HIGH SPECIFICITY OF MOLECULARLY IMPRINTED POLYMER PARTICLES TOWARD TARGET COMPOUND IN COMPETITIVE ENVIRONMENTAL BINDING

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Keywords: bisphenol A, capillary electrophoresis, competitive binding, molecularly imprinted polymers, reusability, specificity

Molecularly imprinted polymer (MIP) particles tailored for bisphenol A (BPA) were prepared using a 1:8:7 molar ratio of BPA the template, methacrylic acid (MAA) the functional monomer, and ethylene glycol dimethacrylate (EGDMA) the cross-linker. These colloidal particles were tested for rapid competitive binding by capillary electrophoresis with ultraviolet detection (CE-UV). Good interface binding efficiencies were obtained for BPA even in the presence of 2-hydroxy-4-methoxy benzophenone (HMB) as a structurally related compound at high concentrations. The specifically bound BPA could be desorbed rapidly out of the interface cavities by 5% triethylamine in methanol. However reusability was demonstrated by repeated injections of BPA that bound to MIP particles without regeneration of the cavities.

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Introduction

Bisphenol A (BPA) (2,2-bis(4-hydroxyphenyl)propane) has recently drawn the attention of scientific community and the general public due to its potent estrogenic activity,[1-4] having a hazard quotient of 2.24 in surface water.[5] Consequently, it is of great importance to develop a treatment technology that can efficiently remove BPA and other contaminants from water to boost human health. About 28 million chemicals are known up to date, which provokes the need for highly selective sorbents.[6] Water treatment demands for inexpensive, highly selective, and reusable sorbents with no significant loss in adsorption capacity make this research field of critical importance.

Molecular imprinting has gained considerable interest as a feasible route to fabricate tailored recognition materials featuring receptor sites in the form of molecularly imprinted polymers (MIPs).[7] The prime approach of imprinting involves the synthesis of reticulated polymers in the presence of a template ranging from small molecules to biological macromolecules as well as microorganisms. Functional monomers and cross-linkers interact with the template to hold it in place during polymerisation.[8] Removal of the template by an appropriate solvent produces a polymer with accessible binding sites that are complementary in shape and functionality to the template.[9] As a promising alternative to traditional SPE sorbents including silica gel, polyamide, ion-exchange resins and reverse-phase packing materials, MIPs have been extensively utilized to overcome the dissatisfactory cross-reactivity of such sorbents.[10] MIPs have been used in a wide range of applications including chemical sensing,[11] extraction of pollutants,[12] chromatography separation,[13] catalysis,[14] drug delivery,[15] and enzyme inhibition.[16] MIPs possess inherent advantages including a high affinity for the template molecule, great chemical and thermal stability, reusability, multiplicity in the choice of functional monomers and cross-linkers, as well as simplicity in preparation at low cost.[17]

A rapid CE-UV method was recently developed in our lab for rapidly testing the binding of MIPs tailored for BPA with various environmentally hazardous compounds.[18] The CE technique allows for a high loading capacity of particles in aqueous suspension for clog-free analysis. After sequential injection of particles and compounds, migration through the capillary provided an opportunity for binding during the momentary overlap. A high binding efficiency of 99±1% was obtained for BPA over a short interaction time of several seconds. MIP selectivity for its target compound in the presence of neutral, cationic and anionic interferences was successfully demonstrated in competitive binding tests.

Reusability of colloidal MIP particles is an important feature that warrants further research to demonstrate the key factor of cost savings, so as to open the opportunity for large-scale applications including water treatments.[19] In this work, a CE-UV reusability test was performed by injecting MIP particles first followed by multiple injections of BPA. The main objective was to demonstrate the repeated use of MIP particles without desorption of the already bound analytes. The reusability test was repeated in the presence of a structurally related compound, 2-hydroxy-4-methoxy benzophenone (HMB), to reveal the excellent specificity of MIP in recognizing its target compound rapidly.

Material and methods

Materials

2,2′-azobis(2-isobutyronitrile) (AIBN) was bought from Pfaltz & Bauer (Waterbury, CT, USA). Bisphenol A (BPA), ethylene glycol dimethacrylate (EGDMA), 2-hydroxy-4-methoxy benzophenone (HMB), and methacrylic acid (MAA) were all obtained from Sigma-Aldrich (Oakville,

ON, Canada). Hydrochloric acid was obtained from Anachemia (Montreal, QC, Canada). Sodium phosphate dibasic was obtained from Fisher Scientific (Fair Lawn, NJ, USA). Triethylamine (TEA) was purchased from Fluka (Buchs, Switzerland). Trifluoroacetic Acid (TFA) was bought from Aldrich (Milwaukee WI, USA). HPLC grade methanol and acetonitrile, spectro grade acetone, and sodium hydroxide were all purchased from Caledon Laboratories (Georgetown, ON, Canada).

