

Supplementary Materials

A Comprehensive GC-MS Approach for Monitoring Legacy and Emerging Halogenated Contaminants in Human Biomonitoring

Rossana Comito ¹, Nicholas Kassouf ², Alessandro Zappi ², Nicolò Interino ³, Emanuele Porru ^{1,*}, Jessica Fiori ^{2,3}, Dora Melucci ² and Francesco Saverio Violante ¹

¹ Occupational Medicine Unit, Department of Medical and Surgical Sciences, Alma Mater Studiorum-University of Bologna, 40138 Bologna, Italy; rossana.comito2@unibo.it (R.C.); francesco.violante@unibo.it (F.S.V.)

² Department of Chemistry “Ciamician”, Alma Mater Studiorum-University of Bologna, 40129 Bologna, Italy; nicholas.kassouf2@unibo.it (N.K.); alessandro.zappi4@unibo.it (A.Z.); jessica.fiori@unibo.it (J.F.); dora.melucci@unibo.it (D.M.)

³ Laboratory of Proteomics, Metabolomics and Bioanalytical Chemistry, IRCCS Institute of Neurological Sciences of Bologna, 40139 Bologna, Italy; nicolo.interino@ausl.bologna.it

* Correspondence: emanuele.porru2@unibo.it

Table S1. IS used for the quantification of each compound.

Compound	Internal standard
2,4,6-Tribromophenol	2,4,6-Tribromophenol-3,5-d2
Allyl 2,4,6-tribromophenyl ether	2,4,6-Tribromophenol-3,5-d2
PCB 18	PCB 77-d6
PCB 31	PCB 77-d6
PCB 28	PCB 77-d6
PCB 52	PCB 77-d6
PCB 44	PCB 77-d6
PCB 95	PCB 77-d6
PCB 101	PCB 77-d6
PCB 99	PCB 77-d6
Tetrabromo-o-chlorotoluene	2,3,4,5,6- Pentabromotoluene- 13C6
PCB 81	PCB 77-d6
PCB 77	PCB 77-d6
PCB 110	PCB 77-d6
PCB 151	PCB 77-d6
PCB 123	PCB 77-d6
PCB 149	PCB 77-d6
PCB 118	PCB 77-d6
2,3,4,5,6- Pentabromotoluene	2,3,4,5,6- Pentabromotoluene- 13C6
PCB 114	PCB 77-d6
PCB 146	PCB 156-d3
PCB 153	PCB 156-d3
PCB 105	PCB 156-d3
PCB 138	PCB 156-d3
PCB 126	PCB 156-d3
PCB 187	PCB 156-d3
PCB 183	PCB 156-d3
PCB 128	PCB 156-d3
PCB 167	PCB 156-d3

Hexabromobenzene	2,3,4,5,6- Pentabromotoluene- 13C6
PCB 177	PCB 156-d3
PCB 156	PCB 156-d3
PCB 157	PCB 156-d3
Hexabromocyclododecane (α,β,γ)	2-ethylhexyl-2,3,4,5-tetrabromobenzoate-d17
PCB 180	PCB 156-d3
2,2',4,4'-Tetrabromo diphenyl ether	2-ethylhexyl-2,3,4,5-tetrabromobenzoate-d17
PCB 169	PCB 156-d3
PCB 170	PCB 156-d3
PCB 189	PCB 156-d3
Pentabromobenzylacrylate	2-ethylhexyl-2,3,4,5-tetrabromobenzoate-d17
2,2-Bis(4-allyloxy-3,5-dibromophenyl)propane	2-ethylhexyl-2,3,4,5-tetrabromobenzoate-d17
2-ethylhexyl-2,3,4,5-tetrabromobenzoate	2-ethylhexyl-2,3,4,5-tetrabromobenzoate-d17
1,2-bis (2,4,6-tribromophenoxy)ethane	1,2-bis (2,4,6-tribromophenoxy)ethane-d4
Bis (2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate	1,2-bis (2,4,6-tribromophenoxy)ethane-d4

Table S2. MS scan parameters.

Time(min)	Group name	Ion number	Total Dwell time (ms)	Cycle Time (Hz)	Resolution	Gain Factor
3.50	1	8	360	2.5738	High	5.0
20.60	2	9	360	2.5636	High	5.0
26.40	3	9	360	2.5740	High	5.0
30.90	4	9	360	2.5662	High	5.0

Table S3. Selected experiments for the D-optimal design.

Exp	X1	X2	X3	X4	X5	X6	X7	X8	X9	X10
1	-1	1	1	1	1	-1	-1	-1	-1	-1
2	-1	1	-1	-1	-1	1	-1	-1	-1	-1
3	1	-1	1	-1	-1	1	-1	-1	-1	-1
4	-1	-1	-1	1	1	1	-1	-1	-1	-1
5	1	1	1	-1	1	-1	1	-1	-1	-1
6	1	1	1	1	-1	1	1	-1	-1	-1
7	1	-1	1	1	1	1	1	-1	-1	-1
8	-1	1	-1	-1	-1	-1	-1	1	-1	-1
9	1	-1	-1	-1	1	-1	-1	1	-1	-1
10	1	1	-1	-1	-1	-1	1	1	-1	-1
11	-1	-1	-1	1	1	-1	1	1	-1	-1
12	-1	-1	1	-1	-1	1	1	1	-1	-1
13	1	-1	-1	1	-1	1	1	1	-1	-1
14	-1	-1	-1	-1	-1	-1	-1	-1	1	-1
15	-1	-1	1	-1	1	-1	-1	-1	1	-1
16	1	1	1	-1	1	1	-1	-1	1	-1
17	1	-1	-1	1	1	1	-1	-1	1	-1
18	1	1	-1	1	-1	-1	1	-1	1	-1
19	1	-1	-1	-1	-1	1	1	-1	1	-1

