Electronic Supplementary Information

MULTIVARIATE ASSESSMENT OF EXTRACTION PROCEDURES FOR THE FRACTIONATION OF MERCURY IN OILY SLUDGE SAMPLES USING COLD VAPOR ATOMIC FLUORESCENCE SPECTROMETRY

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Table S1. Doehlert design applied to the optimization of extractant volume and sample mass using convective heating at 80 °C for 10 minutes and 10 mL of HNO_3 4.0 mol L^{-1}. The response was considered as Hg^{2+} concentration (mg kg^{-1}) and as standard deviation (n=4).

Run	Volume / mL	Sample mass / mg	Hg^{2+}/ mg kg^{-1}		Standard deviation / mg kg^{-1}
1	0(20.0)	0(100)	3.30	3.39	0.74
2	1(35.0)	0(100)	2.65	2.85	0.40
3	0.5(27.5)	0.866(150)	2.00	2.82	0.51
4	-1(5.0)	0(100)	5.20	5.50	1.29
5	-0.5(12.5)	-0.866(50)	6.38	6.84	1.41
6	0.5(27.5)	-0.866(50)	4.07	3.77	0.27
7	-0,5(12.5)	0.866(150)	3.82	4.37	0.55

Table S2. Box-Behnken design matrix and responses associated to Hg^{2+} extraction, organic Hg extraction, CH_3Hg^+ to Hg^{2+} conversion and Hg^{2+} and CH_3Hg^+ recoveries applied to the optimization of temperature, HCl concentration and time of extraction.

Run	Temperature / °C	HCl / mol L^{-1}	Time / min	Extracted Hg^{2+} / %		Extracted Hg_{org} / %		CH_3Hg^+ conversion / %		Hg^{2+} recovery / %		CH_3Hg^+ recovery / %	
1	50	0.0	10	0.12	0.12	0.07	0.03	0.00	0.00	0.0	0.0	0.4	0.4
2	90	0.0	10	0.01	0.03	0.07	0.09	0.07	0.10	0.1	0.0	5.2	5.1
3	50	2.0	10	0.44	0.42	0.29	0.25	0.01	0.01	1.5	1.5	8.4	8.2
4	90	2.0	10	3.38	3.37	0.37	0.44	2.10	1.18	6.7	6.9	17.3	17.3
5	50	1.0	5	0.13	0.13	0.19	0.21	0.03	0.03	0.4	0.4	5.5	5.5
6	90	1.0	5	1.64	1.66	0.37	0.60	0.11	0.03	3.7	3.0	12.1	12.1
7	50	1.0	15	0.30	0.30	0.35	0.29	0.09	0.09	0.5	0.5	9.0	9.0
8	90	1.0	15	2.26	2.49	0.32	0.44	0.00	0.15	3.5	3.4	16.1	16.9
9	70	0.0	5	0.04	0.04	0.07	0.07	0.03	0.00	0.0	0.0	0.9	0.9
10	70	2.0	5	0.60	0.60	0.21	0.04	0.65	0.66	1.8	1.8	9.2	8.8
11	70	0.0	15	0.01	0.01	0.16	0.09	0.03	0.01	0.0	0.0	0.8	0.9
12	70	2.0	15	1.27	1.29	0.02	0.02	0.21	0.25	1.7	2.9	10.5	10.7
13	70	1.0	10	0.55	0.60	0.47	0.48	0.04	0.03	1.0	1.0	7.8	7.8
14	70	1.0	10	0.63	0.60	0.40	0.41	0.01	0.04	1.1	1.1	8.6	8.2
15	70	1.0	10	0.58	0.60	0.34	0.19	0.04	0.02	1.0	1.0	8.0	8.1

Table S3. Box-Behnken design matrix, responses, individual and global desirabilities calculated combining Hg^{2+} extraction efficiency, organic Hg extraction efficiency, CH_3Hg^+ to Hg^{2+}conversion and Hg^{2+} and CH_3Hg^+ recoveries for optimization of the extraction conditions applied to the fractionation of Hg in oily sludge samples using a HNO_3 solution.

