

Supplementary data

In-situ formation of chloroform for dispersive liquid liquidmicroextraction of some aromatic amines from aqueous samples optimized by central composite design prior to GC-MS analysis

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Table S1. Experimental factors, levels, and results for CCD design.

Variables						levels				
						$-\alpha$	-1	0	+1	$+\alpha$
(A) Vortex time (min)						1	3.3	5.5	7.8	10
(B) Chloral hydrate (mg)						140	180	220	260	300
(C) NaCl concentration (% w/v)						0	2.5	5.0	7.5	10
(D) NaOH concentration (mol L ⁻¹)						0.5	0.75	1.0	1.25	1.5
Std	Run	A	B	C	D	Average ER (%) obtained from three repeated determinations of				
						Aniline	4-Toluidine	1-Naphthylamine	Diphenylamine	
16	1	7.8	260	7.5	1.25	48.6	52.9	48.2	53.3	
27	2	5.5	220	5	1	49.1	53.5	48.7	53.9	
28	3	5.5	220	5	1	49.0	53.5	48.6	53.9	
17	4	1.0	220	5	1	52.9	57.7	52.5	58.2	
7	5	3.3	260	7.5	0.75	45.4	49.5	45.0	49.8	
30	6	5.5	220	5	1	44.8	48.8	44.4	49.2	
9	7	3.3	180	2.5	1.25	56.6	61.6	56.1	62.1	
29	8	5.5	220	5	1	49.0	53.5	48.6	53.9	
19	9	5.5	140	5	1	52.2	57.0	51.8	57.4	
22	10	5.5	220	10	1	52.8	57.6	52.4	58.0	
21	11	5.5	220	0	1	68.7	74.9	68.1	75.4	
23	12	5.5	220	5	0.5	76.1	83.0	75.5	83.6	
15	13	3.3	260	7.5	1.25	68.2	74.3	67.6	74.9	
20	14	5.5	300	5	1	47.2	51.5	46.8	51.9	
5	15	3.3	180	7.5	0.75	55.4	60.4	55.0	60.9	
2	16	7.8	180	2.5	0.75	83.0	90.4	82.3	91.1	
13	17	3.3	180	7.5	1.25	55.5	60.5	55.1	61.0	
11	18	3.3	260	2.5	1.25	70.6	77.0	70.1	77.6	
14	19	7.8	180	7.5	1.25	41.4	45.1	41.0	45.4	
24	20	5.5	220	5	1.5	69.9	76.2	69.3	76.8	
3	21	3.3	260	2.5	0.75	50.3	54.8	49.9	55.2	
26	22	5.5	220	5	1	44.8	48.9	44.5	49.2	
25	23	5.5	220	5	1	44.8	48.8	44.4	49.2	
4	24	7.8	260	2.5	0.75	57.8	63.0	57.3	63.4	
10	25	7.8	180	2.5	1.25	53.8	58.6	53.4	59.1	
1	26	3.3	180	2.5	0.75	67.1	73.1	66.6	73.7	
18	27	10.0	220	5	1	47.7	52.0	47.3	52.4	
6	28	7.8	180	7.5	0.75	69.1	2 75.3	68.5	75.8	
8	29	7.8	260	7.5	0.75	46.9	51.1	46.5	51.5	
12	30	7.8	260	2.5	1.25	54.3	59.1	53.8	59.6	

Table S2. Final equations for the ER of analytes in terms of coded factors.

Analytes	Final equations
Aniline	$ER (\%)=Y = 46.93 -1.04 A - 2.08 B -3.95 C -1.6 D - 2.48 AB - 1.43 AC - 5.71 AD +6.79 BD +1.23 CD + 3.34 C^2 + 6.40 D^2$
4-Toluidine	$ER (\%)=Y = 51.15 -1.13 A - 2.26 B -4.30 C -1.75 D - 2.70 AB - 1.56 AC - 6.23 AD +7.40 BD +1.34 CD + 3.64 C^2 + 6.98 D^2$
1-Naphthylamine	$ER (\%)=Y = 46.55 -1.03 A - 2.06 B -3.91 C -1.59 D - 2.46 AB - 1.42 AC - 5.67 AD +6.74 BD +1.22 CD + 3.31 C^2 + 6.35 D^2$
Diphenylamine	$ER (\%)=Y = 51.55 -1.14 A - 2.28 B -4.330 C -1.76 D - 2.72 AB - 1.57 AC - 6.28 AD +7.46 BD +1.35 CD + 3.66 C^2 + 7.03 D^2$

Table S3. Results of ANOVA for CCD design for aniline.

