Supplement Information

Molecularly imprinted fiber array solid-phase microextraction strategy for simultaneous detection of multiple estrogens

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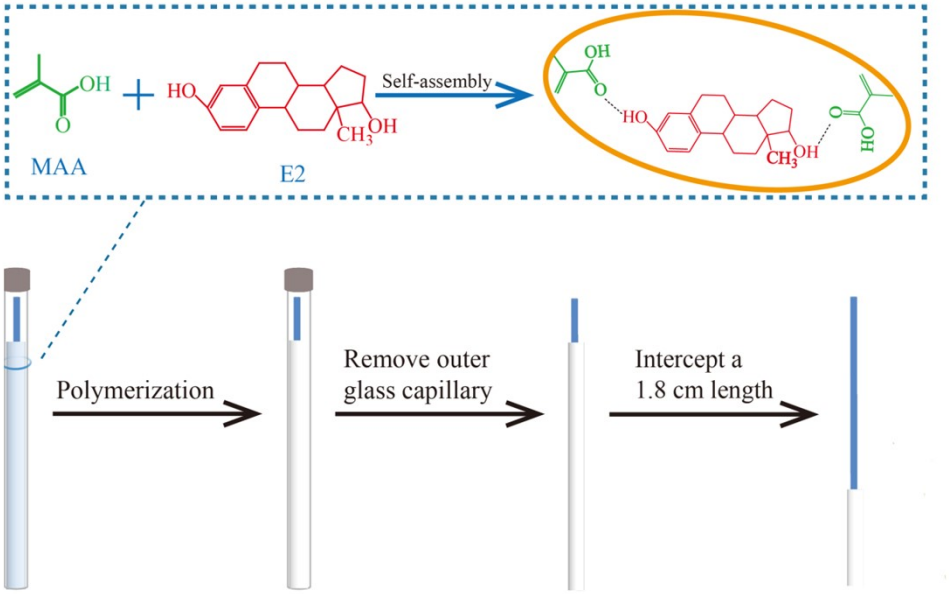

Fig. S1. Schematic diagram of the preparation process of MIP fiber coating.

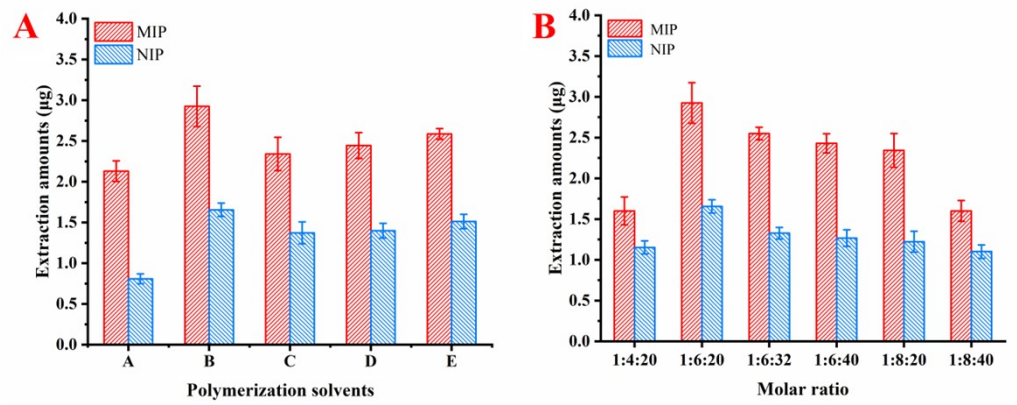

Fig. S2. Polymer solvent optimization (A), a: acetonitrile; b: methanol-acetonitrile (1:1, v/v); c: methanol-acetonitrile (1:2, v/v); d: methanol-acetonitrile (1:3, v/v); e: methanol-acetonitrile (2:3, v/v); and molar ratio optimization among template molecules, functional monomers and crosslinkers (B).

