Supplementary Material

Determination of Parabens and Phenolic Compounds in Dairy Products through the Use of a Two-Step Continuous SPE System Including an Enhanced Matrix Removal Sorbent in Combination with UHPLC−MS/MS

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Table S1. Results obtained for precision and recovery studies for the different types of dairy product samples.

		RSD (%) /Recovery (%) [a]															
		Milk		Yogurt		Custard		Milkshake		Cream		Cheese		Butter		Margarine	
		500 ng/kg	2000 ng/kg	500 ng/kg	2000 ng/kg	500 ng/kg	2000 ng/kg	500 ng/kg	2000 ng/kg	500 ng/kg	2000 ng/kg	500 ng/kg	2000 ng/kg	500 ng/kg	2000 ng/kg	500 ng/kg	2000 ng/kg
Parabens	Methylparaben	6.10[a]	5.28	5.33	10.25	6.46	7.21	7.50	8.67	8.25	9.75	7.25	9.28	6.09	7.19	6.05	7.45
		99 ± 10[a]	101 ± 10	104 ± 7	101 ± 9	95 ± 7	95 ± 7	98 ± 10	101 ± 9	105 ± 9	102 ± 7	96 ± 11	93 ± 7	95 ± 6	102 ± 9	101 ± 6	106 ± 6
	Ethylparaben	9.20	7.16	6.30	11.40	5.39	8.08	7.86	7.27	5.85	7.98	5.69	7.35	6.44	8.91	5.52	8.51
		101 ± 6	99 ± 10	91 ± 8	103 ± 8	105 ± 9	98 ± 5	103 ± 9	92 ± 6	91 ± 8	103 ± 9	101 ± 10	96 ± 8	101 ± 10	97 ± 6	101 ± 6	103 ± 7
	Isopropylparaben	5.28	7.35	7.55	9.87	6.80	9.39	5.33	9.73	8.47	9.50	9.05	5.52	8.34	11.46	6.00	10.37
		103 ± 9	103 ± 10	93 ± 6	97 ± 7	98 ± 10	104 ± 8	95 ± 7	95 ± 7	94 ± 6	91 ± 9	97 ± 6	103 ± 9	103 ± 9	96 ± 9	102 ± 8	95 ± 9
	Butylparaben	5.36	7.83	8.05	7.84	7.21	9.47	6.46	6.27	5.48	9.58	9.38	9.17	5.69	10.81	5.49	10.44
		98 ± 5	99 ± 9	104 ± 8	99 ± 10	98 ± 5	101 ± 6	99 ± 9	103 ± 9	95 ± 6	99 ± 9	104 ± 8	99 ± 9	102 ± 7	104 ± 8	99 ± 6	92 ± 7
	Propylparaben	8.01	9.56	6.21	10.57	7.18	9.87	8.80	6.20	7.87	7.38	11.07	8.54	6.64	6.58	6.62	9.50
		104 ± 8	98 ± 10	104 ± 8	95 ± 6	101 ± 8	106 ± 6	102 ± 9	95 ± 6	104 ± 9	103 ± 9	96 ± 9	98 ± 5	96 ± 6	95 ± 6	102 ± 9	102 ± 7
