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SUPPORTING INFORMATION

Preparation of cucurbit[6]uril-modified polymer monolithic column for microextraction of nitroaromatics

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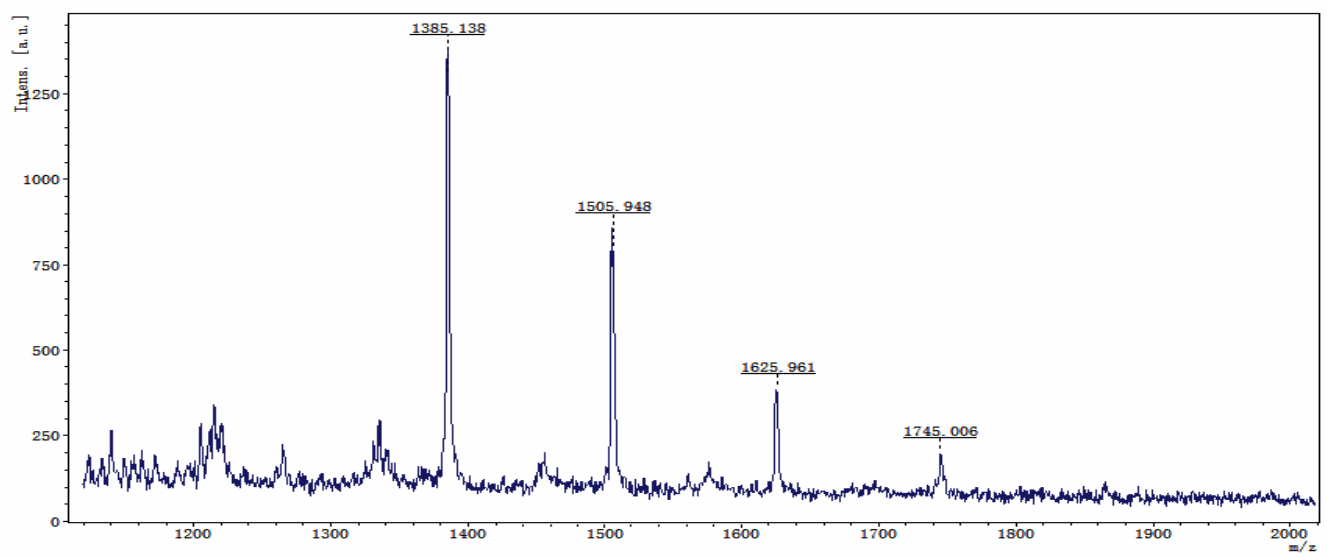

Fig. S1. The MALDI-TOF-MS spectra of CB[6]MR.

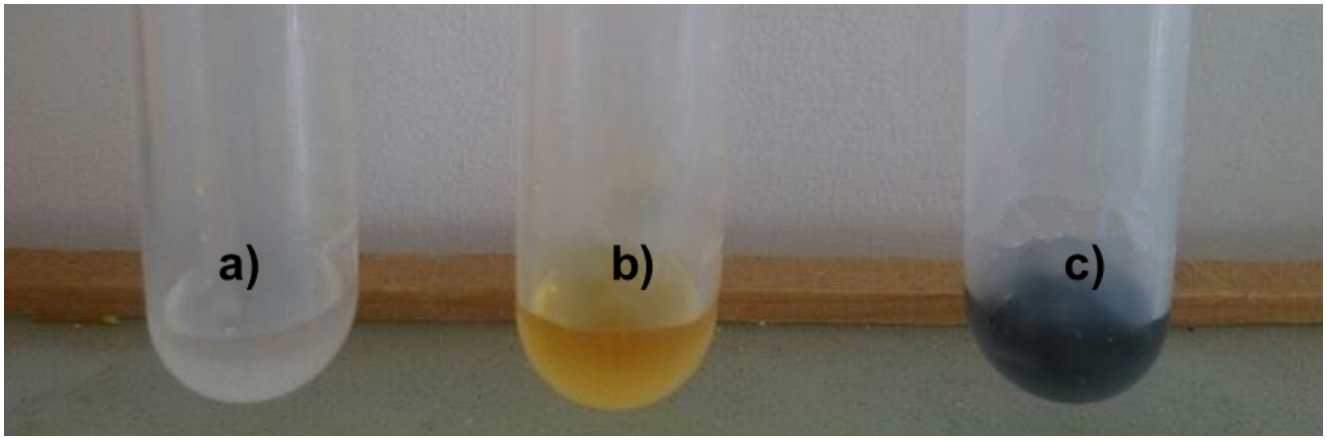

Fig. S2. Chromogenic reaction of phenolic hydroxyl groups (a) CB[6]MR, (b) the solution after color, and (c) $FeCl_3$ solution.