Apparatus and Analytical Method

CE-UV analyses were performed on a modular system built in our laboratory, which includes a Spellman CZE1000R high-voltage power supply (Hauppauge, New York, USA). Fused-silica capillary (51 mm i.d., 356 mm o.d.) was obtained from Polymicro Technologies (Phoenix, AZ, USA). The capillary total and effective lengths were 53.5 cm and 46.1 cm, respectively. The background electrolyte (BGE) was composed of 10 mM Na_2HPO_4 in deionized distilled water (DDW) to attain pH 7.5±0.2. Prior to initial use, the capillary was typically conditioned with 1 M NaOH, 0.1 M NaOH and the BGE. Daily conditioning was done by flushing the capillary with pure methanol, 1.0 M HCl, 1.0 M NaOH, DDW, and the BGE.

All subsequent CE running at an applied voltage of 17 kV had the capillary inlet 2 mm away and below the electrode tip to improve both precision and baseline stability. A Bischoff Lambda 1010 (Leonberg, Germany) UV detector was set up at a wavelength of 200 nm to monitor the analytes (BPA, HMB) and particles. A PeakSimple chromatography data system (SRI model 203, Torrance, CA, USA) was used to acquire the detector output signal. The capillary was re-equilibrated by running the BGE at 17 kV for 1 min in between sample analyses to eliminate any carrryover contamination from the previous electrophoretic run.

Preparation of MIP and NIP Particles

The preparation procedure for BPA-MIP and non-imprinted polymer (NIP) particles was detailed elsewhere.[18] Briefly, at a molar ratio of 1:8:7, BPA the template, MAA the functional monomer, and EGDMA the cross-linker were dissolved in acetone/acetonitrile (1:3 v/v) the porogen. At 2% by weight of the total monomer and crosslinker, AIBN the initiator was added. The pre-polymerization mixture was sonicated, deoxygenated, and placed in a 60°C water bath for 24 h to yield BPA-MIP submicron particles. To generate binding cavities in MIP particles, 5 mL of 5% TEA in methanol was used to wash out the template and any residual monomer or crosslinker. After sonication for 10 min, the suspension of MIP particles was centrifuged for 10 min and then the supernatant was discarded. This washing step was repeated several times to ensure complete removal of the template. Subsequently, the particles were rinsed three times with ACN to remove any TEA remaining in the pores and imprinted cavities. The MIP particles were finally dried overnight to be ready for experimental use. NIP particles were prepared in a similar procedure without BPA.

CE-UV Desorption Test

A suspension was prepared to contain10 mg mL^{-1} BPA-MIP (MIP with BPA in the binding cavities) in the BGE (10 mM Na_2HPO_4, pH 7.5±0.2). Both 5% TEA in methanol and 5% TFA in methanol were evaluated as eluents to elute BPA out of MIP cavities. Capillary desorption tests were performed by sequential injection of BPA-MIP particles first and 5% TEA in methanol next for 3 s at 17 kV of applied voltage. Mesityl oxide (MO) was run individually for ionic charge determination of BPA, TEA, TFA and particles.

External Desorption Test

In-capillary desorption test was confirmed by performing an external desorption test. It was done by mixing 10 mg mL^{-1} of BPA-MIP particles with 5% TEA in methanol or 5% TFA in methanol in the sample vial. After sonication for 5 min, the mixture was analyzed by CE-UV with electrokinetic injection for 3 s at 17 kV.

Reusability of MIP Particles

MIP and NIP suspensions (10 mg mL^{-1}) were prepared in the BGE, as well as a stock solution of BPA (100 ppm) when needed. A stock solution of HMB (5000 ppm) was prepared in methanol due to its insolubility in water. A working solution of 200 ppm HMB was daily prepared by dilution with the BGE. MIP reusability was investigated by injecting MIP particles for 21s followed by up to five injections of BPA, each for 3s. Peak overlapping between NIP particles and BPA restricted the multiple injections of BPA up to 3, following the NIP injection.

Chemical Interference

To study the effect of an interfering compound on BPA % binding, a CE-UV experiment was conducted using first injection of MIP particles for 21s, second injection of HMB for 3s, third injection of BPA for 3s, and finally fourth injection of BPA for 3s. To further investigate the effect of HMB on BPA % binding, gradual increase of HMB injection time was carried out using 6, 9, 12, and 15s of injection time. The experiment was repeated for NIP particles.

