

**Low-viscosity hydrophobic deep eutectic solvent based ferrofluid for
simultaneous vortex-assisted liquid-liquid microextraction of UV
filters and parabens from environmental waters**

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Preparation of Fe₃O₄ magnetic nanoparticles

Firstly, FeCl₃ • 6H₂O (5.2 g) and FeCl₂ • 4H₂O (2.2 g) were added to a 250 mL three necked flask containing 160 mL of ultrapure water. Then, the mixture was sonicated for 20 min, and then mechanically stirred in an 80 °C oil bath for 20 min. With the mixture completely dissolved, 30 mL of ammonia solution was quickly added and continued stirring for 30 min. The entire reaction process was carried out in nitrogen atmosphere. After the reaction was completed, the precipitate, namely Fe₃O₄ nanoparticles, was collected using an external magnet and washed alternately with water and ethanol several times. Finally, the Fe₃O₄ particle was dried in a 60 °C vacuum drying oven for 12 hours.

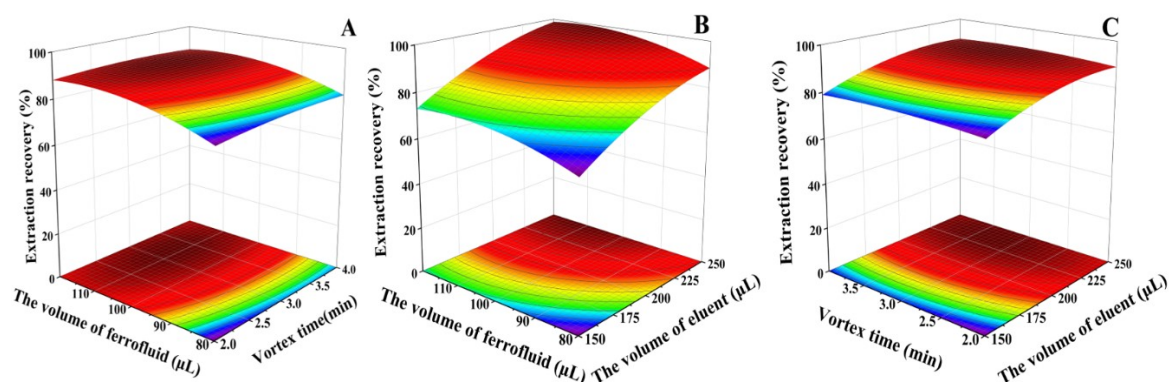


Figure 1 Response surface plots and contour plots for the recovery extraction recovery of UVFs using CCD. (A) The volume of ferrofluid versus vortex time; (B) the volume of ferrofluid versus the volume of eluent; (C) vortex time versus the volume of eluent.