	Isobutylparaben	8.29	7.30	9.66	10.22	7.37	8.42	5.77	8.81	8.48	10.14	7.10	6.54	6.49	7.26	8.59	10.60
		102 ± 7	96 ± 8	94 ± 6	99 ± 9	104 ± 7	101 ± 6	97 ± 5	98 ± 9	99 ± 6	99 ± 10	104 ± 8	101 ± 6	101 ± 8	103 ± 8	99 ± 4	103 ± 10
	Benzylparaben	8.19	8.69	5.95	7.15	8.04	6.82	7.27	8.09	6.82	9.08	5.71	9.62	4.95	7.64	7.04	6.45
		99 ± 7	104 ± 7	93 ± 6	102 ± 6	97 ± 6	98 ± 7	104 ± 9	101 ± 6	101 ± 9	104 ± 8	98 ± 10	104 ± 8	99 ± 10	100 ± 6	99 ± 8	98 ± 7

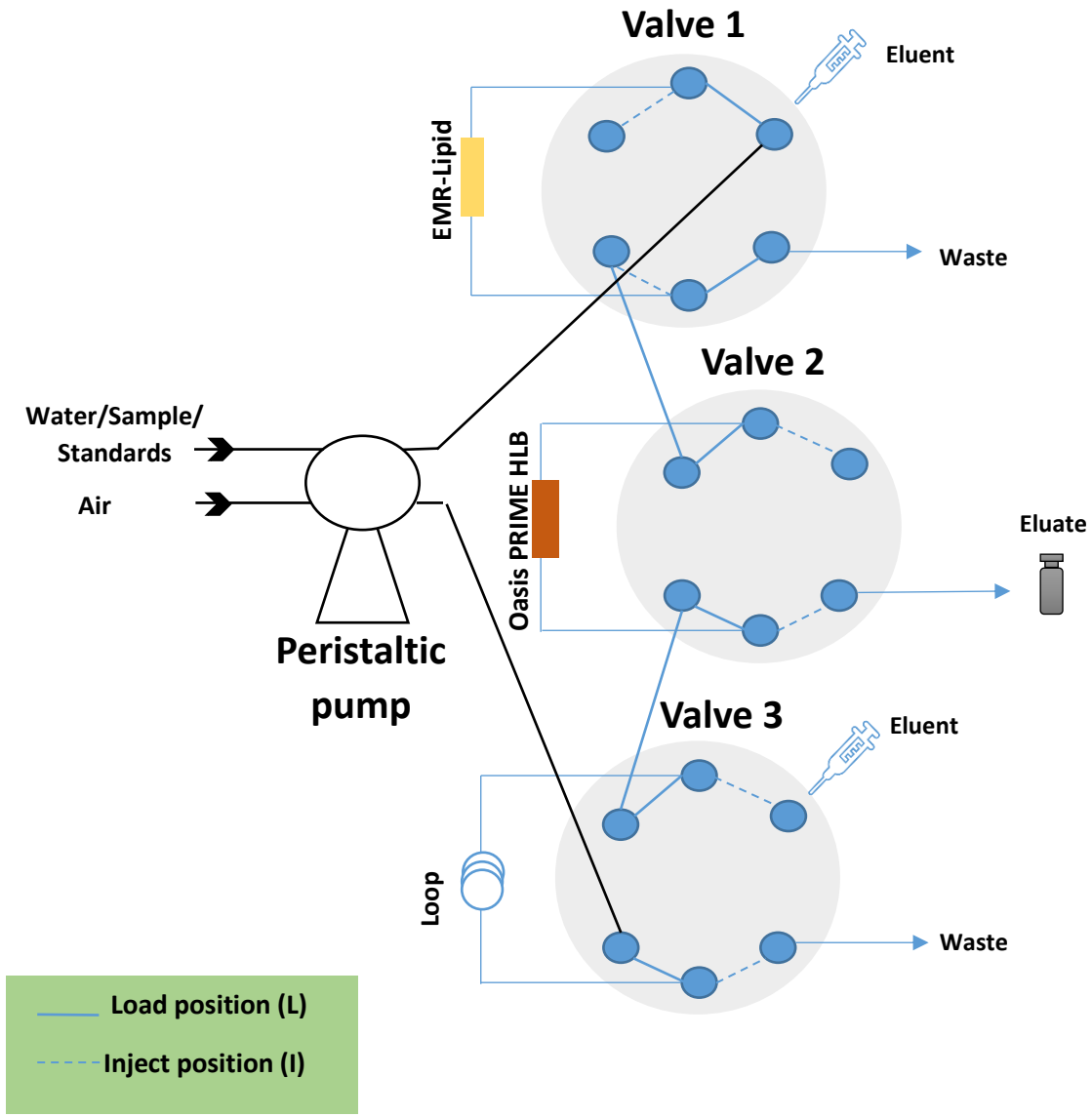
Table S1. Continued

		RSD (%) / Recovery (%)[a]															
		Milk		Yogurt		Custard		Milkshake		Cream		Cheese		Butter		Margarine	
		500 ng/kg	2000 ng/kg	500 ng/kg	2000 ng/kg	500 ng/kg	2000 ng/kg	500 ng/kg	2000 ng/kg	500 ng/kg	2000 ng/kg	500 ng/kg	2000 ng/kg	500 ng/kg	2000 ng/kg	500 ng/kg	2000 ng/kg
Phenols	Pentylphenol	6.49[a]	7.95	7.20	8.77	6.55	10.40	5.69	5.78	7.29	8.16	8.57	8.52	7.83	7.88	6.66	8.30
		98 ± 6[a]	99 ± 5	104 ± 8	97 ± 5	101 ± 6	99 ± 8	99 ± 8	97 ± 6	94 ± 7	104 ± 8	105 ± 10	98 ± 9	95 ± 7	100 ± 5	99 ± 8	105 ± 7
	4-Chloro-3-methylphenol	5.29	9.56	5.20	5.27	10.67	4.65	9.38	9.55	6.10	10.54	8.48	5.34	10.15	6.19	9.15	6.89
		104 ± 8	99 ± 9	105 ± 7	98 ± 9	98 ± 10	101 ± 9	91 ± 8	101 ± 10	93 ± 6	95 ± 7	92 ± 7	103 ± 5	99 ± 8	94 ± 7	103 ± 9	103 ± 9
	4-*tert*-Octylphenol	5.39	8.49	5.65	4.34	7.46	9.50	4.20	10.47	5.40	10.21	8.45	8.33	5.75	8.49	3.59	6.57
		99 ± 9	95 ± 8	99 ± 8	99 ± 8	103 ± 5	104 ± 8	102 ± 7	92 ± 6	94 ± 6	99 ± 9	94 ± 7	93 ± 6	103 ± 9	105 ± 9	98 ± 8	104 ± 9
	Phenol	8.08	8.37	5.95	7.91	9.57	10.34	6.14	8.21	7.24	11.30	6.52	7.53	3.08	6.56	8.88	3.25
		104 ± 9	101 ± 6	101 ± 9	104 ± 8	98 ± 10	104 ± 8	103 ± 9	99 ± 6	98 ± 10	92 ± 7	105 ± 8	105 ± 7	98 ± 10	95 ± 7	100 ± 5	103 ± 5
	4-*tert*-Butylphenol	5.59	11.1	5.44	6.36	7.39	9.34	5.29	9.65	6.27	9.40	9.86	8.40	7.51	9.82	7.01	9.40