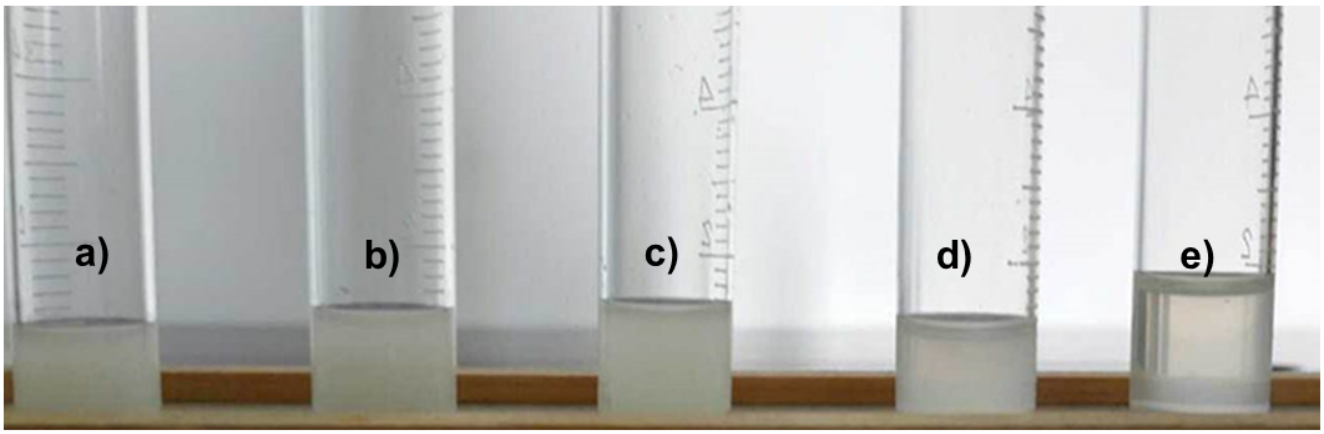

Fig. S3. Precipitation conditions with different proportion of CB[6]MR (placed after a week) A: 20 mg, B: 40 mg C: 60 mg, D: 80 mg and E: 100 mg.

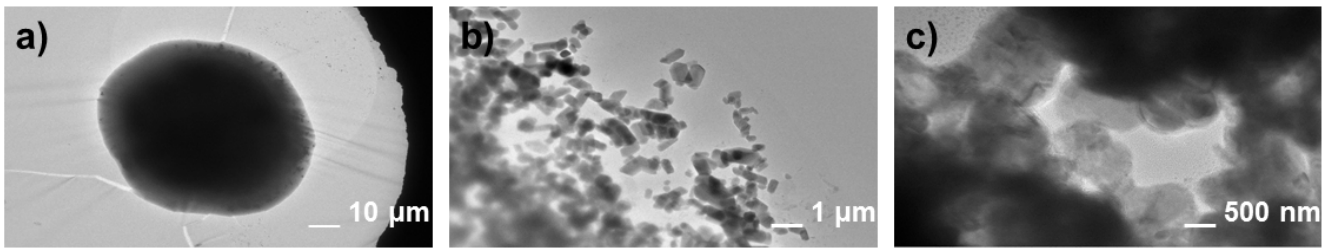

Fig. S4. TEM images of monolithic capillary: A: 10 μm, B: 1 μm, and C: 500 nm.

