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## **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  $\mu$ L of P<sub>4,4,4,12</sub>Br, 100  $\mu$ L of NaBF<sub>4</sub>, 500  $\mu$ L of 2 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, 45 °C solution temperature.



Fig. S3 Comparison of the solidification effect of the final DES phase using HCl, HAc and H<sub>2</sub>SO<sub>4</sub>.



Fig. S4 Effect of the volume of NaBF<sub>4</sub> solution. Extraction conditions: 8 mL of sample solution, 400  $\mu$ L of DecA-Na, 100  $\mu$ L of P<sub>4,4,4,12</sub>Br, 300  $\mu$ L of 2 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, 45 °C solution temperature.



Fig. S5 Effect of salt addition. Extraction conditions: 8 mL of sample solution, 400  $\mu$ L of DecA-Na, 100  $\mu$ L of P<sub>4,4,4,12</sub>Br, 50  $\mu$ L of NaBF<sub>4</sub>, 300  $\mu$ L of 2 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.



Fig. S6 Effect of sample volume. Extraction conditions: 400  $\mu$ L of DecA-Na, 100  $\mu$ L of P<sub>4,4,4,12</sub>Br, 50  $\mu$ L of NaBF<sub>4</sub>, 300  $\mu$ L of 2 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.



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<sup>-1</sup>, 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.