		96 ± 6	103 ± 6	102 ± 7	100 ± 8	99 ± 8	98 ± 5	101 ± 6	99 ± 9	103 ± 9	96 ± 9	98 ± 8	97 ± 9	96 ± 9	104 ± 8	102 ± 9	104 ± 8
	Nonylphenol	7.64	10.31	5.84	9.24	6.65	7.54	5.55	9.37	5.32	9.81	10.77	9.25	5.58	10.74	6.08	7.17
		98 ± 10	101 ± 9	96 ± 11	101 ± 9	101 ± 6	99 ± 9	103 ± 9	103 ± 9	101 ± 10	104 ± 7	93 ± 6	102 ± 6	97 ± 6	101 ± 9	95 ± 6	91 ± 8
	2-*tert*-Butylphenol	5.70	10.44	7.02	9.41	7.57	10.51	7.08	6.17	6.22	9.61	6.38	9.34	5.78	9.50	7.24	8.97
		99 ± 8	102 ± 6	102 ± 7	99 ± 9	98 ± 10	95 ± 7	100 ± 5	96 ± 9	98 ± 5	99 ± 9	104 ± 8	95 ± 6	101 ± 8	106 ± 6	99 ± 9	101 ± 9
	Bisphenol F	5.99	9.55	6.04	8.27	9.41	8.24	5.62	8.3	5.89	7.91	6.50	6.57	6.65	6.24	5.34	11.31
		101 ± 6	94 ± 5	91 ± 8	101 ± 10	93 ± 6	93 ± 7	104 ± 8	103 ± 5	100 ± 5	103 ± 9	94 ± 7	103 ± 9	101 ± 10	96 ± 11	102 ± 7	104 ± 8
	3,4-Dimehylphenol	7.00	10.64	4.29	9.61	8.25	9.35	5.77	9.58	5.56	8.36	6.52	6.40	8.28	6.49	6.24	10.81
		100 ± 5	101 ± 9	95 ± 7	98 ± 10	97 ± 5	104 ± 8	97 ± 5	101 ± 6	93 ± 6	104 ± 8	98 ± 10	98 ± 5	99 ± 8	105 ± 7	103 ± 9	103 ± 9
	2,5-Dimethylphenol	6.69	7.71	5.51	9.32	9.09	10.71	9.81	7.16	5.44	10.64	5.67	9.38	6.43	6.78	7.60	6.38
		100 ± 8	99 ± 8	98 ± 5	95 ± 7	101 ± 6	106 ± 6	103 ± 9	100 ± 8	105 ± 7	91 ± 6	103 ± 6	103 ± 9	97 ± 8	104 ± 8	91 ± 9	95 ± 6
	4-Phenylphenol	5.33	10.13	6.15	9.19	11.30	8.56	8.03	7.23	6.32	10.98	6.76	5.45	5.29	7.25	5.47	8.09
		99 ± 5	93 ± 6	100 ± 5	94 ± 7	100 ± 8	91 ± 8	102 ± 7	96 ± 8	97 ± 6	97 ± 5	95 ± 10	100 ± 5	93 ± 6	100 ± 5	93 ± 6	103 ± 8
	2-Phenylphenol	6.32	9.25	7.25	11.30	6.17	7.26	9.03	6.24	5.25	11.01	5.68	7.55	8.98	9.41	5.55	7.56
		96 ± 6	93 ± 6	102 ± 7	104 ± 6	101 ± 9	104 ± 8	98 ± 5	103 ± 9	99 ± 4	101 ± 10	100 ± 5	93 ± 6	100 ± 5	91 ± 9	101 ± 6	104 ± 7
	Bisphenol S	4.35	10.61	8.26	9.41	6.19	9.45	7.58	6.19	8.94	7.98	8.32	5.44	6.34	6.47	7.18	9.41
