Electronic Supplementary Material

Effervescence tablets based on magnetic ionic liquids as simple microdevices for the *in situ* dispersive liquid-liquid microextraction of urinary biomarkers

Raúl González-Martín[1,2], María J. Trujillo-Rodríguez[1,2,3,*], Mara G. Freire[3], Juan H. Ayala[1], Verónica Pino[1,2,4]

[1]Laboratorio de Materiales para Análisis Químico (MAT4LL), Departamento de Química, Unidad Departamental de Química Analítica, Universidad de La Laguna (ULL), 38206 San Cristóbal de La Laguna, Spain
[2]Unidad de Investigación de Bioanalítica y Medio Ambiente, Instituto Universitario de Enfermedades Tropicales y Salud Pública de Canarias (IUETSP), ULL, 38206 San Cristóbal de La Laguna, Spain
[3]CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[4]Centro de Investigación Biomédica en Red de Enfermedades Infecciosas (Ciberinfec), Instituto de Salud Carlos III, 28029 Madrid, Spain

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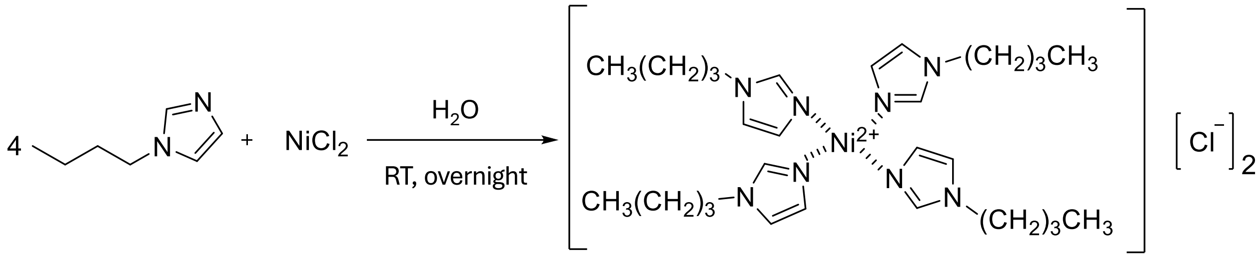


$[Ni(C_4IM)_4]Cl_2$ MIL

Figure S1. Preparation of the $[Ni(C_4IM)_4]Cl_2$ MIL.

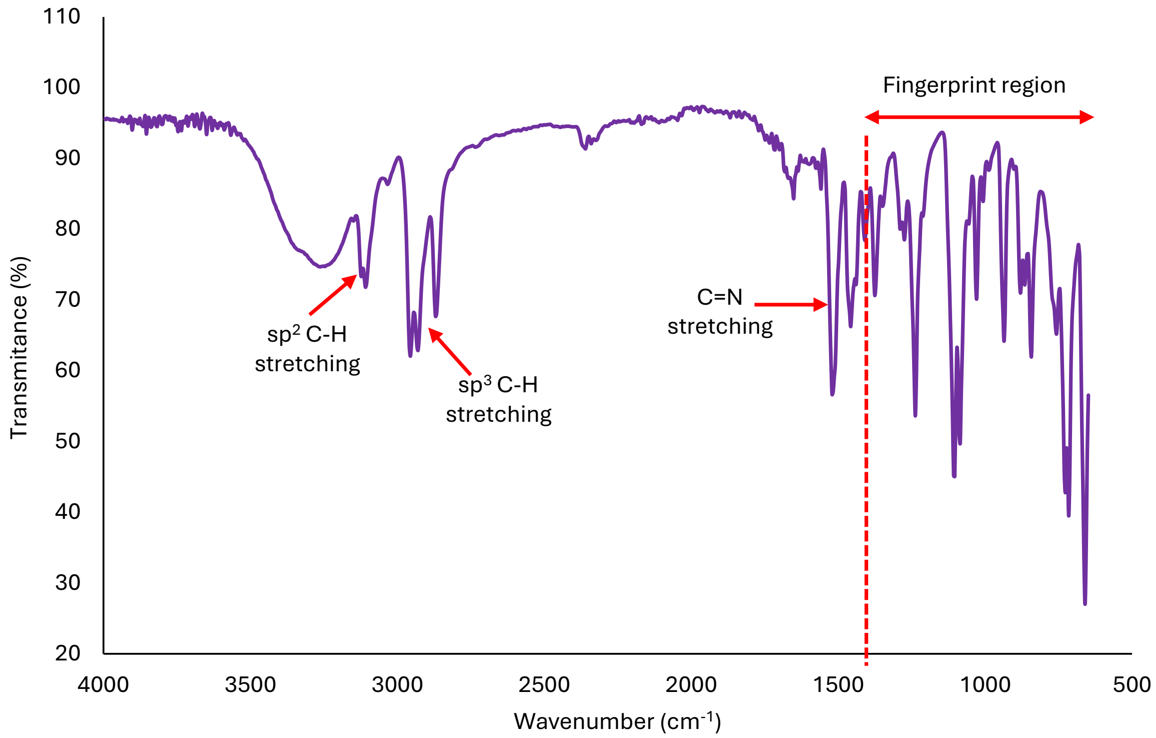


Figure S2. Characterization of the $[Ni(C_4IM)_4]Cl_2$ MIL by FT-IR spectroscopy:

- sp^3 C-H stretching bands at ~2900 cm^{-1}.
- sp^2 C-H stretching bands at 3100 cm^{-1}.
- C=N stretching bands at 1550–1650 cm^{-1}.
- Fingerprint region at 1400–400 cm^{-1}.

