Supplementary Information

Speciation of Chromium in Water Samples after Dispersive Liquid-Liquid Microextraction, and Detection by Means of High-Resolution Continuum Source Atomic Absorption Spectrometry

Daniele S. Porto,[a] Naomi Akiba,[a] Marcone Augusto L. de Oliveira[b] and Ivanise Gaubeur*[a]

[a]Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Av. dos Estados, 5001, 09210-971 Santo André-SP, Brazil

[b]Departamento de Química, Universidade Federal de Juiz de Fora, Campus Universitário, 36036-330 Juiz de Fora-MG, Brazil

Table S1. Absorbance values of the fractional factorial design 2_v^{5-1} for determination of Cr^{III} and Cr^{VI} using APDC

Experiment	pH	APDC / (mmol L^{-1})	Extractant solvent volume / µL	Disperser solvent volume / µL	NaCl (m/v) / %	Integrated absorbance / s	
						Cr^{III}	Cr^{VI}
1	2.0 (−1)	0.4 (−1)	50 (−1)	100 (−1)	5 (1)	0.009	0.340
2	2.0 (−1)	0.4 (−1)	200 (1)	100 (−1)	0 (−1)	0.007	0.176
3	2.0 (−1)	0.4 (−1)	50 (−1)	300 (1)	0 (−1)	0.036	0.449
4	2.0 (−1)	0.4 (−1)	200 (1)	300 (1)	5 (1)	0.020	0.459
5	2.0 (−1)	6.0 (1)	50 (−1)	100 (−1)	0 (−1)	0.025	1.135
6	2.0 (−1)	6.0 (1)	200 (1)	100 (−1)	5 (1)	0.009	1.908
7	2.0 (−1)	6.0 (1)	50 (−1)	300 (1)	5 (1)	0.033	2.974
8	2.0 (−1)	6.0 (1)	200 (1)	300 (1)	0 (−1)	0.006	1.305
9	7.0 (1)	0.4 (−1)	50 (−1)	100 (−1)	0 (–1)	0.007	0.086
10	7.0 (1)	0.4 (−1)	200 (1)	100 (−1)	5 (1)	0.036	0.366
11	7.0 (1)	0.4 (−1)	50 (−1)	300 (1)	5 (1)	0.031	0.162
12	7.0 (1)	0.4 (−1)	200 (1)	300 (1)	0 (–1)	0.033	0.032
13	7.0 (1)	6.0 (1)	50 (−1)	100 (−1)	5 (1)	0.263	0.345
14	7.0 (1)	6.0 (1)	200 (1)	100 (–1)	0 (−1)	0.083	0.565
15	7.0 (1)	6.0 (1)	50 (−1)	300 (1)	0 (−1)	0.212	0.342
16	7.0 (1)	6.0 (1)	200 (1)	300 (1)	5 (1)	0.333	0.210
17	4.5 (0)	3.2 (0)	125 (0)	200 (0)	2.5 (0)	0.021	1.070
18	4.5 (0)	3.2 (0)	125 (0)	200 (0)	2.5 (0)	0.014	1.090
19	4.5 (0)	3.2 (0)	125 (0)	200 (0)	2.5 (0)	0.022	1.310

Concentration of Cr^{III} and Cr^{VI}: 1000 µg L^{-1}.

*e-mail: ivanise.gaubeur@ufabc.edu.br

Table S2. Absorbance values of the fractional factorial design 2_v^{5-1} for determination of Cr^{III} and Cr^{VI} using DDTC

Experiment	pH	APDC / (mmol L^{-1})	Extractant solvent volume / µL	Disperser solvent volume / µL	NaCl (m/v) / %	Integrated absorbance / s	
						Cr^{III}	Cr^{VI}
1	2.0 (−1)	0.4 (−1)	50 (−1)	100 (−1)	5 (1)	0.003	0.277
2	2.0 (−1)	0.4 (−1)	200 (1)	100 (−1)	0 (−1)	0.005	0.129
3	2.0 (−1)	0.4 (−1)	50 (−1)	300 (1)	0 (−1)	0.006	0.685
4	2.0 (−1)	0.4 (−1)	200 (1)	300 (1)	5 (1)	0.014	0.490
5	2.0 (−1)	6.0 (1)	50 (−1)	100 (−1)	0 (−1)	0.024	0.290
6	2.0 (−1)	6.0 (1)	200 (1)	100 (−1)	5 (1)	0.015	0.262
7	2.0 (−1)	6.0 (1)	50 (−1)	300 (1)	5 (1)	0.008	0.445
8	2.0 (−1)	6.0 (1)	200 (1)	300 (1)	0 (−1)	0.003	0.396
9	7.0 (1)	0.4 (−1)	50 (−1)	100 (−1)	0 (–1)	0.007	0.320
10	7.0 (1)	0.4 (−1)	200 (1)	100 (−1)	5 (1)	0.002	0.042
11	7.0 (1)	0.4 (−1)	50 (−1)	300 (1)	5 (1)	0.005	0.010
12	7.0 (1)	0.4 (−1)	200 (1)	300 (1)	0 (−1)	0.002	0.583
13	7.0 (1)	6.0 (1)	50 (−1)	100 (−1)	5 (1)	0.255	0.303
14	7.0 (1)	6.0 (1)	200 (1)	100 (–1)	0 (−1)	0.133	0.228
15	7.0 (1)	6.0 (1)	50 (–1)	300 (1)	0 (−1)	0.486	0.896
16	7.0 (1)	6.0 (1)	200 (1)	300 (1)	5 (1)	0.397	0.641
17	4.5 (0)	3.2 (0)	125 (0)	200 (0)	2.5 (0)	0.018	0.505
18	4.5 (0)	3.2 (0)	125 (0)	200 (0)	2.5 (0)	0.013	0.523
19	4.5 (0)	3.2 (0)	125 (0)	200 (0)	2.5 (0)	0.007	0.402

