

Supplementary Material

Determination of bisphenol A, its chlorinated derivatives, and structural analogues in vegetables by focused ultrasound solid-liquid extraction and GC-MS/MS

Julia Martín,^{A,B} Juan Luis Santos,^A José Luis Malvar,^A Irene Aparicio^A and Esteban Alonso^A

^ADepartment of Analytical Chemistry, Escuela Politécnica Superior, University of Seville. C/ Virgen de África, 7, E-41011 Seville, Spain.

^BCorresponding author. Email: jbueno@us.es

Table S1. Box–Behnken design matrix for FUSLE optimization

Experiment	Power (%)	Sonication time (min)	Solvent volume (mL)
1	60	2.75	6.5
2	60	2.75	6.5
3	60	2.75	6.5
4	60	5.00	10
5	60	0.50	3
6	20	5.00	6.5
7	100	2.75	10
8	20	2.75	3
9	60	5.00	3
10	100	5.00	6.5
11	100	0.50	6.5
12	20	0.50	6.5
13	60	0.50	10
14	20	2.75	10
15	100	2.75	3

Table S2. Box–Behnken design matrix for d-SPE clean-up optimization

Experiment	C18 amount (g)	PSA amount (g)	Florisil amount (g)
1	0.4	0.8	0.0
2	0.8	0.8	0.4
3	0.4	0.0	0.8
4	0.4	0.8	0.8
5	0.8	0.4	0.8
6	0.0	0.8	0.4
7	0.4	0.4	0.4
8	0.4	0.0	0.0
9	0.4	0.4	0.4
10	0.4	0.4	0.4
11	0.0	0.0	0.4
12	0.8	0.4	0.0
13	0.0	0.4	0.8
14	0.8	0.0	0.4
15	0.0	0.4	0.0

Table S3. Recovery (R), and precision, expressed as relative standard deviation (RSD), of the proposed method in turnip and potato samples.

Pollutant	Turnip samples						Potato samples					
	Low spiked level (1 ng g ⁻¹ d.w.)		Medium spiked level (25 ng g ⁻¹ d.w.)		High spiked level (50 ng g ⁻¹ d.w.)		Low spiked level (1 ng g ⁻¹ d.w.)		Medium spiked level (25 ng g ⁻¹ d.w.)		High spiked level (50 ng g ⁻¹ d.w.)	
	R	RSD	R	RSD	R	RSD	R	RSD	R	RSD	R	RSD
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
BPA	76.2	14.8	106.9	4.4	100.1	2.8	94.1	4.7	100.4	1.8	96.2	1.9
Cl-BPA	74.0	2.3	95.9	2.8	91.7	0.9	76.4	1.8	99.8	1.4	90.5	2.0
Cl ₂ -BPA	72.0	1.6	91.2	5.1	82.0	2.7	73.8	1.8	98.0	6.1	85.2	0.7
Cl ₃ -BPA	60.0	2.2	80.2	1.7	82.9	13.8	58.1	2.1	78.4	0.8	100.8	6.6
Cl ₄ -BPA	82.0	1.0	91.1	6.1	97.0	0.1	83.2	0.5	99.4	4.4	96.9	2.1
BPAF	93.0	5.1	80.4	2.2	91.7	0.6	100.0	5.1	82.9	2.2	91.0	1.6
BPF	77.4	13.7	97.2	6.9	84.1	0.6	94.0	3.9	107.2	4.8	84.9	0.7
BPE	74.8	14.3	97.5	4.5	100.8	2.3	91.8	4.6	103.9	4.1	104.1	0.5
BPB	72.8	15.2	101.3	3.4	97.3	0.4	90.3	6.1	106.3	3.4	97.8	1.5
BPS	118.8	8.0	93.3	10.5	83.4	5.4	106.0	6.4	108.3	8.4	90.0	0.1
BPP	102.0	4.9	92.4	0.6	102.3	2.0	95.2	4.6	93.2	0.6	99.5	1.0

Table S4. Bisphenols in lyophilised vegetables

	Concentration (ng g ⁻¹ d.w.)														
	Carrot					Turnip					Potato				
	N1	N2	N3	N4	N5	N1	N2	N3	N4	N5	N1	N2	N3	N4	N5
BPA	3.51	3.61	4.01	5.13	5.36	4.93	3.91	6.13	3.78	4.00	3.22	4.20	3.66	4.17	3.28
BPA-Cl	7.05	6.77	7.08	8.91	-	6.68	7.99	7.60	3.80	8.90	6.77	7.43	6.54	-	6.59
BPA-Cl ₂	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPA-Cl ₃	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPA-Cl ₄	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPAF	1.30	-	-	1.44	-	1.22	-	-	1.23	-	-	-	-	-	-
BPF	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPB	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPS	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPP	-	-	-	<LOQ	-	-	-	-	-	-	-	-	-	-	-

-: no detected; <LOQ: lower than the limit of quantification.

