-line mode has no sample manipulation between the pretreatment and analysis steps, therefore the risk of losing the analyte and contamination are reduced, consumption of organic solvents is lower, the limit of detection, reproducibility and the potential for automation are improved. However, a serious limitation of this on-line mode is that sorbents used in the pretreatment column and in the analytical column must be compatibility [25,26]. In addition, the column-switching system increases the complexity and dead volume of the HPLC system, and increases the analysis cost too. Nowadays, there are also reports [27,28] about using MIPs as HPLC stationary phase to separate and determine target analytes from complex matrices. Because MIPs can be used as enrichment sorbents as well as analytical sorbents, using one MIP column to simultaneously extract, enrich, separate and determine analytes in complex matrices in one analysis process will be an attractive work.

In this study, a fully simultaneous and direct analysis method for ultra-trace analytes in environmental water samples was established using one MIP column in the first time. First the MIPs were synthesized and packed into a HPLC column. Then large volume water samples (40 mL) were directly injected into the column. Due to the highly selective binding characteristics of MIPs, target analyte and its analogues were retained on the column, while a large amount of other interferences in the water were washed away with the injected solution running through the column. Therefore, the analyte and its analogues were extracted from the water and enriched in the column. Later, optimum HPLC conditions were used to separate the target analyte from its analogues and quantify it. Under the optimum conditions, ultra-trace analyte in different water samples can be simultaneously extracted, enriched, separated, determined and quantitated in one analysis process using one MIPs column and UV detector. Bisphenol A (BPA) was chosen as the target analyte in this study because it is an endocrine disrupter widely presented in environment at ultra-trace concentration and methods for its determination are tedious [29–33].

2. Experimental

2.1. Reagents and standards

Bisphenol A, Bisphenol C, diethylstilbestrol, phenol, *p*-nitrophenol, hexoestrol, 4-vinylpyridine (4-VP), and trimethylolpropane trimethacrylate (TRIM) were purchased from Sigma (St. Louis, MO). Azobisisobutyronitrile (AIBN, analytical grade), toluene (analytical grade), methanol (HPLC-grade), acetonitrile (HPLC-grade) and acetic acid (analytical grade) were obtained from Shanghai chemical reagent company (Shanghai, China). 4-VP and TRIM were purified prior to use via general distillation methods in vacuo under argon protection to remove the polymerization inhibitor. The AIBN was recrystallized from methanol and then dried at room temperature in vacuum prior to use. Toluene was distilled before use. Fig. 1 showed the molecular structures of the chemicals used.

Distilled water was quadruplicate. Tap water was collected from Zongguan waterworks (Wuhan, China). Lake water was collected from Xibeihu Lake (Wuhan, China). Tap water and lake water were filtered through a 0.22 um filter before use.

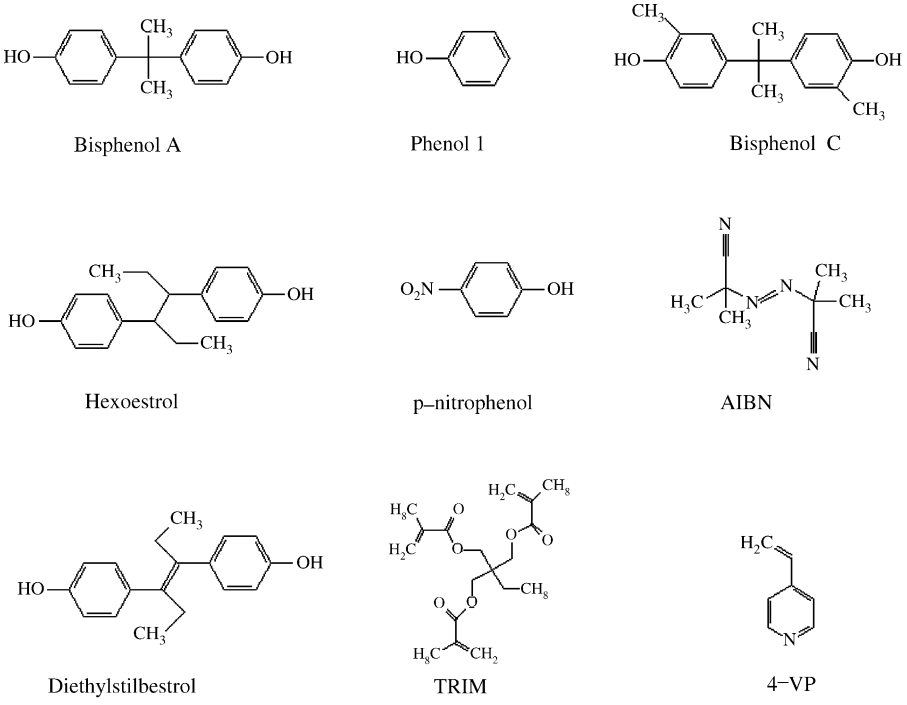

Fig. 1. Names and structures of chemicals used in this study.

