Electronic Supplementary Material (ESI) for Analytical Methods.

Electronic Supplementary Material

Validation of chemometric-assisted single-drop microextraction based on sustainable solvents to analyze PAHs in water samples

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1. Characterization of selected DES

The interactions between the two components resulting in the formation of DES were clarified by recording FT-IR spectra. The synthesis of deep eutectic solvents is achieved by forming hydrogen bonds between choline chloride (ChCl) and oxalic acid (OX), which playact the role of hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD), respectively (Fig. S2). Fig. 2 displays the FT-IR spectra of pure OX, ChCl versus DES consisting of them. The characteristic peaks of OX at 1708, 1438, 1310, 1230, 1218, and 1129 cm^{-1} and peaks of ChCl at 1632, 1478, 1406, 1092, and 949 cm^{-1} can also be observed in the DES. The peaks of OH groups from ChCl and OX are shifted and broaden due to the formation of H-bonding in the DES. The frequency at 3450 cm^{-1} (Fig. 1b) is allocated to the OH stretching frequency associated with Cl—OH of ChCl. The sharp peak around 1475 cm^{-1} is associated with the N—C bond in ChCl and is a distinct feature for identifying ChCl. The OH stretching region of oxalic acid (Fig. 1c) contains broad overlapping bands centered around 3420 cm^{-1} that is typical of carboxylic acid forming strongly bonded dimer rings through intermolecular H-bonding between C=O and O—H groups. The frequencies at 1720 and 1225 cm^{-1} are related to C=O and C—O stretching frequency respectively and can be used to recognize free oxalic acid present in DES.

In the pure ChCl-OX, OH stretching frequency shifted to a lower frequency of 3415 cm^{-1}, but retains its broader nature; in contrast, that of ChCl seems to disappear. C—O stretching frequency too is moved to a lower frequency at 1198 cm^{-1}. ChCl-OX contains both the free and bound carbonyl groups- a sharp peak at 1710 cm^{-1} indicates the presence of free COOH group in the DES and the presence of a peak at 1618 cm^{-1} indicates the presence of OX in the dissolved state, but the relative strengths of these signals are dependent on the processing conditions. In the pure ChCl-OX, the latter peak appeared in a much faint signal compared to former. From the

spectroscopy data, it can be inferred that during the formation of DES, the strong Choline OH…Cl and COOH…COOH bonds in ChCl and OX break down to produce a new stronger intermolecular COOH…Cl bonds, which explains the stability of the liquid phase, lowering of melting point and high viscosity of the ChCl-OX. It is also suggested that multiple types of H bonds in form of OH (OX)—Cl^-, OH (ChCl)—Cl^- and OX—OX can be present in the resultant DES.

2. Enrichment factor

Enrichment factor (EF) is "a means of quantifying the enrichment of a potentially element in an environmental sample relative to a user-defined background composition"[1]. The EF was calculated as:

$$EF(\%) = C_{sed} \times V_{sed} / (C_0 \times V_{aq}) \times 100 \qquad (1)$$

In which, C_{sed} is the final solutions after extraction of the standard Cr solutions obtained from the calibration graph, C_0 is the Cr initial concentration within the sample, V_{sed} is the final volume of sediment phase and V_{aq} is the volume of the aqueous sample[1].

3. Comparative study

The analytical characteristics of the present technique of PAHs analysis were compared with other microextraction techniques that were previously published. The results in Table S8 indicate that DES-HS-SDME approach provides LODs and EFs superior or comparable to other procedures. ChCl-OX DES was applied in this study as an extraction solvent. Thus, the proposed approach is a greener approach compared to the classical-DLLME, DLLME–MSFIA, and HLLME, which they all use toxic chlorine solvents as an extraction phase[2-4]. In this method, sample clean-up, and analyte pre-concentration were simultaneously achieved in a single step. The use of dispersive solvents is evident although relatively safer solvents have been used in

DLLME-SFO and SBSE-DLLME[5, 6]. While ionic liquids are classified as green solvents, their synthesis requires energy, special equipment, and it is time-consuming[7, 8]. Unlike AALLME, the proposed approach does not need any additional process or energy to disperse the extraction phase in solution and formation of the cloudy state[9, 10]. Compared with HLLME[11], AG-LPME[12] and DES-HS-SDME is a centrifuge free procedure, and has extra electronic accessories compared with other microextraction techniques[13, 14]. In addition, thermal desorption system was avoided[8, 12-14]. Thus, it makes the proposed approach one step closer to automation. Further, sample preparation using SPME requires a particular costly device and is more time-consuming than DES-HS-SDME[15, 16]. In comparison with traditional SDME, using improved equipment and DES in the proposed method led to the high stability of the micro drop which allowed extraction in high temperatures and fast stirring rates without any operative problems[11, 17]. Moreover, collecting the extraction medium by micro-syringe after phase separation is a time-consuming and laborious step which is usually neglected in calculating analysis time. In the proposed method, using bell-shaped tube spends less time for this step. Therefore, compared to the time amounts reported in other studies, authors claim that DES-HS-SDME is one of the fastest procedures by considering the analysis time including the duration of extraction, centrifugation, and chromatography. Thus, DES-HS-SDME procedure is more cost-effective and environmentally friendly than the other methods presented in Table S5.