20	-1	1	1	-1	-1	1	1	-1	1	-1
21	-1	1	-1	1	1	1	1	-1	1	-1
22	1	1	1	1	-1	-1	-1	1	1	-1
23	1	1	-1	-1	-1	1	-1	1	1	-1
24	-1	-1	1	1	-1	1	-1	1	1	-1
25	-1	1	1	-1	1	1	-1	1	1	-1
26	-1	1	1	1	-1	-1	1	1	1	-1
27	1	-1	1	-1	1	-1	1	1	1	-1
28	1	1	1	1	1	1	1	1	1	-1
29	1	-1	-1	1	-1	-1	-1	-1	-1	1
30	1	1	-1	-1	1	-1	-1	-1	-1	1
31	-1	-1	1	-1	-1	-1	1	-1	-1	1
32	-1	1	-1	1	1	-1	1	-1	-1	1
33	1	-1	-1	-1	1	1	1	-1	-1	1
34	-1	-1	1	1	-1	-1	-1	1	-1	1
35	-1	1	1	-1	1	-1	-1	1	-1	1
36	1	1	1	-1	-1	1	-1	1	-1	1
37	1	-1	1	1	1	-1	1	1	-1	1
38	-1	-1	-1	-1	1	1	1	1	-1	1
39	1	-1	1	-1	-1	-1	-1	-1	1	1
40	-1	-1	1	1	1	-1	-1	-1	1	1
41	-1	1	-1	-1	1	1	-1	-1	1	1
42	-1	-1	-1	1	-1	-1	1	-1	1	1
43	1	1	1	1	1	-1	1	-1	1	1
44	1	-1	1	1	-1	1	1	-1	1	1
45	-1	-1	1	-1	1	1	1	-1	1	1
46	1	-1	-1	-1	-1	-1	-1	1	1	1
47	1	1	-1	1	1	-1	-1	1	1	1
48	-1	-1	-1	1	-1	1	-1	1	1	1
49	1	-1	1	-1	1	1	-1	1	1	1
50	-1	1	1	-1	-1	-1	1	1	1	1
51	-1	1	-1	-1	1	-1	1	1	1	1
52	1	1	-1	1	-1	1	1	1	1	1
53	1	1	-1	-1	1	1	1	1	1	1
54	-1	1	1	1	1	-1	-1	-1	-1	-1
55	-1	1	-1	-1	-1	1	-1	-1	-1	-1
56	1	-1	1	-1	-1	1	-1	-1	-1	-1
57	-1	-1	-1	1	1	1	-1	-1	-1	-1
58	1	1	1	-1	1	-1	1	-1	-1	-1
54	1	1	1	1	-1	1	1	-1	-1	-1
55	1	-1	1	1	1	1	1	-1	-1	-1
56	-1	1	-1	-1	-1	-1	-1	1	-1	-1
57	1	-1	-1	-1	1	-1	-1	1	-1	-1
58	1	1	-1	1	1	1	-1	1	-1	-1

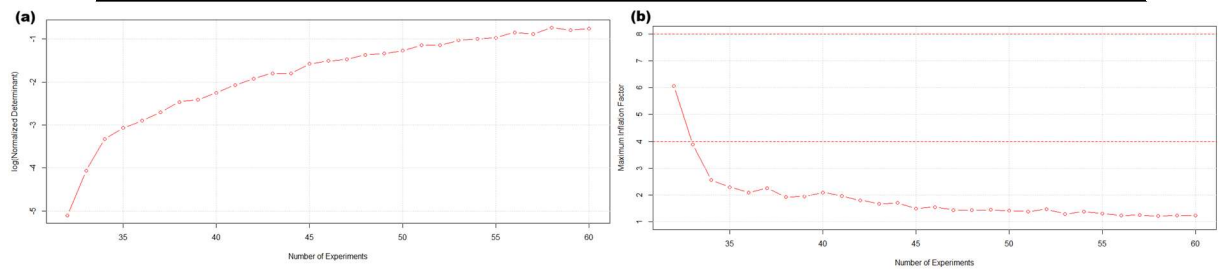


Figure S1. Normalized determinant of the information matrix (a, M -parameter) and maximum inflation factors (b).

Table S4. Selected experiments for the D-optimal design.