Table 1
The preparation conditions, equilibrium dissociation constant (K_d), maximum number of binding sites (B_{max}), surface area and pore characters of MIPM and nMIPM in this study

Polymer	Amount of BPA (mmol)	Acetonitrile (%)	$K_d \times 10^{-5}$ (mol/L)	$B_{max} \times 10^{-2}$ (mmol/g)	N_2 adsorption		
					Surface area (BET) (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)
MIPM 1	0.5	100	1.10	0.801	5.81	0.0056	43.1
MIPM 2	0.5	95					
MIPM 3	0.5	90					
MIPM 4	1	100	0.95	1.050	5.73	0.0051	40.8
MIPM 5	3	100	0.93	0.1208	5.92	0.0062	45.2
MIPM 6	6	100	0.90	1.370	5.43	0.0043	42.6
MIPM 7	8	100	0.88	1.373	5.85	0.0053	42.1
nMIPM	0	100	1.20	0.752	5.76	0.0058	39.2

2.2. Synthesis of the imprinted polymers

BPA imprinted MIPMs as well as non-imprinted polymeric microspheres (nMIPM) were prepared by precipitation polymerization. Table 1 showed the molar amounts of template molecule and porogen used for the preparation of MIPMs and nMIPM in this study. For a general polymerizing procedure, template BPA, monomer 4-VP (6.0 mmol), cross-linker TRIM (12 mmol) and free-radical initiator AIBN (40 mg) were dissolved in 250 mL porogen in a 500 mL round-bottomed flask. The solution was degassed in an ultrasonic bath for 5 min then sparged with oxygen-free nitrogen for 10 min. The flask was then attached to the rotor-arm and rotated slowly (about 50 rpm). The polymerization was induced by heat irradiation at 65 °C for 24 h. After centrifugation, the microspheres were extracted using a Soxhlet apparatus in methanol–acetic acid 9:1 (v/v) for 24 h to remove the template. Then the microspheres were washed by acetonitrile for five times and dried in vacuo overnight at 25 °C. nMIPM were prepared under identical conditions except that the template was omitted.

2.3. Morphology observation

The surface morphology of the particles was observed using a FEI Sirion 200 ultra-high resolution Schottky field emission scanning electron microscope (FESEM). All samples were sputter-coated with gold before FESEM analysis. Pore volumes and surface area were determined by nitrogen adsorption on ASAP 2020M system (Micromeritics,USA).

2.4. Rebinding test

20 mg polymers were shaken with 0.1–0.5 mM BPA acetonitrile solutions at 25 °C for 24 h. BPA in the supernatants (free BPA) were determined by HPLC. Scatchard plot was constructed by plotting the ratio of the adsorbed BPA (B) to the free BPA (free) against the adsorbed BPA (B). K_d (the equilibrium dissociation constant) and B_{max} (the maximum number of binding sites) were decided according to Scatchard plot and the Scatchard equation: $B/[\text{Free}] = -(B/K_d) + (B_{max}/K_d)$.

HPLC analyses were performed using a VARIAN PROSTAR 230 (USA) HPLC system with UV variable wavelength detector operating at 281 nm. The injection volume was 10 μL. Separations were carried out on a 250 mm × 4.6 mm, 5 μm Waters C18 column at 25 °C. The mobile phase was a mixture of acetonitrile–H_2O–acetic acid (50:47:3) and the flow rate was maintained at 1 mL/min. For BPA, the calibration graph was linear in the ranges from 0.001–0.25 mmol/L with $R^2 = 0.9998$. The limit of detection (LOD) (a signal-to-noise ratio of three) was 0.1 umol/L. The limit of quantification (LOQ) was 1 umol/L.

2.5. Selectivity evaluation

The MIPMs were packed into a 50 mm × 4.6 mm stainless-steel column by a slurry packing technique and then coupled to the HPLC system mentioned above. 10 uL BPA solution (0.2 mmol/L in acetonitrile) was injected into the MIPM column. Methanol was used as mobile phase. The flow rate was 1 mL/min. The backpressure for nMIPM, MIPM1, MIPM4-7 was 28, 32, 30, 31, 30, 33 atm, respectively. Each sample was analyzed in triplicate. The imprinting factor was defined as $I = k_{mip}/k_{nmip}$, where k_{mip} and k_{nmip} are the capacity factors of BPA on the imprinted and non-imprinted polymers, respectively [34].