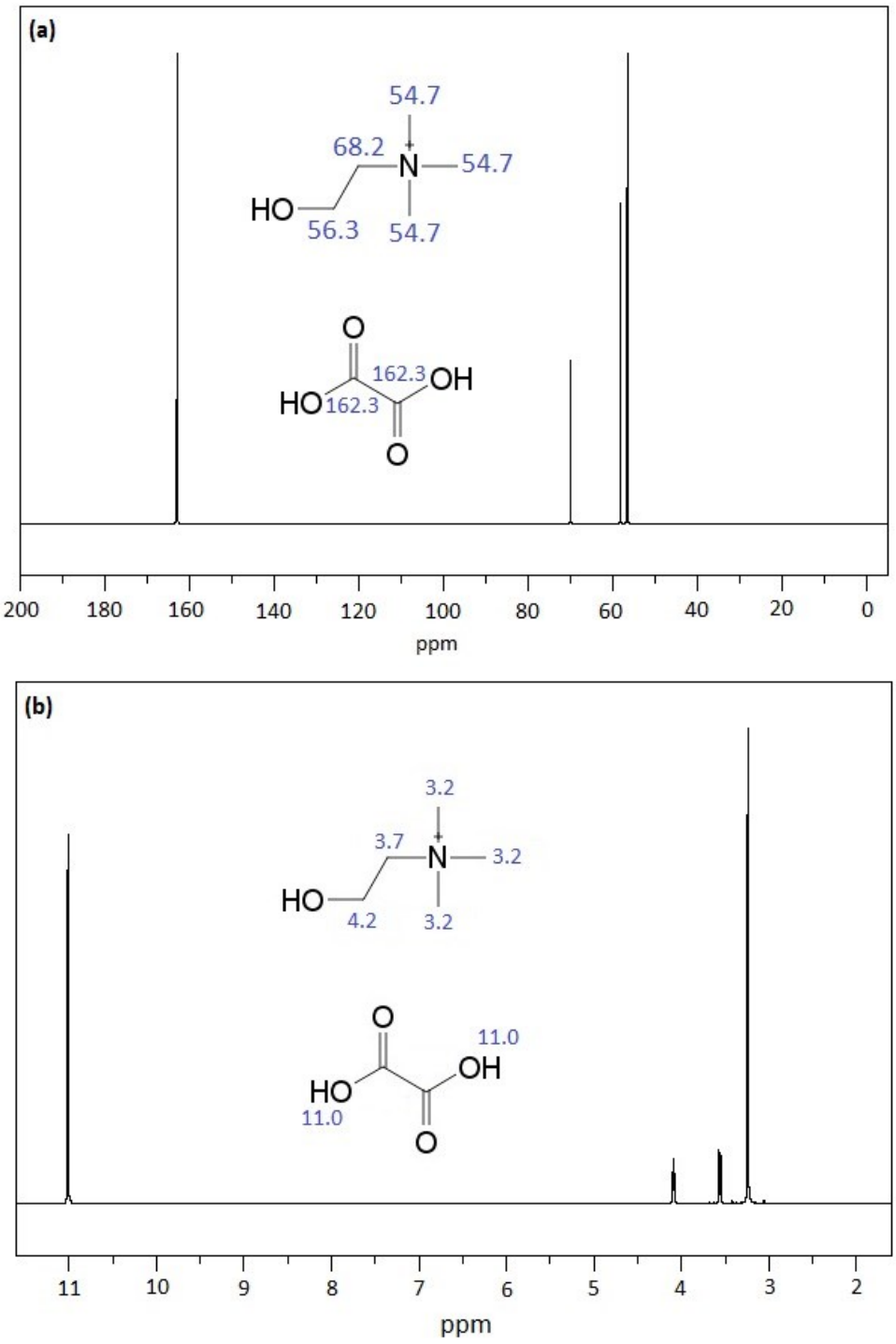


Fig. S1. ^{13}C NMR spectrum (a) and ^{1}H NMR spectrum (b) of DES (ChCl-Ox) in D_2O.

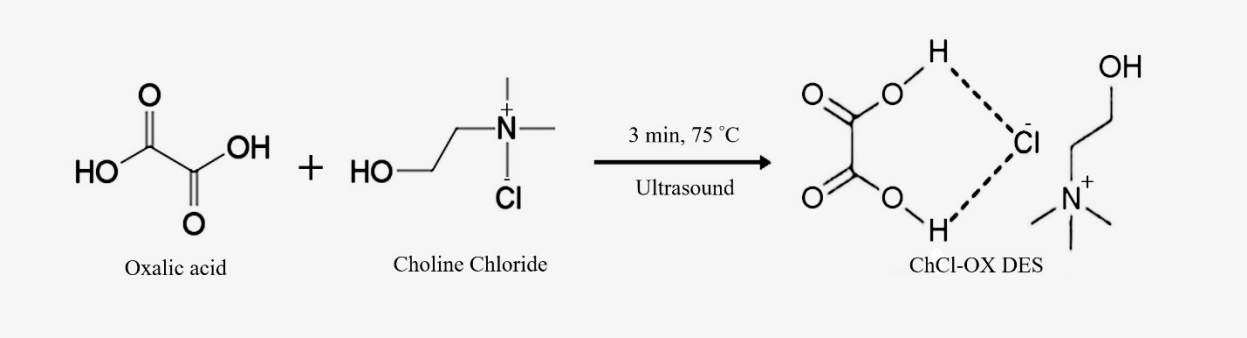


Fig. S2. Chemical structures of compounds and their interactions used to make ChCl-OX DES.

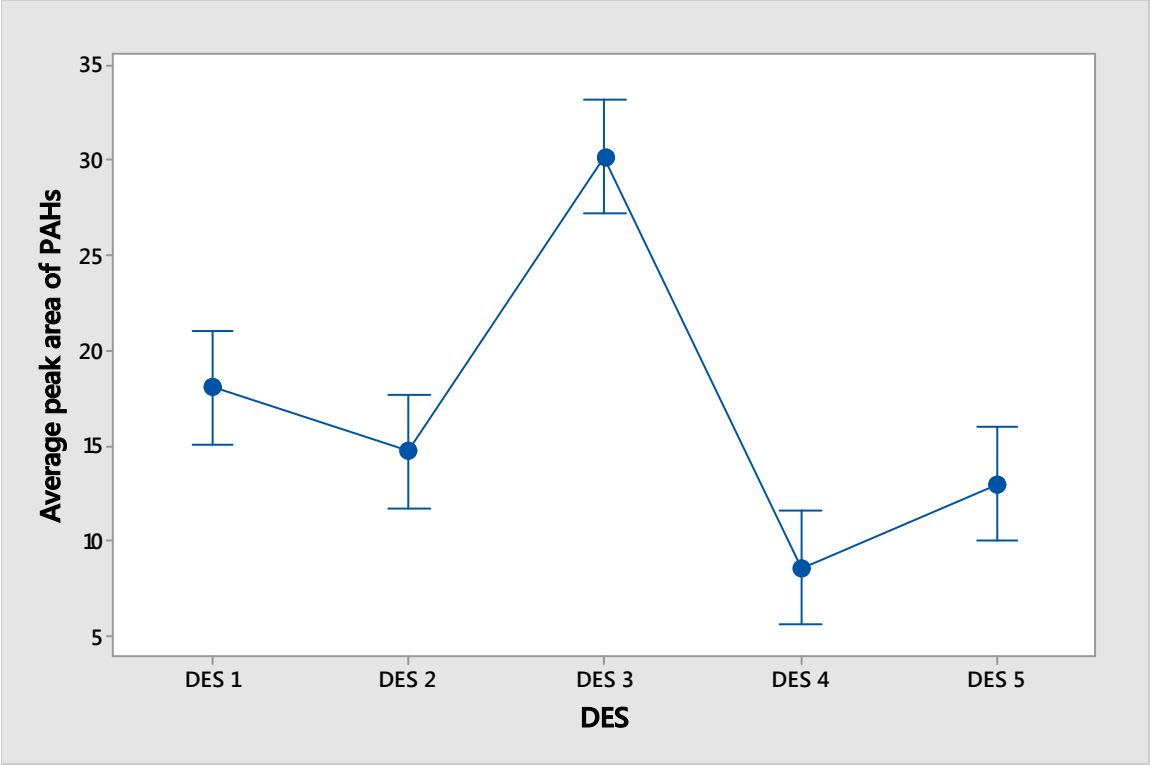


Fig. S3. Interval plot average peak area of PAHs versus DESs at p = 0.05. The pooled standard deviation was used to calculate the intervals.