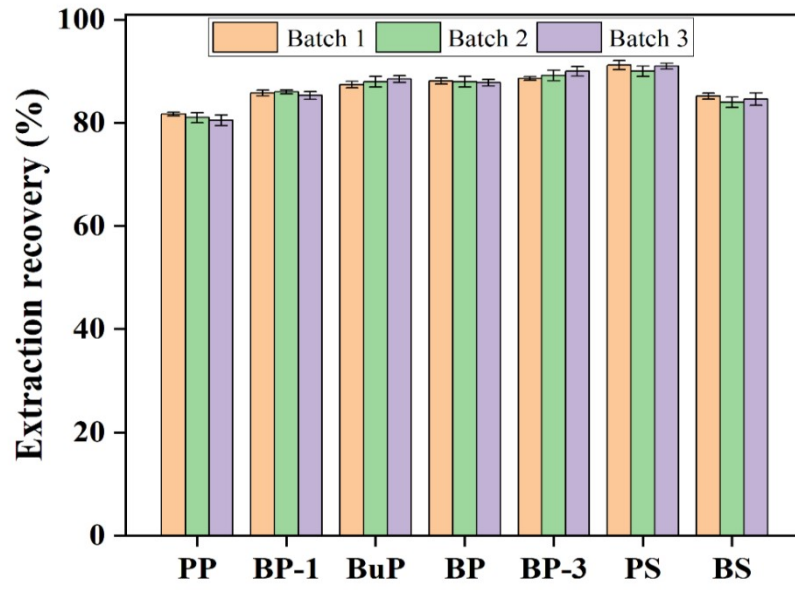


Figure 2 Inter-batch repeatability of the prepared ferrofluids

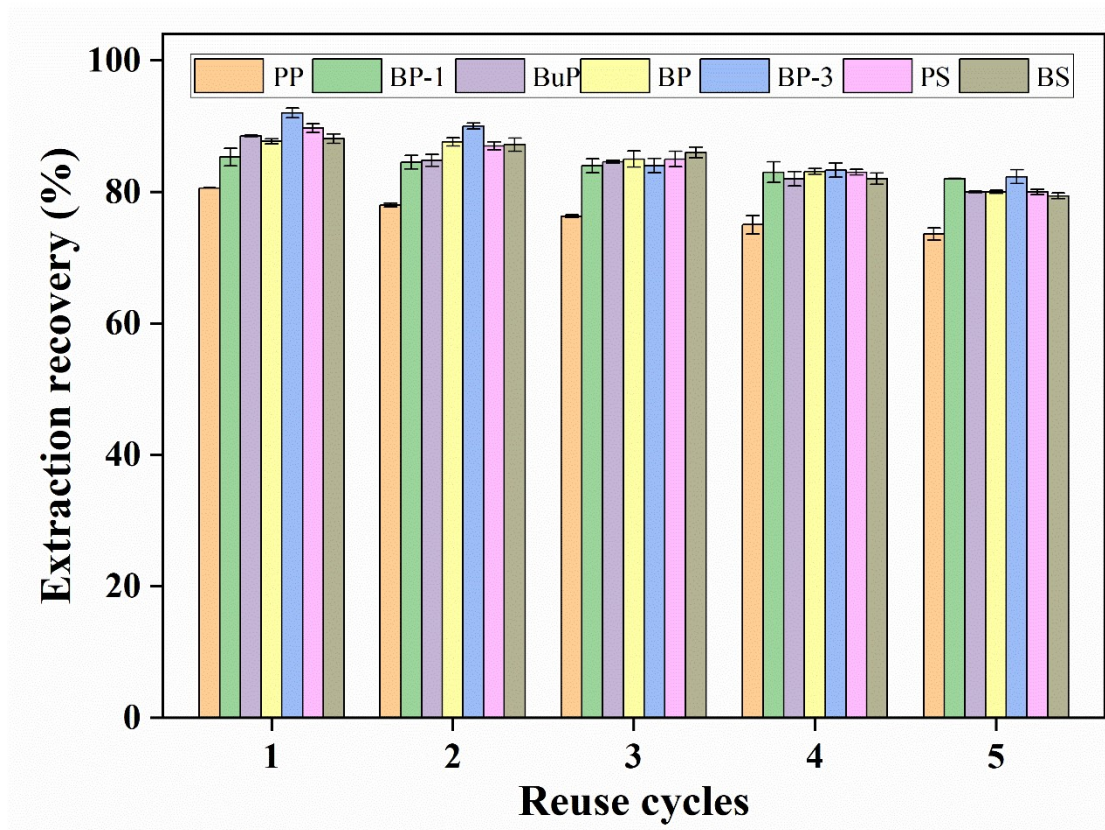


Figure 3 Reusability of $\text{Fe}_3\text{O}_4\text{@PDA}$ for the preparation of ferrofluids for extraction of UVFs and PBs