2.6. Optimized BPA separation conditions in MIPM column

Ten microliters mixed BPA and its analogues solution (0.2 mmol/L each in acetonitrile) was injected into the MIPM6 and nMIPM column. Mobile phase was optimized through using different percentage of methanol in water in order to find the optimum BPA separation conditions in MIPM column. The flow rate was 1 mL/min. Each sample was analyzed in triplicate.

2.7. Direct analysis of BPA in water samples by MIPM6 column

The MIPM6 and nMIPM column was first conditioned with distilled water for 10 min before used. Then 40 mL blank or spiked water sample was injected into the column by a HPLC pump and the optimum HPLC conditions established in 2.6 were used to separate, determine and quantitate BPA. All samples were analyzed in quintuplicate.

2.8. Validation of the BPA peak

Under the same protocol in 2.7, 2 mL efflux corresponding to BPA peak (56–58 min) in blank lake water samples was collected. This collection was repeated five times. Totally 10 mL collected efflux was dry under N_2 stream. The resident was redissolved in 20 uL acetonitrile and was analyzed by HPLC using C18 column under the HPLC condition mentioned in Section 2.4.

3. Results and discussion

3.1. Preparation of MIPMs

Difference ratio of acetonitrile and toluene (Table 1) was chosen as porogen. Particles prepared in pure acetonitrile (MIPM1) (Fig. 2(A)) were globular and narrowly dispersible. As the percentage of acetonitrile decrease from 100 to 90%, the particles' shape changed from globular to irregular and the dispersivity increased (Fig. 2(A–C)). Regular shape of imprinted particles is advantageous in chromatographic applications, and can facilitate system homogenization and mass transfer in ligand rebinding processes. Therefore, acetonitrile was chosen as porogen in the following study.

Table 2
Retention time, capacity factor and imprinted factor for the nMIPM and MIPMs

Polymer	Retention time	k'	I
nMIPM	1.02	1.04	
MIPM 1	1.11	1.2	1.15
MIPM 4	2.60	4.2	4.03
MIPM 5	3.32	5.6	5.38
MIPM 6	3.89	6.8	6.53
MIPM 7	4.01	7.0	6.73

To examine the effects of the amount of template on the performance of MIPMs, different amount of template was used in the preparation. As the morphological and pore characters of MIPM1, MIPM4, MIP5, MIP6, MIPM7 and nMIPM were similar (Table 1). The binding isotherms (Fig. 3(a)) and B_{max} (Table 1) were carried out to evaluate binding capability, and the capacity factor (k) and imprinting factor (I) (Table 2) were used