Results and Discussion

CE-UV Desorption Test

In the presence or absence of BPA, polymerization of MAA and EGDMA in acetone/ acetonitrile (1:3 v/v) at 60°C for 24 h yielded BPA-MIP or NIP submicron particles. The average diameters (or sizes) of these BPA-MIP and NIP particles were first determined by scanning electron microscopy (SEM) and then confirmed by dynamic light scattering. The SEM images illustrated the morphology, size and distribution of the prepared BPA-MIP and NIP particles. Their average diameters were 164±15 nm and 187±7 nm, respectively, as reported with more details elsewhere.[18]

CE-UV analysis was carried out by electrokinetic injection of a BPA-MIP suspension prepared in the BGE. The electrophoretic mobility, which signifies the amount of positive or negative charges carried by the particles, was obtained by subtracting the electroosmotic mobility of the neutral marker (MO) from the apparent mobility of analytes or particles. [20] MIP and NIP particles both migrated after the neutral marker, yielding negative electrophoretic mobility values as presented in Table 1. Both BPA and TEA were determined to be neutral compounds since they migrated at velocities nearly identical to that for MO. TEA is neutral in the BGE because of the presence of methanol that works as an alcohol modifier preventing the protonation of TEA. [21]

Table 1. Electrophoretic mobility values of particles, analytes and eluents signifying the amount of positive or negative charges they carried at pH 7.5±0.2.

	$t_{nmt,}$ min *	MW, g mol^{-1}	φ_{eph}, m^2 V^{-1} s^{-1}
MIP particles	8.1	------	-2.30x10^{-6}
NIP particles	7.1	------	-1.88x10^{-6}
Bisphenol A	3.75	228.29	-1.03x10^{-7}
Mesityl oxide	3.7	98.14	0.00
Triethylamine	3.7	101.19	0.00
CF_3COOH	11.6	114.02	-2.67x10^{-6}

t_{nmt} = Net Migration Time after injection; MW=molecular weight, φ_{eph} = electrophoretic mobility

An in-capillary desorption test was conducted by injecting BPA-MIP particles first and TEA next, each for 3s. The BPA-MIP peak shape changed (after TEA injection) as shown in Fig .1(a) and 1(b). A small peak, appearing around 5.4 min in front of the MIP peak, was suspected to be the eluted BPA. To investigate the identity of this peak, the BPA-MIP suspension was spiked with 100 ppm BPA. An increase in peak area (and height) was observed at 5.4±0.2 min, thus proving the peak to be BPA.

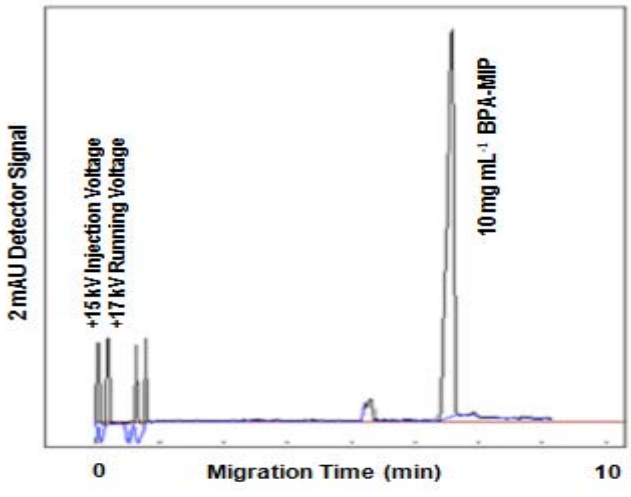


Figure 1(a). CE-UV characterization of BPA-MIP particles. Electrokinetic injection at 15 kV: first injection of BPA-MIP particles for 3s; second injection of BGE for 3 s. CE analysis at 17 kV; UV detection at 200 nm.

Full y-scale represents 2 milli-absorbance units (mAU). This seems to contradict the migration time of 3.75 min for BPA in Table 1. However, it can be explained by the transfer of two protons (H^+) from BPA to 5% TEA, which changed the analyte into a negatively charged ion with an increase in migration time. In future work, TEA can be added to the BGE for in-capillary desorption of BPA from MIP particles