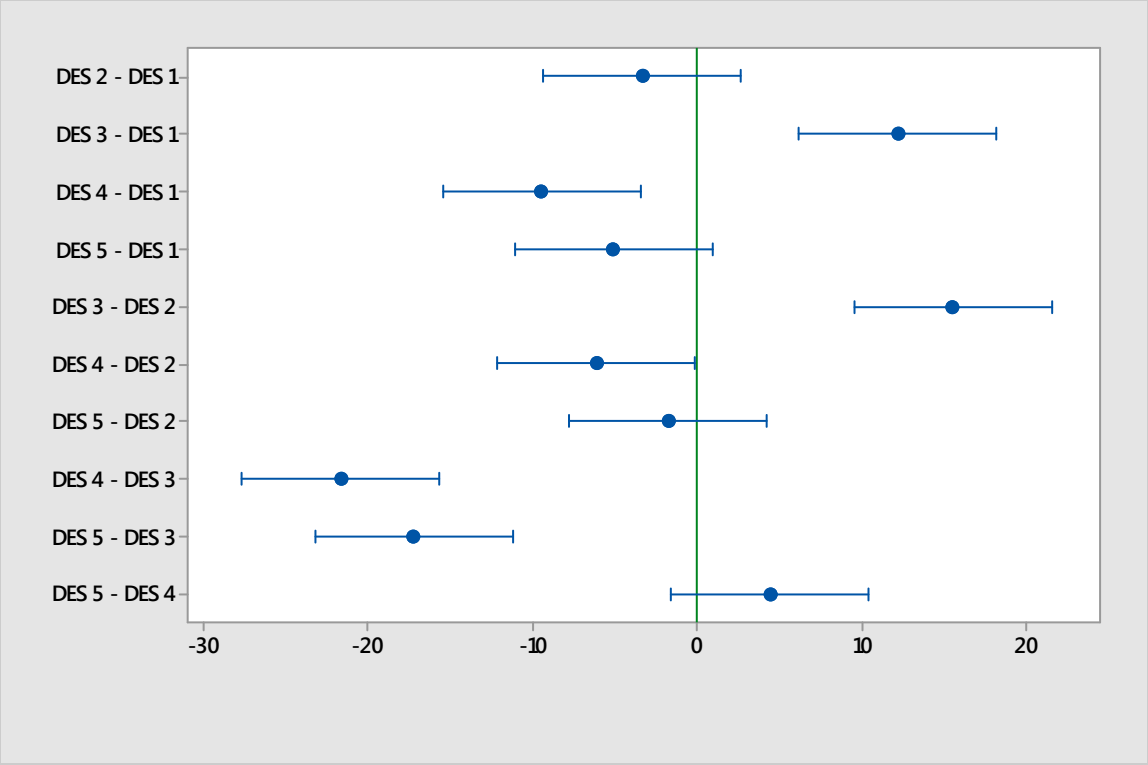
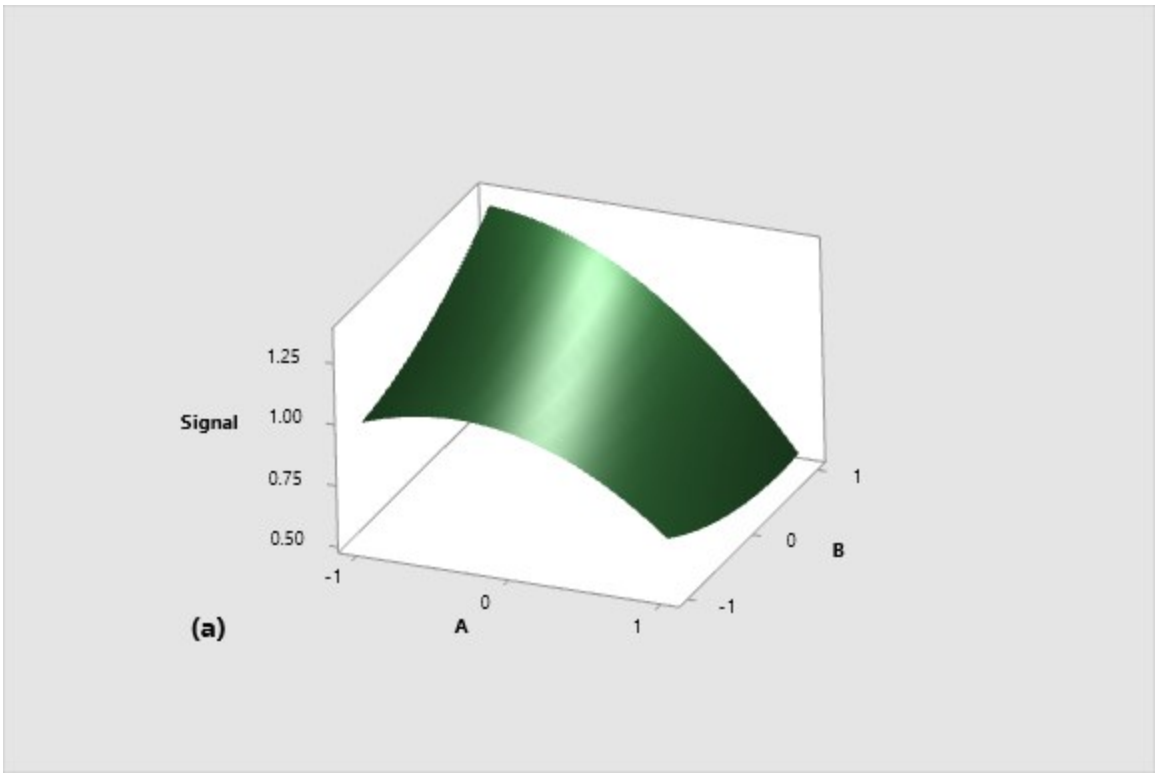


Fig. S4. Tukey Simultaneous 95% CIs, differences of means for DESs. If an interval does not contain zero, the corresponding means are significantly different.