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $									
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Method	Extraction	UV filters	Sample	Organic solvents in	Main operation time	Analytical	LOD	Reference
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		medium			extraction process		range		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$							(µg L <sup>-1</sup> )		
-MS/MS (1) PDMS- FPSE BP-3, IAMC, seawater, swimming- ETC, 2EHMC, pool water pool water pool water of ethyl acetate $(50:50, \psi/v)$ , 1 mL $(50:00, \psi/v)$ ,	FPSE <sup>a</sup> -GC	Sol-gel	EHS, BS, HMS,	Lake, river,	2 mL of	8 min of immersing,	0.2-200,	0.013-4.5	10
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	-MS/MS (1)	PDMS-	BP-3, IAMC,	seawater,	methanol/acetonitril	20 min of magnetic	0.55-200,	ng L <sup>-1</sup>	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		FPSE	4MBC, MA,	swimming-	e (50:50, <i>v</i> / <i>v</i> ), 1 mL	stirring, 3 min of	0.5-200,		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			ETO, 2EHMC,	pool water	of ethyl acetate	desorption	1-200		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	_		EHPABA, OCR						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	SPE <sup>b</sup> -GC-	MIL-101	EHS, BS, HMS,	Mineral, river,	3.2 mL of ethyl	20 min of	0.5-100	1.0-11.7	7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	MS/MS (2)		BP-3, IAMC,	wastewater,	acetate	conditioning,		ng L-1	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			4MBC, MA,	swimming-		eluting, and			
$\begin{array}{c cccccc} \text{Water} & \text{Water}$			ETO, 2EHMC,	pool, sea		redissolving			
NHMSE-HyoridBP-2, BP-1, 4-Swimming-Soo $\mu$ L of methaloi,150 min of suffing5-5001-1044UPLC-DADmonolithhydroxybenzoppool water,150 $\mu$ L of mobileat 1100 rpm, 5 min $\mu$ g L-1(3)BP-3BP-3phaseof stirring at 1100rpmDES-AA-DES (DL-40H-BP, BP-1,Swimming-100 $\mu$ L of DESPull into and push0.5-10000.05-0.234DLLME <sup>4</sup> menthol:BP, BP-3, BP-2,pool, river100 $\mu$ L of DESPull into and push0.5-10000.05-0.234HPLC-DADdecanoicBP-6waterglass syringe(repeated 5 times), 5min ofcentrifugation(4)acid = 1:1)FS, BSpool, well,100 $\mu$ L of DES,Pull into and push0.15-400,0.045-35SFDES <sup>e</sup> -(decanoicPS, BSpool, well,100 $\mu$ L of methanolout using a 1 mL1.5-400,0.54(5)dodecanoicriver waterriver water100 $\mu$ L of methanolout using a 1 mL1.5-400,0.54(5)dodecanoiccid = 2:1)river watercid = 2:00.5, 3 min2.0-800	NHMOEC	Uribrid		water	200 uL of mothemal	150 min of stiming	5 500	1 10	4.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	NHMSE-	Hydrid	BP-2, BP-1, 4-	Swimming-	500 μL of methanol,	at 1100 rpm 5 min	5-500	1-10 u.a. I1	44
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(3)	mononui	henone BP-8	human urine	nhase	of stirring at 1100		μgĽ	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$(\mathbf{J})$		RP-3	numan urme	phase	rnm			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	DFS-AA-	DFS (DL-	40H-RP RP-1	Swimming-	100 µL of DES	Pull into and push	0.5-1000	0.05-0.2	34
HPLC-DAD (4)decanoic acid = 1:1)BP-6waterglass syringe (repeated 5 times), 5 min of centrifugationAA-LLME- SFDESe- (decanoic BP-1, BP, BP-3, Swimming- (f)BP-3, Swimming- 	DLLME <sup>d</sup> -	menthol <sup>.</sup>	BP BP-3 BP-2	pool river		out using a 10 mL	0.5 1000	ug L <sup>-1</sup>	51
(4) $acid = 1:1$ ) (4) $acid = 1:1$ ) (7) $acid = $	HPLC-DAD	decanoic	BP-6	water		glass svringe		r8 -2	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(4)	acid = 1:1				(repeated 5 times), 5			
AA-LLME-DESBP-1, BP, BP-3,Swimming- pool, well, $65 \ \mu L \text{ of DES},$ Pull into and push $0.15-400,$ $0.045 35$ SFDESe-(decanoicPS, BSpool, well, $100 \ \mu L \text{ of methanol}$ out using a 1 mL $1.5-400,$ $0.54$ HPLC-UVDacid:river waterriver waterpipette (repeated 6 $0.50-400,$ $\mu g L^{-1}$ (5)dodecanoicacid = 2:1)of ice-water bathof ice-water bath $0.50-400,$ $0.50-400,$		,				min of			
AA-LLME-DESBP-1, BP, BP-3,Swimming- pool, well, $65 \ \mu L \text{ of DES},$ Pull into and push $0.15-400,$ $0.045 35$ SFDESe-(decanoicPS, BSpool, well, $100 \ \mu L \text{ of methanol}$ out using a 1 mL $1.5-400,$ $0.54$ HPLC-UVDacid:river waterriver waterpipette (repeated 6 $0.50-400,$ $\mu g L^{-1}$ (5)dodecanoicacid = 2:1)of ice-water bath $0.645 0.50-400,$ $0.54$						centrifugation			
SFDESe- HPLC-UVD(decanoic acid:PS, BS river waterpool, well, river water100 $\mu$ L of methanol pipette (repeated 6out using a 1 mL pipette (repeated 61.5-400, ug L^-10.54(5)dodecanoic acid = 2:1)river watertimes, <10 s), 3 min of ice-water bath2.0-800	AA-LLME-	DES	BP-1, BP, BP-3,	Swimming-	65 μL of DES,	Pull into and push	0.15-400,	0.045-	35
HPLC-UVDacid:river waterpipette (repeated 6 $0.50-400$ , $\mu g L^{-1}$ (5)dodecanoictimes, <10 s), 3 min	SFDES <sup>e</sup> -	(decanoic	PS, BS	pool, well,	100 µL of methanol	out using a 1 mL	1.5-400,	0.54	
(5) dodecanoic times, $<10$ s), 3 min 2.0-800 acid = 2:1) of ice-water bath	HPLC-UVD	acid:		river water		pipette (repeated 6	0.50-400,	μg L-1	
acid = 2:1) of ice-water bath	(5)	dodecanoic				times, <10 s), 3 min	2.0-800		
		acid = $2:1$ )		~		of ice-water bath			
DES-UA- DES BP-1, BP, BP-3 Swimming- $30 \text{ mg DES} + 80 \mu\text{L}$ 5 min of sonication, 0.5-500, 0.15-0.30 33	DES-UA-	DES	BP-1, BP, BP-3	Swimming-	$30 \text{ mg DES} + 80 \mu \text{L}$	5 min of sonication,	0.5-500,	0.15-0.30	33
DLLME <sup>T</sup> - ( $N_{8,8,8,1}$ CI: pool, river of methanol 4 min of 1-500 µg L <sup>-1</sup>	DLLME <sup>1</sup> -	$(N_{8,8,8,1}CI:$		pool, river	of methanol	4 min of	1-500	μg L-1	
HPLC-UVD decanoic water centrifugation	HPLC-UVD	decanoic		water		centrifugation			
(6) $acid = 1:3$	(6) In site DES	acid = 1:3		Direct ton	200 . I of mother of	5 min of	2 00 500	0.000	This mode
III-SILU DES- DES DF-2, BF-1, BF- KIVEF, LAP, $200 \mu\text{L}$ OI metinanol S min OI $2.00-500$ , $0.600-$ I fils Wor SECD (D Br: 6 BD 3 bottled contribution 5 5.00, 500, 1.50 m J-	SEOD		Dr-2, Br-1, Br-	kiver, tap,	200 µL of methanol	5 min 01	2.00-300,	0.000-	I HIS WORK
DLIME, decanoic mineral and min of ice bath $\frac{1}{2}$	DLIME-	decanoic	0, D <b>F</b> -3	mineral and		min of ice bath	5.00-500	1.50 µg L	
HPLC-UVD acid = 1.9.4) vitamin water	HPLC-UVD	acid = 1.94		vitamin water					

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.