## Deposition of nickel oxide nanoworms on anodized nickel foil substrate as

## highly effective thin-film microextraction sorbent to determine caffeine

Milad Ghani<sup>1</sup>, Sayed Mehdi Ghoreishi<sup>2</sup>\*, Shokofe Nasrollahi<sup>2</sup> and Hanieh Ansarinejad<sup>2</sup>

<sup>1</sup>Department of Analytical Chemistry, Faculty of Chemistry, University of Mazandaran, Babolsar,

Iran

<sup>2</sup>Department of Analytical Chemistry, Faculty of Chemistry, University of Kashan, Kashan, Iran,

Corresponding author: Sayed Mehdi Ghoreishi, Department of Analytical Chemistry, Faculty of Chemistry, University of Kashan, Kashan, Iran Phone: +98 3155912395

E-mail: s.m.ghoreishi@kashanu.ac.ir

		Le	vel
Factor	Name	Min	Max
		(-1)	(+1)
А	Stirring rate (rpm)	200	700
В	Ionic strength (% w/v)	0	10
С	Extraction time (min)	20	60
D	Desorption time (min)	2	10
Е	Desorption volume (µL)	100	300

**Table S1**Experimental variables and levels of the Plackett–Burman design

Experimental		Factors					
number	Stirring rate	Ionic strength	Extraction time	Desorption volume	Desorption time	(Caffeine)	
1	-1	-1	1	1	1	8810	
2	-1	1	-1	-1	-1	10300	
3	1	1	-1	1	1	8400	
4	-1	1	1	-1	1	8102	
5	1	-1	1	1	-1	16750	
6	-1	-1	-1	-1	-1	7320	
7	1	-1	1	-1	-1	12900	
8	1	1	1	-1	1	8200	
9	1	1	-1	1	-1	15100	
10	-1	1	1	1	-1	18200	
11	-1	-1	-1	1	1	4410	
12	1	-1	-1	-1	1	2010	

 Table S2

 The matrix of the Plackett–Burman design experiments obtained from Minitab and the responses (peak area).

Source	Degree of freedom (D.F)	Adjusted sum of squares (adj. SS)	Adjusted mean squares (adj. MS)	<i>F</i> -value	<i>p</i> -Value
Main effects	5	259769775	51953955	510.33	0.000
Stirring rate	1	3221960	3221960	31.65	0.001
Ionic strength	1	21606200	21606200	212.23	0.000
Extraction time	1	53856507	53856507	529.02	0.000
Desorption volume	1	43464520	43464520	426.94	0.000
Desorption time	1	137620587	137620587	1351.81	0.000
Residual error	6	610829	101805		
Total	11	260380604			

 Table S3

 Analysis of the variance (ANOVA) for the fit of the experimental data to Plackett–Burman design

## Table S4Experimental variables and levels of the CCD

Factor	Norre	Levels					
symbol	Iname	(-2)	(-1)	(0)	(+1)	(+2)	
A	Stirring rate (rpm)	200	325	450	575	700	
В	Ionic strength (% w/v)	0	2.5	5.0	7.5	10	
С	Extraction time (min)	20	30	40	50	60	
D	Desorption volume ( $\mu$ L)	100	150	200	250	300	
Е	Desorption time (min)	2	4	6	8	10	

			factors			
Experimental number	Stirring rate (rpm)	Ionic strength (% w/v)	Extraction time (min)	Desorption time (min)	Desorption volume(µL)	Response
1	-1	+1	+1	-1	+1	95200
2	+1	+1	-1	+1	-1	45560
3	+1	+1	+1	-1	-1	120820
4	-1	+1	+1	+1	-1	36100
5	1	-1	-1	+1	+1	95120
6	0	0	0	0	0	32100
7	+1	+1	+1	+1	+1	34500
8	-1	+1	-1	+1	+1	27720
9	+1	+1	-1	-1	+1	47500
10	-1	-1	+1	-1	-1	65800
11	+2	0	0	0	0	28930
12	+1	-1	-1	-1	-1	23000
13	0	0	0	0	+2	96000
14	0	0	0	0	-2	76800
15	+1	-1	+1	-1	+1	64500
16	-1	-1	-1	-1	+1	71600
17	-2	0	0	0	0	13250
18	0	0	0	0	0	31240
19	-1	+1	-1	-1	-1	29000
20	-1	-1	+1	+1	+1	24600
21	0	0	2	0	0	51250
22	0	0	0	0	0	31250
23	+1	-1	+1	+1	-1	14130
24	0	-2	0	0	0	24100
25	0	+2	0	0	0	36250
26	-1	-1	-1	+1	-1	31250
27	0	0	0	-2	0	85120
28	0	0	0	+2	0	31000
29	0	0	-2	0	0	29560

 Table S5

 The matrix of the CCD experiments obtained from Minitab and the responses (peak area for caffeine).

