Banana peel/silicon glue coated stir bar for extraction of aspirin, diclofenac, ibuprofen and mefenamic acid followed by high performance liquid chromatography –UV detection

Zahra Jafari, Mohammad Reza Hadjmohammadi[*]

Department of Analytical Chemistry, Faculty of Chemistry, University of Mazandaran,

NirooHavayiiboulevard,47416-95447 Babolsar, Iran

[*]Corresponding author: Prof. M.R. Hadjmohammadi, Department of Analytical Chemistry,

Faculty of Chemistry, University of Mazandaran, NirooHavayiiboulevard,47416-95447

Babolsar, Iran

 Tel.: +98 113532350; fax: +98 1135302350.

E-mail address: hadjmr@umz.ac.ir (M.R. Hadjmohammadi)

To optimize the level of these two significant parameters and to estimate their interaction, response surface methodology based on CCD, as a multivariate statistic technique, was applied. CCD is composed of a factorial design (2f) augmented with (2f) star points, where f is the number of factors to be optimized, and with a central point, which can be run n times.

A total of 13 experimental runs are needed, which were carried out randomly. The matrix of CCD experiments obtained from MINITAB and the response (sum of the peak area of the analytes) is indicated in Table S4. The established polynomial model to predict the extraction performance in terms of original factors and interaction of the variable is in accordance with equation 2). The model analysis was carried out by ANOVA (TableS5). The significance of each coefficient was investigated by F-test and P-value(probability). The p-values higher than 5% indicated that the variable has no significant effect on the model and can be removed. Based on ANOVA, lack of fit (LOF) was measured 0.476. High R^2 demonstrated that the prognosticated answer is completely correct. The high value of adjusted R^2 illustrated the correlation between the experimental response and the fitted model (TableS6). It can be derived from the data that the response equation created a suitable and sensible model for CCD. Eventually, the elution solvent volume of 137 µL and desorption time of 7.3 min were chosen as the optimum condition of the method (TableS7).

To examine the capability of the RSM model validation was studied. The predicted peak area taken from the MINITAB software was 245.25 while the mean factual peak area for extraction of analytes under the optimum condition was 251.3. Based on the following equation, the percentage error was calculated to be 2.46%:

$$\% \, Error = \frac{A - B}{B} \times 100$$

In the equation, A and B are the experimental and the predicted peak area, respectively. The obtained small error (%), approved the RSM ability for optimization.

Figure caption

Figure S1. Effect of desorption solvent type on the extraction efficiency.

Figure S2. Pareto chart of the standardized effects obtained from a Plackett-Burman design.

Figure S3. Response surface plots of each pair of the independent factors: desorption time vs. desorption solvent volume.

Figure S4. Profiles for predicted values and desirability function for the extraction target analytes.

Figure S5. Reproducibility and reusability of banana peel-silicon glue bar.

Figure S6. Effect of plasma matrix on determination of analytes.

Table 1

Experimental variables and levels of the Plackett–Burman design

Factor	Name	Level	
		Min (-1)	Max (+1)
A	Extraction time (min)	5	30
B	pH	3	11
C	Desorption Time (min)	2	10
D	Stirring rate (rpm)	100	1500
E	Solvent volume (µL)	100	500

Table 2
The matrix of the Plackett–Burman design experiments obtained from MINITAB and the response (sum of peak area).

Experimental number	Factors					Response (NSAIDs)
	A	B	C	D	E	
1	1	-1	-1	-1	1	27157
2	-1	-1	1	1	1	57589
3	1	-1	1	-1	-1	141689
4	-1	-1	-1	-1	-1	98914
5	-1	1	1	-1	1	22292
6	1	1	-1	1	-1	78486
7	-1	1	1	1	-1	138757
8	-1	-1	-1	1	1	9889
9	1	1	1	-1	1	33440
10	-1	1	-1	-1	-1	115454
11	1	1	1	1	-1	185189
12	1	1	-1	1	1	24775

Table 3
Analysis of the variance for the fit of the experimental data to Plackett–Burman design (for NSAIDs)

Source	Degree of freedom (D.F)	Adjusted sum of squares (adj. SS)	Adjusted mean squares (adj. MS)	F-value	p-Value
Model	5	33957338208	6791467642	15.19	0.002
Linear	5	33957338208	6791467642	15.19	0.002
extraction time	1	190730107	190730107	0.43	0.538
pH	1	958064311	958064311	2.14	0.194
desorption time	1	4191830580	4191830580	9.38	0.022
stirring rate	1	258903010	258903010	0.58	0.475
solvent volume	1	28357810201	28357810201	63.43	0.000
Error	6	2682414691	447069115		
Total	11	36639752899			

Table 4

The matrix of the Central-Composite design experiments obtained from MINITAB and the responses.

