Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

A solidified floating organic drop-dispersive liquid-liquid microextraction based on in-situ formed fatty acid-based deep eutectic solvents for extraction of benzophenone-UV filters from water samples

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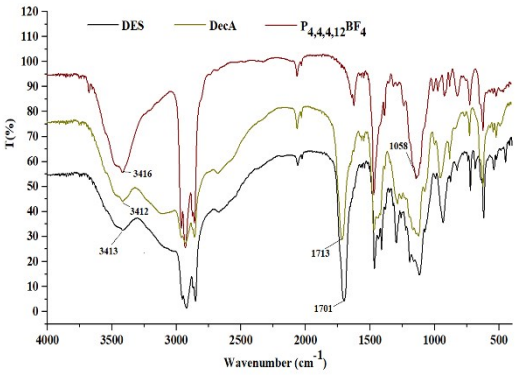

Fig. S1 FTIR spectra of $P_{4,4,4,12}BF_4$, DecA and DES ($P_{4,4,4,12}BF_4$: DecA).

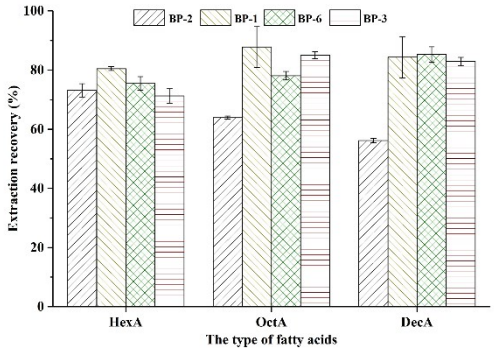

Fig. S2 Effect of the type of fatty acids. Extraction conditions: 8 mL of sample solution, 1 mL of fatty acid sodium solution, 100 μL of $P_{4,4,4,12}Br$, 100 μL of $NaBF_4$, 500 μL of 2 mol L^{-1} H_2SO_4, 45 °C solution temperature.

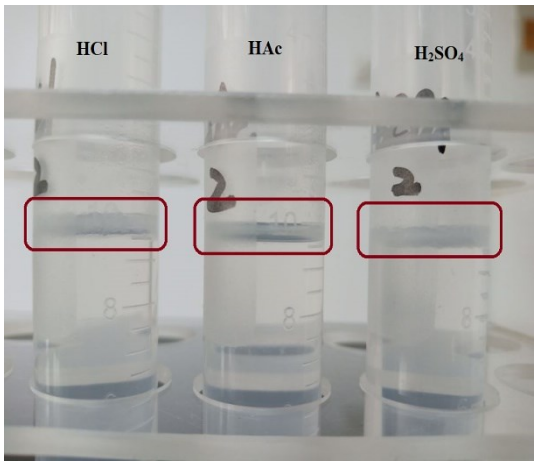

Fig. S3 Comparison of the solidification effect of the final DES phase using HCl, HAc and H_2SO_4.

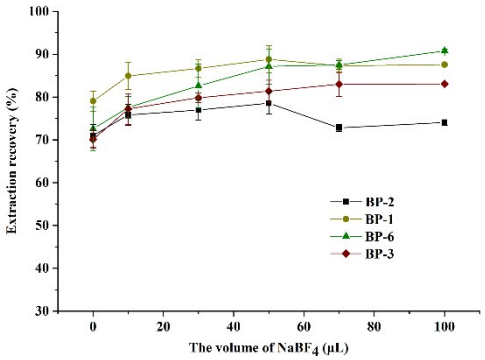

Fig. S4 Effect of the volume of $NaBF_4$ solution. Extraction conditions: 8 mL of sample solution, 400 μL of DecA-Na, 100 μL of $P_{4,4,4,12}Br$, 300 μL of 2 mol L^{-1} H_2SO_4, 45 °C solution temperature.

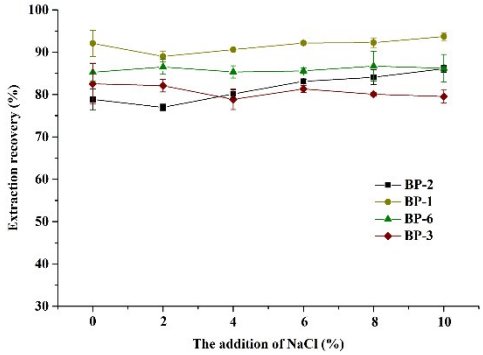

Fig. S5 Effect of salt addition. Extraction conditions: 8 mL of sample solution, 400 μL of DecA-Na, 100 μL of $P_{4,4,4,12}Br$, 50 μL of $NaBF_4$, 300 μL of 2 mol L^{-1} H_2SO_4.