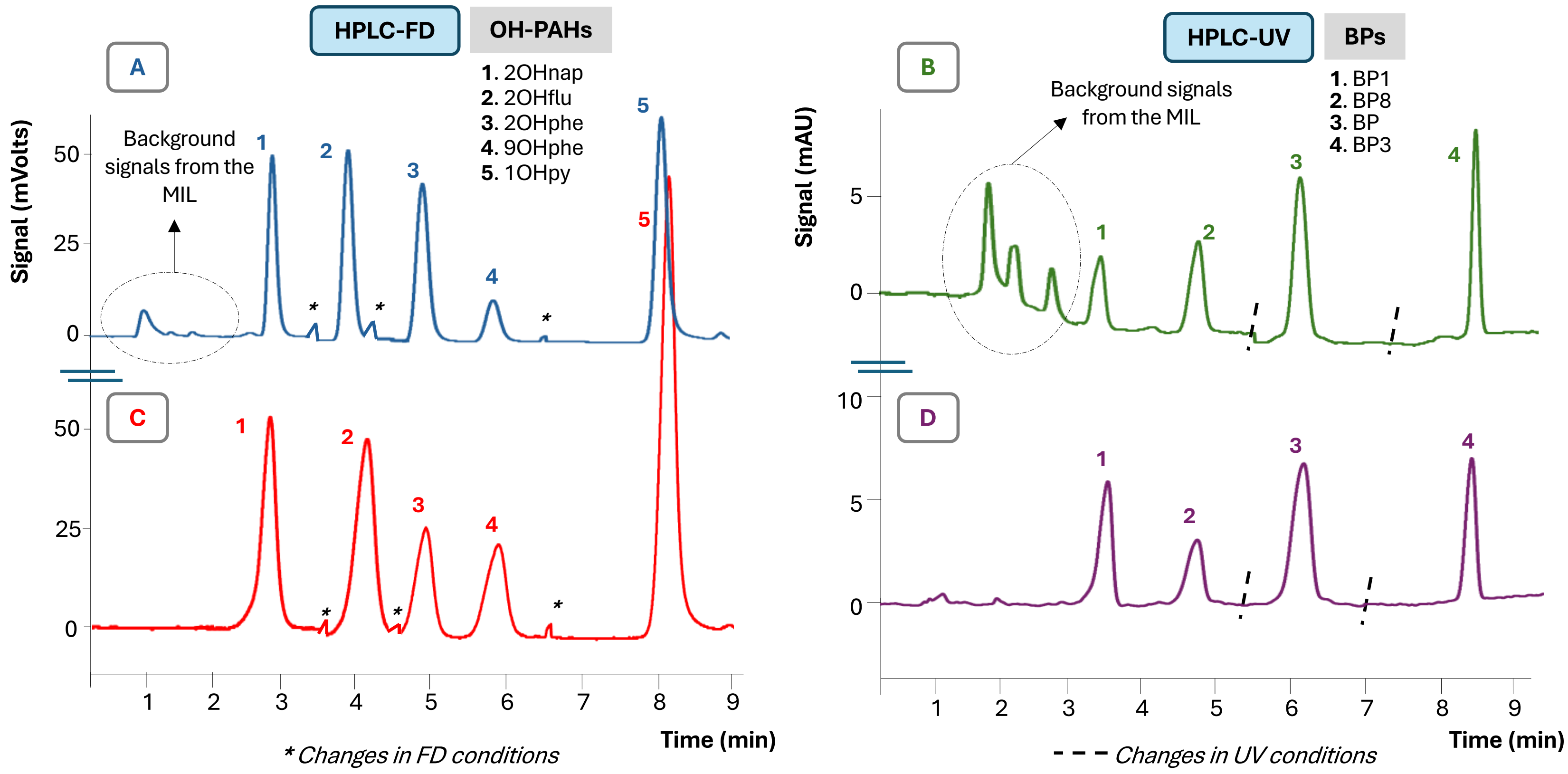


Figure S3. Representative chromatograms of: **(A)** & **(B)** an extract (MIL microdroplet diluted with ACN) obtained after subjecting an aqueous standard solution to the *in situ* MIL-DLLME method (under non-optimum conditions). The concentrations of the aqueous standard were: 4.8 μg·L^{-1} for 2OHflu, 2OHphe, and 1OHpy, 9.6 μg·L^{-1} for 2OHnap and 9OHphe, and 80 μg·L^{-1} for the BPs; **(C)** a standard of the OH-PAHs in ACN at 15 μg·L^{-1} for 2OHflu, 2OHphe and 1OHpy, and 30 μg·L^{-1} for 2OHnap and 9OHphe; **(D)** a standard of the BPs in ACN at 250 μg·L^{-1}.

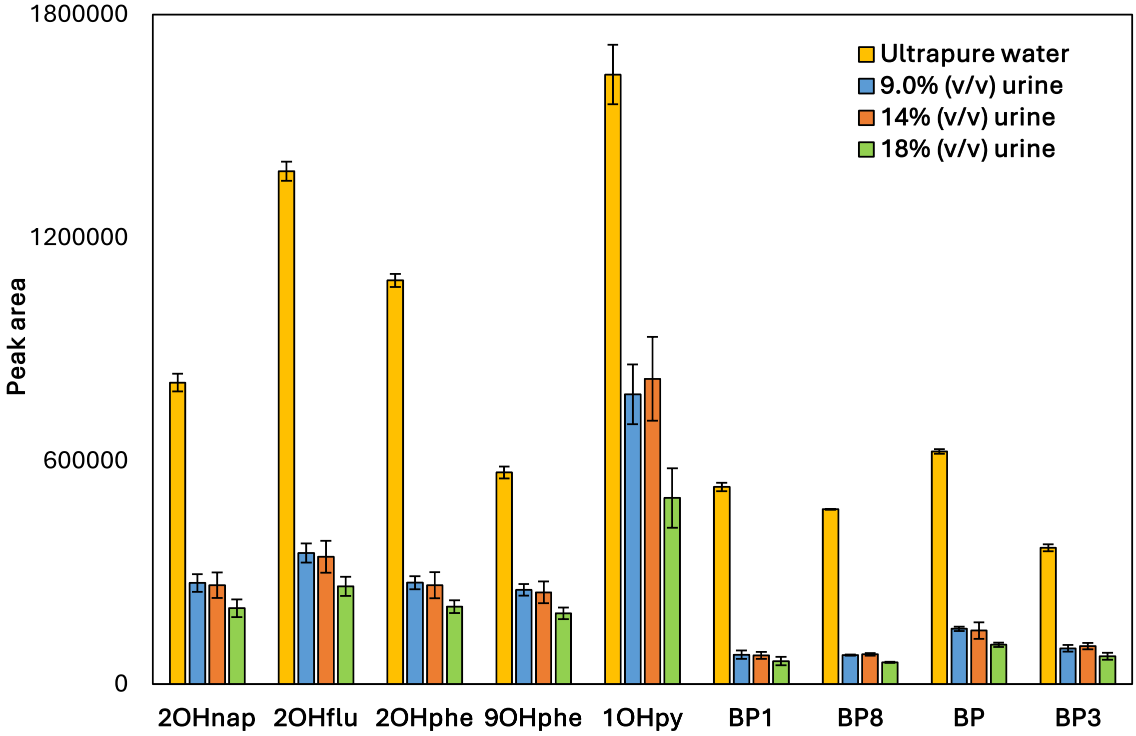


Figure S4. Effect of the urine content in the standard subjected to the *in situ* MIL-DLLME method. Experiments (n = 3) involved 5.0 mL of aqueous standard or diluted urine standard solution. Different urine contents were tested (9.0%, 14%, and 18%, v/v) at pH 5, 300 µL of acetone, and 15 min of equilibration time. The effervescence tablet was composed by 30.0 mg of MIL, 26.0 mg of $LiNTf_2$, 297 mg of NaH_2PO_4, 311 mg of K_2CO_3, and 750 mg of Na_2SO_4 (15%, w/v). The concentration of the standards was 9.6 $\mu g \cdot L^{-1}$ for 2OHnap and 9OHphe, 4.8 $\mu g \cdot L^{-1}$ for the remaining OH-PAHs, and 80 $\mu g \cdot L^{-1}$ for all BPs.

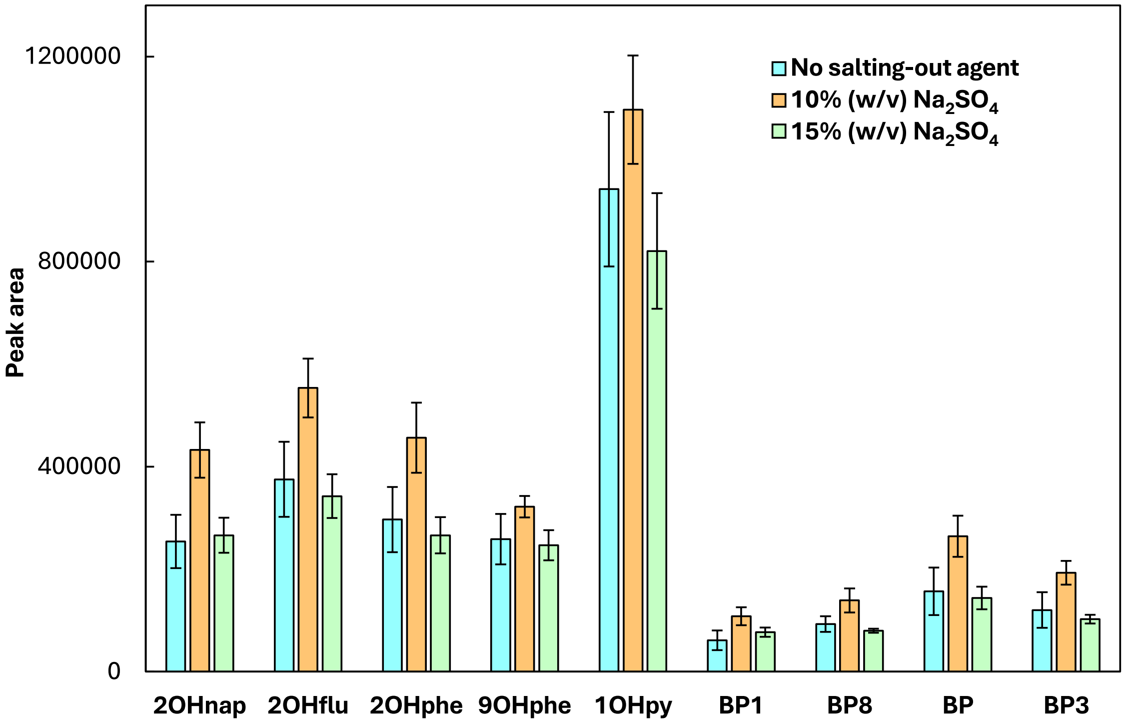


Figure S5. Effect of the concentration of Na_2SO_4 as salting-out agent in the *in situ* MIL-DLLME method. Experiments (n = 3) required 5.0 mL of diluted urine standard solution (14%, v/v, of urine) at pH 5, 300 µL of acetone, and 15 min of equilibration time. The effervescence tablet was composed by 30.0 mg of MIL, 26.0 mg of $LiNTf_2$, 297 mg of NaH_2PO_4, 311 mg of K_2CO_3, and different amounts of Na_2SO_4 depending on the experiment (0, 500 or 750 mg). The concentration of the standards was 9.6 $\mu g \cdot L^{-1}$ for 2OHnap and 9OHphe, 4.8 $\mu g \cdot L^{-1}$ for the remaining OH-PAHs, and 80 $\mu g \cdot L^{-1}$ for all the BPs.