Signal
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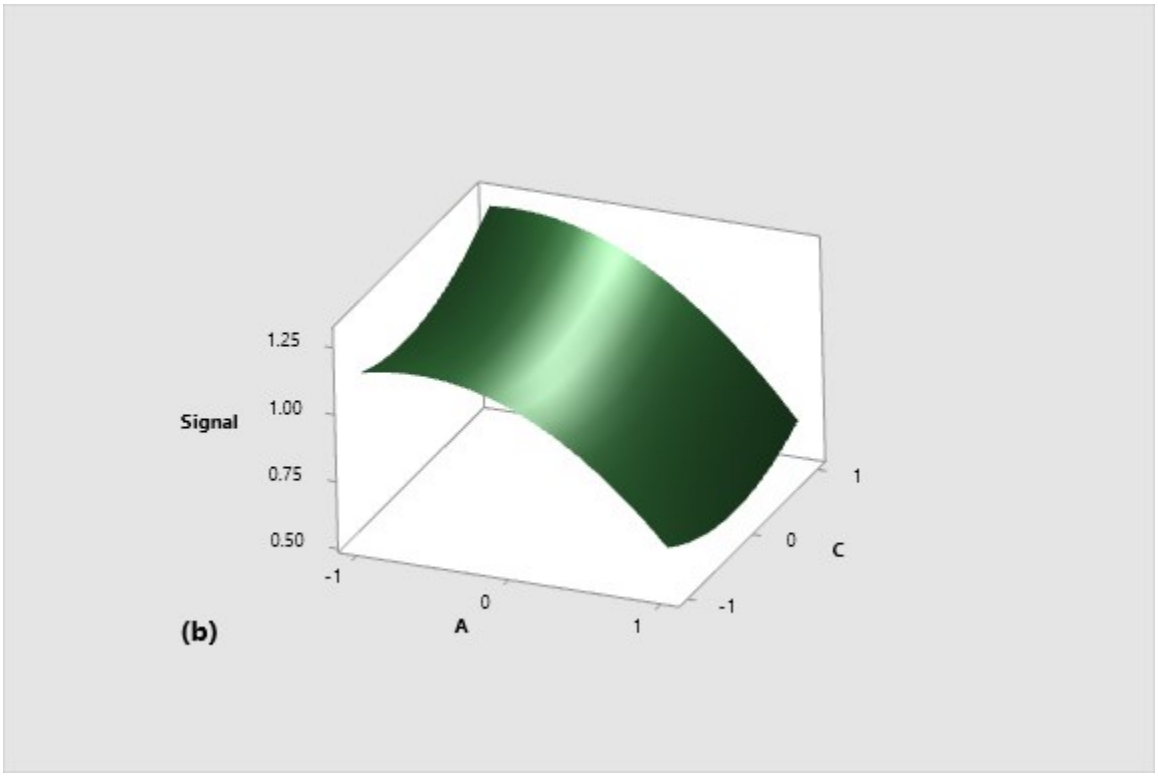
1.00
0.75
0.50
-1
0
1
A
-1
0
1
B
(a)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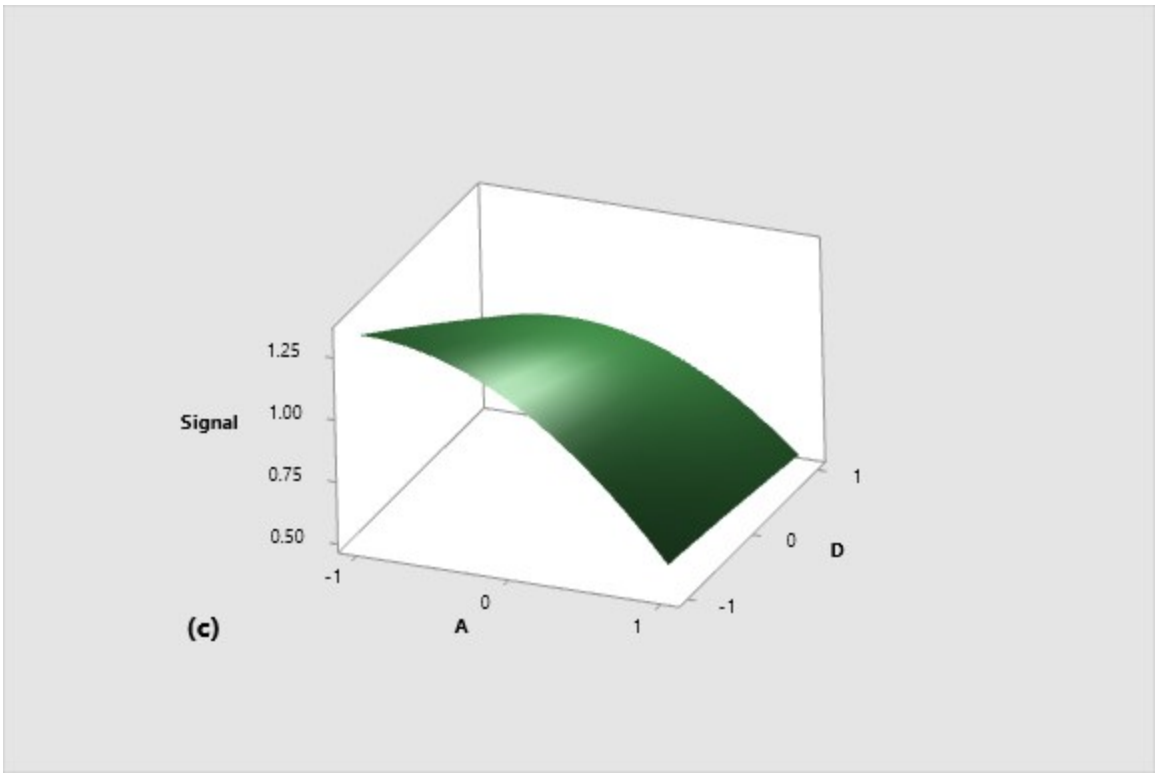
0.75
0.50
-1
0
1
A
-1
0
1
C
(b)