Table S5. Bisphenols in fresh vegetables

	Concentration (ng g ⁻¹)														
	Carrot					Turnip					Potato				
	N1	N2	N3	N4	N5	N1	N2	N3	N4	N5	N1	N2	N3	N4	N5
BPA	0.36	0.37	0.41	0.53	0.55	0.31	0.25	0.39	0.24	0.25	0.56	0.74	0.64	0.73	0.57
BPA-Cl	0.73	0.70	0.73	0.92	-	0.42	0.50	0.48	0.24	0.56	1.18	1.30	1.14	-	1.15
BPA-Cl ₂	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPA-Cl ₃	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPA-Cl ₄	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPAF	0.13	-	-	0.15	-	0.08	-	-	0.08	-	-	-	-	-	-
BPF	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPB	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPS	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BPP	-	-	-	<LOQ	-	-	-	-	-	-	-	-	-	-	-

-: no detected; <LOQ: lower than the limit of quantification.

Figure S1. Optimization of FUSLE procedure. Main standardized-effect Pareto charts for target compounds according to Box-Behnken experimental design. Experiments were carried out with carrot samples spiked at 100 ng g⁻¹ d.w..

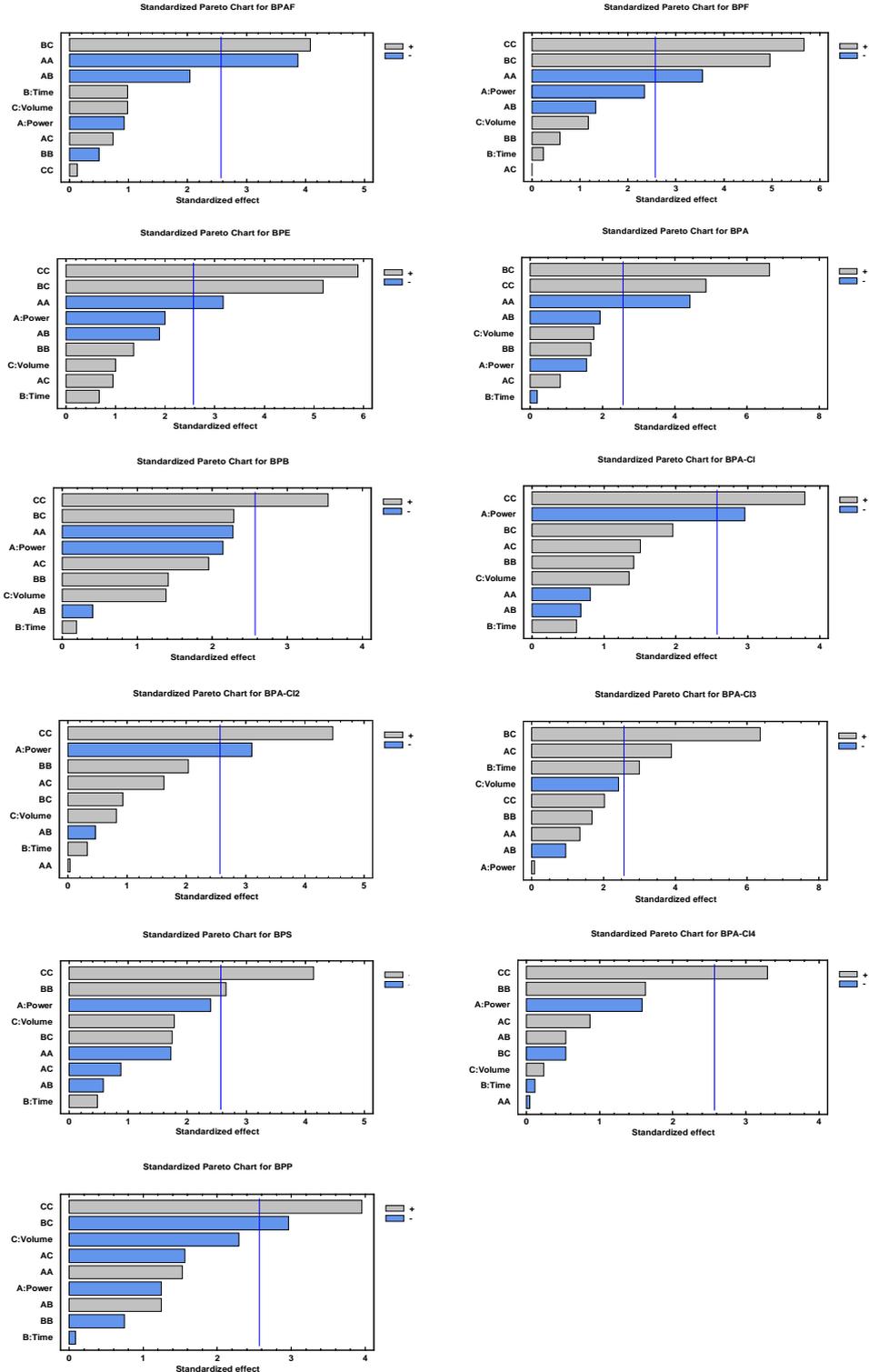


Figure S2. Optimization of d-SPE clean-up step. Main standardized-effect Pareto charts for target compounds according to Box-Behnken experimental design. Experiments were carried out with carrot samples spiked at 100 ng g⁻¹ d.w..

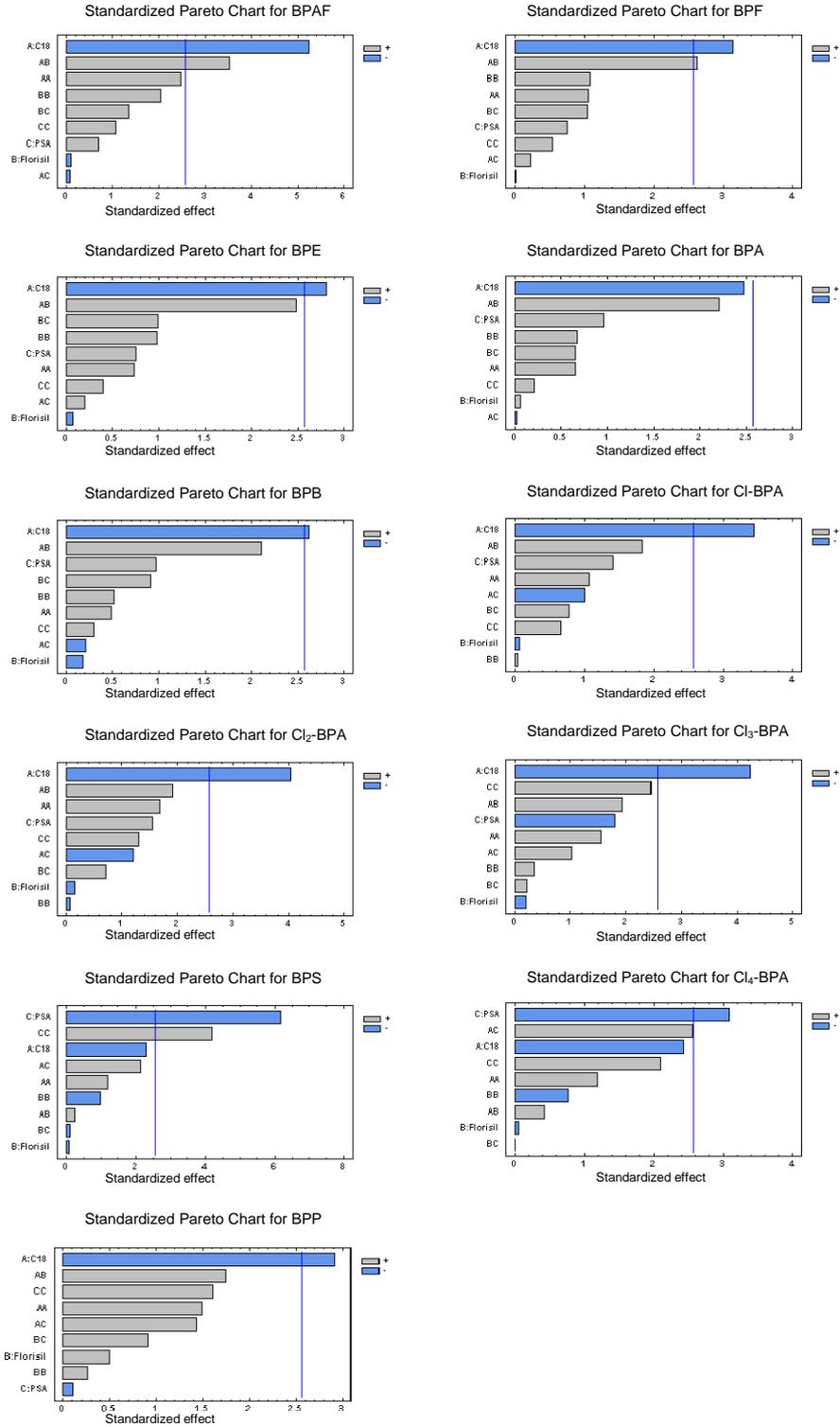


Figure S3. Total ion chromatograms corresponding to BBD experiments in which only one type of disperser sorbent was used (n° 8, 11 and 15 in table S2).