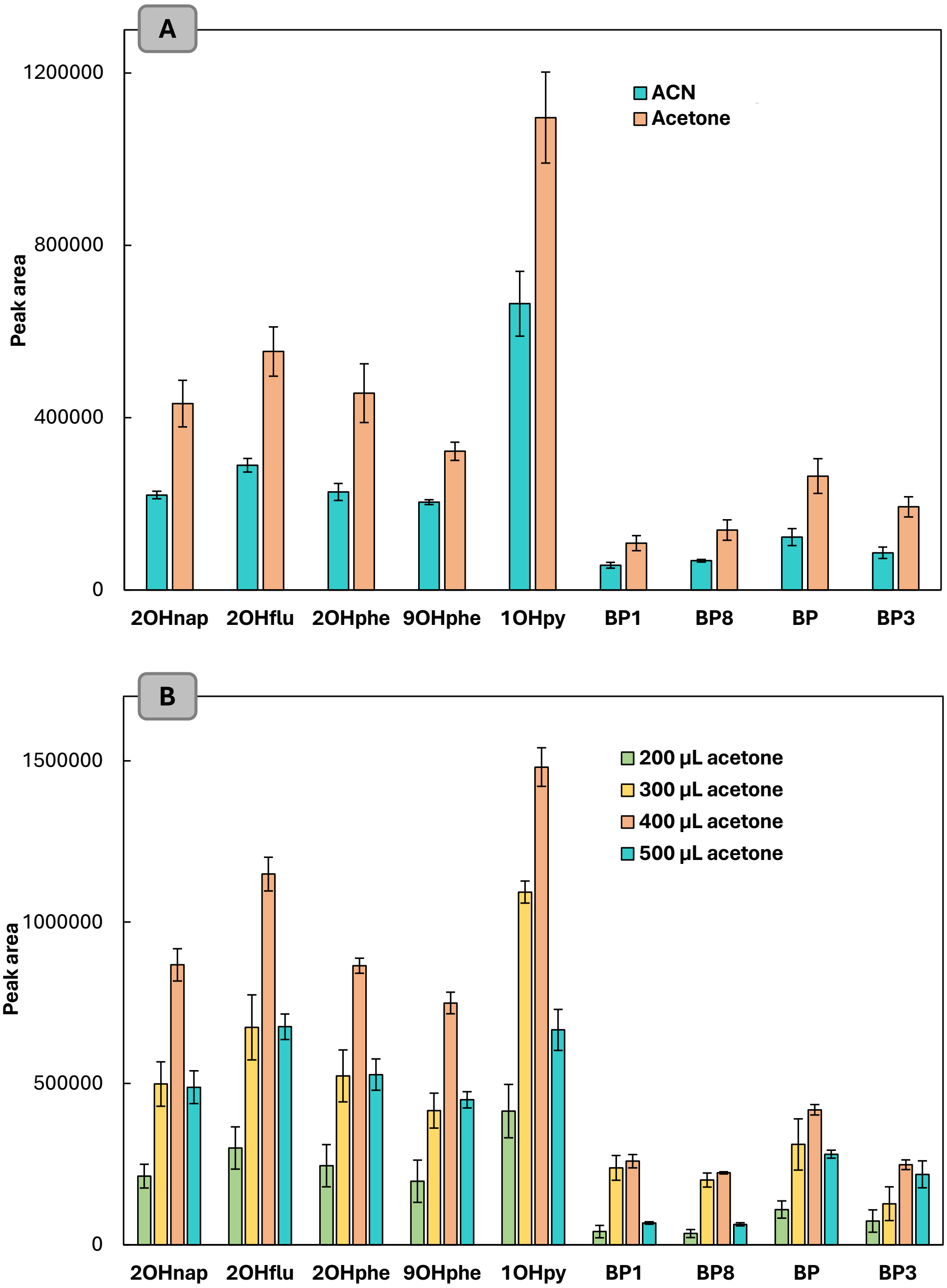


Figure S6. Effect of **(A)** the type of auxiliary solvent (keeping its volume constant at 300 µL); and **(B)** the volume of acetone. In both studies, experiments (n = 3) required 5.0 mL of diluted urine standard solution (14%, v/v, of urine) at pH 5, and 15 min of equilibration time. The effervescence tablet was composed by 30.0 mg of MIL, 26.0 mg of $LiNTf_2$, 297 mg of NaH_2PO_4, 311 mg of K_2CO_3, and 500 mg of Na_2SO_4 (10%, w/v). The concentration of the standards was 9.6 µg·L^{-1} for 2OHnap and 9OHphe, 4.8 µg·L^{-1} for the remaining OH-PAHs, and 80 µg·L^{-1} for all the BPs.

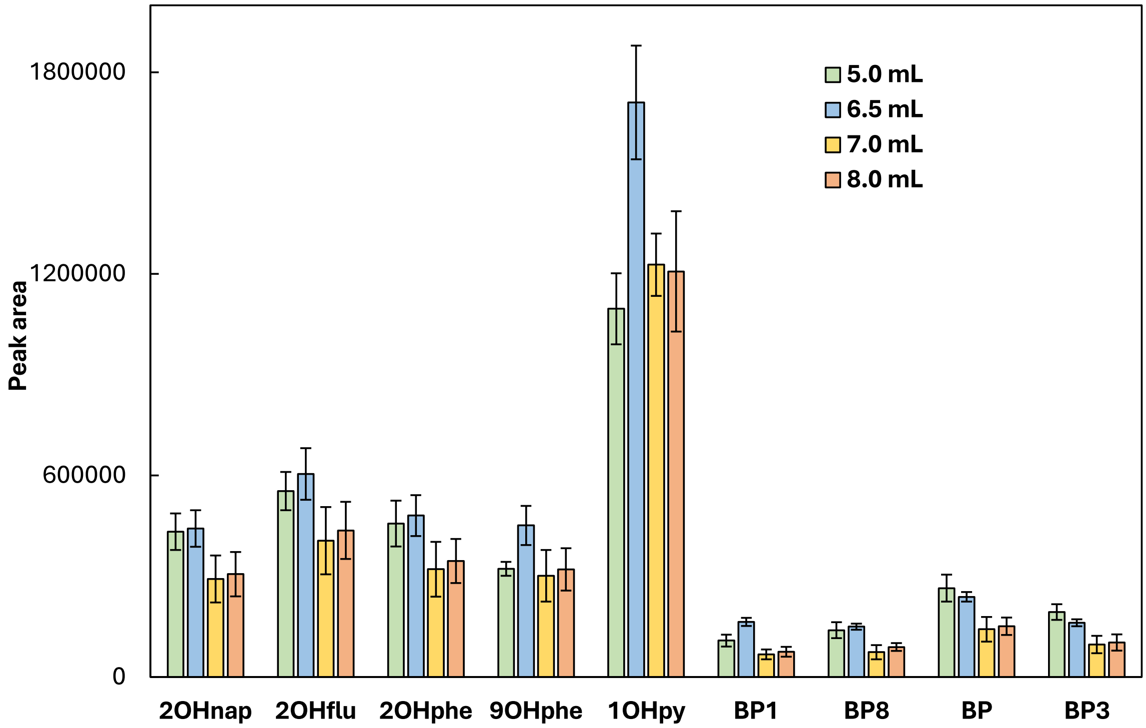


Figure S7. Effect of the sample volume in the *in situ* MIL-DLLME method. Experiments (n = 3) required different volumes (from 5.0 to 8.0 mL) of diluted urine standard solution (14%, v/v, of urine) at pH 5, 400 µL of acetone, and 15 min of equilibration time. The effervescence tablet was composed by 30.0 mg of MIL, 26.0 mg of $LiNTf_2$, 297 mg of NaH_2PO_4, 311 mg of K_2CO_3, and 10% (w/v) of Na_2SO_4. The concentration of the standards was 9.6 $\mu g \cdot L^{-1}$ for 2OHnap and 9OHphe, 4.8 $\mu g \cdot L^{-1}$ for the remaining OH-PAHs, and 80 $\mu g \cdot L^{-1}$ for all the BPs.