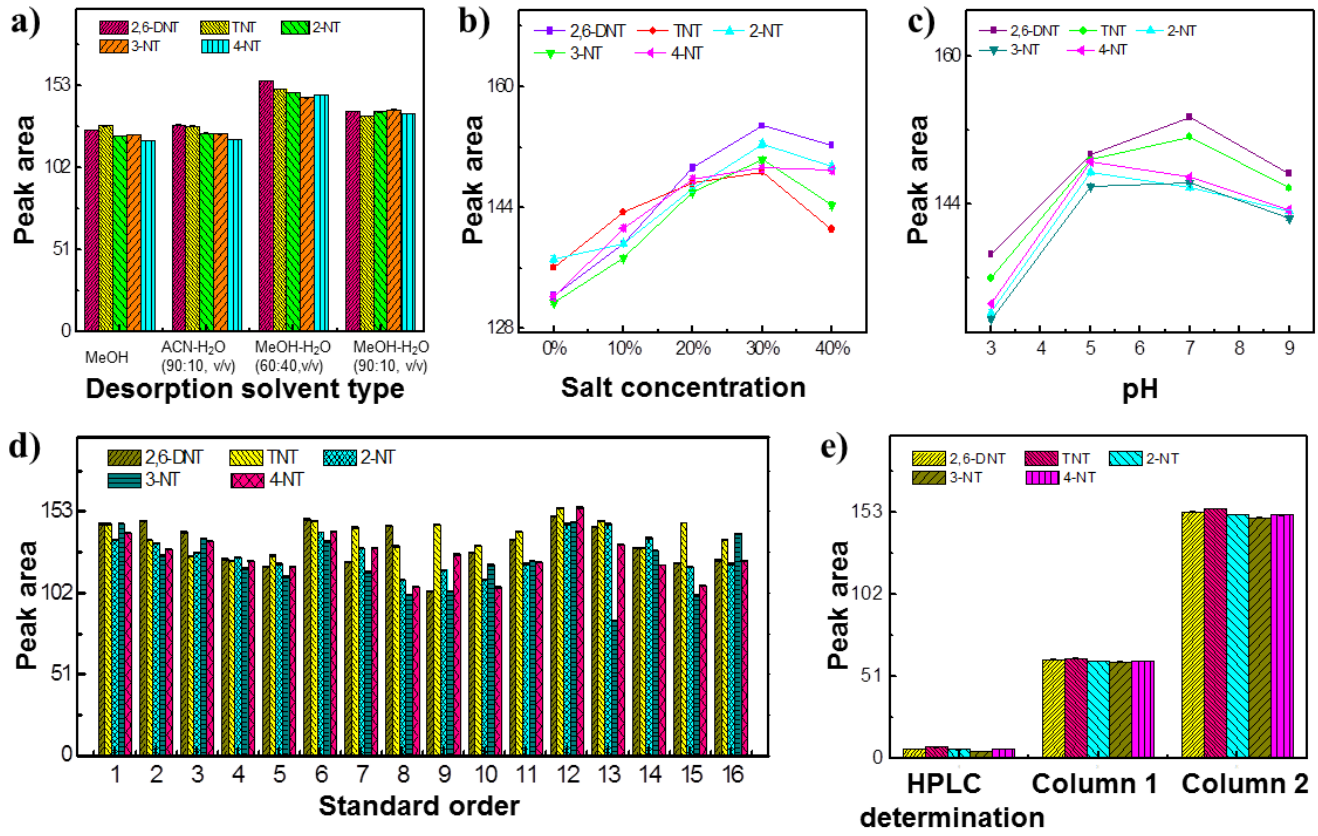

Fig. S5. Effects of various experimental parameters on the extraction efficiency: a), Effect of eluent species, b), Effect of sample pH, c), Effect of salt concentration, d), Results of orthogonal test, and e),Comparison of analytical performance of CB[6]MR@poly(GMA-EDMA) monolithic column (Column 2) with that of poly(GMA-EDMA) monolithic column (Column 1), and direct HPLC analysis. The concentration of nitroaromatics was 20 ng/mL.

Table S1. Composition of the polymerization mixtures used in the preparation of the CB[6]MR-decorated polymer monolithic column.

Column	Monomer/ porogen	Monomers (% w/w)		Porogens (% w/w)		AIBN (mg)	Temperature (°C)	Permeability [a]
		GMA	EDMA	1-Dodecanol	Toluene			
M-1	30/70	18	12	63	7	4.5	60	General
M-2	35/65	21	14	58.5	6.5	4.5	60	Good
M-3	40/60	24	16	54	6	4.5	60	General

[a] The permeabilities of monoliths were determined with flow rates, *i.e.*, the volume was determined when the solution passed through the monolith within certain time.