		103 ± 9	104 ± 8	103 ± 9	105 ± 8	102 ± 8	99 ± 8	101 ± 10	101 ± 9	91 ± 9	99 ± 9	95 ± 8	99 ± 8	105 ± 9	95 ± 8	99 ± 8	99 ± 8
	4-Chlorophenol	6.28	10.90	5.24	10.75	6.35	9.30	7.14	6.30	5.99	6.35	7.57	9.31	5.56	7.41	6.55	8.20
		102 ± 7	98 ± 5	102 ± 6	104 ± 7	105 ± 7	96 ± 8	96 ± 6	102 ± 9	98 ± 5	105 ± 7	99 ± 9	104 ± 8	99 ± 9	98 ± 5	101 ± 10	101 ± 9
	4-Hexylphenol	9.09	11.09	6.46	5.28	8.33	9.41	6.08	6.39	5.31	9.35	6.15	10.41	7.74	10.61	5.35	9.08
		103 ± 9	102 ± 6	98 ± 5	99 ± 9	91 ± 9	94 ± 7	105 ± 7	98 ± 10	105 ± 7	99 ± 10	95 ± 7	100 ± 5	100 ± 7	93 ± 6	100 ± 5	94 ± 7
	Bisphenol A	5.34	8.42	6.86	6.28	7.56	10.81	9.83	9.83	5.91	9.89	7.07	10.50	7.64	9.60	7.21	11.38
		98 ± 8	99 ± 8	101 ± 10	101 ± 9	91 ± 9	98 ± 5	93 ± 7	94 ± 7	97 ± 7	98 ± 5	100 ± 5	93 ± 6	100 ± 5	96 ± 6	103 ± 6	102 ± 7
	Bisphenol B	6.63	7.20	5.68	5.55	10.45	8.27	6.35	8.27	5.42	9.60	6.70	9.51	5.94	8.20	6.25	9.40
		103 ± 5	101 ± 6	99 ± 9	98 ± 8	103 ± 7	103 ± 8	96 ± 11	96 ± 11	105 ± 6	105 ± 8	102 ± 8	96 ± 7	102 ± 7	94 ± 6	91 ± 8	92 ± 7
	4-Heptylphenol	6.35	8.47	5.39	7.22	6.98	6.61	4.68	9.35	8.91	9.30	5.25	10.34	5.84	9.37	6.80	7.44
		101 ± 9	91 ± 8	103 ± 9	99 ± 8	104 ± 7	93 ± 6	100 ± 7	105 ± 8	98 ± 5	105 ± 7	91 ± 8	101 ± 9	106 ± 6	98 ± 5	96 ± 7	95 ± 6
	Bisphenol Z	6.62	9.55	6.28	8.15	7.19	8.45	5.85	6.78	6.13	7.24	7.34	9.35	9.82	8.50	5.29	11.32
		98 ± 10	99 ± 9	99 ± 4	103 ± 10	105 ± 8	92 ± 5	91 ± 6	103 ± 6	106 ± 6	103 ± 9	100 ± 8	94 ± 7	98 ± 8	101 ± 10	91 ± 8	91 ± 8
	Pentachlorophenol	8.85	7.75	7.41	6.88	8.65	6.30	10.32	8.15	7.17	7.48	7.91	11.02	5.82	8.36	6.38	10.94
		105 ± 6	95 ± 8	91 ± 9	94 ± 7	105 ± 7	104 ± 7	105 ± 7	101 ± 6	106 ± 6	93 ± 6	100 ± 9	101 ± 10	98 ± 7	93 ± 6	99 ± 9	96 ± 8
	Triclosan	9.13	5.64	8.23	6.13	7.18	9.40	8.07	7.50	5.55	10.10	6.16	7.22	8.15	10.13	5.24	5.78
		94 ± 7	105 ± 7	105 ± 7	98 ± 10	97 ± 8	105 ± 6	96 ± 9	98 ± 6	104 ± 9	98 ± 8	103 ± 9	102 ± 6	104 ± 8	93 ± 7	105 ± 8	99 ± 8