Experiment	x1	x2	x3	x4	x5
1	1	0	-1	-1	0
2	1	-1	-1	1	-1
3	-1	-1	1	1	-1
4	1	1	1	-1	1
5	0	-1	1	-1	-1
6	1	-1	1	-1	1
7	-1	1	1	-1	-1
8	-1	1	-1	-1	1
9	-1	0	0	-1	1
10	0	-1	0	1	0
11	1	1	0	0	1
12	-1	0	-1	1	-1
13	1	-1	-1	0	1
14	1	-1	1	1	1
15	1	1	-1	-1	-1
16	-1	-1	1	-1	0
17	-1	1	0	1	-1
18	1	1	-1	1	1
19	0	1	-1	0	-1
20	1	1	1	1	-1
21	-1	1	-1	0	0
22	1	-1	0	-1	-1
23	0	0	1	1	1
24	0	-1	-1	-1	1
25	-1	1	1	1	1
26	-1	-1	-1	1	1
27	1	0	1	0	-1
28	-1	-1	1	0	1
29	-1	-1	-1	-1	-1
Validation1	0	0	0	0	0
Valvalidation2	0	0	0	0	0
Validation3	0	0	0	0	0

Table S5. Statistically significant regression coefficients in the MLR model.

Variable		Coefficient	p-value
X2	First oven temperature	-0.091	0.0004
X3	First temperature holding time	0.083	0.0005
X4	Second oven ramp rate	-0.095	0.0003
X2*X3		-0.075	0.0007
X2*X4		0.092	0.0003
X3*X4		-0.078	0.0006
X7*X8		0.031	0.0168

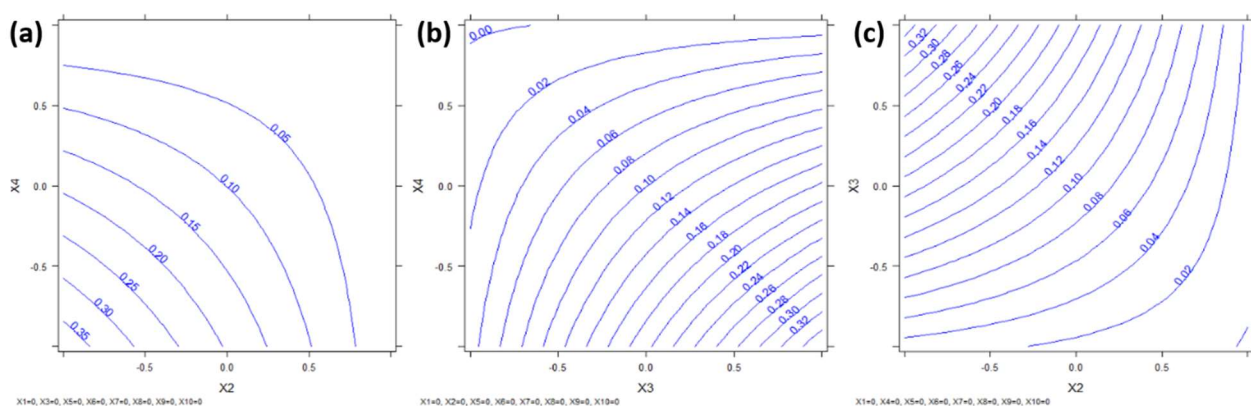


Figure S2. Response surface of the significant variables: (a) x2 vs. x3, (b) x3 vs. x4, (c) x2 vs. x4.

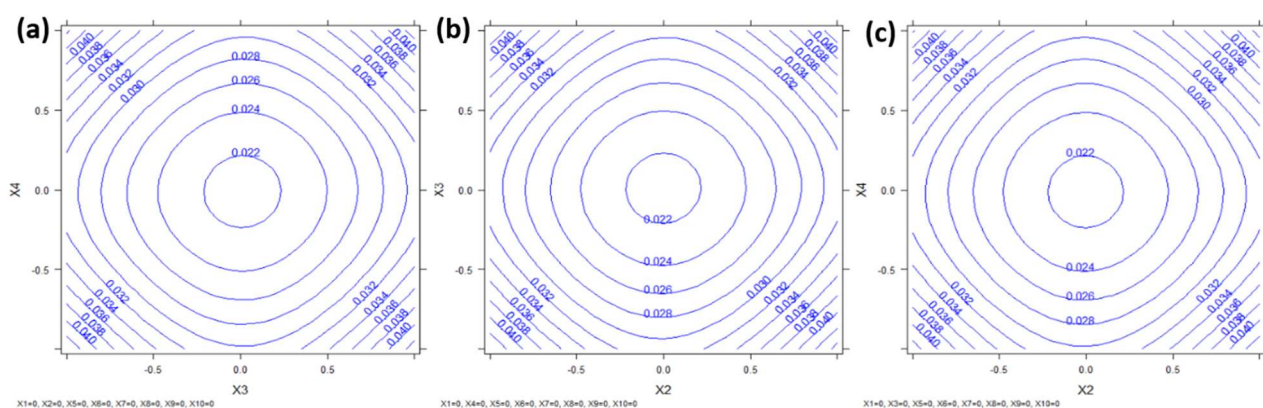


Figure S3. Confidence interval responses: (a) x2 vs. x3, (b) x3 vs. x4, (c) x2 vs. x4.