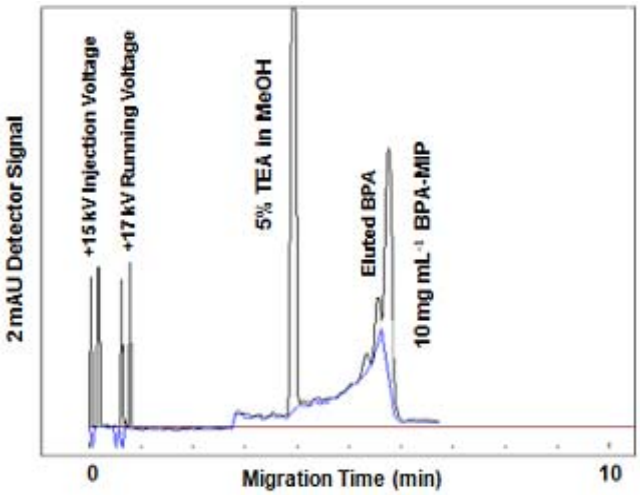


Figure 1(b). CE-UV desorption test. Electrokinetic injection at 15 kV: first injection of BPA-MIP particles for 3 s; second injection of 5 % TEA in methanol for 3 s. CE analysis at 17 kV; UV detection at 200 nm.

External Desorption Test

An external desorption test was next carried out to confirm the eluent ability of TEA. A mixture of BPA-MIP and TEA was sonicated for 5 min before injection for CE-UV analysis. As shown in Fig. 2, other than the TEA and BPA-MIP peaks, a new peak was observed at 4.9±0.1 min. This peak was confirmed to be BPA by spiking the mixture with 100 ppm BPA and observing an increase in peak area (and height). One plausible explanation of this shorter migration time (than 5.4 min above) is the transfer of only one proton from BPA to 2.5% TEA. When 5% TEA was next used, the migration time of BPA increased to 5.4±0.1 min.

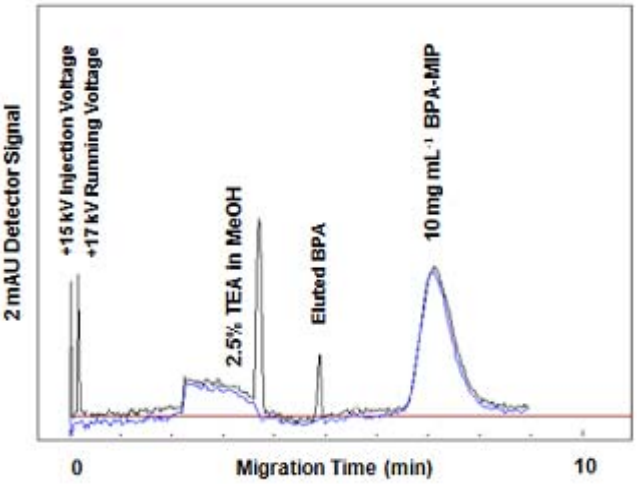


Figure 2. External desorption test. Electrokinetic injection at 15 kV of a mixture of BPA-MIP particles and 2.5% TEA in methanol for 3 s. CE analysis at 17 kV; UV detection at 200 nm.

The selection of an appropriate eluent is crucial for achieving the highest desorption efficiency. Therefore it was necessary to add an acidic/basic modifier with the ability to disrupt the hydrogen bonds formed between BPA and MAA, the functional monomer that provides carboxyl functional groups inside the MIP cavities. [22] Having two phenolic hydroxyl groups, BPA can act as a weak acid (pK_a=9.6). [23] TEA is an organic base that can interfere with the binding equilibrium between BPA and MAA, releasing BPA out of the cavity. Martin *et al.* explored the ability of basic and acidic modifiers to overcome the electrostatic interactions between basic analytes and acidic MIPs. They reached a conclusion that only TEA achieved this with superior performance when compared with TFA. [24] In addition, methanol contains an -OH group that can form a hydrogen bond with MAA and force BPA out of the cavity. However, methanol cannot quantitatively desorb BPA on its own. [25]

After injecting TEA first and BPA next for 3s, proton exchange occurred. As shown in Fig. 3, the BPA peak showed up at a slightly longer migration time due to an increase in its negative charge after the transfer of a proton to TEA. . BPA works as a hydrogen bond donor while TEA is a hydrogen bond acceptor (since it contains a lone pair of electrons on the nitrogen atom). All in all, 5% TEA in methanol is a proper eluent (or elution reagent) that can quantitatively desorb BPA out of the MIP cavities. In spite of the finite time interval required for the elution reagent to desorb all of the bound BPA out of the cavities, in-capillary desorption was demonstrated to be a rapid test for evaluating the desorption ability of an eluent.