[a] RSD: relative standard deviation (n=12) for 500 and 2000 ng/kg ($p < 0.05$), interday. Percent recoveries (% ± SD, n = 3) of analytes spiked to milk and dairy product samples (500 – 2 000 ng/L)

Table S2. Results obtained in the matrix effect studies of the different types of dairy product samples

		Matrix Effect (%)[a]							
		Milk	Yoghourt	Cheese	Milkshake	Cream	Custard	Butter	Margarine
Parabens	Methylparaben	1.03 (3%)	0.98 (-2%)	0.94 (-6%)	1.06 (6%)	0.95 (-5%)	0.97 (-3%)	1.02 (2%)	0.92 (-7%)
	Ethylparaben	0.98 (-2%)	1.04 (4%)	1.05 (5%)	0.93 (-7%)	0.99 (-1%)	1.03 (3%)	0.95 (-5%)	0.93 (-7%)
	Isopropylparaben	1.07 (7%)	0.98 (-2%)	0.94 (-6%)	1.05 (5%)	0.95 (-5%)	1.03 (3%)	1.05 (5%)	0.93 (-7%)
	Butylparaben	1.02 (2%)	0.92 (-8%)	0.99 (-1%)	1.01 (1%)	0.95 (-5%)	0.90 (-10%)	1.01 (1%)	1.02 (2%)
	Propylparaben	1.02 (2%)	0.92 (-7%)	0.95 (-5%)	0.90 (-10%)	1.06 (6%)	0.92 (-8%)	0.90 (-10%)	0.98 (-2%)
	Isobutylparaben	0.95 (-5%)	0.93 (-7%)	0.93 (-7%)	1.04 (4%)	0.93 (-7%)	1.04 (4%)	1.04 (4%)	0.99 (-1%)
	Benzylparaben	0.99 (-1%)	1.05 (5%)	1.03 (3%)	0.98 (-2%)	1.03 (3%)	0.98 (-2%)	0.99 (-1%)	1.05 (5%)
Phenols	Pentylphenol	1.02 (2%)	0.95 (-5%)	0.90 (-10%)	0.98 (-2%)	1.02 (2%)	0.92 (-7%)	0.94 (-6%)	1.04 (4%)
	4-Chloro-3-methylphenol	1.07 (7%)	1.06 (6%)	0.92 (-8%)	0.93 (-7%)	0.93 (-7%)	0.97 (-3%)	0.90 (-10%)	1.04 (4%)
	4-*tert*-Octylphenol	0.95 (-5%)	0.93 (-7%)	0.95 (-5%)	0.93 (-7%)	1.02 (2%)	0.93 (-7%)	0.95 (-5%)	0.93 (-7%)
	Phenol	0.99 (-1%)	1.03 (3%)	0.95 (-5%)	1.04 (4%)	1.05 (5%)	1.06 (6%)	1.04 (4%)	1.02 (2%)
	4-*tert*-Butylphenol	0.95 (-5%)	1.03 (3%)	0.90 (-10%)	0.92 (-7%)	0.96 (-4%)	0.95 (-5%)	0.98 (-2%)	0.99 (-1%)
	Nonylphenol	0.98 (-2%)	0.93 (-7%)	0.97 (-3%)	0.93 (-7%)	0.94 (-6%)	1.03 (3%)	0.99 (-1%)	1.03 (3%)