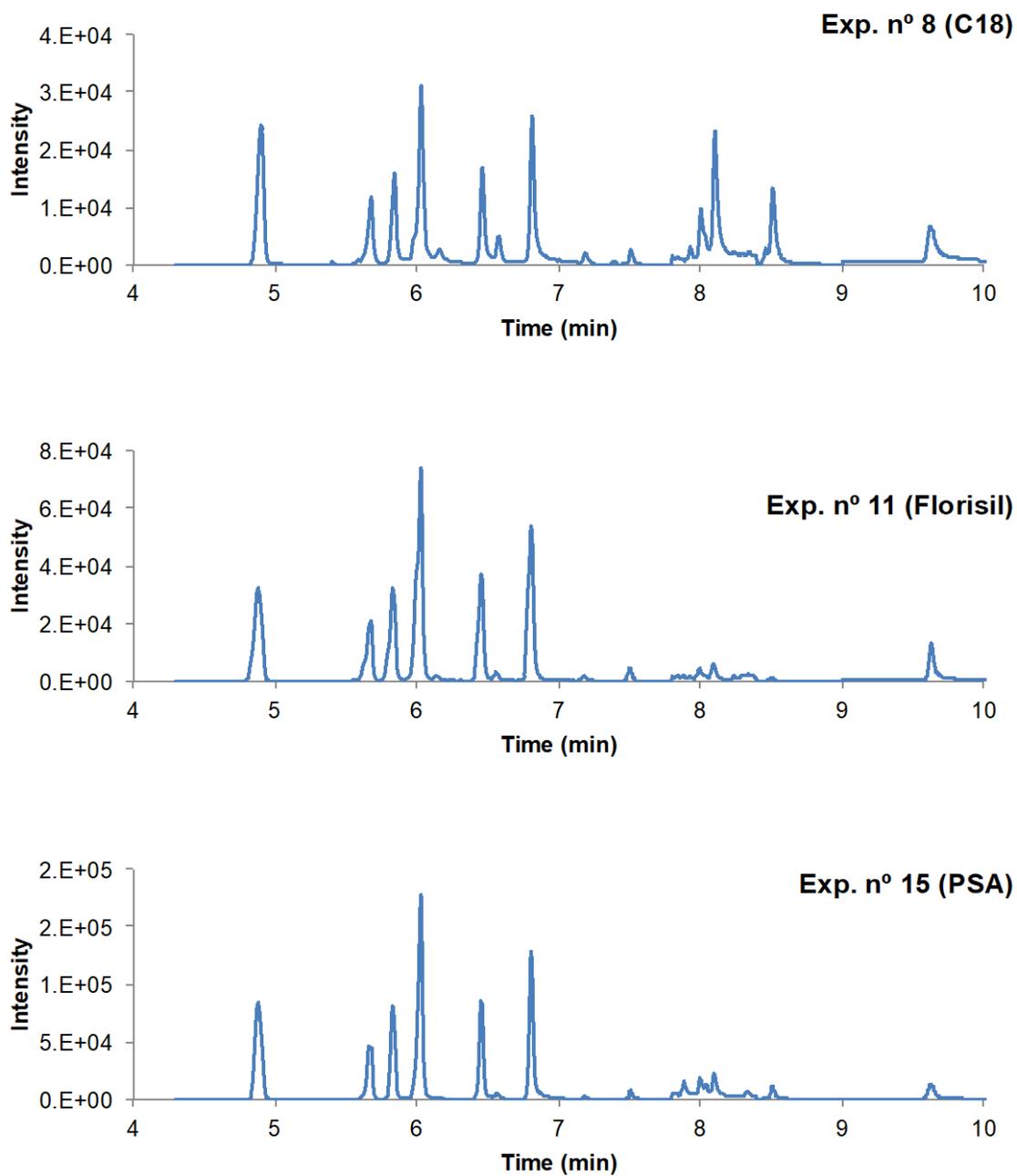


Figure S4. Response surface plots, corresponding to the global desirability function, when optimizing type of sorbents and amounts. A) Results from target compounds excluding BPS and Cl₄-BPA; B) Results from target compounds including BPS and Cl₄-BPA. Experiments were carried out with carrot samples spiked at 100 ng g⁻¹ d.w..