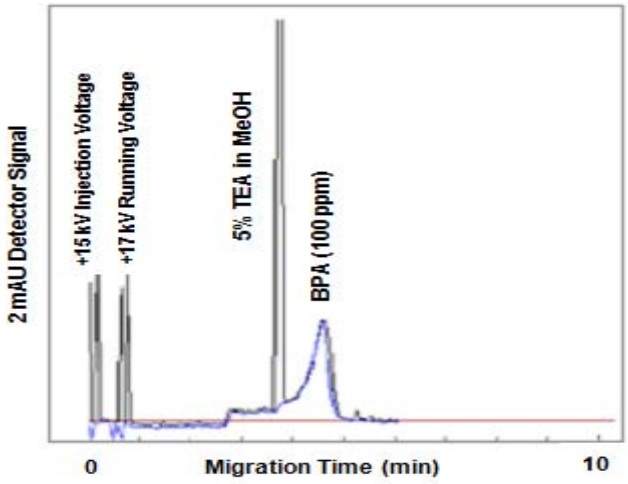


Figure 3. CE-UV binding test. Electrokinetic injection at 15 kV: first injection of 5% TEA in methanol for 3 s; second injection of BPA (100 ppm) for 3s. CE analysis at 17 kV; UV detection at 200 nm.

The elution ability of TFA was next investigated. TFA is negatively charged in the BGE, based on its electrophoretic mobility value presented in Table 1. A mixture of 5% TFA in methanol and 100 ppm BPA in BGE was injected for 3s to examine the interaction of TFA with BPA. 5% TFA in methanol was sufficient to interact quantitatively with BPA and still fell within the dynamic range of CE-UV detection. As shown in Fig. 4, a single peak was observed at 10.9±0.1 min, which is believed to be the TFA-BPA complex. When injected individually, BPA appeared at a migration time of 3.7±0.1 min while TFA appeared at 11.6±0.1 min. Based on the new migration time for the complex peak, the electrostatic interactions between BPA and TFA formed an overall negatively charged complex. Varying concentrations of BPA (10, 50, 100 and 200 ppm) were used to further investigate whether the obtained peak is the TFA-BPA complex. Figure 5 shows an increasing peak area of the TFA-BPA complex as the BPA concentration was increased. This is a convincing proof of the complex formation.

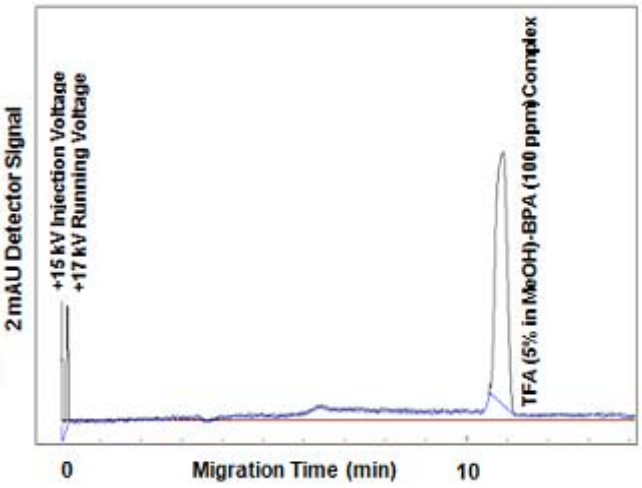


Figure 4. CE-UV binding test. Electrokinetic injection at 15 kV of a mixture of 5% TFA in methanol and 100 ppm BPA in BGE for3 s. CE analysis at 17 kV; UV detection at 200 nm.

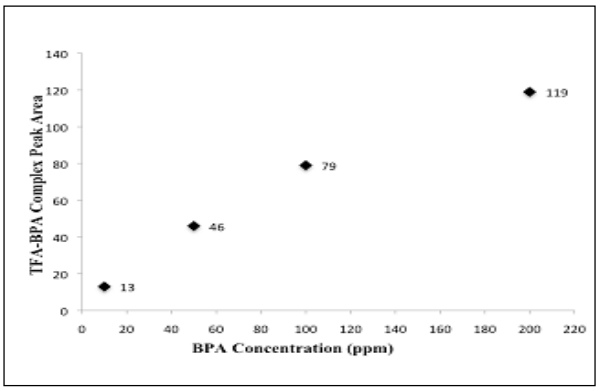
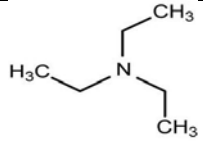
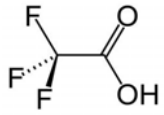


Figure 5. Effect of BPA concentration on area of TFA-BPA complex peak.

10% acetic acid had previously been used to elute BPA out of MIP cavities. TFA had also been utilized as an organic modifier in the mobile phase to elute BPA out of HPLC columns. [26] Although TFA could form a complex with BPA, it was apparently not able to break up the binding interactions between BPA and MAA inside the MIP binding cavities. Both in-capillary and external desorption tests showed no impact of TFA on BPA desorption. It is believed that Coulomb/electrostatic repulsion between TFA and MIP particles would not allow TFA to approach the MIP cavities. It is also possible that TFA just attaches itself to BPA without breaking up with MAA. Consequently, TFA cannot be used as an eluent for BPA bound inside methacrylate-based MIP particles. Table 2 compares TEA and TFA for use as elution reagents.