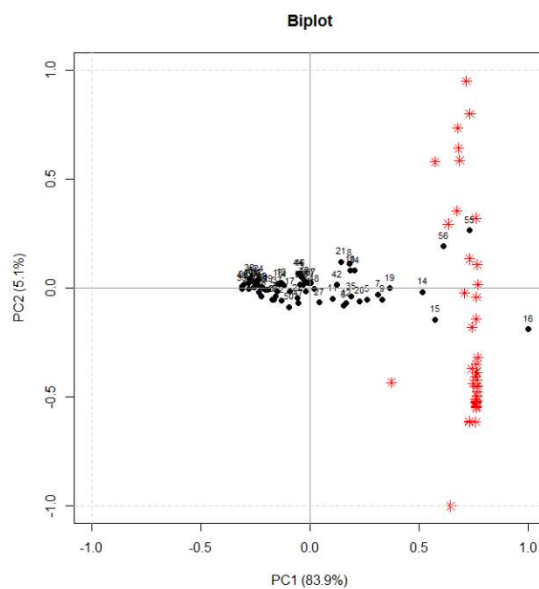


Figure S4. Principal Component Analysis with experiments and A/FWHM for all the compound: score in black, loadings in red.

Table S6. Statistically significant regression coefficients in the MLR model.

Variable	Extended name	Coefficients	p-value
X1	First oven ramp rate (°C/min)	0.6488	0.1093
X2	First oven temperature (°C)	0.8538	0.0537
X3	First temperature holding time (min)	-1.409	0.0082

Variable	Extended name	Coefficients	p-value
X4	Second oven ramp rate (°C/min)	1.903	0.0020
X5	Final temperature (°C)	0.333	0.3687
X6	Final temperature holding time (min)	-0.571	0.1494
X7	Pulse pressure (Psi)	4.188	0.0001
X8	Time of pulse pressure (min)	0.201	0.5745
X9	Purge flow to split vent (mL/min)	0.414	0.2756
X10	Purge time (min)	0.246	0.5098
X1*X2		1.357	0.0088
X1*X3		0.539	0.1664
X1*X4		-0.133	0.7077
X1*X5		0.521	0.1750
X1*X6		0.078	0.8245
X2*X3		0.105	0.7597
X2*X4		-0.206	0.5625
X2*X5		0.895	0.0463
X2*X6		0.540	0.1744
X3*X4		-0.811	0.0563
X3*X5		0.705	0.0889
X3*X6		0.458	0.2280
X4*X5		0.034	0.9219
X4*X6		0.004	0.9892
X5*X6		-0.072	0.8346
X7*X8		-0.549	0.1615
X7*X9		0.179	0.6135
X7*X10		-0.138	0.7062
X8*X9		0.343	0.3553
X8*X10		0.035	0.9210
X9*X10		0.621	0.1307

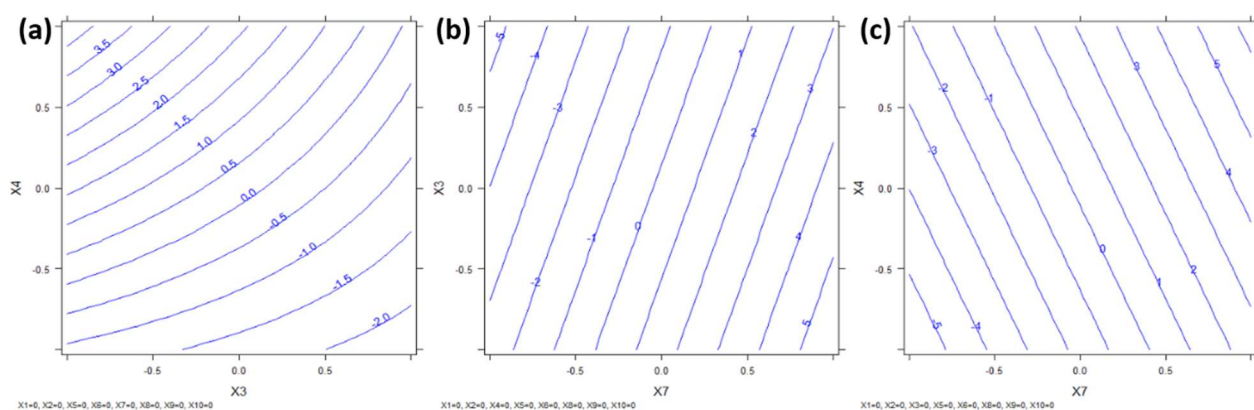


Figure S5. Response surface for method sensitivity and peak shape MLR model: (a) x3 vs. x4, (b) x7 vs. x3, (c) x7 vs. x4.