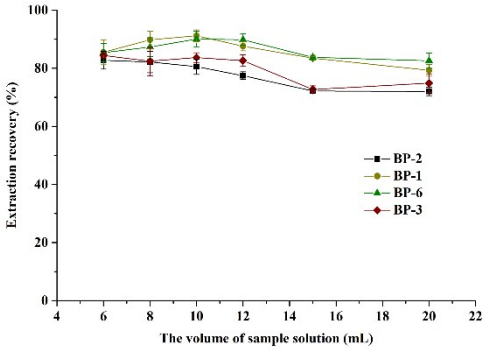

Fig. S6 Effect of sample volume. Extraction conditions: 400 μL of DecA-Na, 100 μL of $P_{4,4,4,12}Br$, 50 μL of $NaBF_4$, 300 μL of 2 mol L^{-1} H_2SO_4.

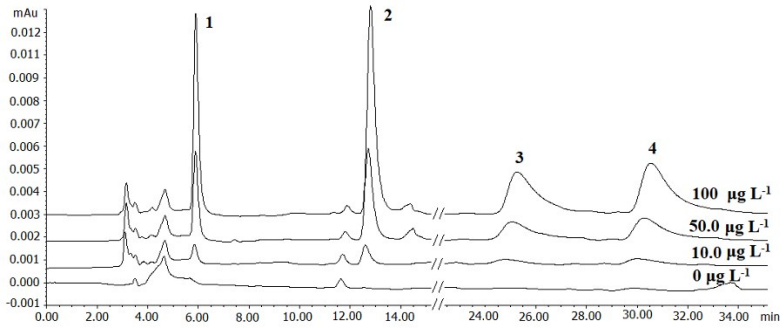

Fig. S7 The HPLC chromatograms of BP-UV filters in the blank and spiked (spiked with 0, 10.0, 50.0 and 100 μg L^{-1}, respectively) tap water: 1. BP-2; 2. BP-1; 3. BP-6; 4. BP-3.