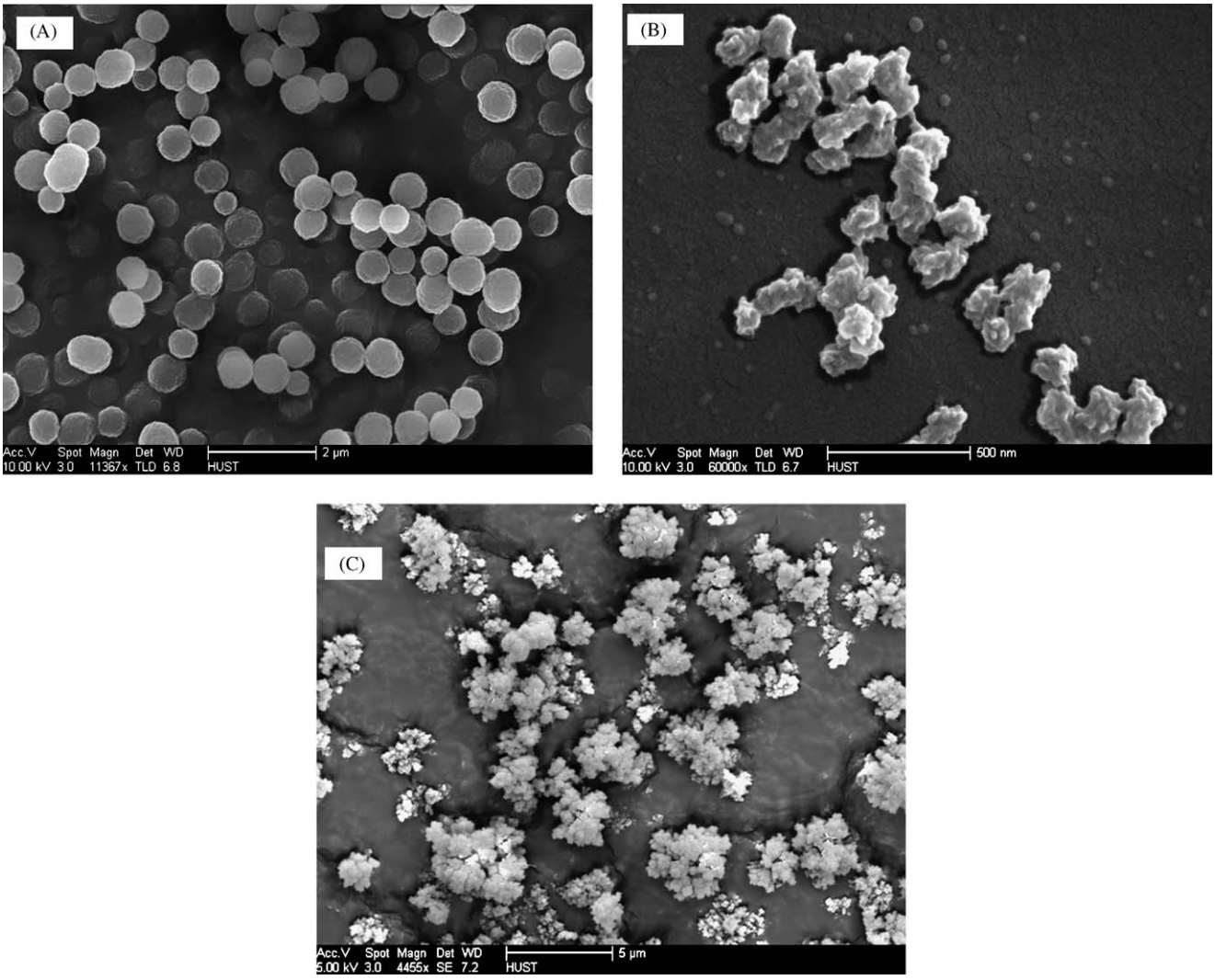

Fig. 2. Scanning electron micrographs of particles prepared in (a) 100%, (b) 95% and (c) 90% acetonitrile.

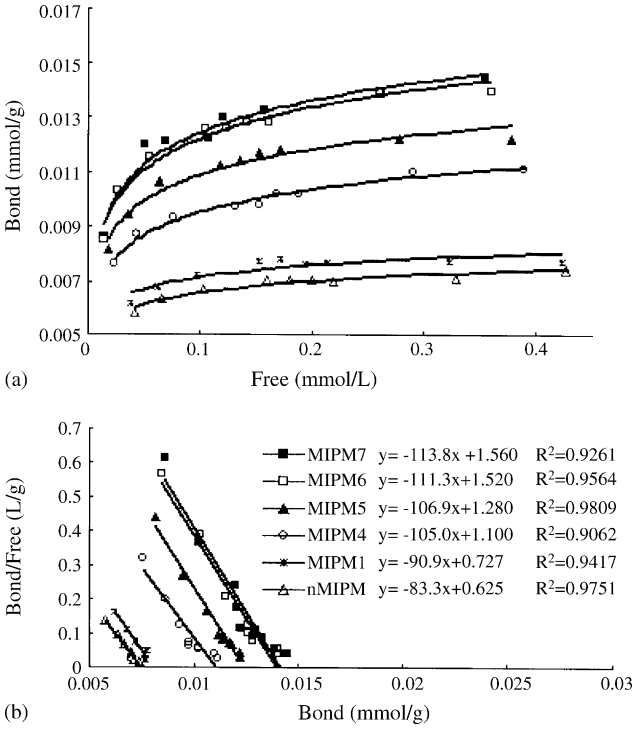

Fig. 3. The binding isotherms (a) and the Scatchard plot (b) of MIPMs and nMIPM.