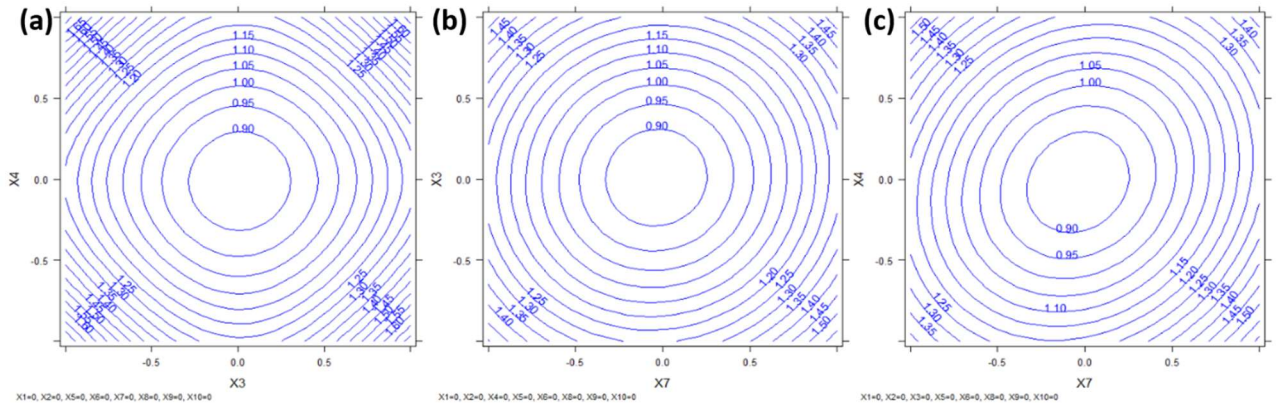


Figure S6. Confidence interval responses: (a) x3 vs. x4, (b) x7 vs. x3, (c) x7 vs. x4.

Table S7. Regression coefficients obtained for the MLR model.

Variable	Extended name	Coefficients	p-value
X2	First oven temperature (°C)	0.109	0.0142
X3	First temperature holding time (min)	0.080	0.0684
X4	Second oven ramp rate (°C/min)	-0.288	0.0000
X7	Pulse pressure (Psi)	0.005	0.8905
X8	Time of pulse pressure (min)	-0.078	0.0595
X2*X3		0.010	0.8201
X2*X4		0.085	0.0707
X2*X7		0.007	0.8773
X2*X8		-0.014	0.7419
X3*X4		0.028	0.5374
X3*X7		0.021	0.6462
X3*X8		0.048	0.2856
X4*X7		-0.033	0.4903
X4*X8		0.137	0.0061
X7*X8		-0.104	0.0392
X2 ²		-0.173	0.0832
X3 ²		0.052	0.5680
X4 ²		0.232	0.0211
X7 ²		-0.001	0.9882
X8 ²		0.112	0.2839

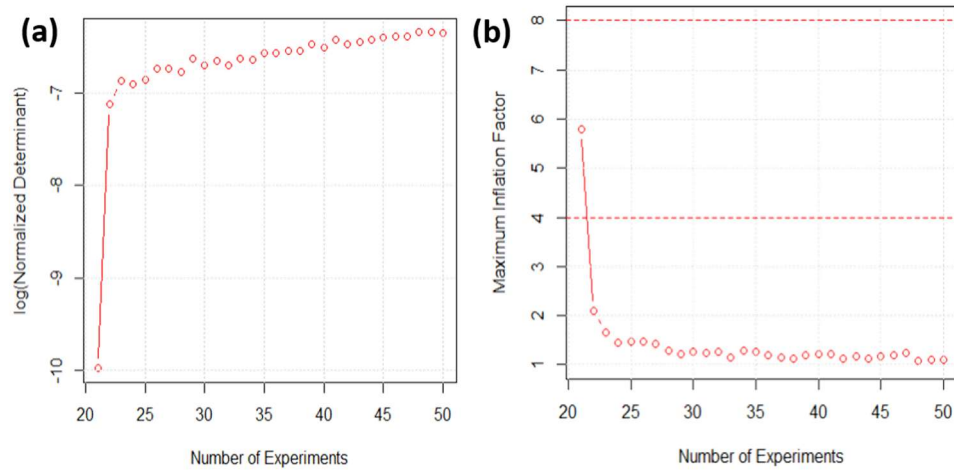


Figure S7. Normalized determinant of the information matrix (M -parameter) and maximum inflation factors.

Table S8. Regression coefficients obtained for the MLR model.

Variable	Extended name	Coefficients	p-value
X2	First oven temperature (°C)	0.298	0.7754
X3	First temperature holding time (min)	0.907	0.4712
X4	Second oven ramp rate (°C/min)	3.326	0.0088
X7	Pulse pressure (Psi)	-2.510	0.0495
X8	Time of pulse pressure (min)	0.625	0.5542
X2*X3		0.949	0.4985
X2*X4		0.520	0.6159
X2*X7		-1.230	0.2940
X2*X8		2.535	0.0417
X3*X4		1.034	0.4670
X3*X7		-4.175	0.0062
X3*X8		2.441	0.0899
X4*X7		-3.933	0.0024
X4*X8		1.134	0.2962
X7*X8		-3.352	0.0085
X2 ²		-2.216	0.2654
X3 ²		0.849	0.7224
X4 ²		-1.303	0.5476
X7 ²		3.516	0.0992
X8 ²		2.230	0.2962

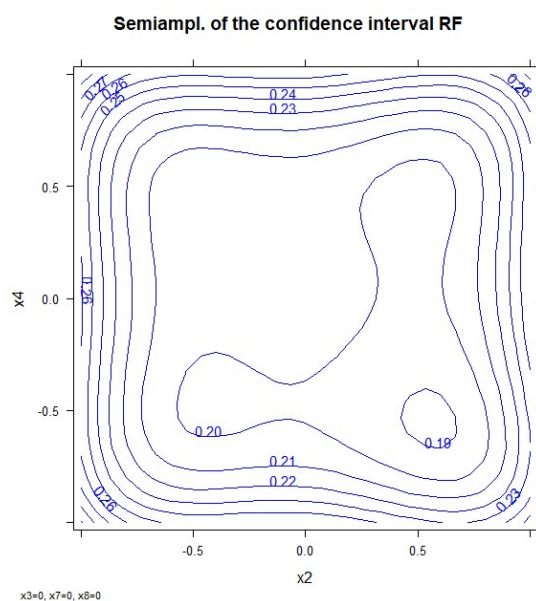


Figure S8. Confidence interval response for X2 vs. X4.