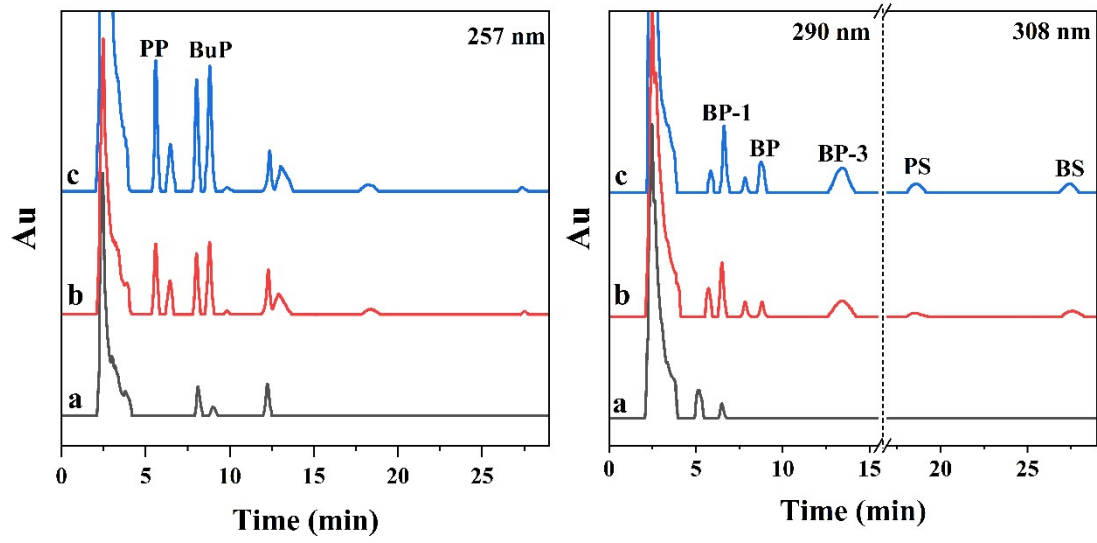


Figure 4 HPLC chromatograms of swimming pool water spiked with (a) 0, (b) 20 and (c) $50 \mu\text{g}\cdot\text{L}^{-1}$ of PP, BuP, BP-1, BP, BP-3, PS and BS.

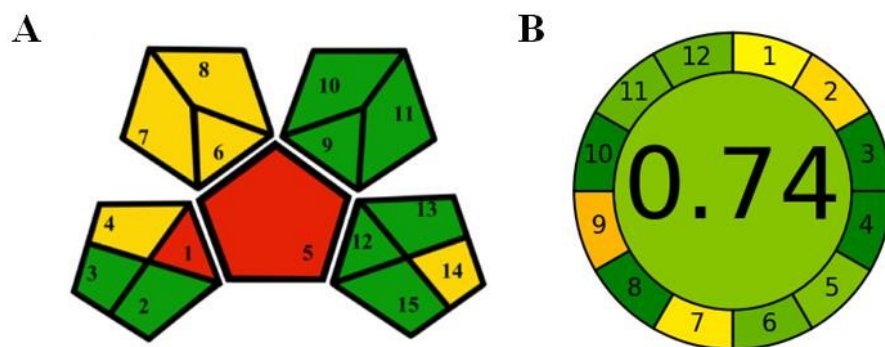
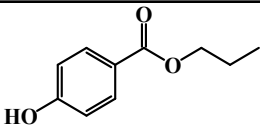
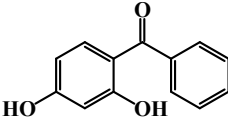
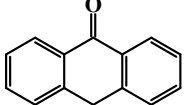
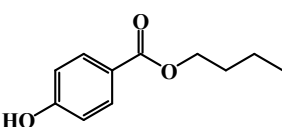
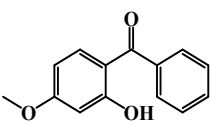
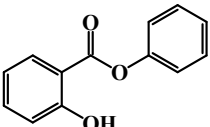
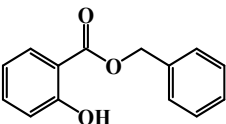


Figure 5 (A) Assessment of the green profile of the method based on the Green Analytical Procedure Index GAPI tool. (B) AGREE for the proposed method.