Table 2. Comparison between TEA and TFA in their capability to elute BPA out of MIP particles.

	5% TEA in MeOH	**5% TFA in MeOH**
Chemical Structure		
pK_a	10.8 (basic) [27]	0.6 (strongly acidic) [28]
Charge in 10 mM Na_2HPO_4	Neutral	Negatively charged
Interaction with BPA	BPA exchanged protons with TEA, resulting in a change in its migration time from 3.7 min to 5.4 min.	TFA and BPA formed a complex (via electrostatic interactions) peak in between the migration times of BPA and TFA.
Ability to break up MAA and BPA	TEA was able to disrupt the binding between MAA and BPA and eventually elute BPA out of MIP cavities.	TFA was not able to break up the binding interactions between MAA and BPA to elute BPA out of MIP cavities.

Reusability of MIP Particles

Reusability was demonstrated over several adsorption tests without regeneration of the MIP particles (by desorbing the already bound analytes). Figure 6(a) shows a typical CE-UV analysis for five consecutive injections of 100 ppm BPA (each for 3s), following one injection of MIP particles. As 48 s of MIP injection was needed to bind 99±1% of the BPA, 21s of MIP injection would not be quantitatively enough even for the first BPA injection. However, all subsequent BPA injections were observed to bind onto the MIP particles, with a gradual decrease in % binding as shown in Fig. 6(b). Similarly, a gradual decrease is observed in Fig. 6(c) even though peak overlapping between NIP particles and BPA allowed only three injections of BPA (following the injection of NIP particles). The % binding results of all adsorption tests are summarized in Table 3 for easy comparison; they also show the significantly higher % binding results obtained from MIP than NIP particles. The progressive decreases in BPA % binding to MIP and NIP particles imply that binding as a physicochemical interaction was dictated by an equilibrium constant (K_{eq}):

$$\text{BPA} + \text{MIP} = \text{BPA-MIP} \qquad (1)$$

The first injection of BPA did not bind completely probably because the effective equilibrium constant does not have a very high value: [29]

$$K_{eq} = \frac{\left[\dfrac{C_i - C_e}{C_e}\right]}{\left[\dfrac{V}{m}\right]} = \frac{\left[\dfrac{\%\,binding}{1-\%\,binding}\right]}{\left[\dfrac{V}{m}\right]} \qquad (2)$$

where C_i is the initial concentration of analyte, C_e is the concentration of analyte at binding equilibrium, V is the volume of solution (mL) and m is the mass of particles (g). An effective equilibrium constant can be calculated for the first injection of BPA binding with MIP particles to be $K_{eq}' = 212$ g mL^{-1}; for NIP particles, $K_{eq}' = 35$ g mL^{-1}. As less and less binding sites were available, all subsequent injections of BPA obtained lower % binding results than the first injection.

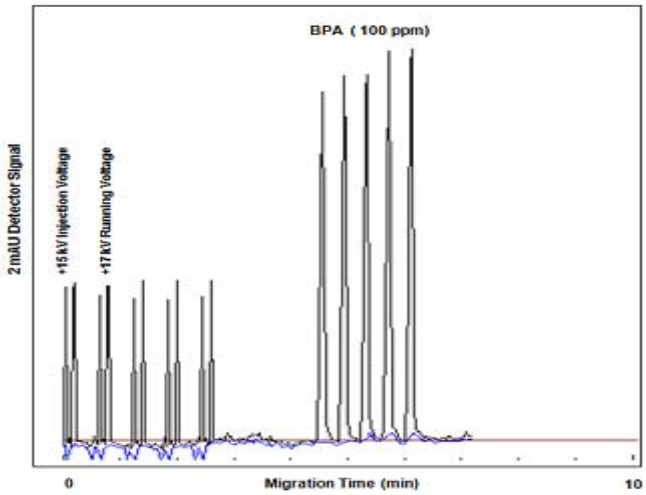


Figure 6(a). CE-UV characterization of multiple BPA (100 ppm) injections (for 3s each). Electrokinetic injection at 15 kV. CE analysis at 17 kV; UV detection at 200 nm.