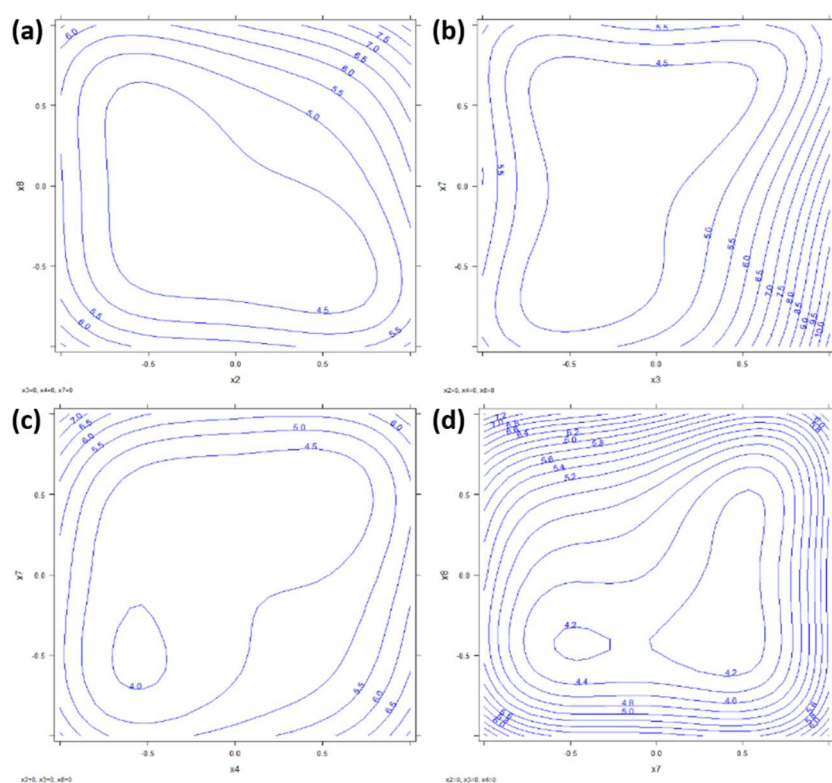


Figure S9. Confidence interval responses: (a) x2 vs. x8, (b) x3 vs. x7, (c) x4 vs. x7, (d) x7 vs. x8.

Table S9. Accuracy (CV %) and precision (bias %).

Analytes	Concentration			
	0.5 ppb (PCBs) e 0.08 ppm (BFRs)			
	CV% intraday	Bias% intraday	CV% interday %	Bias interday%
2,4,6-Tribromophenol	7	9	9	6
Allyl 2,4,6-tribromophenyl ether	6	-6	10	-9
PCB 18	5	-9	4	-10
PCB 31 + PCB 28	6	-8	10	-9
PCB 52	4	3	4	5
PCB 44	5	-10	6	-6
PCB 95	2	-10	4	-5
PCB 101	3	-9	10	-8
PCB 99	4	-9	6	-7
Tetrabromo-o-chlorotoluene	3	-4	9	-6
PCB 81	4	-9	8	-8
PCB 77	4	-9	8	-7
PCB 110	4	-10	9	-4
PCB 151	6	-8	10	-5
PCB 123	6	-10	8	-1
PCB 149	5	-8	7	-2
PCB 118	3	-8	8	-5
2,3,4,5,6-Pentabromotoluene	1	-6	7	-1
PCB 114	5	-9	9	-3
PCB 146	7	-9	7	-5
PCB 153	5	-5	5	-6

PCB 105	2	-8	5	-6
PCB 138	5	-4	5	-7
PCB 126	4	-2	7	-4
PCB 187	6	-9	5	-6
PCB 183	5	-9	4	-3
PCB 128	8	-10	3	-3
PCB 167	1	-10	5	-10
Hexabromobenzene	6	-9	5	-10
PCB 177	5	-9	9	-5
PCB 156	4	-8	5	-8
PCB 157	5	-8	7	-8
PCB 180	6	-6	4	-5
2,2',4,4'-Tetrabromo diphenyl ether	4	-6	3	-6
PCB 169	5	-8	5	-4
PCB 170	6	-7	7	-7
PCB 189	6	-9	4	-6
Pentabromobenzylacrylat e	7	-10	6	-5
2,2-Bis(4-allyloxy-3,5- dibromophenyl)propane	2	6	5	-6
2-ethylhexyl-2,3,4,5- tetrabromobenzoate	8	-9	4	-10
1,2-bis (2,4,6- tribromophenoxy)ethane	2	-9	9	-5
Bis (2-ethylhexyl)-3,4,5,6- tetrabromo-phthalate	4	-7	3	-5
Hexabromocyclododecan e (α,β,γ)	6	9	10	-10

Table S10. MQLs and MDLs for included pollutants.