Signal
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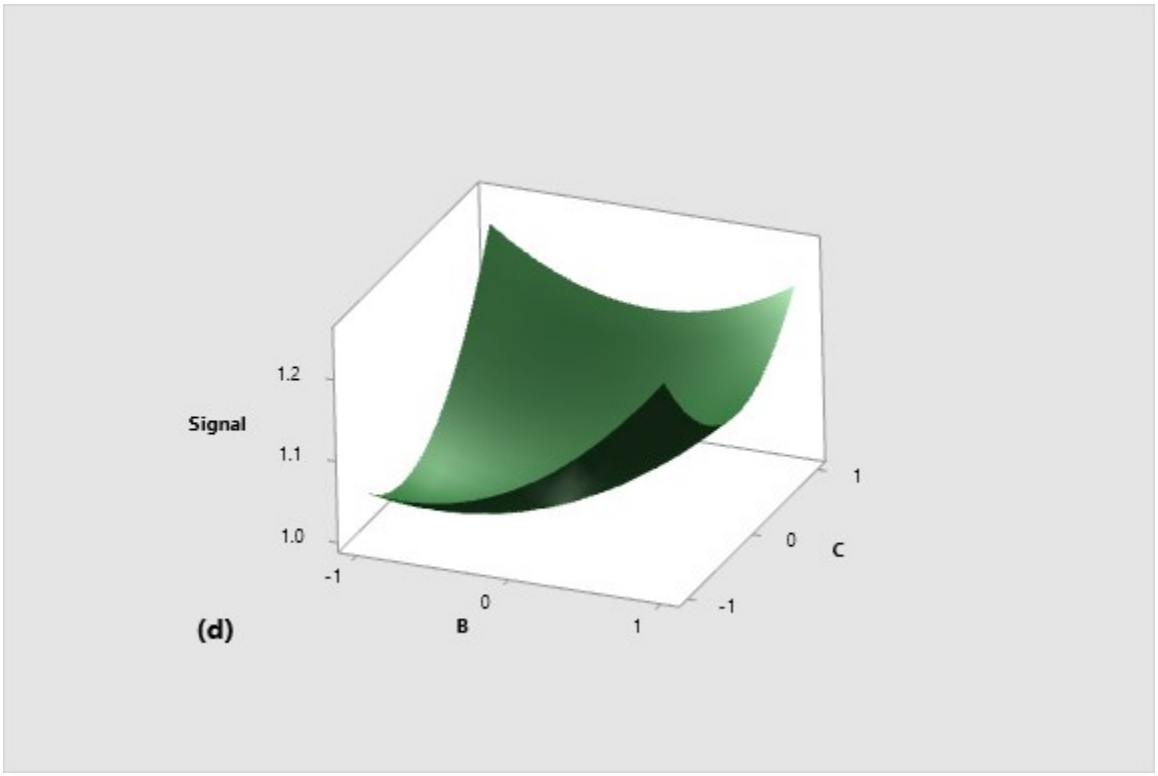
0.75
0.50
-1
0
1
A
-1
0
1
D
(c)


Signal
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1.1
1.0
-1
0
1
B
-1
0
1
C
(d)

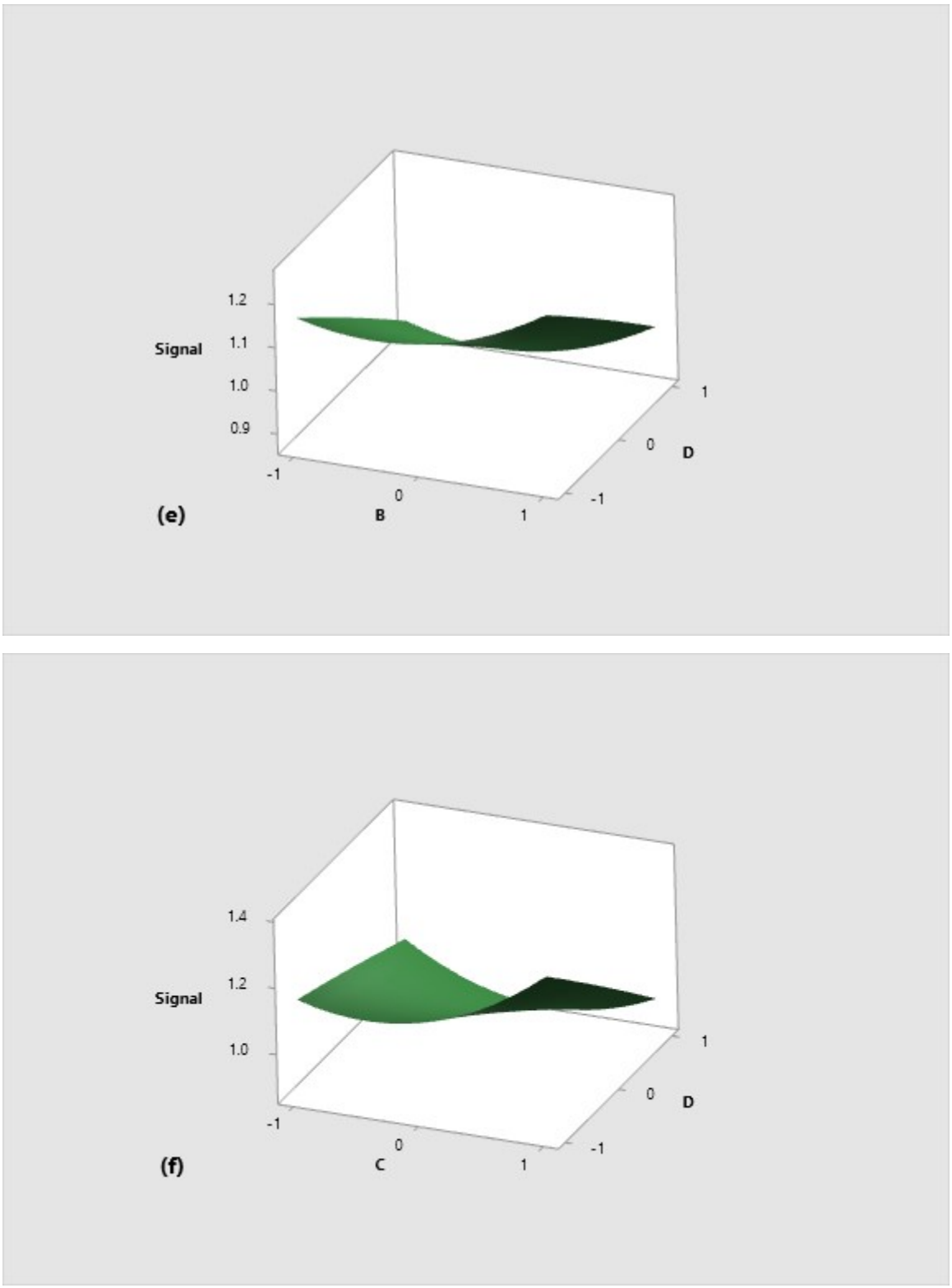


Fig. S5. Response surface plots on the sum of the peak area of PAHs as a□ected by the sample temperature (A), extraction time (B), stirring rate (C), and ionic strength (D).

Table S1. Mass parameters of SIM methods.