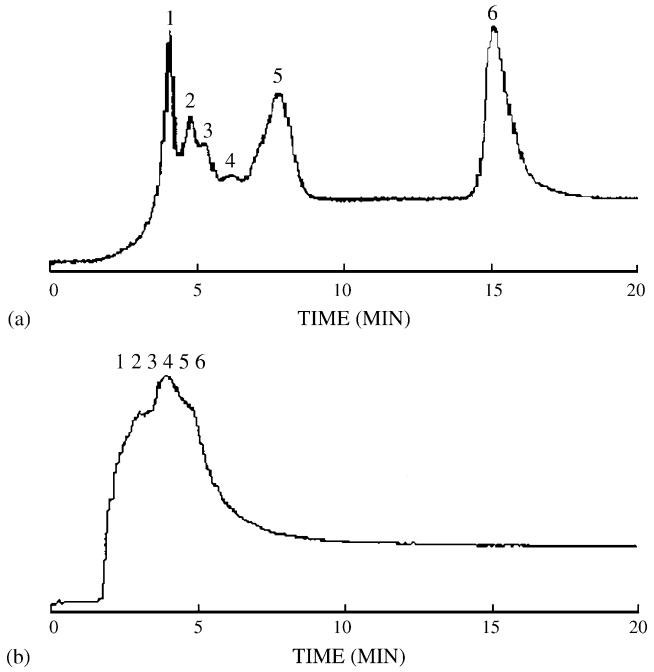

Fig. 4. Chromatograms obtained by using 70% methanol for 13 min then 100% methanol for 7 min as mobile phase. (a) MIPM6 column, (b) nMIPM column. (1) Phenol, (2) *p*-nitrophenol, (3) diethylstilbestrol, (4) hexoestrol, (5) Bisphenol C, and (6) Bisphenol A HPLC conditions: flow rate: 1 mL/min; injection volume, 10 uL; analysts' concentrations: 0.2 mmol/L each in acetonitrile.

to evaluate binding selectivity. It was clear that the binding capability and binding selectivity increased as the amount of template used increased. This may because that in precipitation polymerization excess porogen (typically 95% of the total reaction volume) was used in order to synthesize uniform MIP microspheres [35,36]. Therefore, much of the template dissolves in the porogen instead of reacting with the functional monomers to form pre-polymerization complex. Increase the amount of template would increase the formation of pre-polymeriztion complex and the imprinted efficiency. Compared with other MIPMs, MIPM6 had almost the highest binding capability and selectivity like MIPM7, but was prepared with less amount of template. Therefore, MIPM6 was selected for the following research in this study.

3.2. Optimized BPA separation condition using MIPM6 column

In order to examine the workability of MIPM6 to separate BPA from its analogues, MIPM6 and nMIPM were initially washed with methanol to verify that there was no residual template presented. Then 10 uL mixed BPA and its analogues solution (0.2 mmol/L each in acetonitrile) was injected into the columns, respectively. When distilled water was used as mobile phase, none of the analytes can be eluted within 40 min. This confirmed that under aqueous conditions the analytes primarily interacted with MIPM6 and nMIPM by hydrophobic interactions (non-specific interactions) [37].

In order to facilitate selective analytes isolation, a "molecular recognition step" is necessary in the separation procedure [38–40]. Methanol was then used as mobile phase to elute the analytes. Although BPA had the highest retention time when using methanol as mobile phase, the separation efficiency was unsatisfied. Then 80% and 70% percentage of methanol in water were used as mobile phase, respectively. Results showed that as the percentage of methanol decrease, the separation efficiency increased. Seventy percent methanol can completely separated BPA from its analogues, but the peak of BPA was broad. So 70% methanol for the first 13 min and then 100% methanol for 7 min were used as mobile phase. Suitable separation efficiency was achieved (Fig. 4(a)). Therefore, 70% methanol for the first 13 min and then 100% methanol for 7 min were used as the optimum HPLC assay protocol (Fig. 5). Under the same optimum HPLC conditions, nMIPM column could not separate BPA from its analogues (Fig. 4(b)). Only MIPM6 can selectively extract and efficiently determine BPA.

3.3. Direct injection, enrichment and HPLC analysis of ultra-trace BPA and the analytical characteristics of this method

In order to establish a direct HPLC analysis method for ultra-trace BPA, 40 mL standard solution contained BPA and its analogues (10 nmol/L each) and 40 mL blank distilled water were analyzed using MIPM6 and nMIPM, respectively, according to the established direct analysis protocol (Fig. 5). When 40 mL blank distilled water was analyzed, no obvious peak appeared in either MIPM6 or nMIPM column, demonstrating that no leakage of BPA was detected in this assay. No obvious peak detected during the injection of 40 mL standard solution demonstrated in that BPA and its analogues were extracted and

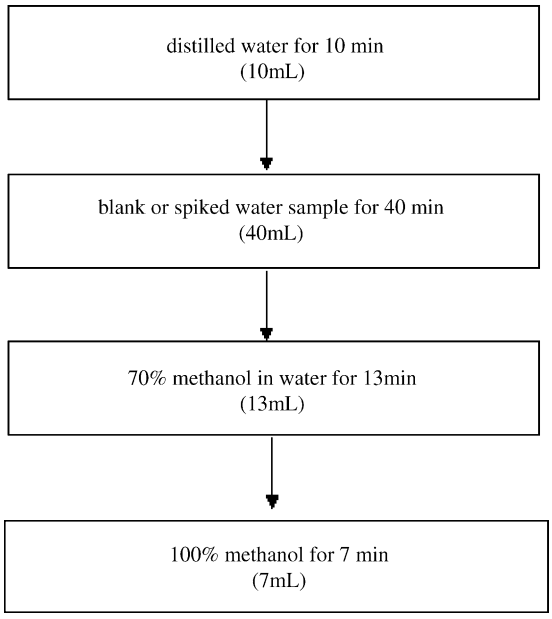

Fig. 5. The entire developed direct analysis protocol.

retained. Then the optimum HPLC protocol was applied to the columns. Chromatograms of MIPM6 (Fig. 6(a)) confirmed that the enrichment, separation and analysis efficiency of MIPM6 were obvious. But chromatograms of nMIPM (Fig. 6(b)) showed that nMIPM could not separate BPA and its analogues. Furthermore, as the total eluted peak area of BPA and its analogues was smaller than that of MIPM6, it was clear that only partial of BPA and its analogues were retained and eluted in nMIPM.