1. Optimisation of the extraction conditions

Extraction time will affect the equilibrium of extraction. The effects of extraction time which included 60, 90, 120, 150, 180, 210 min were investigated to extract E2

from 50 mL of spiked water samples at a concentration of 100.00 μg/L. Polymer coating was then immersed in 0.25 mL desorption solvent of methanol-acetic acid (9:1, v/v). At the same time, the coating was desorbed by ultrasound for 10 minutes. As shown in Fig. 2A, the amount of E2 extracted increases with extraction time. The extraction amount of E2 reaches highest at 120 min. With further increases the extraction time did not significantly increase the extraction amount of the E2. Therefore, 120 min was chosen as sufficient for effective extraction of E2.

This study desorption time of 3, 5, 10, 15 and 20 min were investigated to achieve high desorption efficiency of the E2 from sorbents. No significant difference was seen between 5 minutes and 10 minutes desorption. Thus, 5 min was chosen as optimum desorption time (Fig. 2B).

The desorption solvent is a critical factor during the desorption process which should sufficiently break the hydrogen bonds between the E2 and MAA. Five desorption solvents including acetonitrile-acetic acid (9: 1, v/v), acetonitrile, methanol-acetonitrile (1:1, v/v), methanol and methanol-acetic acid (9:1, v/v) were investigated (Fig. 2C). The best desorption performance of the polymer was achieved when the mixture of methanol-acetic acid (9:1, v/v) was selected as desorption solvent.

Considering ionic strength could affect the binding amount of analytes by squeezing-out and salting-out effects. The effect of ionic strength examined using NaCl solutions varying in mass fractions from 0% to 20%. As shown in Fig. 2D, the adsorption amount of E2 by polymer decreased with the mass fraction increase of NaCl. This may be due to the squeezing-out effect being stronger than that of salting-

out which unfavorable for E2 adsorption. Furthermore, the added ions may penetrate into the diffuse bilayer on surfaces of absorbent, reducing the repulsion between absorbers and producing in a compact aggregate structure [1,2]. Thus, increasing NaCl had adversely influence on adsorption of E2 by polymer. Consequently, experiments were carried out without adding NaCl.

The pH value of extraction solvent could affect the presence forms of the target analytes, so impacting the extraction performance of coating. We use hydrochloric acid (0.1 M HCl) or sodium hydroxide (0.1 M NaOH) to adjust the pH of extracted aqueous solution. E2 has a pKa value of 10.5. At pH 10.5, E2 presents neutral (about 40%) and anionic (about 60%) forms. When value of pH below 8.0, E2 is in its neutral forms (90 to 99%) [3]. When E2 is in molecular form it facilitates the formation of hydrogen bonds between the hydroxyl group in E2 and the carboxyl group in the polymer. Furthermore, the protonation of hydroxyl groups of E2 at pH <4 [4], which weakened the H-bonding between the polymer and E2. So we expect the optimal pH range for the extraction around pH 4.0–8.0. As present in Fig. 2E with the increase of pH value, the extraction amount increase first and then start decreasing, when the pH value is 7.0 the extraction amount reach to the maximum. However, when the pH value is 8.0, the extraction amount decreased significantly. Therefore, the solution pH was maintained at 7.0 to obtain the maximum extraction amount.

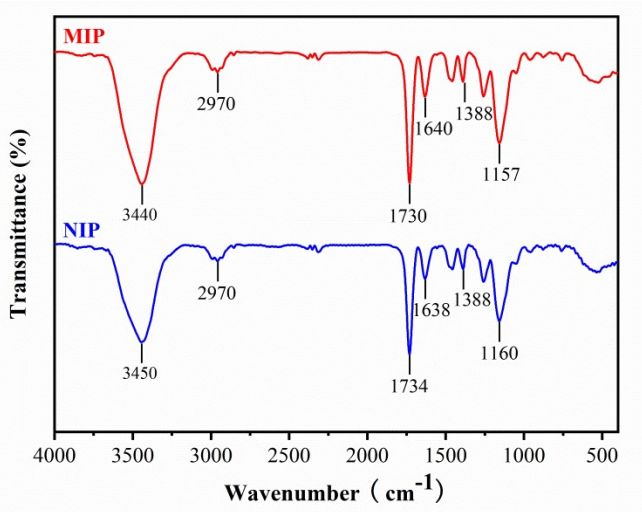

Fig. S3. FT-IR spectra of MIP and NIP coatings.