Experimental number	Factors		Response
	Desorption time	Solvent volume	
1	0	1.4	591657
2	0	0	777817
3	1.4	0	790729
4	0	0	775150
5	-1	1	1302859
6	-1.4	0	587325
7	1	-1	1263245
8	0	0	777075
9	0	0	773783
10	0	0	772615
11	-1	1	491665
12	0	-1.4	1785983
13	1	1	560264

Table 5

Analysis of the variance for the fit of the experimental data to response surface model

Source	Degree of freedom (D.F)	Adjusted sum of squares (adj. SS)	Adjusted mean squares (adj. MS)	*F*-value	*p*-Value
Model	5	1.61488E+12	3.22976E+11	155.05	0.000
Linear	2	1.29510E+12	6.47550E+11	310.87	0.000
A	1	12532745411	12532745411	6.02	0.044
B	1	1.28257E+12	1.28257E+12	615.73	0.000
Square	2	3.16851E+11	1.58426E+11	76.06	0.000
AA	1	18189342016	18189342016	8.73	0.021
BB	1	2.74827E+11	2.74827E+11	131.94	0.000
Interaction	1	2927513342	2927513342	1.41	0.274
AB	1	2927513342	2927513342	1.41	0.274
Error	7	14580946316	2082992331		
Lack-of-Fit	3	14554572108	4851524036	735.80	0.000
Pure Error	4	26374208	6593552		
Total	12	1.62946E+12			

Table 6

Estimated determination coefficient of the CCD design

R^2	R^2 (pred)	R^2 (adj)
99.11	93.65	98.47

Table 7
Optimized value of the factors obtained from CCD design (coded and un-coded values).

Factor	Desorption time	Solvent volume (µL)
Coded value	+ 0.0143	-1.4
un-coded values	7.3	137

Table 8. The pka of the analytes.

Analyte	pka
Aspirin	3.5
Diclofenac	4.1
Ibuprofen	4.8
Mefnamic acid	4.5

Table 9
Summary of results for analysis of target analytes in plasma sample together with relative recovery after and before PP.

