Supplementary Materials

Dispersive micro-solid-phase extraction of dopamine, epinephrine and norepinephrine

from biological samples based on green deep eutectic solvents and Fe₃O₄@MIL-100 (Fe)

core-shell nanoparticles grafted with pyrocatechol

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Figure (1S)

As it can be seen, adsorption time, pH of sample solution and ionic strength are not significant factors. Each factor has a negative or positive effect on the extraction recovery. A positive value for the estimated effect indicates that with the increase in the variable, the response increases. A negative value indicates that a better response is obtained at the lower levels of the variable. pH of sample solution shows a very low positive influence on the analytical response, thus this factor fixed at medium level for further experiment (pH=7). Due to the negative effect of ionic strength and adsorption time on the analytical response, these factors were fixed at a low level. The negative effect with increase in the adsorption time may be explained by occurring new equilibrium occurred between adsorbed analytes and aqueous solution.



Figure (2S)



Figure (3S)



Figure (S4)

Table 1S	Actual and coded values of factors used in FFD for the extraction of DA, E and

NE.

	Levels							
Factors	Low (-1)			Central (0)			High (+1)	
(X ₁) amount of sorbent (mg)	5			12.30			30	
(X ₂) pH		2		7			12	
(X ₃) adsorption time (min)		5		7.5			10	
(X ₄) desorption time (min)	5			7.5			10	
(X ₅) NaCl (% w/v)		0		5			10	
(X ₆) volume of eluent (μ L)		50	75			100		
Run	X_1	X ₂	X ₃	X_4	X ₅	X ₆	EF ^a	
1	-1	-1	-1	-1	-1	-1	44.80	
2	1	-1	-1	-1	1	-1	104.08	
3	-1	1	-1	-1	1	1	36.13	
4	1	1	-1	-1	-1	1	63.16	
5	-1	-1	1	-1	1	1	30.30	
6	1	-1	1	-1	-1	1	56.28	
7	-1	1	1	-1	-1	-1	40.90	
8	1	1	1	-1	1	-1	108.30	
9	-1	-1	-1	1	-1	1	26.90	
10	1	-1	-1	1	1	1	74.90	
11	-1	1	-1	1	1	-1	63.16	
12	1	1	-1	1	-1	-1	142.40	
13	-1	-1	1	1	1	-1	62.17	
14	1	-1	1	1	-1	-1	146.10	
15	-1	1	1	1	-1	1	28.70	
16	1	1	1	1	1	1	64.16	
17 CP	0	0	0	0	0	0	52.45	
18 CP	0	0	0	0	0	0	54.46	

^aEnrichment factor

Factors	Levels				Star point $\alpha = 1.35$	
-	Low (-1)	Central (0)	High $(+1)$	-α	$+\alpha$	
(X_1) amount of sorbent (mg)	10	20	30	6.48	33.53	
(X ₂) volume of eluent (μ L)	40	50	60	36.46	63.53	
(X ₃) desorption time (min)	10	12.30	15	9.11	15.88	
Run	X ₁	X ₂	X ₃	EF ^a		
1	-1	-1	-1	68.4		
2	-1	-1	1	69.3		
3	-1	1	-1	53.4		
4	-1	1	1	68.8		
5	1	-1	-1	97.3		
6	1	-1	1	99.	99.7	
7	1	1	-1	109	.5	
8	1	1	1	120	.8	
9	-1.35	0	0	67.	8	
10	1.35	0	0	112	.8	
11	0	-1.35	0	102	.8	
12	0	1.35	0	123	.9	
13	0	0	-1.35	147	147.6	
14	0	0	1.35	164	.3	
15 CP	0	0	0	168	.8	
16 CP	0	0	0	163	.9	
17 CP	0	0	0	165	.8	

Table 2SActual and coded values of factors used in CCD for the extraction of DA, EP and

NE.

^aEnrichment factor

Factors	Sum of Square (SS)	Degree of Freedom (DF)	Mean Square (MS)	F-value	p-Value
X1 (L ^a)	4468.97	1	4468.97	732.217	0.001363
X1 (Q ^b)	12446.67	1	12446.67	2039.323	0.000490
X2 (L)	184.22	1	184.22	30.184	0.031569
X2 (Q)	6235.79	1	6235.79	1021.703	0.000977
X3 (L)	237.22	1	237.22	38.868	0.024776
X3 (Q)	350.50	1	350.50	57.427	0.016971
X1L by X2L	297.68	1	297.68	48.773	0.019893
X1L by X3L	0.84	1	0.84	0.138	0.745554
X2L by X3L	68.44	1	68.44	11.214	0.078778
Lack of Fit	170.39	5	34.08	5.584	0.158837
Pure Error	12.21	2	6.10		
Total SS	24472.94	16			
R-squared	99.2				
R-adjusted	98.3				

Table 3SANOVA results obtained by CCD.

^aLinear, ^b Quadratic

Table 3S shows the results of the ANOVA for quadratic model. p-value used to investigate the significance of terms. The model equation and related terms were considered to be significant if p-values were less than 0.05 (p-value at 95% confidence level). The lack of fit (LOF) is the variation of data around the fitted model and a special investigative test for the adequacy of a model fit. As shown in Table 3S, the p-value of LOF is 0.158. The insignificant lack of fit relative to the pure error for all investigated variables shows that quadratic polynomial model was satisfactory for accurate prediction of the valid response. Also, the quality of the fit of the polynomial model equation was explained by the coefficient of determination (R-squared=0.992 and R-adjusted=0.983). R-squared is a measure of the amount of deviation around the mean

explained by the model. In other words, the model could describe 99.2% of the variability in the response. The predicted R-squared is in reasonable agreement with the adjusted R-squared.