Analytes	MDLs (ppb)	MQLs (ppb)
2,4,6-Tribromophenol	8.20	25.4
Allyl 2,4,6-tribromophenyl ether	3.50	10.0
PCB 18	0.06	0.21
PCB 31 + PCB 28	0.05	0.16
PCB 52	0.04	0.13
PCB 44	0.05	0.16
PCB 95	0.06	0.20
PCB 101	0.06	0.20
PCB 99	0.06	0.20
Tetrabromo-o-chlorotoluene	3.50	10.0
PCB 81	0.08	0.25
PCB 77	0.05	0.17
PCB 110	0.09	0.32
PCB 151	0.04	0.12
PCB 123	0.09	0.22
PCB 149	0.04	0.12
PCB 118	0.05	0.18
2,3,4,5,6- Pentrabromotoluene	0.80	2.50
PCB 114	0.07	0.23
PCB 146	0.01	0.02
PCB 153	0.01	0.02

PCB 105	0.05	0.18
PCB 138	0.04	0.14
PCB 126	0.06	0.20
PCB 187	0.05	0.17
PCB 183	0.05	0.17
PCB 128	0.04	0.14
PCB 167	0.04	0.14
Hexabromobenzene	2.50	7.50
PCB 177	0.06	0.20
PCB 156	0.04	0.12
PCB 157	0.04	0.12
PCB 180	0.04	0.14
2,2',4,4'-Tetrabromo diphenyl ether	1.20	3.50
PCB 169	0.04	0.14
PCB 170	0.07	0.22
PCB 189	0.08	0.26
Pentabromobenzylacrylate	8.20	25.4
2,2-Bis(4-allyloxy-3,5-dibromophenyl)propane	10.0	25.0
2-ethylhexyl-2,3,4,5-tetrabromobenzoate	7.50	22.3
Hexabromocyclododecane (α,β,γ)	10.5	32.3
1,2-bis (2,4,6-tribromophenoxy)ethane	12.2	37.4
Bis (2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate	14.3	43.2

Table S11. Recovery for validation experiment (n=3).

Analytes	Recovery% $\pm$ standard deviation
2,4,6,tribrphenol (NBFR)	51% $\pm$ 2
Allyl 2,4,5-tribrphenyl_ether (NBFR)	45% $\pm$ 2
3cl-pcb(18)	47% $\pm$ 3
3cl-pcb(31) + 3cl-pcb(28)	72% $\pm$ 6
4cl-pcb(52)	107% $\pm$ 7
4cl-pcb(44)	80% $\pm$ 2
5cl-pcb(95)	86% $\pm$ 4
5cl-pcb(101)	95% $\pm$ 3
5cl-pcb(99)	93% $\pm$ 4
Tetrabr-o-clhorotoluene (NBFR)	91% $\pm$ 2
4cl-pcb(81)	99% $\pm$ 3
4cl-pcb(77)	100% $\pm$ 2
5cl-pcb(110)	97% $\pm$ 4
6cl-pcb(151)	102% $\pm$ 4
5cl-pcb(123)	105% $\pm$ 10
6cl-pcb(149)	100% $\pm$ 5
5cl-pcb(118)	110% $\pm$ 5
PentaBromo_toluene (NBFR)	93% $\pm$ 5
5cl-pcb(114)	100% $\pm$ 5
6cl-pcb(146)	115% $\pm$ 5
6cl-pcb(153)	110% $\pm$ 2
5cl-pcb(105)	97% $\pm$ 2
6cl-pcb(138)	109% $\pm$ 4
5cl-pcb(126)	104% $\pm$ 4
7cl-pcb(187)	102% $\pm$ 2

7cl-pcb(183)	100%± 4
6cl-pcb(128)	101%± 3
6cl-pcb(167)	105%± 4
HexaBromo_benzene (NBFR)	98%± 3
7cl-pcb(177)	102%± 2
6cl-pcb(156)	110%± 1
6cl-pcb(157)	102%± 2
7cl-pcb(180)	100%± 1
Tetrabromo_diphenyl_ether (legacy BFR)	103%± 9
6cl-pcb(169)	101%± 4
7cl-pcb(170)	109%± 6
7cl-pcb(189)	101%± 7
PentaBR_benzyl_acrilate	56%± 1
2,2bis(4alloxy-3,5-dibromophenyl)propane (NBFR)	106%± 2
Hexabromocyclododecane (legacy BFR)	103%± 4
2ethylxyx_tetrabr_benzoate (NBFR)	104%± 3
1,2-bis (2,4,6-tribromophenoxy)ethane (NBFR)	100%± 1
Bis (2-ethylhexyl)-3,4,5,6-tetrabromo- phthalate (NBFR)	101%± 4