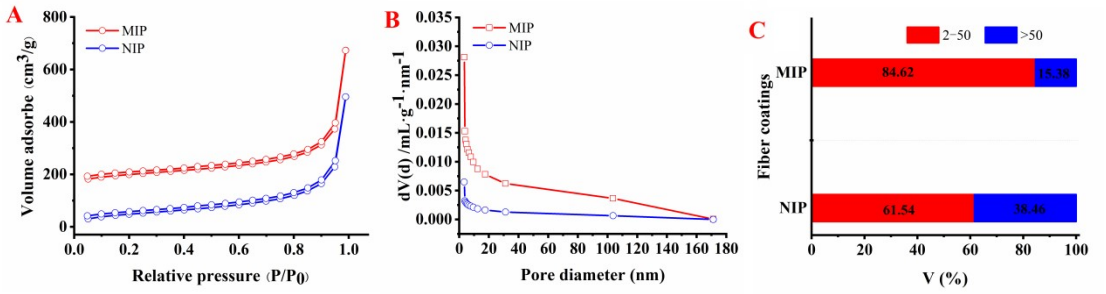

Fig. S4. Nitrogen adsorption-desorption isotherms (A), pore size distribution of the MIP and NIP (B), and different pore size ratio analysis (C).

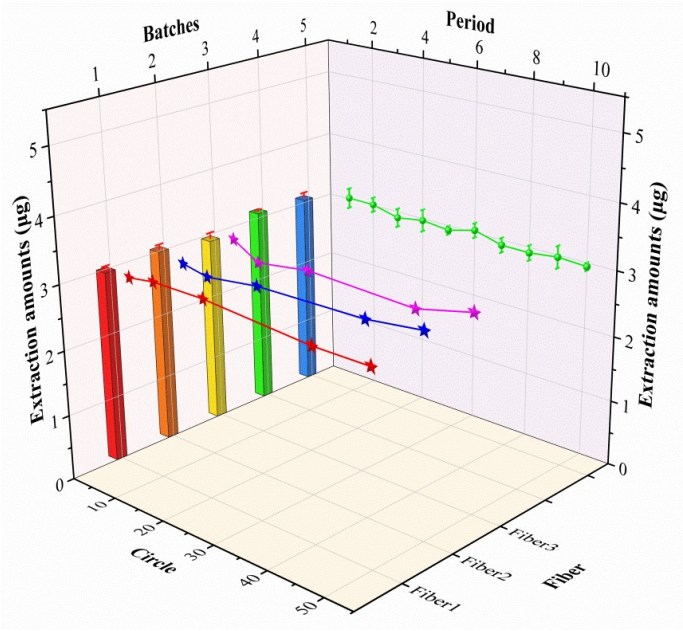

Fig. S5. Evaluation of extraction stability of MIP fiber array. Every 12 hours represent a period.