To check the intra- and inter-day linear range, repeatability, LOQ and LOD of this method, 40 mL 0.01–100 nmol/L standard solution was applied repeatedly ($n = 5$) to MIPM6. Results showed that in the concentration range of 0.1–100 nmol/L, the intra-day RSD is less than 9.5%, and the inter-day RSD is less than 9.6%. The established direct trace BPA analysis method was reproducible. A linear calibration curve in the concentration range of 0.1–100 nmol/L, constructed from peak area (y) versus BPA concentration (x), was $y = 276501x + 102466$, $r^2 = 0.9983$. The LOD (a signal-to-noise ratio of three) was 0.03 nmol/L. The LOQ was 0.1 nmol/L. As the LOQ for C18 column in routine injection volume (10 uL) was 1 umol/L, the enrichment factor for MIPM6 was 10,000 for BPA as 40 mL of water sample was directly injected and analyzed.

3.4. Determination of ultra-trace BPA in environmental water samples

Both blank and spiked tap water (Fig. 7(a)) and lake water (Fig. 7(b)) were analyzed (five times) with the established protocol (Fig. 5) for ultra-trace BPA. Result showed that trace BPA in complex matrices can be enriched, separated, determined and

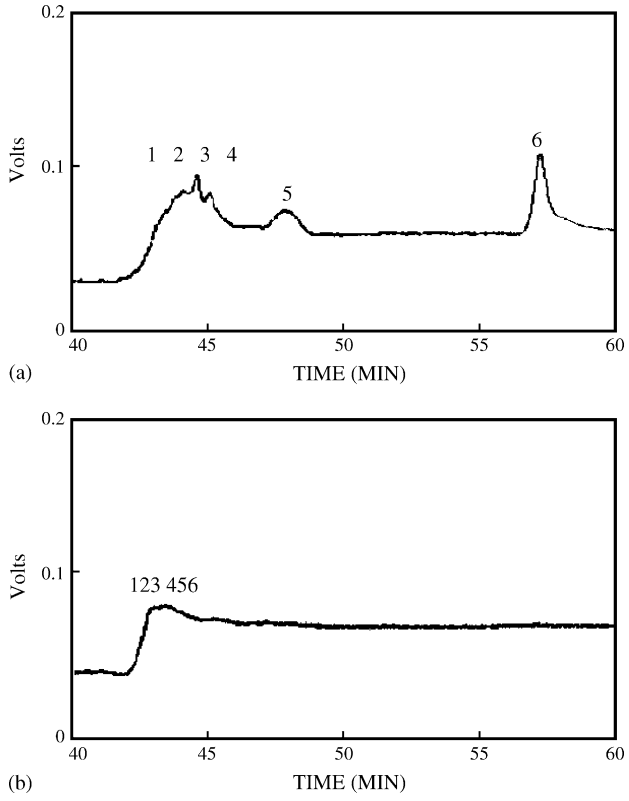

Fig. 6. Chromatograms obtained by directly analysis of standard solution of BPA and it analogues (10 nmol/L each) in MIPM6 column (a) and nMIPM column (b). (1) Phenol, (2) *p*-nitrophenol, (3) diethylstilbestrol, (4) hexoestrol, (5) Bisphenol C, and (6) Bisphenol A HPLC conditions: flow rate: 1 mL/min; mobile phase: direct injecting water for 40 min, 70% methanol in water for 13 min then 100% methanol for 7 min.