	2-*tert*-Butylphenol	0.98 (-2%)	1.02 (2%)	0.93 (-7%)	1.02 (2%)	0.93 (-7%)	0.93 (-7%)	0.93 (-7%)	1.06 (6%)
	Bisphenol F	0.94 (-6%)	1.03 (3%)	0.99 (-1%)	1.03 (3%)	0.99 (-1%)	0.93 (-7%)	1.02 (2%)	1.10 (10%)
	3,4-Dimethylphenol	0.93 (-7%)	1.06 (6%)	1.02 (2%)	0.92 (-7%)	1.02 (2%)	0.93 (-7%)	0.92 (-8%)	0.92 (-8%)
	2,5-Dimethylphenol	0.98 (-2%)	0.92 (-7%)	0.93 (-7%)	1.04 (4%)	0.90 (-10%)	0.98 (-2%)	0.93 (-7%)	0.95 (-5%)
	4-Phenylphenol	0.95 (-5%)	1.04 (4%)	0.90 (-10%)	1.04 (4%)	1.02 (2%)	0.94 (-6%)	1.06 (6%)	0.95 (-5%)
	2-Phenylphenol	1.01 (1%)	1.04 (4%)	0.95 (-5%)	0.93 (-7%)	0.99 (-1%)	1.05 (5%)	1.05 (5%)	0.93 (-7%)
	Bisphenol S	0.99 (-1%)	0.93 (-7%)	1.05 (5%)	1.06 (6%)	0.98 (-2%)	0.92 (-7%)	1.06 (6%)	0.93 (-7%)
	4-Chlorophenol	1.04 (4%)	1.02 (2%)	0.96 (-4%)	0.95 (-5%)	0.99 (-1%)	1.05 (5%)	0.95 (-5%)	1.02 (2%)
	4-Hexylphenol	1.05 (5%)	1.01 (1%)	1.06 (6%)	0.96 (-6%)	0.92 (-8%)	1.02 (2%)	0.93 (-7%)	0.99 (-1%)
	Bisphenol A	1.02 (2%)	0.94 (-6%)	1.04 (4%)	1.01 (1%)	1.06 (6%)	0.98 (-2%)	1.08 (8%)	0.95 (-5%)
	Bisphenol B	0.99 (-1%)	1.05 (5%)	0.95 (-5%)	0.99 (-1%)	0.95 (-5%)	0.99 (-1%)	1.02 (2%)	0.95 (-5%)
	4-Heptylphenol	0.94 (-6%)	1.04 (4%)	1.05 (5%)	1.04 (4%)	0.98 (-2%)	1.02 (2%)	0.93 (-7%)	1.04 (4%)
	Bisphenol Z	0.92 (8%)	1.01 (1%)	1.08 (8%)	0.92 (-8%)	1.08 (8%)	1.05 (5%)	0.92 (-8%)	0.93 (-7%)
	Pentachlorophenol	0.90 (-10%)	1.02 (2%)	1.08 (8%)	1.02 (2%)	0.91 (-9%)	0.98 (-2%)	0.92 (-7%)	0.95 (-5%)
	Triclosan	1.02 (2%)	1.06 (6%)	0.91 (-9%)	1.06 (6%)	1.01 (1%)	0.93 (-7%)	1.06 (6%)	1.06 (6%)



Step	Valve 1	Valve 2	Valve 3
1. ERM-Lipid sorbent conditioning	L	I	I
2. Oasis PRiME HLB sorbent conditioning	I	L	I
3. Introduction of sample or standards	L	L	L
4. Oasis PRiME HLB drying	L	I	L
5. Elution of analytes	L	I	I

Figure S1. Continuous-flow system for the solid-phase with three injection valves and two serially columns.

