Supporting Information

Using Design of Experiments to optimize a screening analytical methodology based on Solid-Phase Microextraction/Gas Chromatography for the determination of volatile methylsiloxanes in water

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Table S1. Factors and values for the proposed central composite design

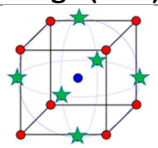
X_i	Factor	-1.607 (-α)	-1 (-)	0	1 (+)	1.607 (+α)	Central Composite Design (CCD)
1	Ionic strength (%NaCl)	0	5	12	20	24	
2	Extraction time (min)	3	11	25	39	48	
3	Desorption time (min)	1	3	6	10	12	
4	Extraction temperature (°C)	22	33	51	69	80	
5	Desorption temperature (°C)	201	210	225	240	249	

Table S2. Proposed central composite design

Run	Pattern	X_1	X_2	X_3	X_4	X_5
1	000(-α)0	12	25	6	22	225
2	++−−	20	39	3	33	210
3	+−+−	20	11	10	33	210
4	−−−−	5	11	3	33	210
5	−++−	5	39	10	33	210
6	+++−+	20	39	10	33	240
7	−+−+	5	39	3	33	240
8	+−−+	20	11	3	33	240
9	−−+−+	5	11	10	33	240
10	0000(-α)	12	25	6	51	201
11	00000	12	25	6	51	225
12	00000	12	25	6	51	225
13	(-α)0000	0	25	6	51	225
14	(+α)0000	24	25	6	51	225
15	00000	12	25	6	51	225
16	00000	12	25	6	51	225
17	00000	12	25	6	51	225
18	00(-α)00	12	25	1	51	225
19	00(+α)00	12	25	12	51	225
20	00000	12	25	6	51	225
21	0(-α)000	12	3	6	51	225
22	0(+α)000	12	48	6	51	225
23	0000(+α)	12	25	6	51	249
24	−+−+−	5	39	3	69	210
25	−−++−	5	11	10	69	210
26	++++−	20	39	10	69	210
27	+−−+−	20	11	3	69	210
28	+−+++	20	11	10	69	240
29	−−−++	5	11	3	69	240
30	−++++	5	39	10	69	240
31	++−++	20	39	3	69	240
32	000(+α)0	12	25	6	80	225

Table S3. Second-order polynomial equation obtained for each target compound and model suitability parameters for the response functions.

Compound	R^2	*F*-ratio	Prob > F	LOF Prob > F
D3	0.94	0.492	0.0003	0.806
$y = 15586 + 1734\,x_2 - 5654x_4 + 2475x_5$				
L3	0.97	8.999	<.0001	0.025
$y = 16053 - 2083\,x_1 + 1128x_2 - 7803x_4$				
D4	0.93	0.823	0.0009	0.615
$y = 34783 - 1762x_1 + 3441x_2 - 7568x_4 - 1951x_2^2 - 3282x_4^2$				
L4	0.84	7.445	0.0347	0.035
$y = 27384 + 2151x_2 - 3358x_4 - 2893x_4^2$				
D5	0.81	6.139	0.0733	0.049
$y = 36532 + 3634x_2 - 2247x_2^2 - 2884x_4^2$				
M4Q	0.70	0.662	0.3533	0.703
$y = 13352 + 2247x_1 + 2032x_1^2$				
L5	0.74	4.973	0.2135	0.070
$y = 38081 + 2514x_1 + 3577x_2$				
D6	0.80	4.522	0.0986	0.082
$y = 30897 + 3034x_2 - 2134x_2^2$				

Table S4. Results from the Student's t-test for the main, quadratic and interaction effects

	Prob > |t|							
	D3	**L3**	**D4**	**L4**	**D5**	**M4Q**	**L5**	**D6**
Intercept	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
X1	0.097	**0.002**	**0.091**	0.875	0.857	**0.023**	**0.057**	0.117
X2	**0.011**	**0.048**	**0.004**	**0.028**	**0.004**	0.826	**0.011**	**0.003**
X3	0.405	0.998	0.438	0.721	0.718	0.842	0.751	0.855
X4	**<0.0001**	**<0.0001**	**<0.0001**	**0.002**	0.114	0.113	0.574	0.202
X5	**0.001**	0.983	0.161	0.813	0.117	0.743	0.538	0.150
X1X2	0.952	0.585	0.679	0.418	0.400	0.690	0.478	0.425
X1X3	0.591	0.634	0.762	0.563	0.723	0.650	0.748	0.829
X2X3	0.136	0.180	0.355	0.294	0.349	0.626	0.487	0.364
X1X4	0.362	0.956	0.214	0.136	0.160	0.436	0.844	0.750
X2X4	0.553	0.900	0.625	0.959	0.468	0.893	0.781	0.756
X3X4	0.590	0.399	0.258	0.316	0.365	0.747	0.347	0.276
X1X5	0.890	0.260	0.665	0.448	0.406	0.765	0.363	0.548
X2X5	0.699	0.705	0.888	0.576	0.557	0.500	0.498	0.245
X3X5	0.903	0.864	0.652	0.301	0.311	0.332	0.318	0.164
X4X5	0.955	0.133	0.933	0.210	0.335	0.858	0.237	0.211
$X1^2$	0.695	0.270	0.169	0.144	0.131	**0.045**	0.231	0.209
$X2^2$	0.732	0.946	**0.075**	0.191	**0.054**	0.109	0.124	**0.025**
$X3^2$	0.785	0.541	0.842	0.922	1.000	0.917	0.737	0.766
$X4^2$	0.376	0.254	**0.007**	**0.007**	**0.018**	0.340	0.190	0.111
$X5^2$	0.779	0.804	0.502	0.432	0.476	0.752	0.522	0.745