Source	Sum of Squares	d _f	Mean Square	F-value	p-value	
Model	3299.19	14	235.66	66.35	< 0.0001	Significant
A-Vortex time	25.86	1	25.86	7.28	0.0165	
B-Chloral hydrate amount	103.61	1	103.61	29.17	< 0.0001	
C-Salt effect	373.64	1	373.64	105.20	< 0.0001	
D-NaOH concentration	61.53	1	61.53	17.32	0.0008	
AB	98.06	1	98.06	27.61	< 0.0001	
AC	32.75	1	32.75	9.22	0.0083	
AD	522.53	1	522.53	147.13	< 0.0001	
BC	14.39	1	14.39	4.05	0.0625	
BD	737.70	1	737.70	207.71	< 0.0001	
CD	24.35	1	24.35	6.86	0.0194	
A ²	14.55	1	14.55	4.10	0.0611	
B ²	9.23	1	9.23	2.60	0.1278	
C ²	305.29	1	305.29	85.96	< 0.0001	
D ²	1123.98	1	1123.98	316.47	< 0.0001	
Residual	53.27	15	3.55			
Lack of Fit	25.82	10	2.58	0.4701	0.8550	Not significant
Pure Error	27.46	5	5.49			
Cor Total	3352.46	29				

Table S4. Results of ANOVA for CCD design for 4-toluidine.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3919.76	14	279.98	66.35	< 0.0001	Significant
A-Vortex time	30.73	1	30.73	7.28	0.0165	
B-Chloral hydrate amount	123.10	1	123.10	29.17	< 0.0001	
C-Salt effect	443.92	1	443.92	105.20	< 0.0001	
D-NaOH concentration	73.10	1	73.10	17.32	0.0008	
AB	116.50	1	116.50	27.61	< 0.0001	
AC	38.91	1	38.91	9.22	0.0083	
AD	620.82	1	620.82	147.13	< 0.0001	
BC	17.09	1	17.09	4.05	0.0625	
BD	876.46	1	876.46	207.71	< 0.0001	
CD	28.93	1	28.93	6.86	0.0194	
A ²	17.29	1	17.29	4.10	0.0611	
B ²	10.96	1	10.96	2.60	0.1278	
C ²	362.71	1	362.71	85.96	< 0.0001	
D ²	1335.40	1	1335.40	316.47	< 0.0001	
Residual	63.29	15	4.22			
Lack of Fit	30.67	10	3.07	0.4701	0.8550	Not significant
Pure Error	32.62	5	6.52			
Cor Total	3983.06	29				

Table S5. Results of ANOVA for CCD design for 1-naphthylamine.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3245.96	14	231.85	66.35	< 0.0001	Significant
A-Vortex time	25.45	1	25.45	7.28	0.0165	
B-Chloral hydrate amount	101.94	1	101.94	29.17	< 0.0001	
C-Salt effect	367.61	1	367.61	105.20	< 0.0001	
D-NaOH concentration	60.54	1	60.54	17.32	0.0008	
AB	96.48	1	96.48	27.61	< 0.0001	
AC	32.22	1	32.22	9.22	0.0083	
AD	514.10	1	514.10	147.13	< 0.0001	
BC	14.15	1	14.15	4.05	0.0625	
BD	725.80	1	725.80	207.71	< 0.0001	
CD	23.96	1	23.96	6.86	0.0194	
A ²	14.32	1	14.32	4.10	0.0611	
B ²	9.08	1	9.08	2.60	0.1278	
C ²	300.36	1	300.36	85.96	< 0.0001	
D ²	1105.85	1	1105.85	316.47	< 0.0001	
Residual	52.41	15	3.49			
Lack of Fit	25.40	10	2.54	0.4701	0.8550	Not significant
Pure Error	27.02	5	5.40			
Cor Total	3298.37	29				