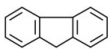
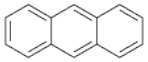
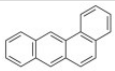
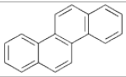
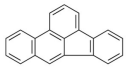
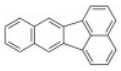
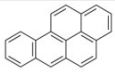
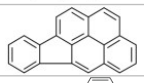
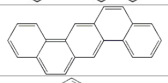
Compound	Molecular Structure	[a]t_r (min)	CAS Number	Target ion in SIM (*m/z*)	Dwell time (ms)
Nap		6.88	91-20-3	128.00 127.00	50 50
Acy		9.14	208-96-8	152.00 151.00	50 50
Ace		9.38	83-32-9	154.00 153.00	50 50
Flu		10.09	86-73-7	166.05 165.05	50 50
Ant		11.48	120-12-7	178.05	50
Phe		11.62	85-01-8	178.05 176.05	50 50
Flt		13.16	85-01-8	202.05 200.05	50 50
Pyr		13.67	129-00-0	202.05 200.05	50 50
BaA		15.24	56-55-3	228.10 226.10	50 50
Chr		15.37	218-01-9	228.10 226.05	50 50
BbF		16.85	205-99-2	252.10 250.05	50 50
BkF		17.01	207-08-9	252.10 253.00	50 50
BaP		18.15	50-32-8	252.00 253.10	50 50
Ind		20.43	193-39-5	276.05	50
DBA		20.65	53-70-3	278.00	40
BgP		21.77	191-24-2	276.05 138.00	50 50

Table S2. Analysis of Variance (ANOVA) for one-way analysis of DES type.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
DES	4	1611.7	402.94	42.01	0.000
Error	25	314.7	12.59		
Total	29	1926.4			

Table S3. Experimental variables, levels, design matrix and results (total peak area) in the Box-Behnken design.

Variables	Coded	Levels		
		Low (-1)	Center (0)	High (+1)
Extraction temperature (°C)	A	45	55	65
Extraction time (min)	B	2	4	6
Stirring rate (rpm)	C	1000	1500	2000
Ionic strength (%)	D	10	15	20

Run	Order	Block	A	B	C	D	Total peak area (AU)
27	1	1	0	0	0	0	153450
12	2	1	1	0	0	1	97650
2	3	1	1	-1	0	0	97650
9	4	1	-1	0	0	-1	192200
1	5	1	-1	-1	0	0	142600
8	6	1	0	0	1	1	150350
23	7	1	0	-1	0	1	150350
11	8	1	-1	0	0	1	134850
14	9	1	0	1	-1	0	206150
6	10	1	0	0	1	-1	213900
13	11	1	0	-1	-1	0	165850
5	12	1	0	0	-1	-1	170500
4	13	1	1	1	0	0	86800
20	14	1	1	0	1	0	91450
22	15	1	0	1	0	-1	186000
15	16	1	0	-1	1	0	182900
7	17	1	0	0	-1	1	145700
24	18	1	0	1	0	1	134850
25	19	1	0	0	0	0	158100
21	20	1	0	-1	0	-1	198400
10	21	1	1	0	0	-1	97650
16	22	1	0	1	1	0	190650
3	23	1	-1	1	0	0	215450
17	24	1	-1	0	-1	0	187550
26	25	1	0	0	0	0	161200
18	26	1	1	0	-1	0	97650
19	27	1	-1	0	1	0	204600

Table S4. Analysis of variance for the fitted quadratic polynomial model of the proposed method.

Source	**DF**	**SS**	**MS**	***F*-value**	***P*- value**
Model	14	1.67929	0.119949	13.78	0.000
Regression	4	1.14065	0.285162	32.75	0.000
A	1	0.89653	0.896533	102.98	0.000
B	1	0.02341	0.023408	2.69	0.127
C	1	0.01267	0.012675	1.46	0.251
D	1	0.20803	0.208033	23.89	0.000
Square	4	0.39914	0.099784	11.46	0.000
A^2	1	0.18584	0.185837	21.35	0.001
B^2	1	0.02225	0.022245	2.56	0.136
C^2	1	0.05833	0.058334	6.70	0.024
D^2	1	0.00009	0.000093	0.01	0.920
2-Way Interaction	6	0.13950	0.023250	2.67	0.070
A×B	1	0.07290	0.072900	8.37	0.013
A×C	1	0.00563	0.005625	0.65	0.437
A×D	1	0.03422	0.034225	3.93	0.071
B×C	1	0.01102	0.011025	1.27	0.282
B×D	1	0.00010	0.000100	0.01	0.916
C×D	1	0.01562	0.015625	1.79	0.205
Error	12	0.10447	0.008706		
Lack of fit	10	0.10321	0.010321	16.30	0.059
Pure error	2	0.00127	0.000633		
Total	26	1.78376			

Table S5. Concentrations of PAHs determined in real water samples.