Run	T / °C	[HNO_3] / mol L^{-1}	Time / min	Response										Individual desirability					Global desirability
				Hg^{2+} ext. / %		Hg_{org} ext. / %		CH_3Hg^+ conversion / %		Hg^{2+} recovery / %		CH_3Hg^+ recovery / %		Hg^{2+} ext. / %	Hg_{org} ext. / %	CH_3Hg^+ conv. / %	Hg^{2+} rec. / %	CH_3Hg^+ rec. / %	
1	50	0.0	10	0.12	0.12	0.07	0.03	0.00	0.00	0.0	0.0	0.4	0.4	0.00	0.00	0.00	0.00	0.00	0.00
2	90	0.0	10	0.01	0.03	0.07	0.09	0.07	0.08	0.0	0.0	5.2	5.2	0.00	0.01	0.02	0.00	0.06	0.00
3	50	8.0	10	4.31	4.47	0.44	0.54	0.23	0.21	6.1	6.1	17.3	17.8	0.07	0.09	0.05	0.08	0.23	0.09
4	90	8.0	10	58.34	61.38	4.07	3.74	5.15	3.13	80.0	80.1	76.4	74.1	1.00	0.77	1.00	1.00	1.00	0.95
5	50	4.0	5	0.44	0.44	0.13	0.18	0.00	0.00	1.0	1.0	9.5	9.3	0.01	0.02	0.00	0.01	0.12	0.00
6	90	4.0	5	10.01	9.96	0.25	0.56	0.03	0.00	20.7	22.9	38.3	38.5	0.17	0.07	0.00	0.27	0.51	0.09
7	50	4.0	15	1.39	1.41	0.62	0.74	0.00	0.05	1.7	1.6	11.6	11.8	0.02	0.13	0.01	0.02	0.15	0.04
8	90	4.0	15	15.65	15.40	5.48	4.65	0.00	0.00	30.3	38.3	38.9	34.3	0.26	1.00	0.00	0.43	0.48	0.00
9	70	0.0	5	0.04	0.04	0.07	0.07	0.03	0.00	0.0	0.0	0.9	0.9	0.00	0.00	0.00	0.00	0.01	0.00
10	70	8.0	5	8.99	9.67	1.48	1.56	0.36	0.46	13.0	12.6	23.3	23.1	0.16	0.29	0.10	0.16	0.30	0.19
11	70	0.0	15	0.01	0.01	0.16	0.09	0.03	0.01	0.0	0.0	0.8	0.9	0.00	0.01	0.00	0.00	0.01	0.00
12	70	8.0	15	12.15	12.54	1.98	2.01	0.57	0.93	23.1	19.8	24.9	25.3	0.21	0.39	0.18	0.27	0.33	0.26
13	70	4.0	10	2.85	2.85	0.00	0.33	0.93	0.00	3.9	3.7	10.8	10.5	0.05	0.02	0.11	0.05	0.14	0.06
14	70	4.0	10	2.60	3.13	0.28	0.14	0.00	0.10	4.2	3.6	12.1	12.4	0.05	0.03	0.01	0.05	0.16	0.04
15	70	4.0	10	2.73	2.94	0.12	0.15	0.43	0.00	4.1	4.1	12.0	12.2	0.05	0.02	0.05	0.05	0.16	0.05

Table S4. Mercury concentrations determined in oily sludge samples unspiked and spiked with Hg^{2+} and CH_3Hg^+ and submitted to microwave-assisted digestion and determination using CV-AFS.

Sample	Unspiked sample (mg kg^{-1})	Hg^{2+} spike (mg kg^{-1})	CH_3Hg^+ spike (mg kg^{-1})
A	24.3 ± 0.3	45.6 ± 0.3[a]	43.0 ± 1.3[a]
B	63.7 ± 0.1	241 ± 8[b]	234 ± 1[b]
C	354 ± 9	549 ± 7[b]	527 ± 7[b]

[a] Sample spiked with 20.0 mg kg^{-1} Hg^{2+} and CH_3Hg^+

[b] Samples spiked with 200.0 mg kg^{-1} Hg^{2+} and CH_3Hg^+

Table S5. ANOVA table for Hg^{2+} extraction (mg kg^{-1}) from an oily sludge sample following sample mass and extractant solution volume evaluation by Doehlert design using convective heating at 80 °C for 10 min and 10 mL 4.0 mol L^{-1} HNO_3 (R^2 = 0,9333).

Factor	SS	Df	MS	F	P	
Volume (L)	15.3385	1	15.3385	146.7452	0.000006	Significant
Volume (Q)	0.6644	1	0.6644	6.3567	0.039738	Significant
Sample mass (L)	8.2055	1	8.20552	78.5030	0.000047	Significant
Sample mass (Q)	1.3244	1	1.3244	12.6710	0.009224	Significant
Vol. x Samp. Mass	0.5289	1	0.5289	5.0603	0.059241	
Lack of Fit	1.0865	1	1.0865	10.3951	0.014569	Significant
Pure error	0.73167	7	0.10452			
Total SS	27.26031	13				

L = linear, Q = quadratic, SS = sum squared, Df = degrees of freedom, MS = media squared

Figure S1: Schematic representation of the analytical sequence adopted to carry out the evaluation of fractionation analysis of mercury in oily sludge samples using CV-AFS.