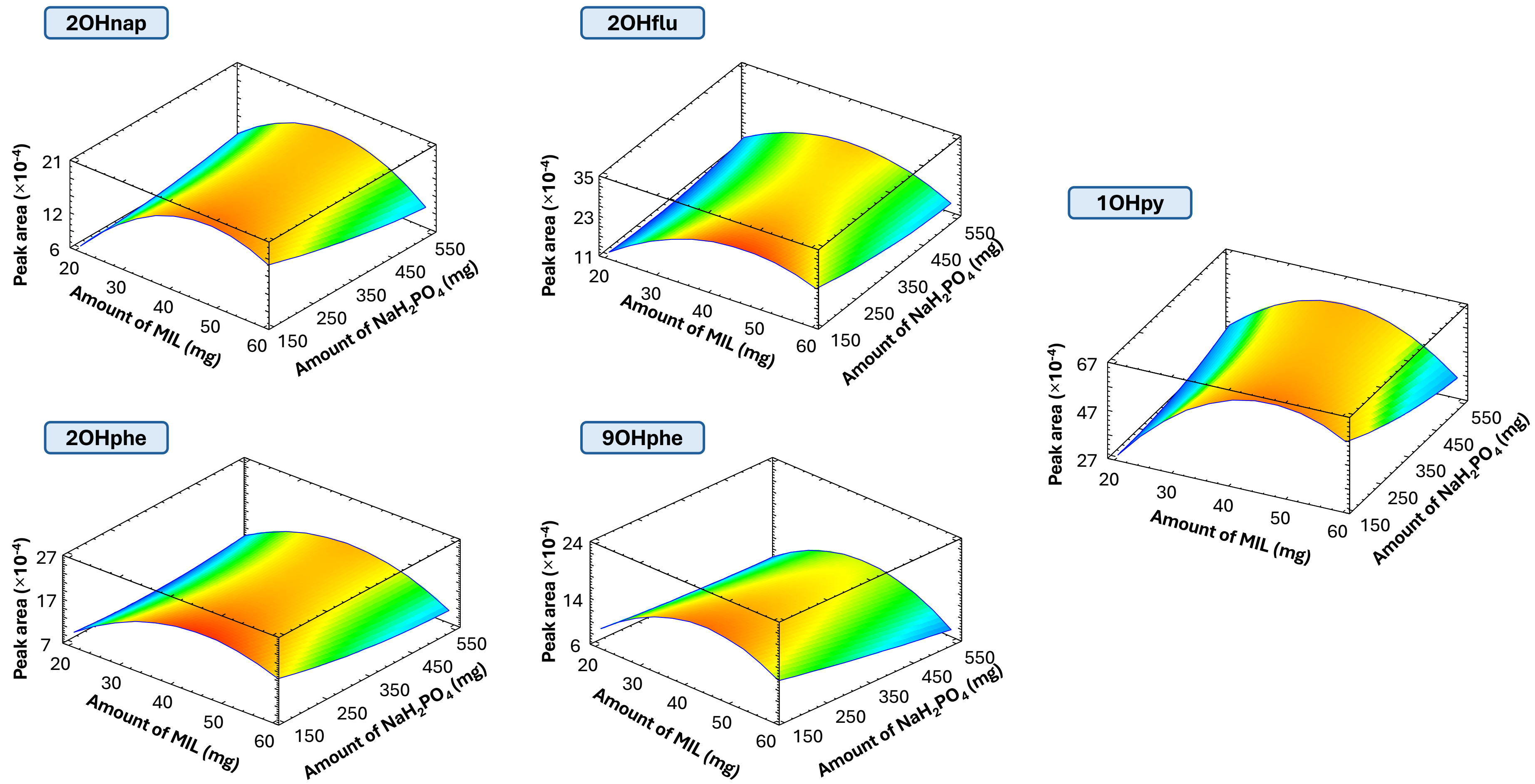


Figure S8. Individual BBD response surfaces of the OH-PAHs. Each response surface was plotted by fixing the equilibration time (variable C) at its optimum value for each analyte.

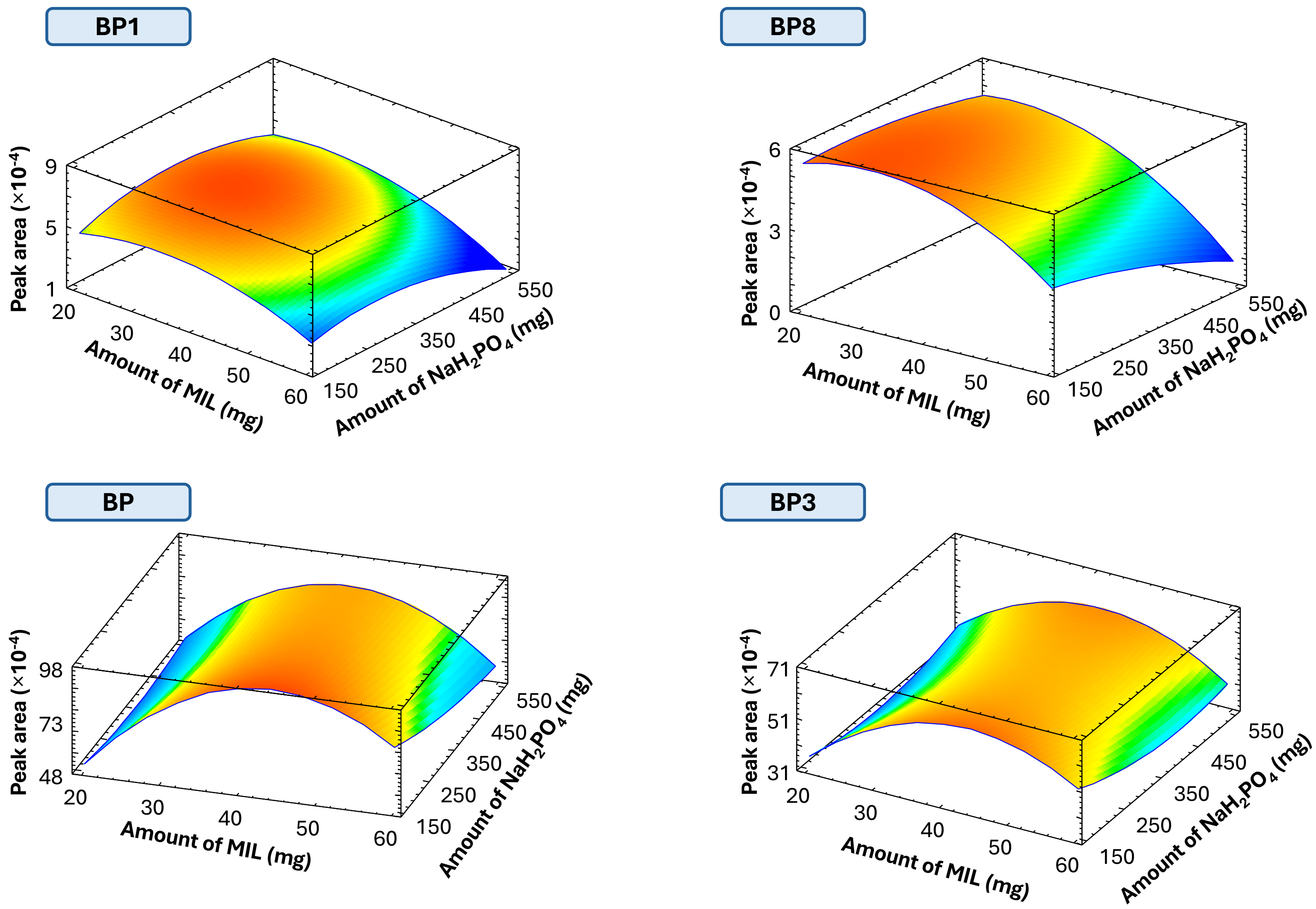


Figure S9. Individual BBD response surfaces of the BPs. Each response surface was plotted by fixing the equilibration time (variable C) at its optimum value for each analyte.