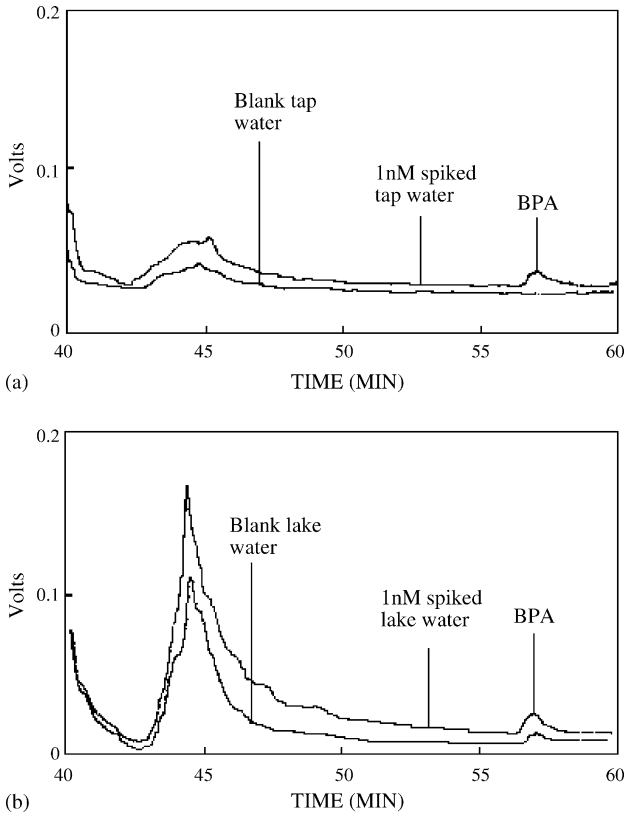

Fig. 7. Chromatograms obtained by directly analysis of BPA in (a) tap water, and (b) lake water. HPLC conditions: flow rate: 1 mL/min; mobile phase: direct injecting water for 40 min, 70% methanol in water for 13 min then 100% methanol for 7 min.

Table 3
Repeatability and recovery data for water samples analysis

Water sample	Background (nmol/L)	Spiked concentration (nmol/L)	Measured concentration (nmol/L)	Repeatability (RSD %, $n = 5$)	Recovery (%)
Tap water	N.D.[a]	0.1	0.096	8.9	96.0
		1	1.001	3.6	100.1
		10	9.991	1.6	99.9
Lake water	0.532	0.1	0.631	8.1	99.0
		1	1.550	4.0	101.8
		10	10.672	1.2	101.4

[a] Not detected.

correctly quantitated using MIPM6 and UV detector in one analysis process. The analysis data (Table 3) showed the recoveries for spiked tap water and lake water ranged from 96 to 101.8% with RSD lower than 10%, which demonstrated that this analysis method was completely suitable for ultra-trace BPA in environmental water samples.

3.5. Confirmation of BPA peak

To prove the peak with the retention time of 57 min was BPA, totally 10 mL efflux of the peak (56–58 min efflux, 2 mL per time for five times) in blank lake water assay was collected and analyzed by HPLC using a C18 column. In HPLC analysis only BPA was detected, showing the peak in the retention time of 57 min was BPA.

4. Conclusions

A fully simultaneous and direct analysis method for ultra-trace analytes in environmental water samples was established by large injection volume (40 mL), direct enrichment and HPLC analysis using one narrowly dispersible MIPM column and UV detector. Since, BPA was widely presented in environment at trace concentration, it was chosen as the representative analytes. Due to the high retention and specific HPLC characters of BPA imprinted MIPM6 to BPA, ultra-trace BPA in 40 mL water samples can be simultaneously extracted, enriched, separated, determined and quantitated in one analysis process under optimum conditions. The calibration graph of BPA standard solution was linear in the concentration ranges of 0.1–100 nmol/L with less than 9.6% intra- and inter-day RSD. For spiked (0.1–10 nmol/L) tap water and lake water samples the RSD was less than 8.9% and the recoveries were 96–101.8%. The enrichment factor for BPA was 10,000 as 40 mL water sample was directly injected and analyzed. MIPM6 was successful applied to ultra-trace BPA determination in environmental water samples with high accurate and repeatability using commonly used UV detector. This methodology may provide a useful tool for accurate investigation and determination of BPA levels in the environmental and biological matrices.