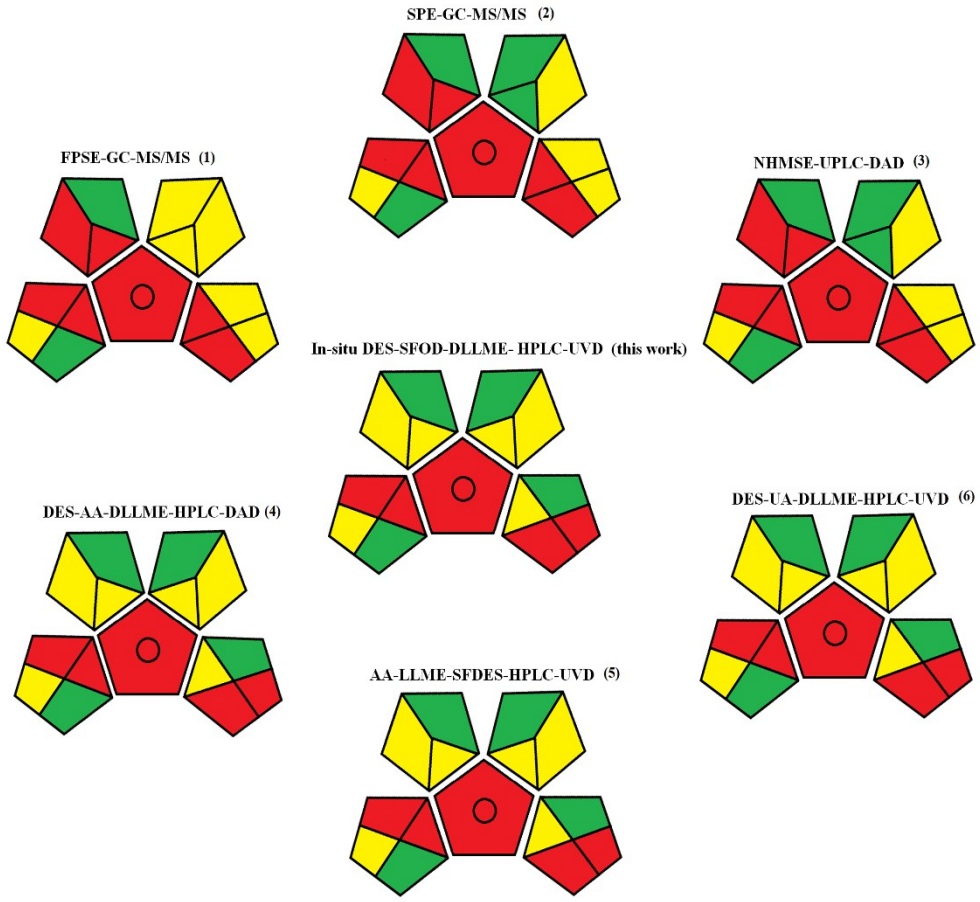

Fig. S8 Greenness assessment of the developed and reported methods for the determination of UV filters by GAPI approach.

Table S1 Comparison of the proposed method with reported methods for the extraction of UV filters.

Method	Extraction medium	UV filters	Sample	Organic solvents in extraction process	Main operation time	Analytical range ($\mu g\ L^{-1}$)	LOD	Reference
FPSE[a]-GC-MS/MS (1)	Sol-gel PDMS-FPSE	EHS, BS, HMS, BP-3, IAMC, 4MBC, MA, ETO, 2EHMC, EHPABA, OCR	Lake, river, seawater, swimming-pool water	2 mL of methanol/acetonitrile (50:50, *v*/*v*), 1 mL of ethyl acetate	8 min of immersing, 20 min of magnetic stirring, 3 min of desorption	0.2-200, 0.55-200, 0.5-200, 1-200	0.013-4.5 $ng\ L^{-1}$	10
SPE[b]-GC-MS/MS (2)	MIL-101	EHS, BS, HMS, BP-3, IAMC, 4MBC, MA, ETO, 2EHMC, OCR	Mineral, river, wastewater, swimming-pool, sea water	3.2 mL of ethyl acetate	20 min of conditioning, eluting, and redissolving	0.5-100	1.0-11.7 $ng\ L^{-1}$	7
NHMSE[c]-UPLC-DAD (3)	Hybrid monolith	BP-2, BP-1, 4-hydroxybenzophenone, BP-8, BP-3	Swimming-pool water, human urine	300 μL of methanol, 150 μL of mobile phase	150 min of stirring at 1100 rpm, 5 min of stirring at 1100 rpm	5-500	1-10 $\mu g\ L^{-1}$	44
DES-AA-DLLME[d]-HPLC-DAD (4)	DES (DL-menthol: decanoic acid = 1:1)	4OH-BP, BP-1, BP, BP-3, BP-2, BP-6	Swimming-pool, river water	100 μL of DES	Pull into and push out using a 10 mL glass syringe (repeated 5 times), 5 min of centrifugation	0.5-1000	0.05-0.2 $\mu g\ L^{-1}$	34
AA-LLME-SFDES[e]-HPLC-UVD (5)	DES (decanoic acid: dodecanoic acid = 2:1)	BP-1, BP, BP-3, PS, BS	Swimming-pool, well, river water	65 μL of DES, 100 μL of methanol	Pull into and push out using a 1 mL pipette (repeated 6 times, <10 s), 3 min of ice-water bath	0.15-400, 1.5-400, 0.50-400, 2.0-800	0.045-0.54 $\mu g\ L^{-1}$	35
DES-UA-DLLME[f]-HPLC-UVD (6)	DES ($N_{8,8,8,1}Cl$: decanoic acid = 1:3)	BP-1, BP, BP-3	Swimming-pool, river water	30 mg DES + 80 μL of methanol	5 min of sonication, 4 min of centrifugation	0.5-500, 1-500	0.15-0.30 $\mu g\ L^{-1}$	33
In-situ DES-SFOD-DLLME-HPLC-UVD	DES ($P_{4,4,4,12}Br$: decanoic acid = 1:9.4)	BP-2, BP-1, BP-6, BP-3	River, tap, bottled mineral and vitamin water	200 μL of methanol	5 min of centrifugation, 5 min of ice bath	2.00-500, 5.00-500	0.600-1.50 $\mu g\ L^{-1}$	This work

a. Fabric phase sorptive extraction;

b. Solid-phase extraction;

c. Nanostructured hybrid monolith stirring extraction;

d. Air-assisted dispersive liquid-liquid microextraction based on a new hydrophobic deep eutectic solvent;

e. Air-assisted liquid-liquid microextraction based on solidification of floating deep eutectic solvent;

f. Deep eutectic solvent-based ultrasound-assisted dispersive liquid-liquid microextraction.