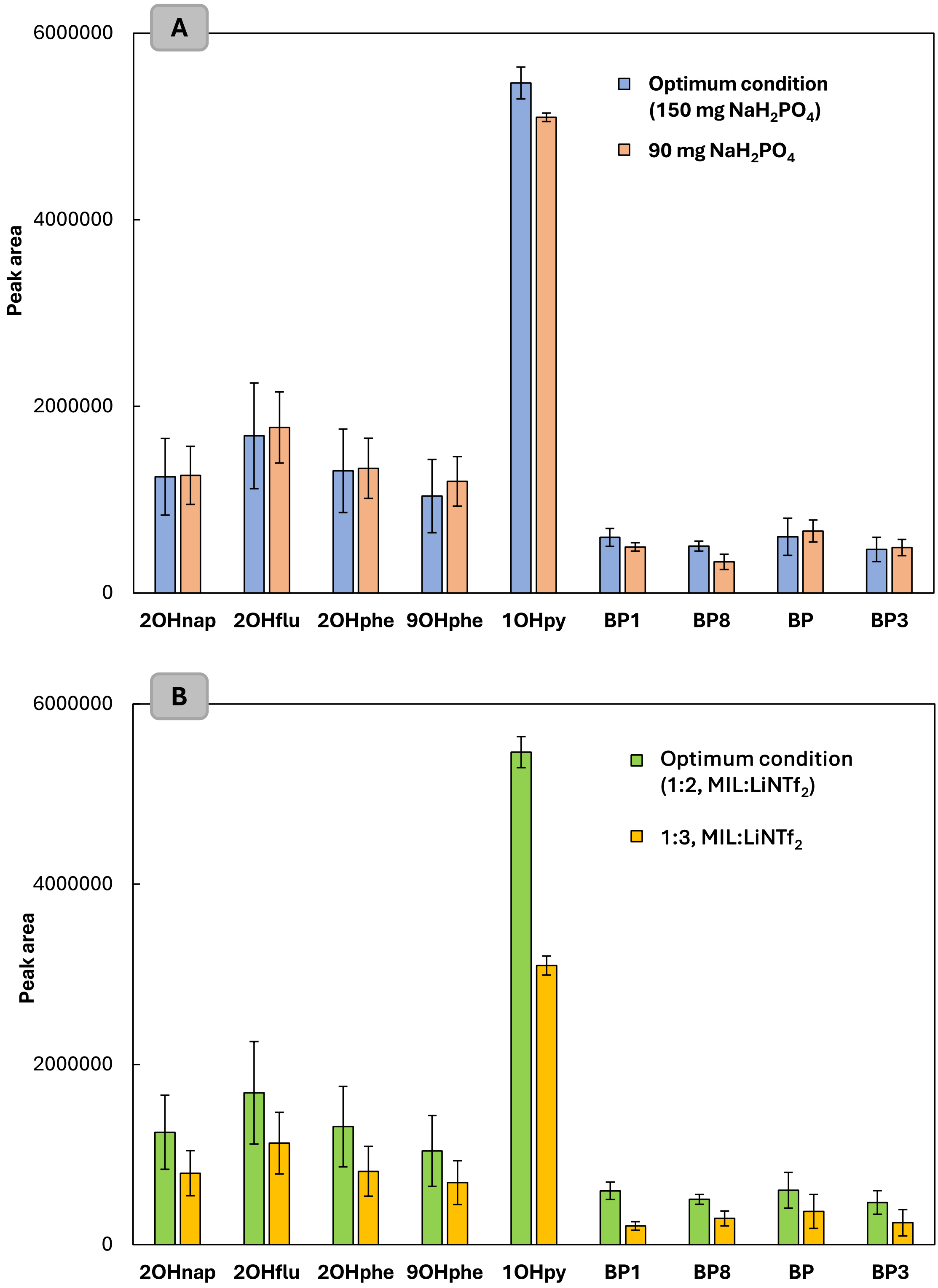


Figure S10. Study of the robustness of the *in situ* MIL-DLLME method when performing slight modifications of the optimum conditions obtained in the BBD: **(A)** decreasing of the amount of NaH_2PO_4; **(B)** increasing of the amount of $LiNTf_2$ while maintaining the optimum amount of MIL.

Figure S11. Sustainability assessment of the proposed *in situ* MIL-DLLME method and other IL- and MIL-DLLME methods already reported in the literature, using the SPMS tool.

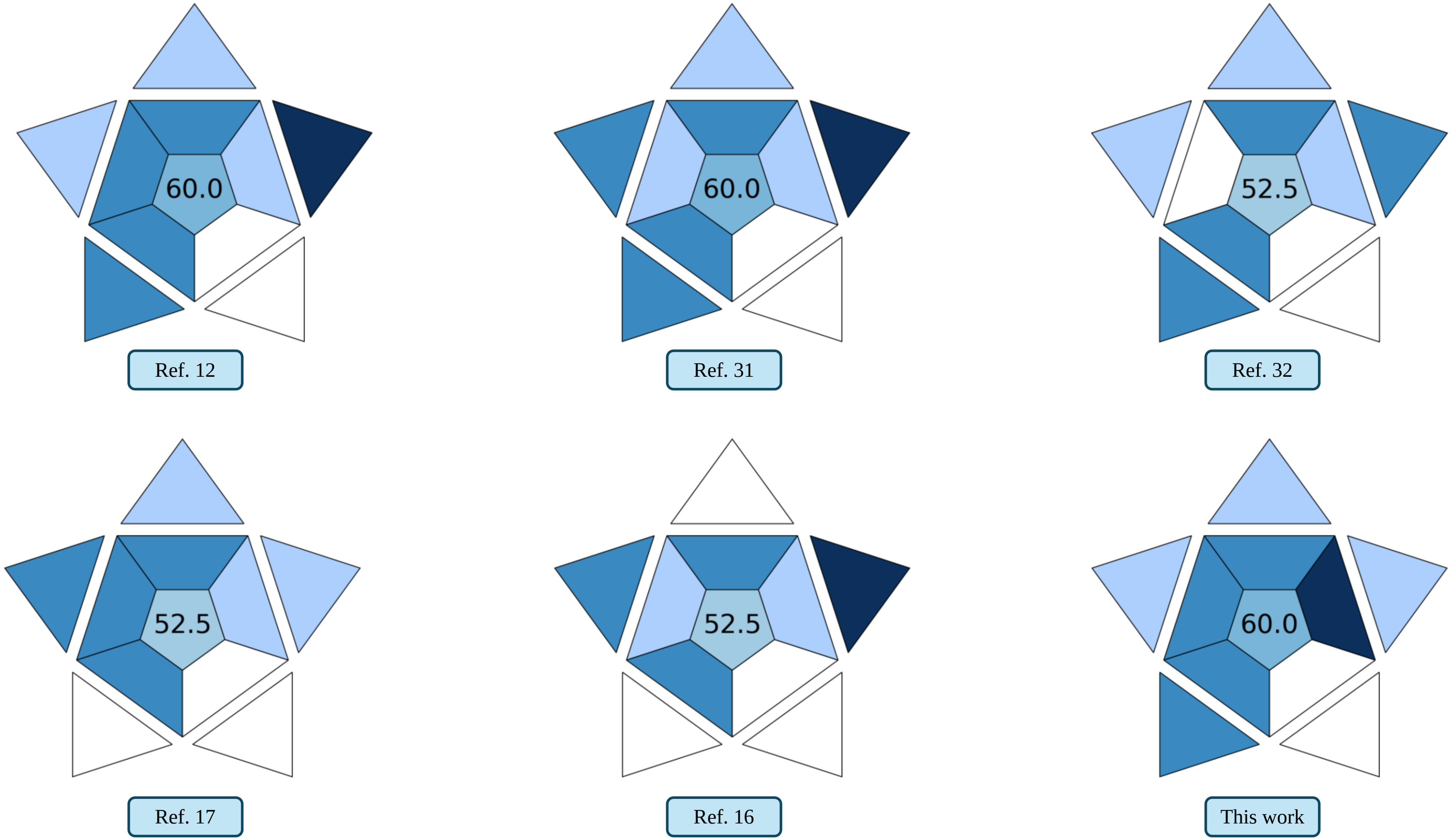
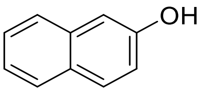
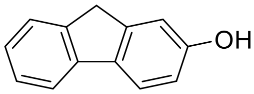
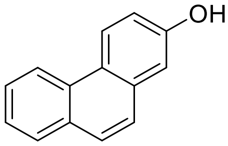
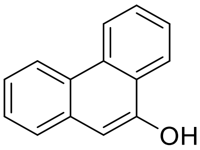
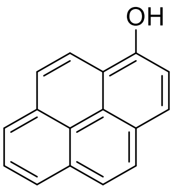
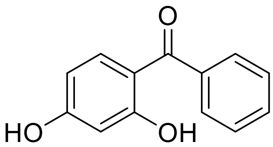
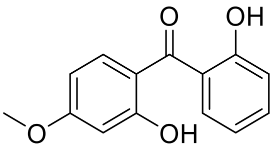
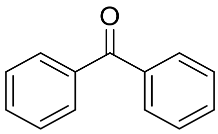
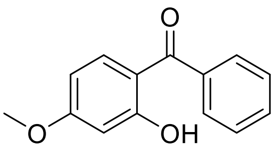