Table S6. Results of ANOVA for CCD design for diphenylamine.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3980.13	14	284.29	66.35	< 0.0001	Significant
A-Vortex time	31.20	1	31.20	7.28	0.0165	
B-Chloral hydrate amount	125.00	1	125.00	29.17	< 0.0001	
C-Salt effect	450.76	1	450.76	105.20	< 0.0001	
D-NaOH concentration	74.23	1	74.23	17.32	0.0008	
AB	118.30	1	118.30	27.61	< 0.0001	
AC	39.51	1	39.51	9.22	0.0083	
AD	630.38	1	630.38	147.13	< 0.0001	
BC	17.36	1	17.36	4.05	0.0625	
BD	889.96	1	889.96	207.71	< 0.0001	
CD	29.37	1	29.37	6.86	0.0194	
A ²	17.56	1	17.56	4.10	0.0611	
B ²	11.13	1	11.13	2.60	0.1278	
C ²	368.30	1	368.30	85.96	< 0.0001	
D ²	1355.97	1	1355.97	316.47	< 0.0001	
Residual	64.27	15	4.28			
Lack of Fit	31.14	10	3.11	0.4701	0.8550	Not significant
Pure Error	33.13	5	6.63			
Cor Total	4044.40	29				

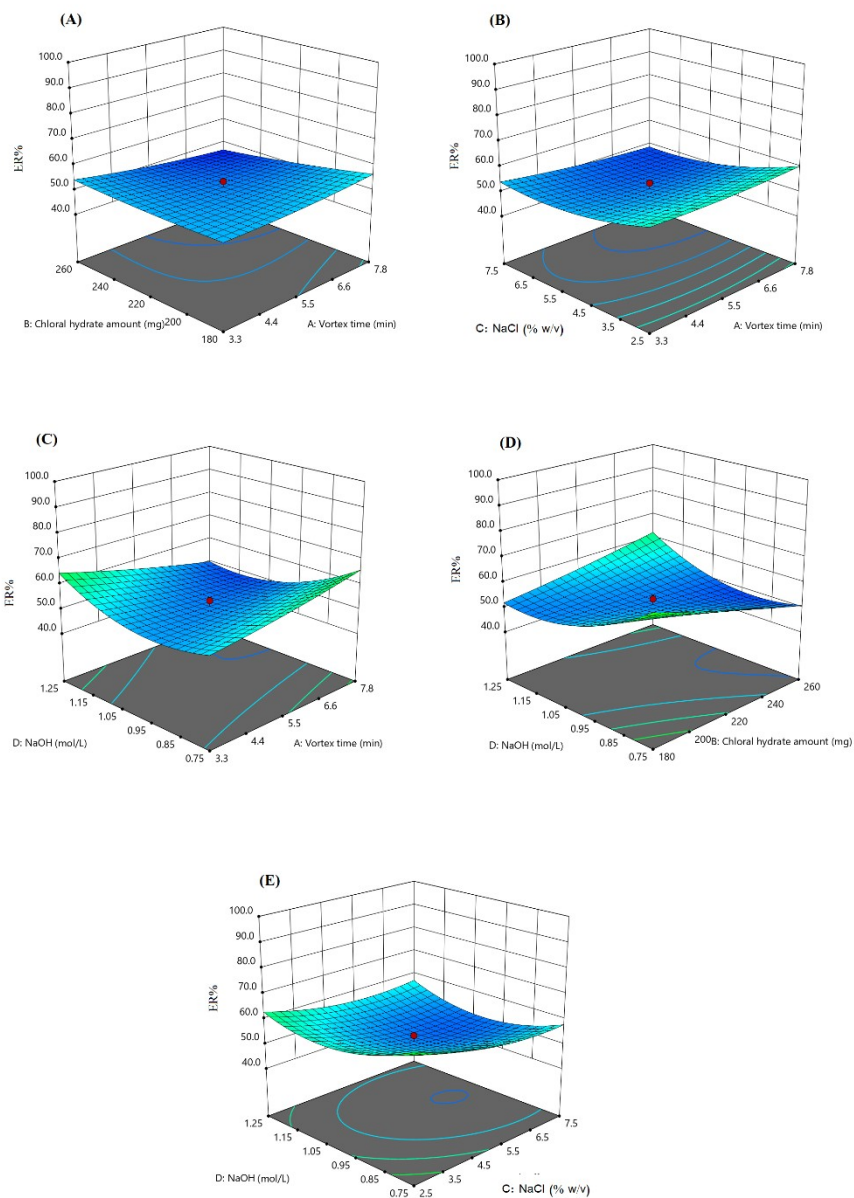


Fig. S1. Response surface and contour plots for 4-toluidine using CCD.