Concentration of Cr^{III} and Cr^{VI}: 1000 µg L^{-1}.

Table S3. Absorbance values of the factorial design 3^2 to determine Cr^{III} using APDC and DDTC

Experiment	pH	Disperser solvent volume / µL	Integrated absorbance / s	
			APDC	DDTC
1	6.0 (−1)	250 (−1)	0.031	0.136
2	6.5 (0)	250 (−1)	0.030	0.387
3	7.0 (1)	250 (−1)	0.019	0.639
4	6.0 (−1)	275 (0)	0.024	0.140
5	6.5 (0)	275 (0)	0.071	1.029
6	7.0 (1)	275 (0)	0.136	0.592
7	6.0 (−1)	300 (1)	0.033	0.096
8	6.5 (0)	300 (1)	0.036	0.608
9	7.0 (1)	300 (1)	0.020	0.639
10	6.5 (0)	275 (0)	0.076	1.133
11	6.5 (0)	275 (0)	0.038	0.594

Concentration of Cr^{III}: 1000 µg L^{-1}.

Table S4. Analysis of variance for fitting the model of prediction for the Cr^{III} with APDC

Source of variation	Sum of square (SS)	Number of degrees freedom	Mean of square (MS)
Model	0.005911	5	0.00118
Residual	0.006476	5	0.00130
Lack of fit	0.005612	3	0.00187
Pure error	0.000864	2	0.00043
Total	0.012388		

Variation explained = 91.27%; maximum of variation explained = 93.02%.

Table S5. Analysis of variance for fitting the model of prediction for the Cr^{III} with DDTC

Source of variation	Sum of square (SS)	Number of degrees freedom	Mean of square (MS)
Model	0.861832	5	0.17237
Residual	0.302985	5	0.06060
Lack of fit	0.139773	3	0.04659
Pure error	0.163212	2	0.08161
Total	1.164817		

Variation explained = 73.99%; maximum of variation explained = 85.99%.

Table S6. Factors and levels evaluated in the Plackett-Burman design to study concomitant species

Factor	Level / (µg L^{-1})		
	−1	0	+1
Aluminum	175	350	700
Barium	670	1,340	2,680
Cadmium	8	16	32
Calcium	25,000	50,000	100,000
Lead	25	50	100
Chloride	25,000	50,000	100,000
Cobalt	35	70	140
Copper	30	60	120
Iron	120	240	480
Manganese	50	100	200
Magnesium	9,850	19,700	39,400
Nickel	80	160	320
Nitrate	25,000	50,000	100,000
Potassium	2,500	5,000	10,000
Sodium	25,000	50,000	100,000
Sulfate	25,000	50,000	100,000
Zinc	100	200	400

Concentration of Cr^{III} and Cr^{VI}: 50 µg L^{-1}.

Table S7. Absorbance values obtained in the study of concomitant species at pH 2.0 value, integrated absorbance (IA)