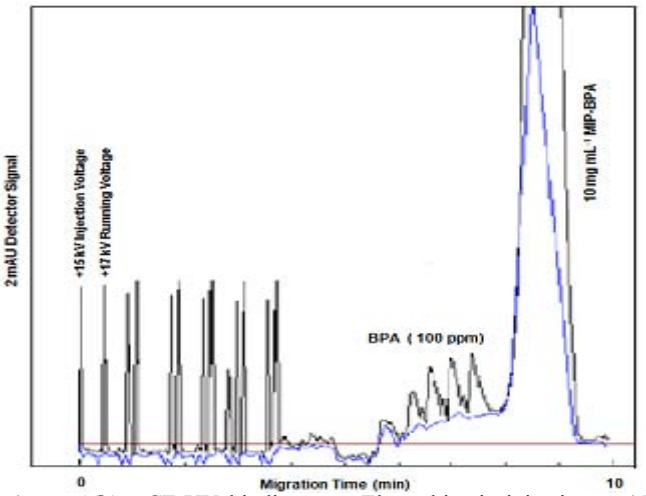


Figure 6(b). CE-UV binding test. Electrokinetic injection at 15 kV: first injection of MIP particles for 21s, followed by five injections of BPA (100 ppm) for 3s each. CE analysis at 17 kV; UV detection at 200 nm.

Table 3. % binding results for multiple injections of BPA (injection time = 3s each) with MIP and NIP particles (injection time = 21s) at pH 7.5.

% Binding	Injection of BPA				
	1st	2nd	3rd	4th	5th
MIP	68±2	62±1	60±1	58±1	51±2
NIP	26±1	23±1	22±1	--------	---------

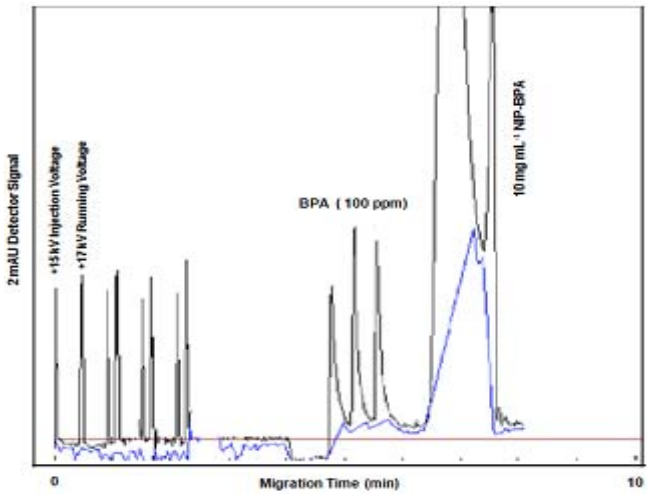


Figure 6(c). CE-UV binding test. Electrokinetic injection at 15 kV: first injection of NIP particles for 21 s, followed by three injections of BPA (100 ppm) for 3 s each. CE analysis at 17 kV; UV detection at 200 nm.

Chemical Interference

The presence of other organic compounds in real-world samples can interfere with the % binding of BPA with MIP. A structurally related compound, HMB, was next employed for the investigation of chemical interference. HMB, also known as oxybenzone, is an organic compound used in sunscreen and other cosmetics because it absorbs UVB and short-wave UVA rays. It was nice to observe that 3s of 200 ppm HMB injection had no significant effect on BPA % binding onto either MIP or NIP particles, in spite of the high % bindings of HMB with both MIP and NIP particles as shown in Fig. 7. As discussed elsewhere, [18] HMB has high affinity to non-specific binding sites as it demonstrated a complete binding to NIP particles. Next, the HMB injection time was increased to 6, 9, 12 and 15s.

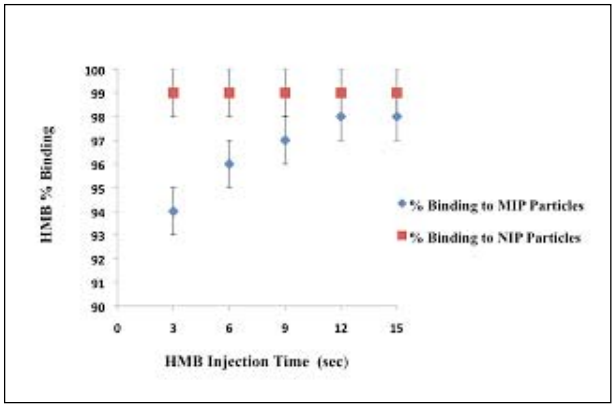


Figure 7. CE-UV investigation of HMB (200 ppm) binding efficiencies with MIP and NIP particles (21s of injection).

In spite of the large quantity of HMB bound to the (non-specific binding sites inside) MIP particles, BPA % binding to MIP particles was not significantly decreased in the two next injections. Figure 8(a) presents the results of BPA % binding to MIP particles after the first injection of HMB over various time durations. Apparently, HMB had only slight impact (due to occupation of non-specific binding sites) on decreasing the BPA % binding to MIP particles in the second injection. The notable decreases in BPA % binding to MIP particles (from the second injection to the third injection) could be explained by a lower number of specific binding sites available. Figure 8(b) presents the results of BPA % binding to NIP particles at different injection time durations of HMB.