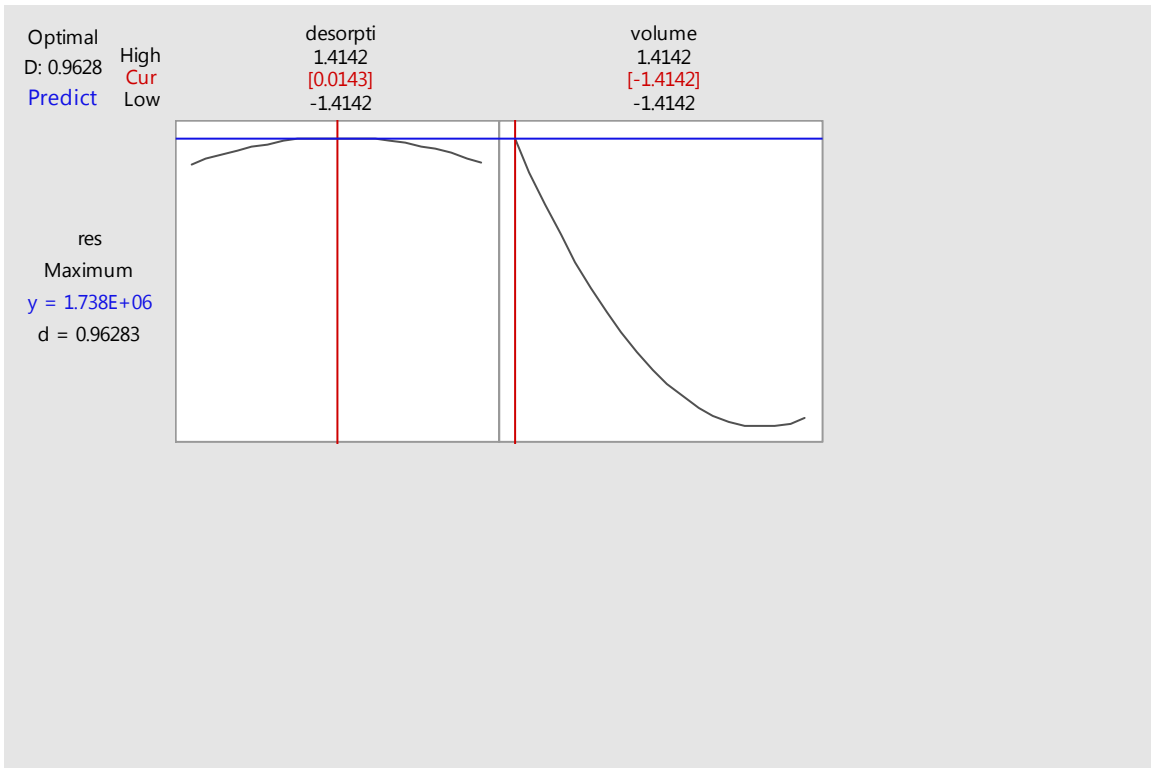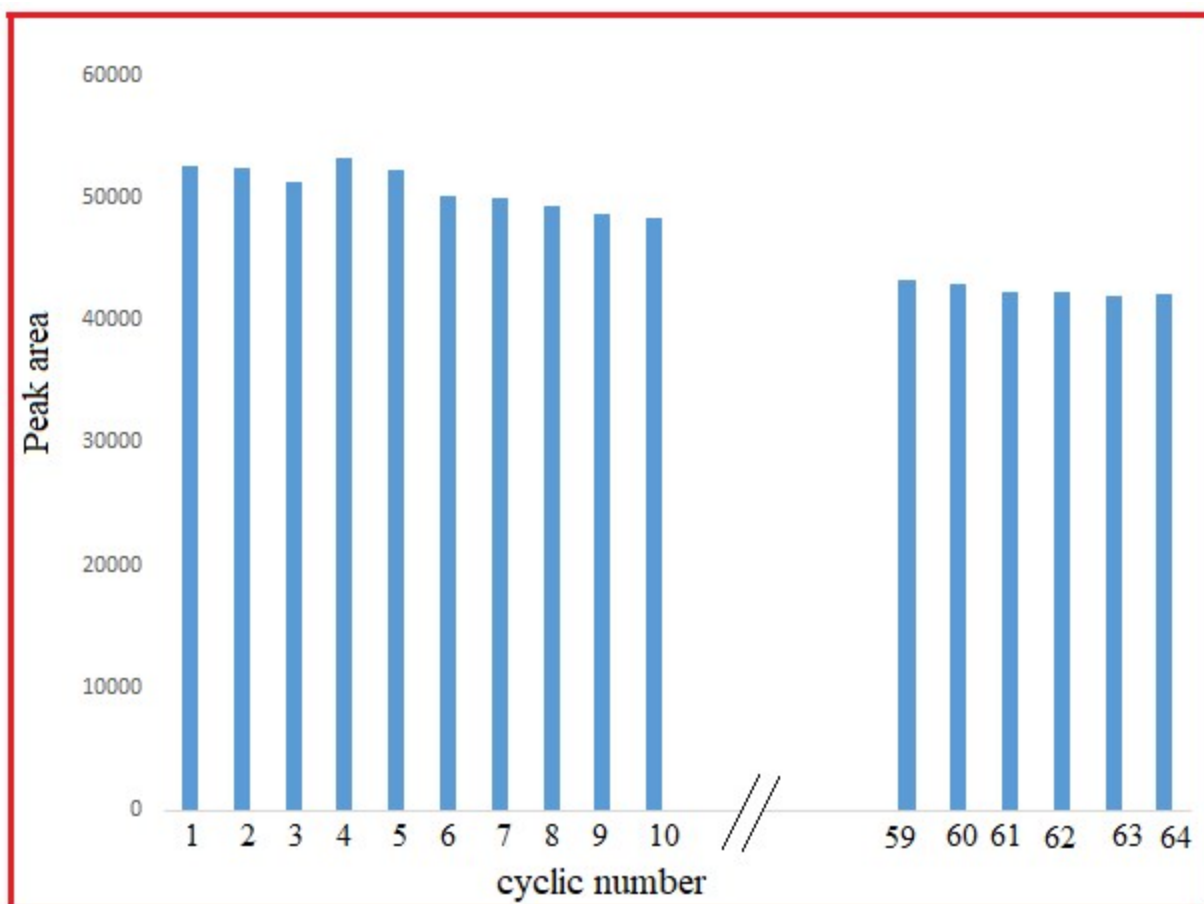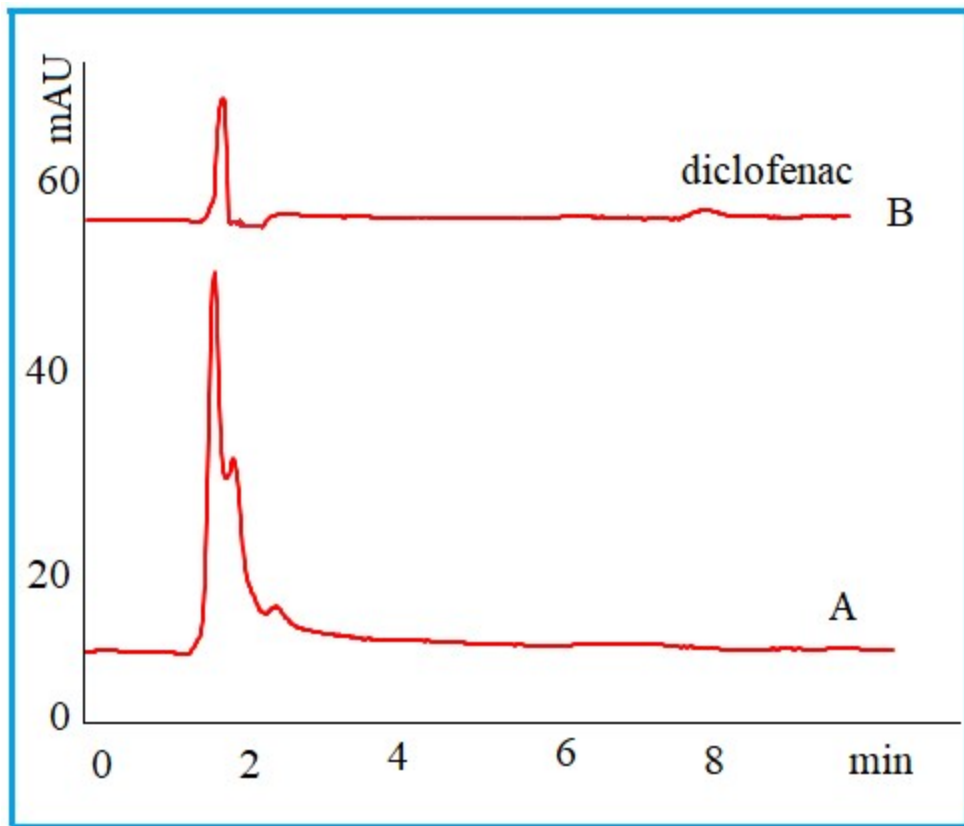| Sample		Aspirin	diclofenac	Ibuprofen	Mefenamic acid
Plasma (before pp)	Found (μg L^{-1})	11	13.6	11.4	12.2
	Added (μg L^{-1})	20	20	20	20
	Relative recovery	55(3.8)[a]	68(4.2)	57(4.5)	61(5.3)
Plasma (after PP)	Measured (μg L^{-1})	16.6	17.2	17.6	16.8
	Added (μg L^{-1})	20	20	20	20
	Relative recovery	83(1.8)	86(2.1)	88(3.1)	84(3.8)