(A) Chloral hydrate amount (mg) vs vortex time (min); (B) salt concentration (% w/v) vs vortex time (min); (C) NaOH concentration (mol L^{-1}) vs vortex time (min); (D) NaOH concentration (mol L^{-1}) vs chloral hydrate amount (mg), and (E) NaOH concentration (mol L^{-1}) vs salt concentration (% w/v).

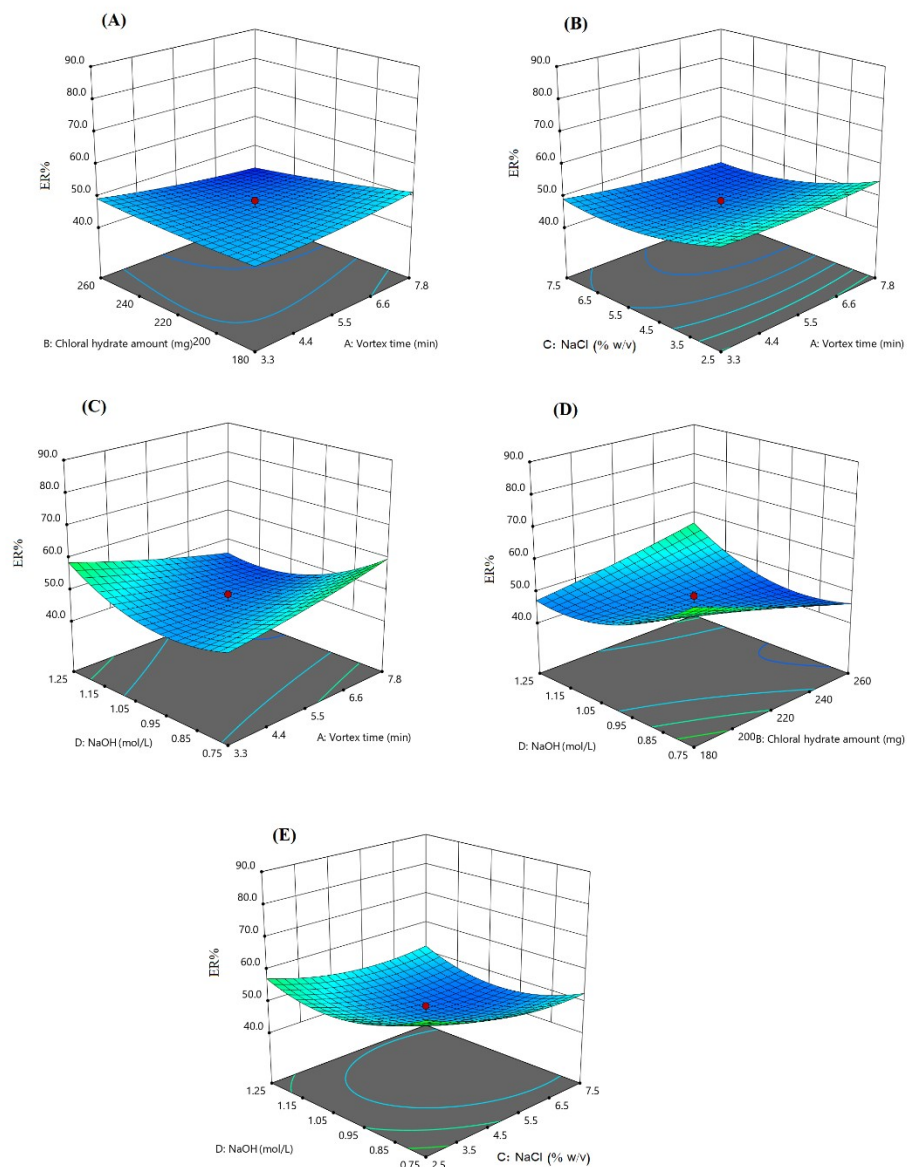


Fig. S2. Response surface and contour plots for 1-naphthylamine using CCD.

(A) Chloral hydrate amount (mg) vs vortex time (min); (B) salt concentration (% w/v) vs vortex time (min); (C) NaOH concentration (mol L^{-1}) vs vortex time (min); (D) NaOH concentration (mol L^{-1}) vs chloral hydrate amount (mg), and (E) NaOH concentration (mol L^{-1}) vs salt concentration (% w/v).

