Supplementary Information

Method development and optimization of DLLME factors using RSM with DF for the determination of organic contaminants in water samples by UHPLC–QTOF–MS: Risk and greenness assessment

Tlou Auguston Makwakwa [a, b], Elsie Dineo Moema [a], Titus Alfred Makudali Msagati [b*]

[a]Department of Chemistry, College of Science, Engineering and Technology, University of South Africa, Florida, 1709, Johannesburg, South Africa.

[b]Institute for Nanotechnology and Water Sustainability, College of Science, Engineering and Technology, University of South Africa, Florida, 1709, Johannesburg, South Africa.

* Corresponding author Email: msagatam@unisa.ac.za, Tel +27 11 670 9482

Table S1 Retention times and mass measurements of molecular ions of target compounds in a mixture standard solution.

Compound	Retention time (min)	Elemental composition	Experimental mass (m/z)	Theoretical mass (m/z)	Error	
					mDa	ppm
ESI (+) mode						
Mifepristone (MIF)	4.13	$[M + H]^+$ $C_{29}H_{36}NO_2$	430.2747	430.2741	-0.7	-1.5
Benzophenone (BP)	5.52	$[M + H]^+$ $C_{13}H_{11}O$	183.0806	183.0804	-0.2	-1.1
ESI (–) Mode						
Eicosapentaenoic acid (EPA)	7.78	$[M–H]^-$ $[C_{20}H_{29}O_2$	301.2172	301.2173	0.4	1.3
Docosahexaenoic acid (DHA)	8.47	$[M–H]^-$ $[C_{22}H_{31}O_2$	327.2330	327.2328	0.3	1.0

Table S2 Elemental composition and accurate mass measurement for product ions obtained in a standard solution using the Q–TOF mode.

Compound	Precursor ion (m/z)	Product ions			Error	
Compound		Elemental composition	Experimental mass	Theoretical mass	mDa	ppm
MIF (ESI+)	430	$[C_9H_{11}N] + H^+$	134.0965	134.0964	-0.0	0.7
		$[C_{26}H_{31}NO^-]H^+$	372.2329	372.2322	-0.7	1.9
BP (ESI+)	183	$[C_6H_5]^+$	77.0382	77.0386	0.4	-5.2
		$[C7H5O]^+$	105.0336	105.0335	-0.1	0.9
EPA (ESI-)	301	$[C_{19}H_{29}]^-$	257.2277	257.2280	0.6	-1.2
DHA (ESI-)	327	$[C^9H^{14}] - H^-$	121.1023	121.1023	-0.0	0.1
		$[C_{17}H_{25}]^-$	229.1964	229.1962	-0.2	0.8
		$[C_{21}H_{31}]^-$	283.2432	283.2431	-0.1	0.4

Table S3 Method relative standard deviations (RSD) and enrichment factors (EF)

Compound	Influent (% RSD)	Influent (EF)	Effluent (% RSD)	Effluent (EF)	River (% RSD)	River (EF)
MIF	0.65	39.71	1.08	52.34	1.13	51.72
BP	4.78	72.72	10.37	59.66	6.91	47.28
DHA	10.34	61.40	14.03	11.66	8.86	33.14
EPA	11.63	32.42	14.12	15.57	10.23	42.52