Compound	Spiked (µg L^{-1})	Tap water				River water				Well water				Waste water			
		Found (µg L^{-1})	RR% (±SD) (n=3)	Bias (%)	[a]t_{exp}	Found (µg L^{-1})	RR% (±SD) (n=3)	Bias (%)	t_{exp}	Found (µg L^{-1})	RR% (±SD) (n=3)	Bias (%)	t_{exp}	Found (µg L^{-1})	RR% (±SD) (n=3)	Bias (%)	t_{exp}
Nap	0	Nd[b]	-	-	2.06	Nd	-	-	2.23	5.41	-	-	1.98	9.53	-	-	1.57
	5	4.98	99.60 (0.81)	-0.40		4.82	96.31 (0.42)	-3.69		9.96	99.20 (1.24)	-0.80		14.41	97.80 (0.74)	-2.20	
	10	9.81	98.10 (0.21)	-1.90		9.60	95.98 (0.48)	-4.12		14.91	95.00 (0.93)	-5.00		19.80	102.70 (1.21)	2.70	
	15	15.89	105.93 (1.09)	5.93		14.72	98.15 (0.61)	-1.85		20.14	98.20 (0.67)	-1.80		24.65	100.80 (0.76)	0.80	
Acy	0	Nd	-	-	1.44	Nd	-	-	1.52	Nd	-	-	1.07	84.60	-	-	2.11
	5	5.04	100.80 (0.92)	0.80		4.86	97.21 (0.52)	-2.79		4.86	97.09 (0.91)	-2.91		89.80	104.00 (0.95)	4.00	
	10	9.68	96.80 (0.56)	-3.20		9.93	99.31 (1.07)	-0.69		10.01	100.08 (1.12)	0.08		94.58	99.81 (0.81)	-0.19	
	15	15.34	102.27 (0.29)	2.27		15.20	101.31 (0.91)	1.31		14.89	99.24 (0.64)	-0.76		99.12	96.8 0 (0.69)	-3.20	
Ace	0	Nd	-	-	1.19	Nd	-	-	1.27	7.05	-	-	1.29	Nd	-	-	1.02
	5	5.09	101.80 (1.03)	1.80		4.89	97.80 (0.49)	-2.20		11.99	98.80 (1.03)	-1.20		5.01	100.10 (0.63)	0.10	
	10	10.12	101.20 (0.82)	1.20		9.75	97.50 (0.98)	-2.50		17.12	100.68 (0.82)	0.68		10.13	101.31 (0.86)	1.31	
	15	14.86	99.07 (1.12)	-0.93		15.16	101.07 (0.91	1.07		21.53	96.52 (1.12)	-3.48		14.60	97.31(1.32)	-2.89	
Flu	0	Nd	-	-	1.95	Nd	-	-	1.08	3.91	-	-	2.09	8.27	-	-	0.79
	5	4.85	97.00 (0.86)	-3.00		5.02	100.40 (0.77)	0.40		9.14	104.61 (1.11)	4.61		13.19	98.31 (1.08)	-2.69	
	10	10.49	104.90 (1.07)	4.90		10.07	100.70 (0.73)	0.70		13.82	99.07 (0.96)	-0.93		18.17	99.01 (0.76)	-0.99	
	15	14.36	95.73 (0.74)	4.27		15.11	100.73 (0.69)	0.73		18.37	96.37 (0.85)	-3.63		23.39	100.83 (0.59)	0.83	
Phe	0	Nd	-	-	1.83	Nd	-	-	1.86	2.64	-	-	1.11	20.44	-	-	2.26
	5	5.12	102.40 (0.66)	2.40		5.06	101.11 (0.52)	1.11		7.56	98.34 (1.06)	-1.66		25.61	103.40 (0.66)	3.40	
	10	9.68	96.80 (1.10)	-3.20		10.40	104.01 (1.13)	4.01		12.72	100.81 (0.59)	0.81		31.10	106.60 (0.84)	6.60	
	15	15.35	102.33 (.91)	2.33		14.73	98.17 (0.61)	-1.83		17.93	101.91 (0.99)	1.91		32.22	97.02 (0.79)	-2.98	
Ant	0	Nd	-	-	2.26	0.81	-	-	1.58	Nd	-	-	2.21	17.67	-	-	1.94
	5	4.72	94.40 (1.14)	-5.60		5.72	98.21 (0.85)	-1.89		4.94	98.82 (0.93)	-1.18		22.44	95.40 (0.88)	-3.60	
	10	9.68	96.80 (1.02)	-3.20		10.97	101.60 (0.67)	1.60		9.65	96.53 (0.68)	-3.47		27.50	98.30 (0.93)	-1.70	
	15	15.66	104.40 (0.58)	4.40		15.69	99.20 (095)	-0.80		14.34	95.61(1.09)	-4.39		32.58	99.41 (0.85)	-0.59	
Flt	0	Nd	-	-	0.99	Nd	-	-	1.07	Nd	-	-	1.63	1.91	-	-	1.55
	5	5.09	101.80 (0.94)	1.80		4.96	99.21 (0.46)	-0.79		4.90	97.91 (0.94)	-2.09		6.76	97.06 (0.74)	-2.94	
	10	9.99	99.90 (0.71)	-0.10		9.95	99.53 (0.86)	-0.47		9.85	98.51 (0.88)	-1.49		11.72	98.14 (0.69)	-1.86	
	15	15.07	100.47 (0.83)	0.47		14.74	98.28(1.20)	-1.72		14.85	99.02 (1.19)	-0.98		17.11	101.35 (0.86)	1.35	
Pyr	0	Nd	-	-	1.81	Nd	-	-	1.84	1.47	-	-	1.08	23.62	-	-	0.69
	5	5.13	102.60 (0.59)	2.60		4.89	97.80 (0.94)	-2.20		6.59	102.35 (1.27)	2.35		28.66	100.80 (0.49)	0.80	
	10	9.74	97.40 (0.69)	-2.60		9.61	96.12 (0.88)	-3.88		11.56	100.94 (0.91)	0.94		33.73	101.10 (0.62)	1.10	
	15	15.40	102.67 (0.66	2.67		15.14	100.93 (1.19)	0.93		16.19	98.16 (0.83)	-1.84		38.42	98.66 (0.55)	-1.44	
BaA	0	Nd	-	-	1.66	Nd	-	-	2.10	Nd	-	-	1.96	Nd	-	-	1.44
	5	4.89	97.80 (1.07)	-2.20		4.79	95.61 (1.52)	-4.39		4.80	96.08 (0.69)	-3.92		4.97	99.40 (1.11)	-0.60	
	10	10.16	101.60 (0.91)	1.60		9.82	98.20 (1.06)	-1.80		9.81	98.11 (1.08)	-1.89		9.62	96.20 (0.81)	-3.80	
	15	15.32	102.13 (0.86)	2.13		14.58	97.19 (0.75)	-2.81		15.12	100.83 (0.87)	0.83		15.64	104.27 (0.97)	4.27	

Chr	0	Nd	-	-	1.38		Nd	-	-	2.22		0.92	-	-	1.27		Nd	-	-	1.74
	5	4.89	97.80 (0.93)	-2.20			5.20	104.04 (0.91)	4.04			6.02	102.07 (1.12)	2.07			4.95	99.04 (0.39)	-0.96	
	10	9.75	97.50 (0.94)	-2.50			9.61	96.12 (0.81)	-3.88			10.82	99.04 (0.91)	-0.96			9.49	94.88 (1.27)	-3.12	
	15	15.16	101.07 (0.78)	1.07			14.54	96.91 (0.59)	-3.09			15.56	97.61 (0.77)	-2.39			14.55	97.01 (0.94)	-2.99	
BbF	0	Nd	-	-	0.67		Nd	-	-	1.49		Nd	-	-	1.35		Nd	-	-	1.89
	5	5.02	100.40 (0.66)	0.40			5.01	100.10 (0.63)	0.10			4.87	97.35 (1.08)	-2.65			5.05	100.98 (0.84)	0.98	
	10	10.07	100.70 (0.73)	0.70			10.13	101.31 (0.86)	1.31			9.86	98.64 (0.67)	-1.36			9.63	96.33 (0.69)	-3.67	
	15	15.11	100.73 (0.86)	0.73			14.60	97.31(1.32)	-2.69			14.90	99.34 (0.89)	-0.66			14.71	98.07 (0.99)	-1.93	
BkF	0	Nd	-	-	1.15		Nd	-	-	1.15		Nd	-	-	1.06		Nd	-	-	1.52
	5	5.19	103.80 (1.12)	3.8			4.95	99.07 (0.76)	-0.93			4.89	97.81 (0.94)	-2.19			4.89	97.80 (0.86)	-2.20	
	10	9.94	99.40 (0.94)	-0.60			9.62	96.16 (1.52)	-3.84			9.90	99.04 (0.83)	-0.66			9.75	97.50 (0.77)	-2.50	
	15	15.20	101.33 (0.88)	1.33			15.29	101.94 (1.29)	1.94			15.02	100.12 (1.08)	0.12			15.16	101.07 (0.92)	1.07	
BaP	0	Nd	-	-	2.24		Nd	-	-	1.09		Nd	-	-	2.17		Nd	-	-	1.05
	5	5.21	104.20 (0.64)	4.20			4.91	98.14 (0.83)	-1.86			5.25	105.08 (0.94)	5.08			4.82	96.44 (0.78)	-3.56	
	10	9.64	96.40 (0.99)	-3.60			9.94	99.37 (1.04)	-0.63			10.13	101.32 (0.67)	1.32			9.86	98.61 (0.76)	-1.39	
	15	15.38	102.53 (085)	2.53			14.71	98.05 (0.95)	-1.95			14.79	98.61 (1.11)	-1.39			15.24	101.62 (1.06)	1.62	
DBA	0	Nd	-	-	1.97		Nd	-	-	1.18		Nd	-	-	2.26		Nd	-	-	1.45
	5	4.87	97.40 (1.14)	-3.60			5.06	101.14 (0.83)	1.14			4.75	94.89 (1.09)	-5.11			4.86	97.09 (0.84)	-3.91	
	10	9.76	97.60 (0.97)	-3.40			9.94	99.43 (1.04)	-0.57			9.80	98.04 (0.67)	-1.96			10.24	102.37 (0.93)	2.37	
	15	15.08	100.53 (0.83)	0.53			15.16	101.05 (0.95)	1.05			15.24	101.60 (0.83)	1.60			15.30	101.97 (1.04)	1.97	
BgP	0	Nd	-	-	1.83		Nd	-	-	1.84		Nd	-	-	1.09		Nd	-	-	1.29
	5	4.97	99.40 (0.75)	-0.60			4.89	97.82 (0.46)	-2.18			5.03	100.62 (0.88)	0.62			5.16	103.17 (0.66)	3.17	
	10	9.62	96.20 (0.91)	-3.80			9.95	99.53 (0.86)	-0.47			9.93	99.34 (1.04)	-0.66			10.08	100.83 (0.71)	0.83	
	15	15.64	104.27 (1.07)	4.27			15.54	103.61 (1.20)	3.61			14.71	98.06 (0.58)	-1.94			14.80	98.67 (0.90)	-1.23	
Ind	0	Nd	-	-	2.29		Nd	-	-	2.08		Nd	-	-	1.88		Nd	-	-	1.03
	5	4.86	97.20 (0.58)	-2.80			4.89	97.80 (0.94)	-2.20			5.15	103.06 (0.79)	3.06			5.21	104.16 (0.55)	4.16	
	10	9.54	95.40 (0.67)	-4.60			9.82	98.16 (0.88)	-1.84			9.86	98.64 (1.07)	-1.36			9.78	97.83 (0.80)	-2.17	
	15	14.27	95.13 (0.93)	-4.87			15.21	101.39 (1.19)	1.39			14.79	98.60 (0.71)	-1.40			15.10	100.64 (0.73)	0.64	