Figure S12. Assessment of the proposed *in situ* MIL-DLLME method and other IL- and MIL-DLLME methods already reported in the literature, using the BAGI tool.

Table S1. Chemical structures and main physicochemical properties of the target biomarkers studied, obtained from the SciFinder® database (2024).

Analyte (abbreviation)	**Chemical structure**	**MW[a] (g·mol^{-1})**	**pK_a**	**Log K_{ow}[b] at 25ºC**
OH-PAHs				
2-hydroxynaphthalene (2OHnap)		144.17	9.57	2.724
2-hydroxyfluorene (2OHflu)		182.22	9.94	3.646
2-hydroxyphenanthrene (2OHphe)		194.23	9.57	3.909
9-hydroxyphenanthrene (9OHphe)		194.23	9.40	3.909
1-hydroxypyrene (1OHpy)		218.25	9.40	4.367
BPs				
2,4-dihydroxybenzophenone (BP1)		214.22	7.72	3.152
2,2′-dihydroxy-4-methoxybenzophenone (BP8)		244.24	7.11	4.311
benzophenone (BP)		182.22	-	3.214
2-hydroxy-4-methoxybenzophenone (BP3)		228.24	7.56	3.995

[a] Molecular weight.

[b] Logarithm of the octanol/water partition coefficient at 25ºC.

Table S2. Chromatographic retention times for the target biomarkers, obtained with the optimum elution gradient, together with the optimum detection conditions set in the FD and UV systems.

Analyte	**Retention time (min) ± SD**[a]	**λ_{ex}**[b] **(nm)**	**λ_{em}**[c] **(nm)**	**λ_{abs}**[d]
OH-PAHs				
2OHnap	2.71 ± 0.04	225	350	-
2OHflu	4.01 ± 0.08	260	350	-
2OHphe	4.87 ± 0.02	240	384	-
9OHphe	5.87 ± 0.09	240	384	-
1OHpy	8.19 ± 0.05	240	387	-
BPs				
BP1	3.38 ± 0.01	-	-	289
BP8	4.65 ± 0.01	-	-	289
BP	6.13 ± 0.02	-	-	254
BP3	8.52 ± 0.04	-	-	289

[a] Standard deviation for n = 50.
[b] Excitation wavelength set in the FD.
[c] Emission wavelength set in the FD.
[d] Absorption wavelength set in the UV.

Table S3. Quality analytical parameters and precision of the chromatographic method, using standards of the biomarkers in ACN.

Analytes	(Slope ± t·S_b[a]) ·10^{-3}	R^{2b}	$S_{y/x}$[c]·10^{-4}	LOD[d] (μg·L^{-1})	LOQ[e] (μg·L^{-1})	Low conc. level[h]		Intermediate conc. level[i]	
						Intraday RSD range[f] (%)	Intermediate precision RSD[g] (%)	Intraday RSD range[f] (%)	Intermediate precision RSD[g] (%)
OH-PAHs									
2OHnap	22 ± 1	0.999	6.9	0.600	2.00	1.0–4.6	6.5	0.30–0.90	2.8
2OHflu	58.2 ± 0.7	0.999	2.7	0.200	0.700	0.20–2.6	3.7	0.70–0.90	1.8
2OHphe	43.9 ± 0.8	0.999	2.5	0.300	1.00	0.20–1.3	1.7	1.1–2.8	2.4
9OHphe	21.5 ± 0.5	0.999	2.8	0.600	2.00	0.30–2.2	2.0	0.10–2.3	2.0
1OHpy	132 ± 2	0.999	7.7	0.100	0.300	1.7–3.3	3.6	1.5–3.0	3.7
BPs									
BP1	0.31 ± 0.05	0.998	2.3	15.0	50.0	2.4–4.0	5.2	3.2–3.6	3.6
BP8	0.40 ± 0.04	0.998	1.7	30.0	100	2.5–2.7	3.0	1.8–2.4	3.1
BP	1.46 ± 0.05	0.999	2.7	10.0	30.0	0.20–3.1	3.1	0.40–1.2	2.2
BP3	0.82 ± 0.03	0.999	1.4	7.50	25.0	2.2–3.1	2.1	1.3–1.8	3.9

[a] Uncertainty of the slope within the calibration range (n = 5 for all the analytes; 2–200 μg·L^{-1} for 2OHnap and 9OHphe, 0.8–100 μg·L^{-1} for 2OHflu, 1–100 μg·L^{-1} for 2OHphe, 0.3–100 μg·L^{-1} for 1OHpy, 50–1500 μg·L^{-1} for BP1, 100–1500 μg·L^{-1} for BP8, 30–1500 μg·L^{-1} for BP, and 25–1500 μg·L^{-1} for BP3), for a confidence level of 95%.

[b] Determination coefficient.

[c] Standard deviation of the residuals.

[d] Limit of detection, determined by decreasing the concentration of the standards in ACN until a S/N ratio of 3 was obtained.

[e] Limit of quantification, estimated as 10/3 times the LOD, and experimentally verified by injection of the standards in ACN at the concentrations predicted.

[f] Range (day 1 to day 3) of relative standard deviation for intra-day precision (n = 3), tested with a standard in ACN not included as calibration point.

[g] Relative standard deviation for intermediate precision (n = 9, 3 non-consecutive days), tested with a standard in ACN not included as calibration point.

[h] Low concentration level for precision studies: 8 μg·L^{-1} for 2OHnap and 9OHphe; 16 μg·L^{-1} for 2OHflu, 2OHphe and 1OHpy; 300 μg·L^{-1} for all the BPs.

[i] Intermediate concentration level for precision studies: 50 μg·L^{-1} for 2OHnap and 9OHphe; 100 μg·L^{-1} for 2OHflu, 2OHphe and 1OHpy; 800 μg·L^{-1} for all BPs.

Table S4. Experimental values of the variables assessed through a three-factor Box-Behnken design, together with the set values of the interdependent variables.