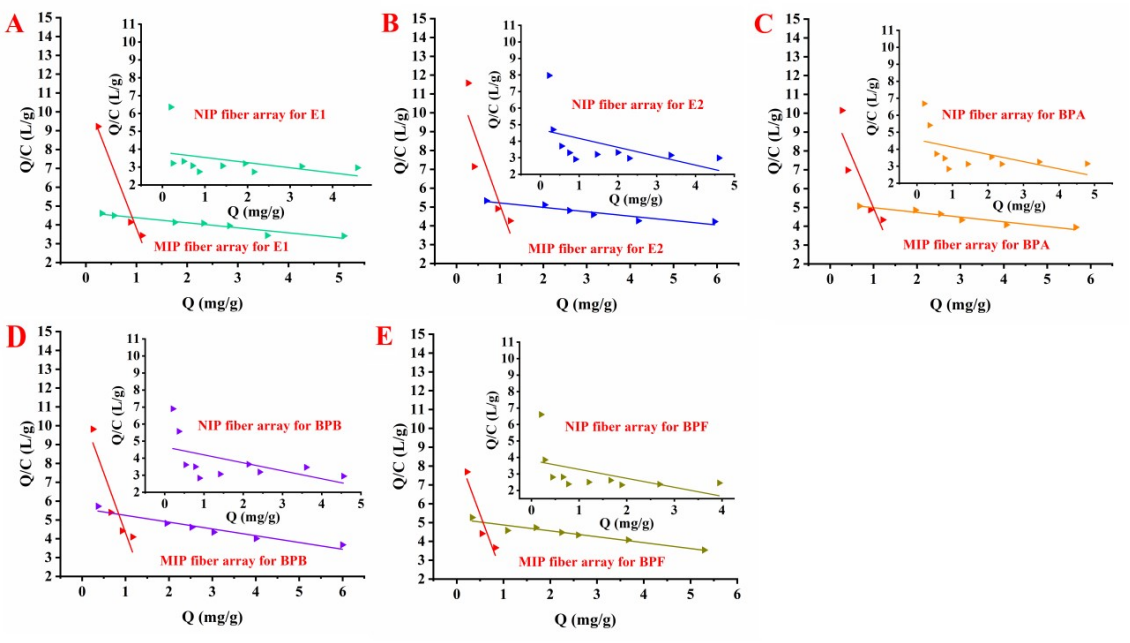

Fig. S6. Scatchard fitting curves. MIP fiber array adsorption estrogens (A)-(E), and insets show NIP fiber array adsorption estrogens, respectively.

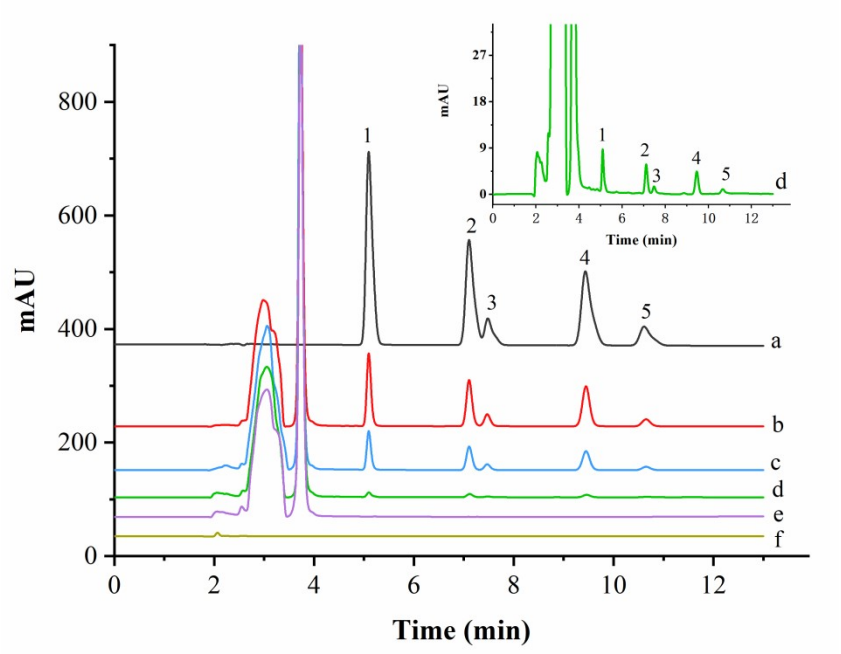

Fig. S7. Chromatograms for the analysis of five estrogens in milk. (a) 20.00 mg/L mixed standard; (b), (c), (d), The spiked sample of the 100.00, 50.00, 5.00 μg/L estrogens mixed standard solution was extracted by the MIP-SPME fiber array, respectively; (e) The sample extracted by the MIP-SPME fiber array; (f) The sample used for direct detection; (1) bisphenol F, (2) bisphenol A, (3) 17β-estradiol, (4) bisphenol B, (5) estrone.

Supplementary tables

Table S1. Atomic charges in 17β-estradiol (E2) and methacrylic acid (MAA).