[a] $t_{(0.025, 8)} = 2.30$. [b] Not detected.

Table S6. Comparison of the characteristics of microextraction procedure and its varieties for analysis of PAHs with the proposed method in this study.

Analytical method	Number of PAHs	LOD (μg L^{-1})	EF[a]	ES[b]	Sample size (mL)	Analysis Time (min)[c]	Extraction Time (min)	Ref.
DLLME[d]-GC-FID	16	0.007-0.020	603-1113	C_2Cl_4	5	≈ 38	<1	[2]
DLLME–MSFIA[e]–LC-FLD	15	0.02-0.60	86–95	Trichloroethylene	4	≈ 27	<1	[3]
HLLME[f]-GC-FID	9	0.02-0.18	225-257	$CHCl_3$-CH_3OH	2.5	≈ 46	<1	[4]
DLLME-SFO[g]-LC	5	0.045-0.86	67-104	1-undecanol	10	≈ 27	<1	[5]
SBSE[h]-DLLME-SFO-LC-UV	5	0.007-0.010	1630-2637	1-undecanol	100	≈ 75	55	[6]
IL[i]-DLLME-LC-FLD/UV	16	0.02-0.56	109-228	IL	5	≈ 70	10	[7]
SBDLME[j]-GC-MS	9	0.0005-0.0087	18-717	MIL[k]	25	≈ 40[†]	10	[8]
TC-IL[l]-DLLME-LC-UV	16	0.0005-0.88	-[**]	IL[i]	10	≈ 100	30	[9]
AALLME[m]-LC-UV	5	0.04-0.60	114-156	1-dodecanol	10	≈ 25	<6	[10]
HS-SDME[n]-LC-FLD	5	0.004-0.247	18-53	β-cyclodextrin	10	≈ 22	10	[11]
AG-LPME[r]-GC-MS	4	0.009–0.014	89-177	1-octanol	10	≈68	50	[12]
AA[m]-DLLME-LC-UV	5	0.002-0.8	310-325	2-ethyl-1-hexanol	40	≈ 36	<1	[13]
SFO[g]-GC-FID	12	0.07–1.67	35-60	1-undecanol	8	≈ 60	35	[14]
In-tube-SPME[s]-LC-UV	10	0.001–0.01	268- 2497	-[*]	60	≈ 86	60[‡]	[15]
HS-SPME[t]-GC-FID	8	0.02-0.09	-[**]	-[*]	10	≈ 67	45	[16]
ELLME-DES[o]-LC-UV	7	0.02-6.8	151-170	DES[p]	1.5	≈ 60	20	[17]
USA[u]-DLLME- GC-MS	21	0.004-0.01	-[**]	DES [v]	10	≈ 75	<20	[18]
MSPE[q]-LC-UV	5	0.02–0.1	242-600	-[*]	2.0	≈ 37	20[⁂]	[19]
Proposed method	16	0.01-0.14		DES [w]	10	≈ 60	<8	-

[a]Enrichment factor; [b] Extraction solvent; [c] Analysis time including extraction time, centrifugation time, and chromatography run time; [d] Dispersive liquid-liquid microextraction, [e]Multi syringe flow injection analysis; [f]Homogeneous liquid-liquid microextraction;[g] Solidification of floating organic drop; [h] Stir bar sorptive extraction; [i]Ionic liquid; [j]Stir bar dispersive liquid microextraction; [k] Magnetic ionic liquid; [l]Temperature-controlled ionic liquid dispersive liquid-liquid microextraction; [m]Air assisted liquid liquid microextraction; [n] Headspace-single drop microextraction; [o]Emulsification liquid-liquid microextraction based on deep eutectic solvent; [p]Deep eutectic solvent, choline chloride-phenol[ChCl][Ph], 1:2;[q]Magnetic solid phase extraction; [r] Agarose gel disc-liquid phase microextraction;[s]In tube solid phase microextraction; [t]Head space-solid phase microextraction;[u]Ultrasoundassisted; [v] Deep eutectic solvent thymol-conphor[Th][C], 1:1,[w] Deep eutectic solvent, choline chloride-oxalic acid[ChCl][OX], 1:2; [*] Not used; [†] Thermal desorption system was used; [**] Not reported; [‡] Solvent desorption (ACN) was used; [⁂] Solvent desorption (1-propanol) was used.

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