Table S2. The experimental design based on Taguchi's L_{16} (4^5) orthogonal array and the response of the peak area count by HPLC.

Standard order	Factor [a]					Response [b] (peak area)	
	A	B	C	D	E	Sum_1 [c]	Sum_2
1	0.08	0.60	0.04	0.06	6.5	710.9	709.4
2	0.08	0.80	0.05	0.07	7.0	670.5	672.3
3	0.08	1.00	0.06	0.08	7.5	663.3	660.1
4	0.08	1.20	0.07	0.09	8.0	609.1	612.8
5	0.09	0.60	0.05	0.08	8.0	594.8	587.6
6	0.09	0.80	0.04	0.09	7.5	710.7	711.3
7	0.09	1.00	0.07	0.06	7.0	640.1	645.2
8	0.09	1.20	0.06	0.07	6.5	592.4	590.3
9	0.10	0.60	0.06	0.09	7.0	593.4	593.9
10	0.10	0.80	0.07	0.08	6.5	594.3	594.1
11	0.10	1.00	0.04	0.07	8.0	639.0	638.2
12	0.10	1.20	0.05	0.06	7.5	752.7	755.3
13	0.11	0.60	0.07	0.07	7.5	652.3	652.1
14	0.11	0.80	0.06	0.06	8.0	644.8	644.8
15	0.11	1.00	0.05	0.09	6.5	591.6	592.3
16	0.11	1.20	0.04	0.08	7.0	639.6	638.8

[a] Factors: A, sample flow rate (mL/min); B, sample volume (mL); C, eluent flow rate (mL/min); D, eluent volume; E, sample pH; [b] Peak areas; [c] Total peak area of five explosives

Table S3. The analysis of the variance of the main factors on the respective peak area of HPLC in water samples.

Source [a]	Sum of Squares	df	Mean Square	*F*-value	Sig. [b]
A	2444.657	3	814.886	0.170	
B	1160.857	3	386.952	0.081	*
C	7430.497	3	2476.832	0.516	*
D	10587.967	3	3529.322	0.735	
E	14396.207	3	4798.735	1.000	**
Error	14396.21	3	4798.73		

[a] A, sample flow rate; B, sample volume; C, eluent flow rate; D, eluent volume; E, sample pH

[b] Significant level $\alpha = 0.05$

* and **: significant at $P \leq 0.01$ and $P \leq 0.001$, respectively.

Table S4. Analytical performance of the PMME method.

Analytes	Correlation coefficient	Linear range (ng/mL)	Limit of detection (ng/mL)	Limit of quantification (ng/mL)	Enrichment factor	RSD (%) (n = 5)	
						Intra-day	Inter-day
2,6-DNT	0.9995	10–500	0.025	0.078	24.5	1.7	2.1
TNT	0.9984	10–500	0.022	0.069	27.8	1.8	2.0
2-NT	0.9990	10–500	0.034	0.090	28.3	2.2	2.4
3-NT	0.9996	10–500	0.036	0.106	35.5	2.8	2.9
4-NT	0.9997	10–500	0.056	0.163	26.9	2.2	2.6

Table S5. Comparison of different sample preconcentration and detection methods for the determination of nitroaromatics.

Preconcentration method	Detection method	LOD (ng/mL)	Samples	Ref.
MEPS	HPLC-UV	0.06–0.09	Human blood	34
SFE [a]	GC-ECD	0.02–0.16	Water samples	41
MAE	GC-ECD	0.06–0.18	Soil samples	42
SPE	LC-MS	0.01–0.07	Water samples	43
DLLME [b]	HPLC	0.04–0.40	Water samples	44
SPME	GC-MS	0.05–2.0	Urine samples	45
SPE and SOX	HPLC	0.05–0.30	Water samples	46
LLE	HPLC	>0.014	Marine sediments	47
PMME	HPLC	0.022–0.056	Human blood	This work

[a] supercritical fluid extraction; [b] dispersive liquid-liquid microextraction

Table S6. Application to real water and blood samples.