[a] RSD% value (n=3).
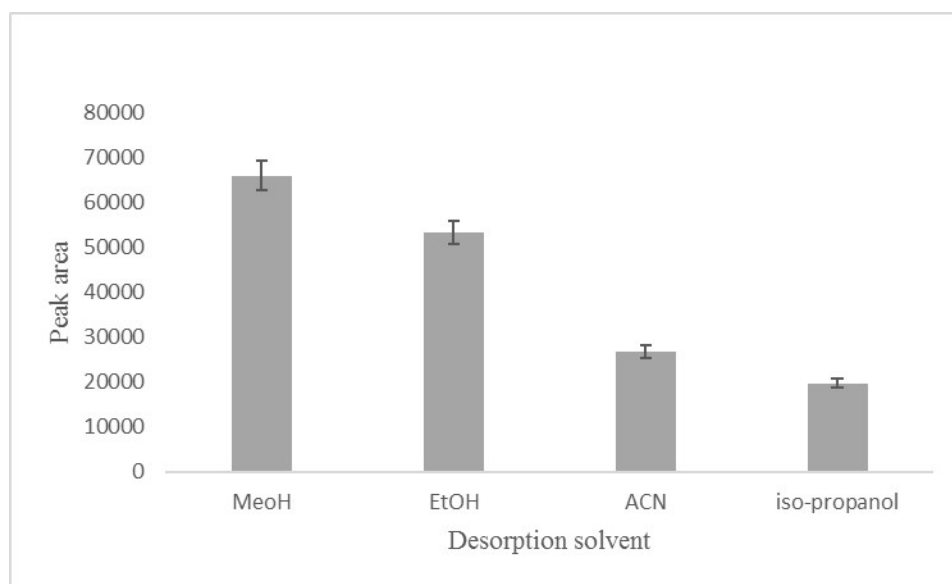
Figure S1
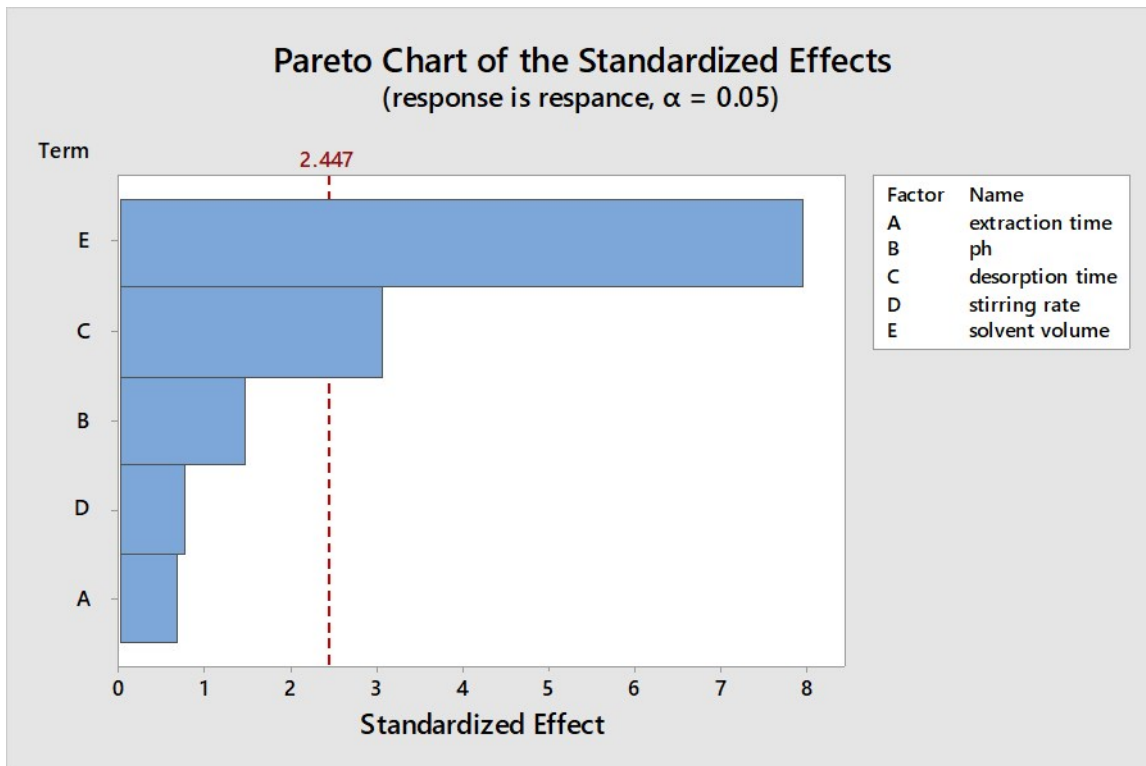
Figure S2
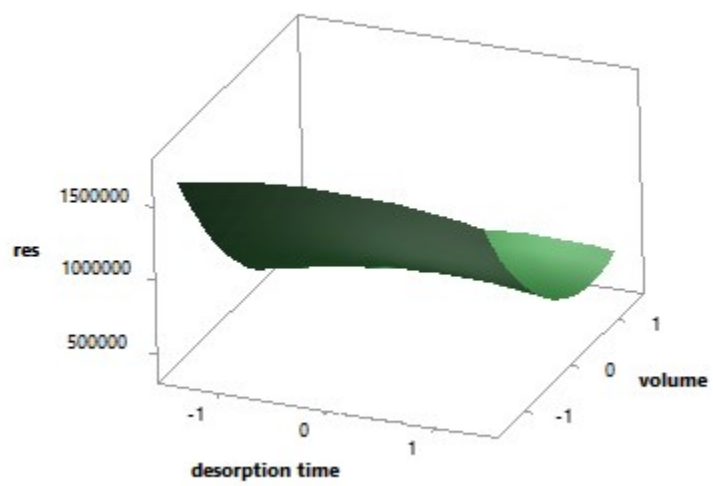
Figure S3

Figure S4

Figure S5

Figure S6