Blue – Prob > |t| below 0.05
Light Blue – Prob > |t| below 0.01

Table S5. Additional testing to prove the applicability of the proposed empirical model

	A *(Pattern:* (-α) (-α) (-α) (-α) (-α)*)*				**B** *(Pattern:* (-α)++-+*)*				**C** *(Pattern:* ++(-α)-+*)*			
	Area	**±SD**	**Area Pred.**	**±SD**	**Area**	**±SD**	**Area Pred.**	**±SD**	**Area**	**±SD**	**Area Pred.**	**±SD**
D3	17262	1252	26048	11778	25804	3928	27427	6304	24072	870	25331	6320
L3	18363	1150	32056	10488	28472	2306	29690	5614	25959	2592	25425	5628
D4	20708	1515	34806	19667	41941	4294	48279	10526	42032	2319	48155	10553
L4	15259	1483	23147	17575	25282	3490	32171	9407	33625	3446	31926	9431
D5	16554	1187	27017	20679	33931	5102	41404	11023	39518	3933	41067	11096
M4Q	2243	914	15521	17662	6163	998	11987	9454	12941	414	16887	9477
L5	11983	527	28646	24448	21688	4745	37222	13086	44364	5197	40263	13118
D6	8410	318	21282	16294	21678	3077	33773	8721	34266	4076	31788	8743

	D *(Pattern: +0+-+)*				**E** *(Pattern:* (+α) (+α) (+α) (+α) (+α)*)*			
	Area	**±SD**	**Area Pred.**	**±SD**	**Area**	**±SD**	**Area Pred.**	**±SD**
D3	24225	3326	23475	4052	17986	1304	14047	11778
L3	25819	2791	22775	3609	2795	304	1500	10488
D4	40009	2593	40242	6768	25900	1068	14299	19667
L4	31807	3398	31277	6048	11886	351	14799	17575
D5	39584	5264	40796	7116	32985	105	32215	20679
M4Q	11834	2897	19058	6078	14146	43	16352	17662
L5	40281	7298	40503	8413	35961	754	43107	24448
D6	32088	6804	34212	5607	34523	1809	39860	16294