			2,6-DNT	TNT	2-NT	3-NT	4-NT
South Lake	Found (ng/mL)		< LOD	< LOD	< LOD	< LOD	< LOD
	RR[a] ± RSD (%)	Level 1[b]	88.2 (4.5)	87.1 (5.2)	95.9 (4.3)	95.6 (5.2)	85.4 (4.7)
		Level 2[c]	97.3 (5.2)	98.2 (4.3)	101.0 (4.9)	99.3 (5.9)	96.8 (6.3)
Yitong River	Found (ng/mL)		0.56	< LOD	< LOD	< LOD	< LOD
	RR ± RSD (%)	Level 1	94.3 (5.7)	97.2 (6.2)	89.1 (4.6)	88.3 (5.9)	83.2 (6.9)
		Level 2	106.0 (5.8)	102.1 (5.7)	98.7 (6.2)	104.1 (5.7)	87.3 (11.2)
Ground water	Found (ng/mL)		< LOD	< LOD	0.43	< LOD	< LOD
	RR ± RSD (%)	Level 1	92.7 (4.2)	88.2 (7.8)	98.4 (8.3)	93.2 (6.8)	94.3 (4.1)
		Level 2	102.1 (4.7)	95.3 (8.2)	107.9 (8.6)	94.2 (8.9)	106.3 (5.4)
Drinking water	Found (ng/mL)		< LOD	< LOD	< LOD	< LOD	< LOD
	RR ± RSD (%)	Level 1	84.9 (7.2)	95.2 (4.7)	86.4 (8.8)	89.3 (7.6)	101.1 (9.1)
		Level 2	97.2 (7.8)	98.3 (5.4)	95.4 (9.3)	102.6 (9.2)	106.2 (9.7)
Blood sample 1	Found (ng/mL)		< LOD	< LOD	< LOD	< LOD	< LOD
	RR ± RSD (%)	Level 1	93.3 (4.2)	94.1 (3.3)	93.3 (3.7)	92.7 (5.1)	98.2 (3.2)
		Level 2	106.4 (4.7)	105.4 (4.1)	101.9 (4.5)	105.4 (5.7)	109.9 (3.3)
Blood sample 2	Found (ng/mL)		< LOD	< LOD	0.33	0.48	< LOD
	RR ± RSD (%)	Level 1	89.2 (4.3)	91.3 (3.2)	94.5 (2.1)	97.5 (2.8)	91.8 (4.6)
		Level 2	98.4 (5.1)	107.2 (3.9)	106.9 (2.5)	112.5 (5.3)	104.3 (6.1)
Blood sample 3	Found (ng/mL)		< LOD	< LOD	0.37	< LOD	< LOD
	RR ± RSD (%)	Level 1	97.2 (7.1)	88.2 (4.4)	98.1 (7.2)	93.5 (4.3)	88.7 (5.5)
		Level 2	110.9 (8.9)	100.9 (5.7)	110.3 (8.7)	102.1 (5.6)	103.2 (6.9)
Blood sample 4	Found (ng/mL)		< LOD	< LOD	< LOD	< LOD	< LOD
	RR ± RSD (%)	Level 1	98.2 (3.1)	95.2 (2.7)	93.8 (4.6)	100.9 (5.1)	99.3 (4.2)
		Level 2	110.1 (3.8)	109.2 (3.4)	101.8 (5.3)	111.8 (6.2)	110.9 (5.6)
Blood sample 5	Found (ng/mL)		< LOD	< LOD	< LOD	< LOD	< LOD
	RR ± RSD (%)	Level 1	93.7 (2.3)	97.5 (3.4)	92.4 (3.1)	90.9 (2.8)	88.5 (3.7)
		Level 2	95.3 (2.9)	95.4 (3.5)	98.6 (3.7)	97.2 (4.1)	98.7 (5.1)
Blood sample 6	Found (ng/mL)		< LOD	0.19	< LOD	< LOD	< LOD
	RR ± RSD (%)	Level 1	89.5 (5.3)	93.7 (2.4)	90.7 (7.1)	96.3 (4.2)	92.8 (5.1)
		Level 2	102.3 (6.2)	111.7 (3.2)	98.3 (9.6)	109.2 (4.5)	100.9 (6.7)

[a] Real recovery; [b] 20 ng/mL spiked; [c] 50 ng/mL spiked.