

## Supplementary materials

**Table S1.** The results obtained for different extraction systems containing chloroform for DLLME.

No	Dispersive agent	Volume, mL	Observation
1		0.5	lack of drop
2		1.0	
3	Acetonitrile	1.2	unstable drop
4		1.5	stable drop
5		1.7	unstable drop
6		0.2	stable drop
7		0.4	
8	Methanol	0.5	unstable drop
9		1.0	lack of drop
10		1.5	
11		0.5	lack of drop
12		0.6	
13	Acetone	0.8	unstable drop
14		1.0	stable drop
15		1.2	lack of drop
16		1.0 + 0.5	lack of drop
17	Acetone+acetonitrile	0.50 + 0.50	
18		0.33 + 0.66	stable drop
19		0.25 + 0.75	
20		1.0+0.5	lack of drop
21		0.75+0.75	
22	Methanol+acetonitrile	0.5+1.0	stable drop
23		0.4+1.1	
24		1.0+0.5	lack of drop
25		0.5+0.5	
26	Methanol+acetone	0.2+0.8	
27		0.2+1.0	stable drop
28		0.5+1.0	

**Table S2.** Analytical performance of the DLLME with binary solvents as dispersive agent for the determination of PAHs in waters.

PAHs	LOD, ng/L		LOQ, ng/L		Linearity range , ng/L		Intra-day precision (n=16)		Inter day precision (n=10)	
	HPLC-FD/ PDA	GC-MS	HPLC-FD/ PDA	GC-MS	HPLC-FD/ PDA	GC-MS	HPLC-FD/ PDA	GC-MS	HPLC-FD/ PDA	GC-MS
Naph	0.07	6.0	0.20	20	0.20 – 1000	20 – 7500	6.5	7.1	7.0	8.2
2-MN	0.05	4.5	0.15	15	0.15 – 1000	15 – 7500	6.5	7.8	5.5	7.6
Biph	0.05	4.5	0.15	15	0.15 – 1000	15 – 7500	5.1	6.5	5.8	6.7
Acy	0.05	4.5	0.15	15	0.15 – 1000	15 – 7500	4.9	5.2	5.2	5.8
Ace	0.05	4.5	0.15	15	0.15 – 1000	15 – 7500	4.2	4.5	5.3	6.1
Flu	0.05	3.0	0.15	10	0.15 – 1000	10 – 7500	5.1	5.5	5.2	6.2
Phe	0.05	3.0	0.15	10	0.15 – 1000	10 – 7500	3.1	3.7	4.8	6.3
Anth	0.05	3.0	0.15	10	0.15 – 1000	10 – 7500	4.2	4.0	4.7	5.8
Pyr	0.05	3.0	0.15	10	0.15 – 1000	10 – 7500	3.3	3.9	4.6	5.7
Fluor	0.05	3.0	0.15	10	0.15 – 1000	10 – 7500	3.8	3.7	4.5	5.9
B[a]A	0.03	3.0	0.10	10	0.10 – 750	10 – 7500	4.4	4.0	4.3	5.8
Chry	0.03	3.0	0.10	10	0.10 – 750	10 – 7500	4.1	4.5	4.5	5.4
Triph	0.03	3.0	0.10	10	0.10 – 750	10 – 7500	3.9	4.2	4.4	5.5
B[b]F	0.03	3.0	0.10	10	0.10 – 750	10 – 7500	4.5	5.1	5.2	6.0
B[k]F	0.03	3.0	0.10	10	0.10 – 750	10 – 7500	4.3	5.2	4.5	5.9
B[a]P	0.03	3.0	0.10	10	0.10 – 750	10 – 7500	4.2	5.3	5.3	5.8
B[e]P	0.03	3.0	0.10	10	0.10 – 750	10 – 7500	4.3	5.0	5.1	6.1
I[1,2,3-c,d]P	0.03	3.0	0.10	10	0.10 – 750	10 – 7500	3.4	3.8	4.7	5.8
D[a,h]A	0.03	3.0	0.10	10	0.10 – 750	10 – 7500	3.3	3.9	4.8	5.9
B[g,h,i]P	0.03	3.0	0.10	10	0.10 – 750	10 – 7500	3.2	3.7	4.5	5.5