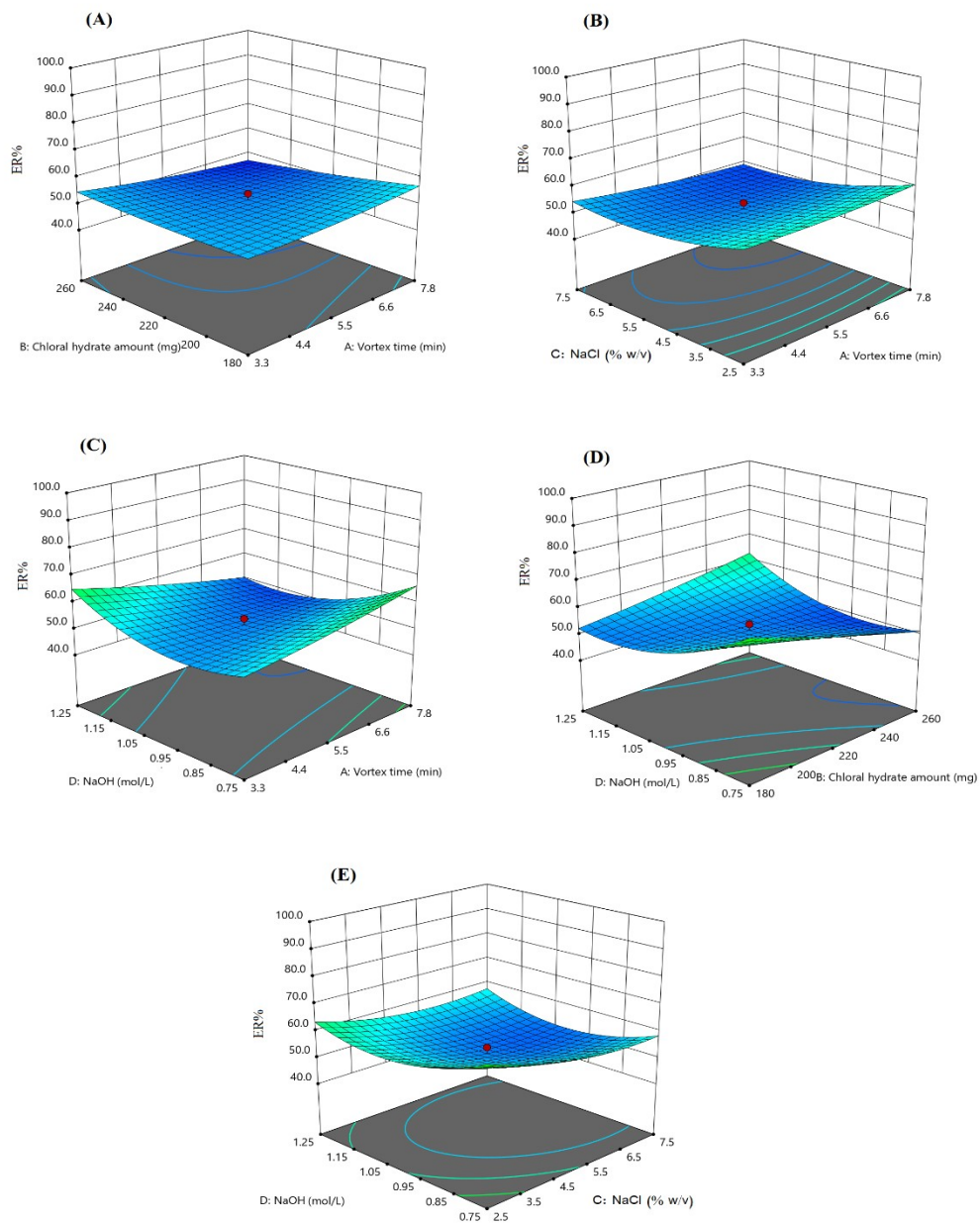


Fig. S3. Response surface and contour plots for diphenylamine using CCD.

(A) Chloral hydrate amount (mg) vs vortex time (min); (B) salt concentration (% w/v) vs vortex time (min); (C) NaOH concentration (mol L^{-1}) vs vortex time (min); (D) NaOH concentration (mol L^{-1}) vs chloral hydrate amount (mg), and (E) NaOH concentration (mol L^{-1}) vs salt concentration (% w/v).