E2		MAA	
Atom	Atomic charge	Atom	Atomic charge
C (1)	-0.078	C (1)	-0.01
C (2)	-0.12	C (2)	-0.176
C (3)	0.277	C (3)	0.49
C (4)	-0.146	C (4)	-0.23
C (5)	0.045	O (5)	-0.421
C (6)	0.044	O (6)	-0.416
C (7)	-0.192	H (7)	0.113
C (8)	-0.158	H (8)	0.085
C (9)	-0.109	H (9)	0.081
C (10)	-0.154	H (10)	0.107
C (11)	-0.087	H (11)	0.107
C (12)	-0.128	H (12)	0.271
C (13)	-0.117		
C (14)	-0.167		
C (15)	-0.163		
C (16)	-0.161		
C (17)	0.165		
C (18)	-0.187		
O (19)	-0.476		
O (20)	-0.441		
H (21)	0.07		
H (22)	0.077		
H (23)	0.054		
H (24)	0.098		
H (25)	0.087		
H (26)	0.088		
H (27)	0.076		
H (28)	0.089		
H (29)	0.113		
H (30)	0.083		
H (31)	0.082		
H (32)	0.085		
H (33)	0.106		
H (34)	0.092		
H (35)	0.084		
H (36)	0.09		
H (37)	0.106		
H (38)	0.085		

H (39)	0.064
H (40)	0.073
H (41)	0.064
H (42)	0.079
H (43)	0.253
H (44)	0.258

110

111 **Table S2.** Brunauer-Emmett-Teller (BET) measures surface area and pore parameters.

Fibers	Surface area (m^2/g)	Average pore Diameter (nm)	Total pore volume (cm^3/g)
MIP	235.935	1.413	8.337
NIP	237.875	6.673	7.936

112

113 **Table S3.** The RSD of inter-day, inter-day, batches and cycles.

	inter-day	intra-day	batches	cycles
RSD (%)	4.16	3.92	3.47	3.59

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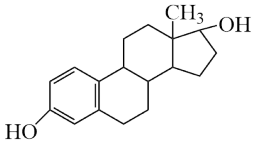
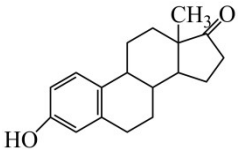
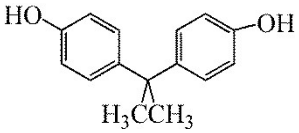
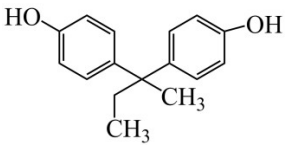
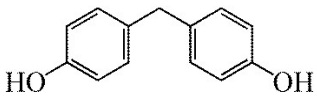
115 **Table S4.** Structure of the seven analogues.

Compounds	Structure	Molecular weight	pKa (predicted)
17β-estradiol		272.38	10.27
Estrone		270.37	10.25
Bisphenol A		228.29	10.29
Bisphenol B		242.31	10.27
Bisphenol F		200.23	9.91

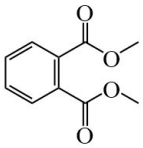
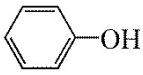
Dimethyl phthalate		194.18	3.42
Phenol		94.11	9.86

Table S5. Distribution coefficients (*Kd*), enrichment factor (*EF*) and imprinting factor (*IF*) calculated from the selectivity study.

Analytes	*Kd* MIP	*Kd* NIP	*EF* MIP	*EF* NIP	*IF*
E2	9924.90	9901.07	133.16	101.08	1.32
E1	9912.84	9885.57	114.73	87.39	1.31
BPA	9920.98	9889.52	126.55	97.73	1.29
BPB	9915.08	9893.30	118.03	93.72	1.26
BPF	9907.39	9866.51	99.60	77.91	1.28
DMP	9526.13	9480.30	21.10	19. 24	1.10
Phenol	7242.90	6901.56	3.63	3. 23	1.12

Table S6. Analysis of desorption rate and extraction rate (100.00 μg/L).

Analytes	Desorption rate /%		Extraction rate /%	
	MIP	NIP	MIP	NIP
E2	84.29	84.20	78.99	60.03
E1	83.56	83.28	68.64	52.47
BPA	83.35	82.51	75.91	54.85
BPB	81.19	81.53	76.59	57.48
BPF	86.87	86.76	62.15	43.17
DMP	88.51	95.17	11.92	10.11
Phenol	83.59	80.60	2.17	1.46

134 **Table S7.** Scatchard fitting parameter analysis.