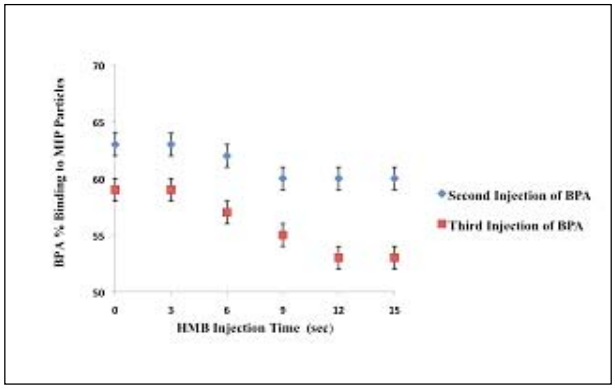


Figure 8(a). CE-UV investigation of BPA (100 ppm) binding efficiencies with MIP particles (21s of injection) after injection of HMB (200 ppm) for various time durations.

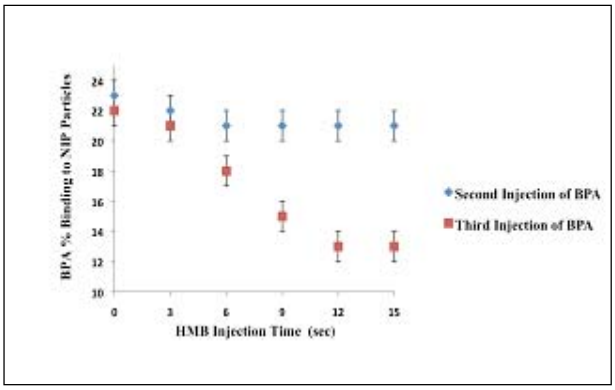


Figure 8(b). CE-UV investigation of BPA (100 ppm) binding efficiencies with NIP particles (21 s of injection) after injection of HMB (200 ppm) for various time durations.

In summary, HMB exhibited almost insignificant impact on decreasing BPA % binding to MIP particles in the second and third injections, demonstrating that MIP particles are not affected by the non-specific binding of HMB despite its large quantities (injection of 200 ppm over 3–15s). MIP particles can still remove a reasonably high percentage of BPA in the next two injections (2^{nd} and 3^{rd}). This is an excellent demonstration of MIP capability to recognize and specifically bind BPA in the presence of interfering compounds. These results are in agreement with the results obtained by Watabe *et al*. They concluded that the removal of interferences from water by the surface modified MIP particles through non-specific binding did not hinder BPA binding to MIP cavities. [30]

Conclusions

A rapid CE-UV desorption test was demonstrated using 5% TEA in methanol to elute BPA out of the interface cavities of colloidal MIP particles. The ability of TEA was

confirmed by an external desorption test. On the contrary, 5% TFA in methanol did not work well as an eluent due to electrostatic repulsion between the negatively charged TFA and MIP particles. Reasonably high % bindings of BPA were attained after one injection of MIP particles for 21s followed by multiple injections of BPA for 3s each. This ascertained the reusability of MIP particles over several adsorption cycles (without regeneration of the interface cavities by desorbing the already bound analyte) until all specific binding sites were occupied. It was further demonstrated that the MIP particles had excellent capability to recognize BPA even in the presence of large quantities of HMB (3–15s of injection of 200 ppm). Such high specificity of colloidal MIP particles toward the target compound in a rapid competitive binding test represents a major advantage of MIP over non-specific SPE sorbents in targeting water contaminants individually. The colloidal state would allow MIP particles to stay suspended in water over an extended period of time for removing any new introduction of contaminants.

Abbreviations

AIBN	2,2′-azobis(2-isobutyronitrile)
BGE	background electrolyte
BPA	bisphenol A
CE	capillary electrophoresis
DDW	deionized distilled water
EGDMA	ethylene glycol dimethacrylate
HMB	2-hydroxy-4-methoxybenzophenone
MAA	methacrylic acid
MIP	molecularly imprinted polymer
MO	mesityl oxide
NIP	non-imprinted polymer
TEA	triethylamine
TFA	trifluoroacetic acid
UV	ultraviolet

Acknowledgements

Financial support from NSERC Canada is gratefully acknowledged. S. Alsudir thanks the Saudi Ministry of Higher Education for her scholarship.

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Received: 30.11.2012.
Accepted: 18.12.2012.