Experiment	Variable A: Amount of MIL (mg)		Amount of $LiNTf_2$[b] (mg)	Variable B: Amount of NaH_2PO_4 (mg)		Amount of K_2CO_3[c] (mg)	Variable C: Equilibration time (min)	
	Coded	***Uncoded***		***Coded***	***Uncoded***		***Coded***	***Uncoded***
1[a]	0	40.0	35.0	0	325	340	0	18.5
2	0	40.0	35.0	1	500	523	1	30.0
3	-1	20.0	17.0	0	325	340	-1	7.00
4[a]	0	40.0	35.0	0	325	340	0	18.5
5	-1	20.0	17.0	0	325	340	1	30.0
6	0	40.0	35.0	-1	150	157	-1	7.00
7	-1	20.0	17.0	-1	150	157	0	18.5
8	1	60.0	52.0	-1	150	157	0	18.5
9	1	60.0	52.0	0	325	340	-1	7.00
10	1	60.0	52.0	1	500	523	0	18.5
11	1	60.0	52.0	0	325	340	1	30.0
12	0	40.0	35.0	-1	150	157	1	30.0
13	-1	20.0	17.0	1	500	523	0	18.5
14	0	40.0	35.0	1	500	523	-1	7.00
15[a]	0	40.0	35.0	0	325	340	0	18.5

[a] Center point, performed in triplicate.

[b] These values were selected according to the values of variable A, to maintain the stoichiometry of the metathesis reaction (1:2, MIL:$LiNTf_2$).

[c] These values were selected according to the values of variable B, to maintain the same excess of the proton donor agent with respect to the theoretical stoichiometry of the effervescence reaction (1.1:1, NaH_2PO_4:K_2CO_3).

Table S5. Main effects and interactions between the variables studied with the Box-Behnken experimental design.

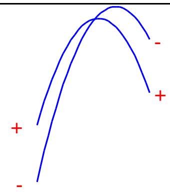
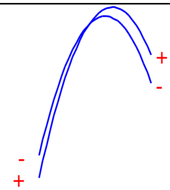
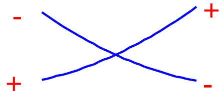
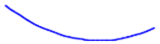
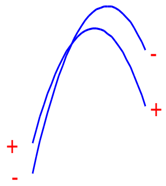
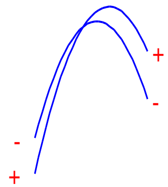
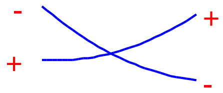
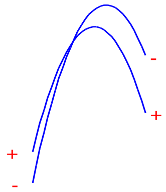
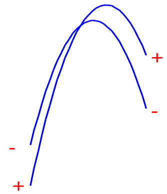
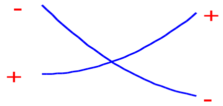
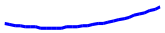
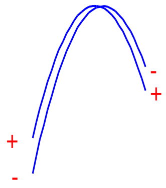
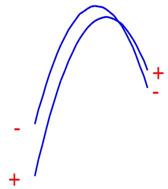
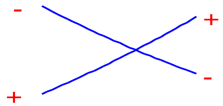
Analytes	**Main effects of the variables**			**Interactions between the variables**		
	Variable A[a]	**Variable B**[b]	**Variable C**[c]	**AB**[d]	**AC**[e]	**BC**[f]
2OHnap						
2OHflu						
2OHphe						
9OHphe						

Table S5 (continued)

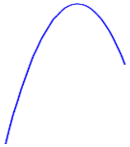
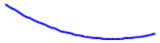
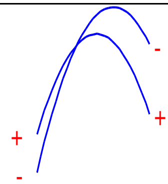
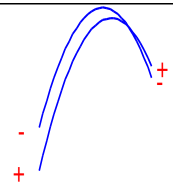
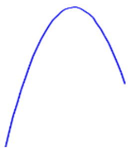
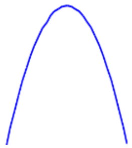
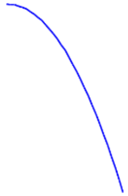
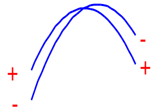
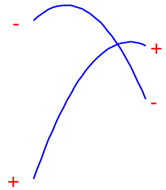
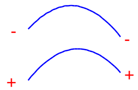
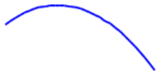
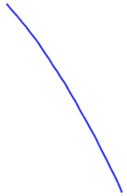
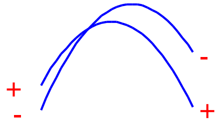
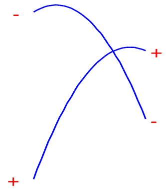
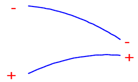
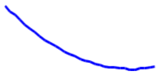
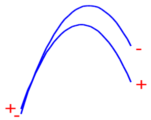
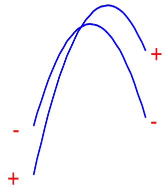
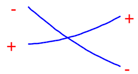
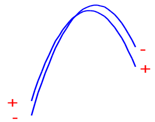
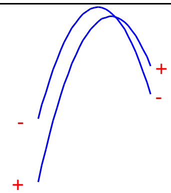
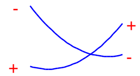
Analytes	Main effects of the variables			Interactions between the variables		
	Variable A[a]	**Variable B**[b]	**Variable C**[c]	**AB**[d]	**AC**[e]	**BC**[f]
1OHpy						
BP1						
BP8						
BP						

Table S5 (continued)

Analytes	Main effects of the variables			Interactions between the variables		
	Variable A[a]	**Variable B[b]**	**Variable C[c]**	**AB[d]**	**AC[e]**	**BC[f]**
BP3						

[a] Amount of MIL (mg).

[b] Amount of NaH_2PO_4 (mg).

[c] Equilibration time (min).

[d] Interaction between the amount of MIL and the amount of NaH_2PO_4.

[e] Interaction between the amount of MIL and the equilibration time.

[f] Interaction between the amount of NaH_2PO_4 and the equilibration time.

Table S6. Individual optimum conditions for each biomarker obtained with the Box-Behnken experimental design and optimum conditions obtained from the desirability, using the multiple response methodology.

Analytes	**Individual optimum conditions**			**Optimum conditions from the desirability**		
	MIL amount (mg)	**NaH_2PO_4 amount (mg)**	**Equilibration time (min)**	**MIL amount (mg)**	**NaH_2PO_4 amount (mg)**	**Equilibration time (min)**
OH-PAHs						
2OHnap	47.5	150	14.0	43.9	150	13.0
2OHflu	45.8	150	15.2			
2OHphe	45.3	150	14.2			
9OHphe	43.8	150	10.7			
1OHpy	46.8	150	15.9			
BPs						
BP1	31.5	326	7.00	43.9	150	13.0
BP8	30.4	163	7.00			
BP	43.2	150	16.4			
BP3	43.8	150	13.9			

Table S7. Statistical tests to assess the differences between the chromatographic peak areas obtained with the *in situ* MIL-DLLME method when incorporating a slight modification in the optimum amount of NaH_2PO_4.

Analytes	***F* test**[a] **Result**[b]	**Student's *t* test**[c] **Variances comparison**	t_{cal}[d]	t_{crit}[e]	**Result**[f]	**Significant differences**
OH-PAHs						
2OHnap	$F_{cal} > F_{crit}$	Heterogeneous	2.6	13	$t_{cal} < t_{crit}$	**No**
2OHflu	$F_{cal} > F_{crit}$	Heterogeneous	3.0	13	$t_{cal} < t_{crit}$	**No**
2OHphe	$F_{cal} > F_{crit}$	Heterogeneous	2.6	13	$t_{cal} < t_{crit}$	**No**
9OHphe	$F_{cal} > F_{crit}$	Heterogeneous	2.9	13	$t_{cal} < t_{crit}$	**No**
1OHpy	$F_{cal} < F_{crit}$	Homogeneous	18	3.2	$t_{cal} > t_{crit}$	**Yes**
BPs						
BP1	$F_{cal} < F_{crit}$	Homogeneous	8.9	3.2	$t_{cal} > t_{crit}$	**Yes**
BP8	$F_{cal} > F_{crit}$	Heterogeneous	2.5	13	$t_{cal} < t_{crit}$	**No**
BP	$F_{cal} < F_{crit}$	Homogeneous	4.7	3.2	$t_{cal} > t_{crit}$	**Yes**
BP3	$F_{cal} > F_{crit}$	Heterogeneous	3.5	13	$t_{cal} < t_{crit}$	**No**

[a] *F* statistical test for variances (comparing the peak areas obtained using 90 mg of salt with those obtained under optimum conditions with 150 mg of salt, see Figure S9 (A)).