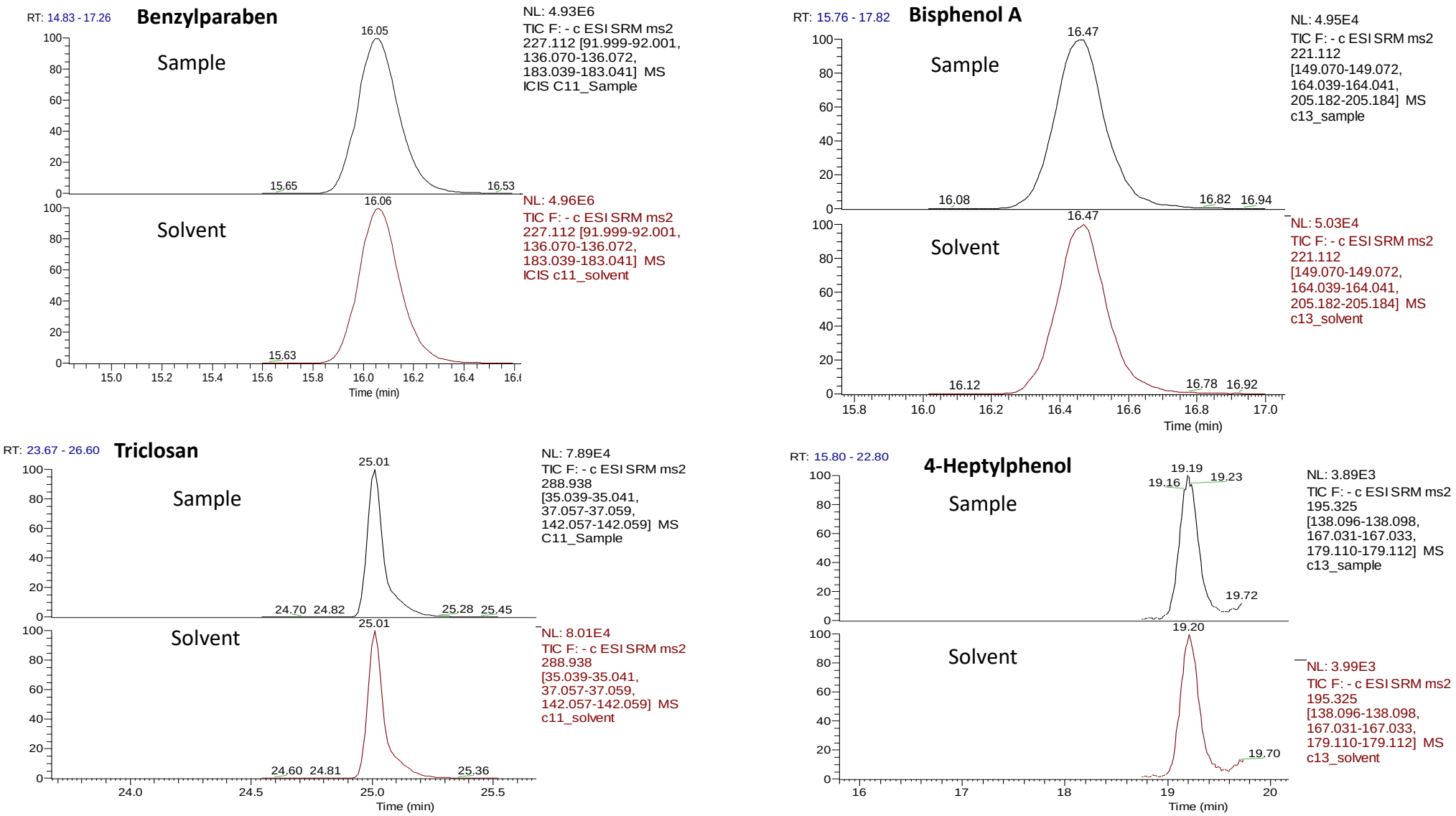


Figure S2. Extract ion chromatograms for four analytes (benzylparaben, bisphenol A, triclosan and 4-heptylphenol). In one chromatogram, the analyte is spiked in the solvent, and in the other the analyte is spiked in a milk sample.