Fiber array	Analytes	Low-affinity sites		High-affinity sites	
		Ka (mg/L)	Q_{max} (mg/g)	*Ka* (mg/L)	Q_{max} (mg/g)
MIP	E2	4.28	23.31	0.15	1.79
	E1	3.74	17.40	0.14	1.57
	BPA	4.00	20.97	0.18	1.91
	BPB	2.78	15.56	0.16	1.68
	BPF	3.20	16.58	0.15	1.31
NIP	E2	1.86	8.75	/	/
	E1	2.08	7.45	/	/
	BPA	2.34	10.64	/	/
	BPB	2.14	9.98	/	/
	BPF	1.84	7.03	/	/

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136 **Table S8.** The established method in dairy products sample.

Analytes	Linear range (μg/L)	Liner equation	R^2	LOD (μg/L)	LOQ (μg/L)
E2	1.00−200.00	Y=0.0233X+0.0713	0.9992		
E1	1.00−200.00	Y=0.0205X+0.0371	0.9995		
BPA	1.00−200.00	Y=0.0707X+0.1430	0.9998	0.33	1.00
BPB	1.00−200.00	Y=0.0790X+0.1155	0.9998		
BPF	1.00−200.00	Y=0.0655X+0.2751	0.9967		

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138 **Table S9.** The spiked recovery of the milk and yogurt dairy product samples analysis.

Samples	Analytes	Found (μg/L)	Spiked concentration (μg/L)								
			5.00			50.00			100.00		
			Detected[a] (μg/L)	Recovery (%)	RSD (%)	Detected[a] (μg/L)	Recovery (%)	RSD (%)	Detected[a] (μg/L)	Recovery (%)	RSD (%)
Milk-1	E2	/	5.14	102.87	8.25	54.12	108. 23	6.06	103.66	103.66	0.52
	E1		5.05	101.07	7.92	59.53	119.05	7.09	97.37	97.37	4.02
	BPA	/	5.22	104.35	9.42	51.38	102.76	6.86	100.11	100.11	2.45
	BPB	/	4.62	92.41	9.40	51.40	102.79	5.65	101. 21	101.21	6.23
	BPF	/	4.59	91.79	7.41	58.95	117.90	3.61	98.10	98.10	2.42
Milk-2	E2	/	4.02	80.43	5.54	48.40	96.80	9.42	107.31	107.31	5.67
	E1	/	4.13	82.54	5.88	46.75	93.50	5.82	92.70	92.70	5.07
	BPA	/	5.69	113.83	2.87	59.70	119.41	4.78	113.74	113.74	1.40
	BPB	/	4.19	83.70	6.53	56.07	112.13	6.02	118.55	118.55	6.50
	BPF	/	5.12	102.47	5.99	55.78	111.56	7.59	118.35	118.35	3.94
Milk-3	E2	/	3.74	74.75	6.54	42.92	85.83	0.92	93.79	93.79	8.52
	E1	/	4.38	87.54	9.07	56.56	113.11	062	103.35	103.35	5.06

	BPA	/	5.74	114.78	6.86	53.82	107.63	1.81	110.77	110.77	6.80
	BPB	/	4.62	92.41	7.21	58.95	117.90	0.47	110.01	110.01	6.66
	BPF	/	4.04	80.70	8.08	48.60	97. 20	4. 25	114.40	114.40	8.48
Yogurt-1	E2	/	3.77	75.42	9.22	38.78	77.55	6.09	83.62	83.62	5.72
	E1	/	5.45	108.94	1.23	49. 25	98.51	6.45	100.89	100.89	7.39
	BPA	/	5.97	119.35	3.04	55.45	110.89	9.02	112.79	112.79	2.83
	BPB	/	5.42	108.94	1.48	59. 24	118.47	7.27	117.05	117.05	3.79
	BPF	/	5.94	118.72	5.92	57.65	115.30	2.51	117.98	117.98	3.93

"/" means not found.

[a]Data were expressed as the mean Detected concentration determined from triplicate independent experiments.

References

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