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References

[1] K. Shea, D.Y. Sasaki, J. Am. Chem. Soc. 113 (1991) 4109.
[2] G. Wulff, S. Schauhoff, J. Org. Chem. 56 (1991) 395.
[3] J. Svenson, I.A. Nicholls, Anal. Chim. Acta 435 (2001) 19.
[4] G. Vlatakis, L.I. Andersson, R. Muller, K. Mosbach, Nature 361 (1993) 645.
[5] F. Lanza, B. Sellergren, Macromol. Rapid Commun. 25 (2004) 59.
[6] L.I. Andersson, J. Chromatogr. B 745 (2000) 3.
[7] L. Schweitza, L.I. Andersson, S. Nilsson, J. Chromatogr. A 817 (1998) 5.
[8] L.I. Andersson, J. Chromatogr. B 739 (2000) 163.
[9] N. Masque, R.M. Marce, F. Borrull, Trends Anal. Chem. 20 (2001) 477.
[10] E. Caro, R.M. Marc'e, P.A.G. Cormack, D.C. Sherrington, F. Borrull, J. Chromatogr. B 813 (2004) 137.
[11] P. Martin, G.R. Jones, F. Stringer, I.D. Wilson, Analyst 128 (2003) 345.
[12] B. Dirion, F. Lanza, B. Sellergren, C. Chassaing, R. Venn, C. Berggren, Chromatographia 56 (2002) 237.
[13] G. Theodoridis, C.K. Zacharis, P.D. Tzanavaras, D.G. Themelis, A. Economou, J. Chromatogr. A 1030 (2004) 69.
[14] W.M. Mullett, E.P.C. Lai, Microchem. J. 61 (1999) 143.
[15] K.S. Boos, C.T. Fleischer, Fresenius J. Anal. Chem. 371 (2001) 16.
[16] N. Zheng, Y.Z. Li, W.B. Chang, Z.M. Wang, T.J. Li, Anal. Chim. Acta 452 (2002) 277.
[17] F.G. Tamayo, M.M. Titirici, A. Martin-Esteban, B. Sellergren, Anal. Chim. Acta 542 (2005) 38.
[18] C. Baggiani, G. Giraudi, C. Giovannoli, F. Trotta, A. Vanni, J. Chromatogr. A. 883 (2000) 119.
[19] C. Baggiani, F. Trotta, G. Giraudi, G. Moraglio, A. Vanni, J. Chromatogr. A 786 (2000) 23.
[20] M.L. Mena, P. Martínez-Ruiz, A.J. Reviejo, J.M. Pingarrón, Anal. Chim. Acta 451 (2002) 297.
[21] E. Caro, R.M. Marcé, P.A.G. Cormack, D.C. Sherrington, F. Borrull, J. Chromatogr. A 995 (2003) 233.
[22] M. Abert Vian, V. Tomao, S. Gallet, P.O. Coulomb, J.M. Lacombe, J. Chromatogr. A 1085 (2005) 224.
[23] W. Yoshiyuki, K. Takuya, M. Masatoshi, T. Nobuo, H. Jun, H. Ken, J. Chromatogr. A 1032 (2004) 45.
[24] G. Theodoridis, C.K. Zacharis, P.D. Tzanavaras, D.G. Themelis, A. Economou, J. Chromatogr. A 1030 (2004) 69.
[25] A.C. Hogenboom, M.P. Hofman, D.A. Jolly, W.M.A. Niessen, U.A.Th. Brinkman, J. Chromatogr. A 885 (2000) 377.
[26] M.C. Hennion, J. Chromatogr. A 856 (1999) 3.
[27] W.M. Mullett, E.P.C. Lai, B. Sellergren, Anal. Commun. 36 (1999) 217.
[28] F.G. Tamayo, A. Martin-Esteban, J. Chromatogr. A 1098 (2005) 116.
[29] R. Steinmetz, N.A. Mitchner, A. Grant, D.L. Allen, R.M. Bigsby, N. Ben-Jonathan, Endocrinology 138 (1997) 1780.
[30] K. Inoue, Y. Yoshie, S. Kondo, Y. Yoshimura, H. Nakazawa, J. Chromatogr. A 946 (2002) 291.
[31] Y. Sun, M. Wada, N. Kuroda, K. Hirayama, H. Nakazawa, K. Nakashima, Anal. Sci. 17 (2001) 697.

[32] F. Takuma, K. Kurunthachalam, J.P. Giesy, S. Masunaga, Water Res. 38 (2004) 4491.
[33] D. Li, J. Park, J.R. Oh, Anal. Chem. 73 (2001) 3089.
[34] S.H. Cheong, S. McNiven, A. Rachkov, R. Levi, K. Yano, I. Karube, Macromolecules 30 (1997) 1317.
[35] L. Ye, K. Mosbach, React. Funct. Polym. 48 (2001) 149.
[36] J.F. Wang, A. Peter, G. Cormack, D.C. Sherrington, K. Ezat, Angew. Chem. Int. Ed. 42 (2003) 5336.
[37] G. Theodoridis, C.K. Zacharis, P.D. Tzanavaras, D.G. Themelis, A. Economou, J. Chromatogr. A 1030 (2004) 69.
[38] G. Theodoridis, P. Manesiotis, J. Chromatogr. A 948 (2002) 163.
[39] G. Theodoridis, A. Kantifes, P. Manesiotis, N. Raikos, H.T. Papadopoulou, J. Chromatogr. A 987 (2003) 103.
[40] C. Berggren, S. Bayoudh, D. Sherrington, K. Ensing, J. Chromatogr. A 889 (2000) 105.