Experiment	Al^{3+}	Ba^{2+}	Cd^{2+}	Ca^{2+}	Pb^{2+}	Cl^{-}	Co^{2+}	Cu^{2+}	Fe^{3+}	Mn^{2+}	Mg^{2+}	Ni^{2+}	NO_3^{-}	K^{+}	Na^{+}	SO_4^{2-}	Zn^{2+}	IA / s
1	1	−1	−1	−1	−1	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	0.102
2	1	1	−1	−1	−1	−1	1	−1	1	−1	−1	1	1	−1	−1	1	1	0.050
3	1	1	1	−1	−1	−1	−1	1	−1	1	−1	−1	1	1	−1	−1	1	0.111
4	1	1	1	1	−1	−1	−1	−1	1	−1	1	−1	−1	1	1	−1	−1	0.051
5	1	1	1	1	1	−1	−1	−1	−1	1	−1	1	−1	−1	1	1	−1	0.088
6	−1	1	1	1	1	1	−1	−1	−1	−1	1	−1	1	−1	−1	1	1	0.142
7	1	−1	1	1	1	1	1	−1	−1	−1	−1	1	−1	1	−1	−1	1	0.145
8	−1	1	−1	1	1	1	1	1	−1	−1	−1	−1	1	−1	1	−1	−1	0.119
9	1	−1	1	−1	1	1	1	1	1	−1	−1	−1	−1	1	−1	1	−1	0.047
10	1	1	−1	1	−1	1	1	1	1	1	−1	−1	−1	−1	1	−1	1	0.041
11	−1	1	1	−1	1	−1	1	1	1	1	1	−1	−1	−1	−1	1	−1	0.095
12	−1	−1	1	1	−1	1	−1	1	1	1	1	1	−1	−1	−1	−1	1	0.068
13	1	−1	−1	1	1	−1	1	−1	1	1	1	1	1	−1	−1	−1	−1	0.083
14	1	1	−1	−1	1	1	−1	1	−1	1	1	1	1	1	−1	−1	−1	0.126
15	−1	1	1	−1	−1	1	1	−1	1	−1	1	1	1	1	1	−1	−1	0.140
16	−1	−1	1	1	−1	−1	1	1	−1	1	−1	1	1	1	1	1	−1	0.098
17	1	−1	−1	1	1	−1	−1	1	1	−1	1	−1	1	1	1	1	1	0.055
18	−1	1	−1	−1	1	1	−1	−1	1	1	-1	1	-1	1	1	1	1	0.082
19	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	1	−1	1	1	1	0.133
20	−1	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	1	−1	1	1	0.101
21	−1	−1	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	1	−1	1	0.122
22	−1	−1	−1	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	1	−1	0.069
23	−1	−1	−1	−1	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	1	0.097
24	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	0.211
25	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.143
26	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.129
27	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.087

Table S8. Absorbance values obtained in the study of concomitant species at pH 7.0 value

Experiment	Al^{3+}	Ba^{2+}	Cd^{2+}	Ca^{2+}	Pb^{2+}	Cl^{-}	Co^{2+}	Cu^{2+}	Fe^{3+}	Mn^{2+}	Mg^{2+}	Ni^{2+}	NO_3^-	K^+	Na^+	SO_4^{2-}	Zn^{2+}	IA[a] / s
1	1	−1	−1	−1	−1	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	0.200
2	1	1	−1	−1	−1	−1	1	−1	1	−1	−1	1	1	−1	−1	1	1	0.088
3	1	1	1	−1	−1	−1	−1	1	−1	1	−1	−1	1	1	−1	−1	1	0.177
4	1	1	1	1	−1	−1	−1	−1	1	−1	1	−1	−1	1	1	−1	−1	0.096
5	1	1	1	1	1	−1	−1	−1	−1	1	−1	1	−1	−1	1	1	−1	0.131
6	−1	1	1	1	1	1	−1	−1	−1	−1	1	−1	1	−1	−1	1	1	0.128
7	1	−1	1	1	1	1	1	−1	−1	−1	−1	1	−1	1	−1	−1	1	0.145
8	−1	1	−1	1	1	1	1	1	−1	−1	−1	−1	1	−1	1	−1	−1	0.161
9	1	−1	1	−1	1	1	1	1	1	−1	−1	−1	−1	1	−1	1	−1	0.230
10	1	1	−1	1	−1	1	1	1	1	1	−1	−1	−1	−1	1	−1	1	0.156
11	−1	1	1	−1	1	−1	1	1	1	1	1	−1	−1	−1	−1	1	−1	0.096
12	−	−1	1	1	−1	1	−1	1	1	1	1	1	−1	−1	−1	−1	1	0.151
13	1	−1	−1	1	1	−1	1	−1	1	1	1	1	1	−1	−1	−1	−1	0.162
14	1	1	−1	−1	1	1	−1	1	−1	1	1	1	1	1	−1	−1	−1	0.132
15	−1	1	1	−1	−1	1	1	−1	1	−1	1	1	1	1	1	−1	−1	0.114
16	−1	−1	1	1	−1	−1	1	1	−1	1	−1	1	1	1	1	1	−1	0.210
17	1	−1	−1	1	1	−1	−1	1	1	-1	1	-1	1	1	1	1	1	0.082
18	−1	1	−1	−1	1	1	−1	−1	1	1	−1	1	−1	1	1	1	1	0.124
19	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	1	−1	1	1	1	0.133
20	−1	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	1	−1	1	1	0.125
21	−1	−1	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	1	−1	1	0.155
22	−1	−1	−1	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	1	−1	0.113
23	−1	−1	−1	−1	1	−1	1	−1	−1	1	1	−1	−1	1	1	−1	1	0.217
24	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	0.214
25	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.148
26	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.096
27	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.195

IA = integrated absorbance.

Table S9. Graphite furnace temperature program for chromium determination

Step	Temperature / ^{o}C	Ramp / (°C s^{-1})	Hold / s	Ar flow rate / (L min^{-1})
Drying	90	5	20	2.0
Drying	105	3	20	2.0
Drying	130	2	20	2.0
Pyrolysis	1700	250	15	2.0
Atomization	2500	1200	5	0
Cleaning	2800	500	4	2.0

Sample volume: 20 µL; chemical modifier: 3 µL (0.5 g L^{-1} $Mg(NO_3)_2$); linear range: 2.5-50 µg L^{-1}; LOD: 0.03 µg L^{-1}; LOQ: 0.10 µg L^{-1}.