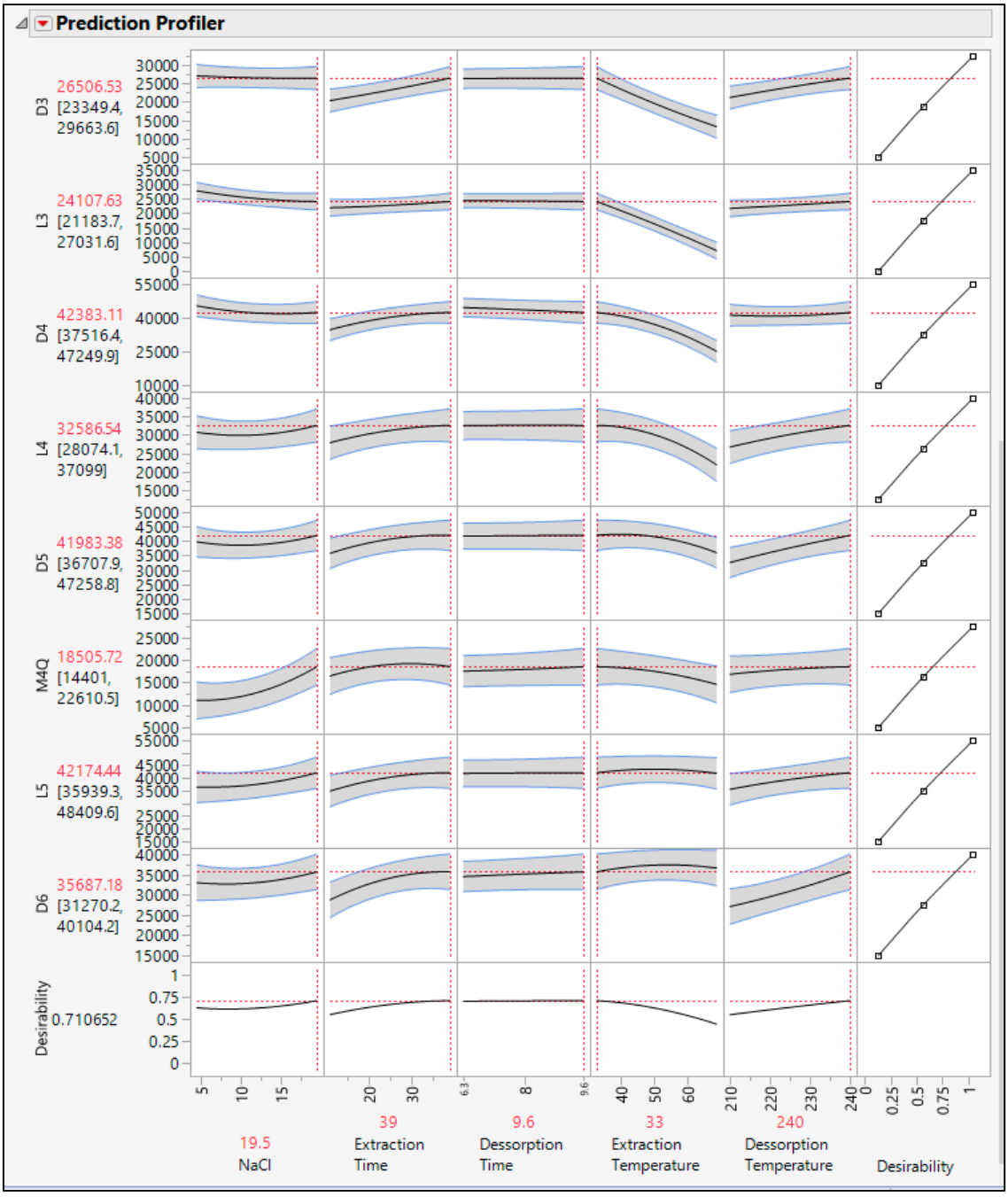
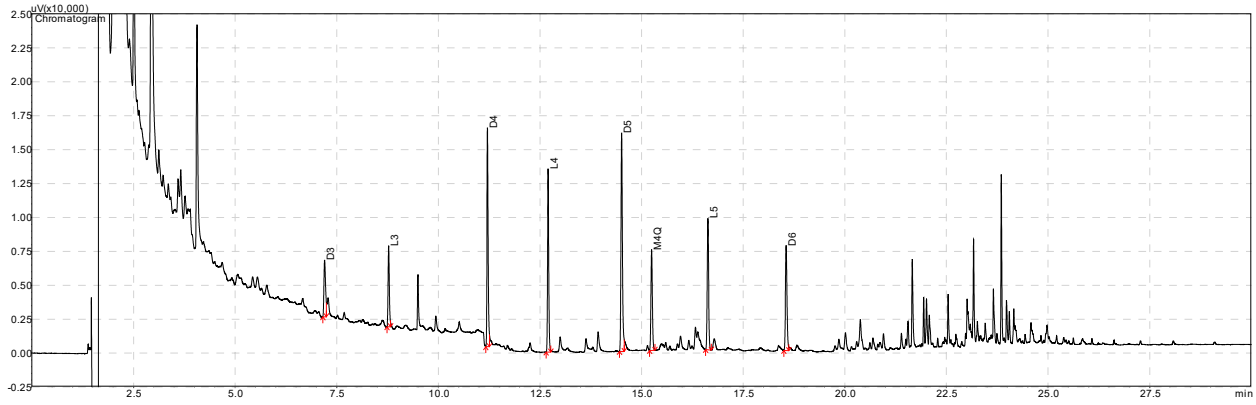


Figure S1. Optimal conditions and desirability function

(A)



(B)

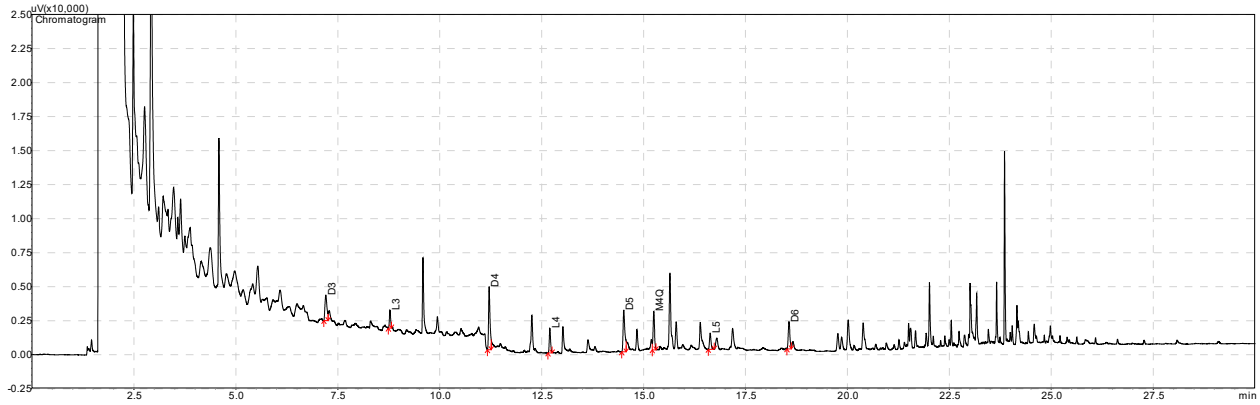


Figure S2. Chromatogram of a 3 µg L^{-1} calibration standard (A) and wastewater sample (B).