Table	<b>S6</b>
	$\sim \circ$

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

Source	Degree of freedom (D.F)	Sum of squares (seq. SS)	Adjusted sum of squares (adj. SS)	Adjusted mean squares (adj. MS)	F-value	<i>p</i> -Value
Regression	19	22833887199	22833887199	1201783537	954.00	0.000
Linear	5	6192676233	6192676233	1238535247	983.17	0.000
Stirring rate	1	377785350	377785350	377785350	299.89	0.000
Ionic strength	1	208270417	208270417	208270417	165.33	0.000
Extraction time	1	685656600	685656600	685656600	544.29	0.000
Desorption volume	1	4178592600	4178592600	4178592600	3317.04	0.000
Desorption time	1	742371267	742371267	742371267	589.31	0.000
Square	4	6375199616	6375199616	1593799904	1265.19	0.000
Stirring rate*Stirring rate	1	886240848	155438741	155438741	123.39	0.000
Extraction time* Extraction time	1	22763667	147107190	147107190	116.78	0.000
Desorption volume*Desorption volume	1	467684484	1197932790	1197932790	950.94	0.000
Desorption time* Desorption time	1	4998510617	4998510617	4998510617	3967.90	0.000
Interaction	10	10266011350	10266011350	1026601135	814.93	0.000
Stirring rate*Ionic strength	1	202066225	202066225	202066225	160.40	0.000
Stirring rate*Extraction time	1	96825600	96825600	96825600	76.86	0.000
Stirring rate*Desorption volume	1	355511025	355511025	355511025	282.21	0.000
Stirring rate*Desorption time	1	22231225	22231225	22231225	17.65	0.002
Ionic strength*Extraction time	1	2227368025	2227368025	2227368025	1768.12	0.000
Ionic strength*Desorption volume	1	493284100	493284100	493284100	391.58	0.000
Ionic strength*Desorption time	1	1372702500	1372702500	1372702500	1089.67	0.000
Extraction time*Desorption volume	1	4406968225	4406968225	4406968225	3498.33	0.000
Extraction time*Desorption time	1	1075512025	1075512025	1075512025	853.76	0.000
Desorption volume*Desorption time	1	13542400	13542400	13542400	10.75	0.010
<b>Residual Error</b>	9	11337622	11337622	1259736		
Lack-of-Fit	7	10850222	10850222	1550032	6.36	0.143
Pure Error	2	487400	487400	243700		
Total	28	22845224821				

## Table S7

Estimated regression coefficients of y (peak area) for the proposed model of CCD design together with standard error and *t*-value

Term	Coefficient	Standard error of coefficient	<i>t</i> -value	<i>p</i> -Value
Constant (β <sub>0</sub> )	30988.0	501.9	61.736	0.000
Stirring rate $(\beta_1)$	3967.5	229.1	17.317	0.000
Ionic strength $(\beta_2)$	2945.8	229.1	12.858	0.000
Extraction time $(\beta_3)$	5345.0	229.1	23.330	0.000
Desorption volume ( $\beta_4$ )	-13195.0	229.1	-57.594	0.000
Desorption time ( $\beta_5$ )	5561.7	229.1	24.276	0.000
Stirring rate*Stirring rate ( $\beta_6$ )	-2447.6	220.3	-11.108	0.000
Extraction time* Extraction time ( $\beta_7$ )	2381.1	220.3	10.806	0.000
Desorption volume*Desorption volume $(\beta_8)$	6794.9	220.3	30.837	0.000
Desorption time* Desorption time ( $\beta_9$ )	13879.9	220.3	62.991	0.000
Stirring rate* Ionic strength ( $\beta_{10}$ )	3553.7	280.6	12.665	0.000
Stirring rate*Extraction time ( $\beta_{11}$ )	-2460.0	280.6	-8.767	0.000
Stirring rate*Desorption volume ( $\beta_{12}$ )	4713.8	280.6	16.799	0.000
Stirring rate*Desorption time ( $\beta_{13}$ )	-1178.7	280.6	-4.201	0.002
Ionic strength* Extraction time ( $\beta_{14}$ )	11798.7	280.6	42.049	0.000
Ionic strength* Desorption volume ( $\beta_{15}$ )	-5552.5	280.6	-19.788	0.000
Ionic strength* Desorption time ( $\beta_{16}$ )	-9262.5	280.6	-33.010	0.000
Extraction time*Desorption volume ( $\beta_{17}$ )	-16596.3	280.6	-59.147	0.000
Extraction time*Desorption time ( $\beta_{18}$ )	-8198.8	280.6	-29.219	0.000
Desorption volume*Desorption time ( $\beta_{19}$ )	920.0	280.6	3.279	0.010

 $y=30988.0 + 3967.5 \text{ A} + 2945.8 \text{ B} + 5345.0 \text{ C} - 13195.0 \text{ D} + 5561.7 \text{ E} - 2447.6 \text{ A}^2 + 2381.1 \text{ C}^2 + 6794.9 \text{ D}^2 + 13879.9 \text{ E}^2 + 3553.7 \text{ A} \times \text{B} - 2460.0 \text{ A} \times \text{C} + 4713.8 \text{ A} \times \text{D} - 1178.7 \text{ A} \times \text{E} + 11798.7 \text{ B} \times \text{C} - 5552.5 \text{ B} \times \text{D} - 9262.5 \text{ B} \times \text{E} - 16596.3 \text{ C} \times \text{D} - 8198.8 \text{ C} \times \text{E} + 920.0 \text{ D} \times \text{E}$ 

Figure S1. CV of the anodized Ni foil at a constant voltage of +60 V at 45 min

**Figure S2.** Energy dispersive x-ray spectroscopy (EDX) of prepared NiO nanoworm/anodized Ni film.

**Figure S3**. Effect of desorption solvent type on extraction efficiency of the method, conditions: stirring rate: 300 rpm, extraction time: 20 min, desorption time: 5 min, desorption volume:  $100\mu$ L and salt concentration of 0% (w/v).

Figure S4. Pareto chart of the main effects obtained from the Plackett-Burman design

**Figure S5**. Response surface plots of each pair of the independent factors: (A) The desorption volume vs. desorption time, (B) extraction time vs. the desorption time, (C) the extraction time vs. the desorption volume, (D) the ionic strength vs. desorption time, (E) the ionic strength vs. desorption volume, (F) the ionic strength vs. extraction time (G) the stirring rate vs. desorption time and (H) stirring rate vs. desorption volume.



re S1



Figure S2



Figure S3



Figure S4

![](_page_13_Figure_0.jpeg)

Figure S5