Table 1 Structures and LogKow of the studied UV filters and preservatives

Analyte	Structural formula	Molecular formula	LogKow ^a
PP		C ₁₀ H ₁₂ O ₃	2.93
BP-1		C ₁₃ H ₁₀ O ₃	2.96
BP		C ₁₃ H ₁₀ O	3.18
BuP		C ₁₁ H ₁₄ O ₃	3.57
BP-3		C ₁₄ H ₁₂ O ₃	3.64
PS		C ₁₃ H ₁₀ O ₃	3.82
BS		C ₁₄ H ₁₂ O ₃	4.01

^a: Exper. Ref: Hansch, C et al. (1995)

Table 2 Experimental variables and levels of PBD

Factors	Level	
	Low (-1)	High (+1)
The volume of ferrofluid (μL)	60	100
Vortex time (min)	1	4
Temperature ($^{\circ}\text{C}$)	25	45
The pH of the sample solution	4	6
The concentration of NaCl ($\text{mol}\cdot\text{L}^{-1}$)	0	0.1
The volume of eluent (μL)	100	200
Desorption time (s)	30	90

Table 3 Design matrix together with its response

Factors		Level				
		$-\alpha$	-1	0	1	$+\alpha$
(X ₁) The volume of ferrofluid (μL)		66.36	80	100	120	133.64
(X ₂) Vortex time (min)		1.32	2	3	4	4.68
(X ₃) The volume of eluent (μL)		115.91	150	200	250	284.09

Run order	X ₁	X ₂	X ₃	Response (%)	
				PBs	UVFs
1	100	3	200	83.3	89.6
2	80	2	250	75.4	80.6
3	133.64	3	200	81.2	85.6
4	100	3	200	82.2	88.9
5	100	3	200	83.4	89.5
6	100	3	284.09	82.5	88.1
7	100	1.32	200	77.3	84.1
8	66.36	3	200	61.9	67.9
9	80	4	150	62.4	68.9
10	100	4.68	200	81.2	87.2
11	120	2	200	73.5	79.9
12	80	4	250	76.1	82.4
13	100	3	200	82.8	89.9
14	120	4	150	74.5	80.0
15	120	4	250	83.4	89.2
16	100	3	200	82.3	88.1
17	100	3	200	82.4	88.0
18	100	3	115.91	59.2	68.2
19	80	2	150	57.6	65.4
20	120	2	250	82.7	88.2

Table 4 Results of ANOVA analysis for CCD (UVFs, $\alpha=1.682$)

Source of variation	Sum of squares	Degree of freedom	Mean squares	F-value	p-value
Model	1306.62	9	145.18	304.85	<0.0001
X ₁	356.42	1	356.42	748.41	<0.0001
X ₂	9.88	1	9.88	20.74	0.0011
X ₃	464.74	1	464.74	975.87	<0.0001
X ₁ X ₂	2.20	1	2.20	4.63	0.0569
X ₁ X ₃	15.68	1	15.68	32.93	0.0002
X ₂ X ₃	0.080	1	0.080	0.17	0.6906
X ₁ ²	278.91	1	278.91	585.67	<0.0001
X ₂ ²	22.61	1	22.61	47.49	<0.0001
X ₃ ²	219.68	1	219.68	461.29	<0.0001
Residual	4.76	10	0.48		
Lack of Fit	1.52	5	0.30	0.47	0.7866
Pure Error	3.24	5	0.65		
Cor Total	1311.39	19			
R-Sq= 99.64%					
R-Sq(adj)= 99.31%					
R-Sq(pred)= 98.66%					

Table 5 Performance characteristics of the HDES-FF-VA-LLME

Analyte	Liner range ($\mu\text{g L}^{-1}$)	R^2	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	Inter-day RSD (%)	Intra-day RSD (%)	EF	ME (%)
PP	0.2-200	0.9994	0.05	0.2	≤ 2.3	≤ 1.7	22	-3.1
BuP	0.5-200	0.9986	0.1	0.5	≤ 2.1	≤ 2.2	25	1.3
BP-1	0.5-200	0.9983	0.1	0.5	≤ 3.3	≤ 2.1	28	-1.3
BP	0.2-400	0.9993	0.05	0.2	≤ 0.2	≤ 3.0	29	-3.5
BP-3	0.2-400	0.9987	0.05	0.2	≤ 0.9	≤ 1.6	26	3.1
PS	0.5-400	0.9990	0.1	0.5	≤ 1.9	≤ 1.6	24	1.2
BS	1.0-400	0.9994	0.25	1.0	≤ 1.5	≤ 1.5	25	1.0