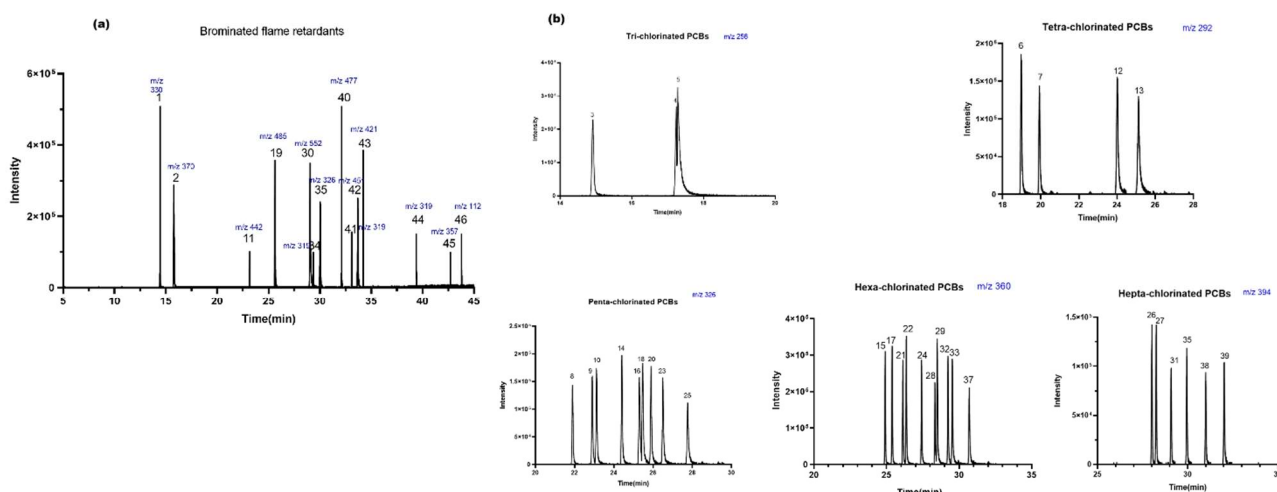


Figure S10. Chromatogram obtained with GC-HRMS: a) BFR: 2,4,6-Tribromophenol (1), Allyl 2,4,6-tribromophenyl ether (2), Tetrabromo-ochlorotoluene (11), 2,3,4,5,6- Pentabromotoluene (19), Hexabromobenzene (30), 2,2',4,4'-Tetrabromo diphenyl ether (36), Pentabromobenzylacrylate (40), 2,2-Bis(4-allyloxy-3,5-dibromophenyl)propane (41), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (43), 1,2-bis (2,4,6-tribromophenoxy)ethane (45), Bis (2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (46), Hexabromocyclododecane (α,β,γ) (34,42,44); b) PCB: PCB-18 (3), PCB-31 (4), PCB-28 (5), PCB-52 (6), PCB-44 (7), PCB-95 (8), PCB-101 (9), PCB-99 (10), PCB-81 (12), PCB-77 (13), PCB-110 (14), PCB-151 (15), PCB-123 (16), PCB-149 (17), PCB-118 (18), PCB-114 (20), PCB-146 (21), PCB-153 (22), PCB-105 (23), PCB-138 (24), PCB-126 (25), PCB-187 (26), PCB-183 (27), PCB-128 (28), PCB-167 (29), PCB-177 (31), PCB-156 (32), PCB-157 (33), PCB-180 (35), PCB-169 (37), PCB-170 (38), PCB-189 (39);.

Table S12. Reference values for PCBs in certified human serum.

Compound	Population age	Year	Reference value ($\mu\text{g/L}$)[32,33]
----------	----------------	------	---

PCB 138	9-11 age	1998/99	0.3
	18-19 age	1997/99	0.4
	20-29 age	1997/99	0.6
	30-39 age	1997/99	0.9
	40-49 age	1997/99	1.4
	50-59 age	1997/99	1.7
	60-69 age	1997/99	2.2
PCB 153	9-11 age	1998/99	0.4
	18-19 age	1997/99	0.6
	20-29 age	1997/99	0.9
	30-39 age	1997/99	1.6
	40-49 age	1997/99	2.2
	50-59 age	1997/99	2.8
	60-69 age	1997/99	3.3
PCB 180	9-11 age	1998/99	0.3
	18-19 age	1997/99	0.3
	20-29 age	1997/99	0.6
	30-39 age	1997/99	1.0
	40-49 age	1997/99	1.6
	50-59 age	1997/99	2.1
	60-69 age	1997/99	2.4
Σ PCB (138+153+180)	9-11 age	1998/99	0.9
	18-19 age	1997/99	1.1
	20-29 age	1997/99	2.0
	30-39 age	1997/99	3.2
	40-49 age	1997/99	5.1
PCB 28	50-59 age	1997/99	6.4
	60-69 age	1997/99	7.8
	7-14 age	2003/06	< 0.1
PCB 52	7-14 age	2003/06	< 0.1
PCB 101	7-14 age	2003/06	< 0.1

References

32. Esser, A.; Schettgen, T.; Kraus, T. Assessment of a Potential PCB Exposure among (Former) Underground Miners by Hydraulic Fluids. *J. Toxicol. Environ. Health A* **2020**, *83*, 219–232. <https://doi.org/10.1080/15287394.2020.1742261>.
33. Kiridena, W.; Wiegand, P.; Booth, M.; Lindelien, C. A Comparative Assessment of Low- and High-Resolution Gas Chromatography / Mass Spectrometry Methods for Polychlorinated Biphenyl Congener Analysis in Industry Wastewater. *J. Chromatogr. Open* **2024**, *5*, 100124. <https://doi.org/10.1016/j.jcoa.2024.100124>.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.