[b] Result of the *F* test, considering n – 1 degrees of freedom (n = 3) and a confidence level of 95% (α = 0.05).

[c] Student's *t* statistical test for means comparison (considering equal variances or different variances, depending on the result of the *F* test).

[d] Calculated *t* value.

[e] Critical *t* value.

[f] Result of the *t* test, considering $n_1 + n_2 – 2$ degrees of freedom and a confidence level of 95%, being n_1 and n_2 the number of peak area data for each amount of NaH_2PO_4 (n = 3, see Figure S9 (A)).

Table S8. Enrichment factors and extraction efficiencies obtained with the *in situ* MIL-DLLME-HPLC-UV/FD method, using diluted urine standard solutions (with a urine content of 14%, v/v).

Analytes	Low concentration level[a]		Intermediate concentration level[b]	
	EF[c]	**E_R[d] (%)**	**EF[c]**	**E_R[d] (%)**
OH-PAHs				
2OHnap	2.3	15	2.0	13
2OHflu	2.2	14	2.0	13
2OHphe	2.2	14	2.0	13
9OHphe	2.0	13	1.6	10
1OHpy	2.0	13	2.0	13
BPs				
BP1	3.0	19	3.5	22
BP8	3.3	21	2.8	18
BP	1.6	10	1.6	10
BP3	2.1	13	2.1	13

[a] 1.6 $\mu g \cdot L^{-1}$ for 2OHnap and 9OHphe; 0.80 $\mu g \cdot L^{-1}$ for 2OHflu, 2OHphe and 1OHpy; and 30 $\mu g \cdot L^{-1}$ for all the BPs.

[b] 16 $\mu g \cdot L^{-1}$ for 2OHnap and 9OHphe; 8.0 $\mu g \cdot L^{-1}$ for 2OHflu, 2OHphe and 1OHpy; and 150 $\mu g \cdot L^{-1}$ for all the BPs.

[c] Enrichment factor, calculated as the ratio between the concentration found in the MIL microdroplet extract (using the calibration curves of the chromatographic method, see Table S3 of the ESM) and the initial concentration of the diluted urine standard subjected to the method.

[d] Extraction efficiency, calculated as the ratio (as a percentage) between the E_F and the maximum enrichment factor (E_{Fmax} = 16).

Table S9. Analytical performance of the *in situ* MIL-DLLME-HPLC-UV/FD method with non-hydrolyzed smoker urine samples, in terms of precision and relative recovery.

Analytes	Smoker male urine[a]		Smoker female urine[a]	
	Intra-day RSD[b] (%)	**(RR ± SD)[c] (%)**	**Intra-day RSD[b] (%)**	**(RR ± SD)[c] (%)**
OH-PAHs				
2OHnap	8.6	135 ± 12	3.0	84 ± 3
2OHflu	6.1	73 ± 12	2.5	93 ± 2
2OHphe	7.3	79 ± 13	0.30	94.3 ± 0.3
9OHphe	8.4	102 ± 9	0.20	47.6 ± 0.1
1OHpy	3.6	94 ± 3	3.9	92 ± 4
BPs				
BP1	2.5	100 ± 5	1.2	78.9 ± 3
BP8	11	121 ± 22	1.1	109 ± 2
BP	8.9	128 ± 18	7.7	107 ± 9
BP3	4.9	157 ± 10	10	103 ± 11

[a] Spiked level: 1.6 $\mu g \cdot L^{-1}$ for 2OHnap and 9OHphe; 0.80 $\mu g \cdot L^{-1}$ for 2OHflu, 2OHphe and 1OHpy; 30 $\mu g \cdot L^{-1}$ for all the BPs.

[b] Relative standard deviation for intra-day precision (n = 3).

[c] Average relative recovery and standard deviation (n = 3).

Table S10. Comparison of operational parameters (in terms of simplicity and energy consumption) of the effervescence-assisted *in situ* MIL-DLLME method together with other methods reported in the literature involving the use of ILs and/or MILs in both non-effervescence and effervescence-assisted DLLME strategies.

Extraction material[a] / amount	**Effervescence tablets components[b]**	**Sample preparation steps (time)**	**Energy consumption (kW·h)[c]**	**Analytes (number)**	**Sample**	**Analytical technique[d]**	**Ref.**
IL- or MIL-DLLME without effervescence assistance							
$[Ni(C_4IM)_4]Cl_2$ & $[Ni(BeIM)_4]Cl_2$ MILs / 20 mg & 30 mg	-	vortex (3 min) + magnetic separation (~0.5 min) + dilution (~0.5 min)	0.002	organic pollutants (10)	water	HPLC-UV	[12]
$[C_8MIm][PF_6]$ IL / 50 µL	-	vortex (1 min) + freezing (5 min) + centrifugation (5 min) + redissolution (~0.5 min)	0.08	UV filters (3)	water	HPLC-DAD	[31]
$[C_4(3Cl2OHC_3)Im][PF_6]$ IL / 20 µL	-	ultrasounds (3 min, 50ºC) + freezing (4 min) + centrifugation (3 min) + dilution (~0.5 min)	0.06	brilliant blue (1)	beverage & candy chewing gum	UV-Vis	[32]

Table S10 (continued)

Extraction material[a] / amount	Effervescence tablets components[b]	Sample preparation steps (time)	Energy consumption (kW·h)[c]	Analytes (number)	Sample	Analytical technique[d]	Ref.
IL- or MIL-DLLME with effervescence assistance							
$[C_4MIm][PF_6]$ IL / 500 µL	citric acid + $NaHCO_3$ + IL@Fe_3O_4 + glycerine	effervescence (n.r.) + freezing (7.5 min) + evaporation (n.r.) + reconstitution (~0.5 min)	0.6	drugs (8)	water	HPLC-DAD	[17]
$[C_4MIm][HSO_4]$ IL / 440 mg	Na_2CO_3 + IL + NaCl	effervescence (n.r.) + addition of $LiNTf_2$ (~0.5 min) + centrifugation (5 min) + back-extraction (3 min) + centrifugation (3 min) + evaporation (n.r.) + reconstitution (~0.5 min)	0.8	bisphenols (3)	milk & milky tea	HPLC-FD	[16]
$[Ni(C_4IM)_4]Cl_2$ MIL / 44 mg	NaH_2PO_4 + K_2CO_3 + MIL + $LiNTf_2$ + Na_2SO_4	effervescence (1 min) + equilibration time (13 min) + magnetic separation (~0.5 min) + dilution (~0.5 min)	0	biomarkers (9)	urine	HPLC-UV/FD	This work

n.r.: non-reported.

[a] ILs and MILs cations and anions: $[Ni(C_4IM)_4]^{2+}$ for tetra(butylimidazole)nickel(II), $[Ni(BeIM)_4]^{2+}$ for tetra(benzylimidazole)nickel(II), $[C_nMIm]^+$ for 1-alkyl-3-methylimidazolium (alkyl: butyl for n=4; octyl for n=8), $[PF_6]^-$ for hexafluorophosphate, $[C_4(3Cl2OHC_3)Im]^+$ for 3-(3-chloro-2-hydroxypropyl)-1-butyl-1H-imidazol-3-ium, $[HSO_4]^-$ for hydrogen-sulfate.

[b] Abbreviations: $LiNTf_2$ for lithium bis[(trifluoromethyl)sulfonyl]imide.

[c] Average energy consumption of the analytical sample preparation method (starting when the extractant is put in contact with the sample and ending with the reconstitution and/or dilution of the extractant phase prior the analytical determination step), considering the power consumed by each apparatus per hour and the time for which each apparatus is used.

[d] Abbreviations: HPLC for high-performance liquid-chromatography, UV for ultraviolet detection, DAD for diode-array detection, UV-Vis, for ultraviolet-visible spectrophotometry, FD for fluorescence detection.

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