Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.

Electronic supplementary information

Table S1. Cadmium and Pb signal response for CCD design using KR-ICP-OES. ICP-OES operating conditions: Q_g: 0.7 L min^{-1}; Q_l: 0.4 mL min^{-1}. Analyte concentration: 1 mg L^{-1}.

pH	APDC concentration (% w w^{-1})	Reactor length (cm)	Elution flow (mL min^{-1})	Integrated signal · 10^3 (counts)	
				Cd	Pb
3	0.27	100	0.23	55±2	20.0±0.5
7	0.8	256	0.23	268±2	25.0±0.5
5	0.54	178	0.11	257±2	20.0±0.7
5	0.54	178	0.34	113±1	17.0±0.6
5	0.54	178	0.56	126±2	13.0±0.5
3	0.27	100	0.45	165±1.7	20.0±0.8
5	0.54	334	0.34	149±1.7	19.0±0.7
3	0.8	100	0.45	165±2	25.0±1.2
3	0.8	100	0.23	45±1.3	22.0±0.8
5	0.54	22	0.34	31±1.0	17.0±0.7
7	0.8	100	0.45	46±1.3	19.0±0.7
3	0.27	256	0.23	103±2	14.0±0.6
5	1.07	178	0.34	145±2	19.0±0.6
5	0.54	178	0.34	113±3	17.0±0.7
9	0.54	178	0.34	160±2	17.0±0.7
5	0.005	178	0.34	83±1.5	12.0±0.5
7	0.27	100	0.23	30.0±1.4	11.8±0.5
7	0.8	256	0.45	63±3	20.0±0.7
7	0.27	256	0.23	47±2	16.0±0.8
3	0.8	256	0.23	25±6	42.0±0.2
3	0.27	256	0.45	95±2	17.0±0.5
1	0.54	178	0.34	170±6	28.0±0.8
7	0.27	256	0.45	60±2	15.0±0.5
7	0.27	100	0.45	38±1.8	14.8±0.3
7	0.8	100	0.11	56±2	15.5±0.6

Table S2. As, Cd and Pb signal response for a CCD design using DLLME. Q_g: 0.7 L min^{-1}; Q_l: 0.4 mL min^{-1}; supramolecular/acetic acid dilution ratio: 1:0.5; analyte concentration: 1 mg L^{-1}.

				Integrated signal (counts))·10^3		
pH	APDC concentration (% w w^{-1})	Alcohol mass (mg)	THF volume (mL)	As	Cd	Pb
3	0.1	80	0.15	23.0±0.5	50.0±1.3	7.9±0.3
6	0.25	160	0.025	13.0±0.3	190±7	8.7±0.5
9	0.4	80	0.15	14.0±0.3	93.0±5	6.7±0.2
9	0.4	80	0.4	27.0±0.6	170±9	10.5±0.2
3	0.4	80	0.15	21.0±0.4	100±5	11.0±0.4
6	0.55	160	0.275	20.0±0.5	300.0±1.0	22.0±0.8
12	0.25	160	0.275	23.0±0.4	130±6	3.0±0.2
9	0.1	240	0.4	25.0±0.6	110±4	14.0±0.2
9	0.4	240	0.4	30.0±0.8	190±6	21.7±0.4
6	0.25	160	0.275	23.0±0.7	260±9	20.2±0.2
0	0.25	160	0.275	27.0±0.9	72±4	3.0±0.2
6	0.25	160	0.275	20.0±0.7	260±9	18.0±0.6
3	0.4	240	0.4	27.0±0.8	120±5	10.0±0.4
3	0.4	80	0.4	31.0±0.9	160±5	20.0±0.7
6	0	160	0.275	21.0±0.8	56±2	4.6±0.2
6	0.25	160	0.525	30.0±1.0	300±10	18.0±0.5
9	0.1	80	0.15	17.0±0.7	139±3	8.0±0.3
6	0.25	0	0.275	0	0	0
9	0.1	80	0.4	29.0±0.8	289±9	16.5±0.7
3	0.1	80	0.4	25.0±0.8	275±9	17.9±0.4
9	0.1	240	0.15	18.0±0.5	131±6	5.2±0.2
9	0.4	240	0.15	20.0±0.6	184±6	8.4±0.5
6	0.25	320	0.275	22.0±0.7	280±9	13.2±0.2
3	0.4	240	0.15	18.0±0.7	170±4	6.0±0.4
3	0.1	240	0.4	30.0±1.0	127±2	12.2±0.5
3	0.1	240	0.15	16.0±0.9	150±9	3.20±0.05

Table S3. Metals recovery assay for different commodities with KR and DLLME. All values are percentual (%)

	KR		DLLME		
Sample	**Cd**	**Pb**	**As**	**Cd**	**Pb**
Mussel	86 ± 4	89 ± 5	98 ± 4	98 ± 3	97 ± 5
Chocolate	97 ± 7	87 ± 5	97 ± 7	101 ± 4	98 ± 5
Rice	90 ± 4	79 ± 6	97 ± 5	98 ± 6	102 ± 5
Wine	93 ± 5	97 ± 2	96 ± 5	98 ± 3	99 ± 5

Recovery (%) = 100×[(found – initial)/added

Table S4.

Elemental analysis of the mussel sample by means of ICP-based techniques. ICP-OES experimental conditions: Q_g: 0.7 L min^{-1}; Q_l: 0.4 mL min^{-1}.

	Concentration (mg kg^{-1})		
Element	**KR-ICP-OES**	**DLLME-ICP-OES**	**ICP-MS**
As	-	10.3±0.3	10.5±0.4
Cd	3.8±0.8	3.4±0.3	3.2±0.3
Pb	<LOD	0.40±0.05	0.30±0.01

Table S5. As, Cd and Pb maximum allowed levels in several foods according to EU 1881/2006 policy and theoretical LODs for KR- and DLLME-ICP-OES considering an acid digestion treatment of 0.5 g sample and dilution up to 25 mL.

			LOD (μg kg^{-1})	
Element	Food	Maximum allowed level (μg kg^{-1})	KR	DLLME
As	Pancakes, wafers, cookies and rice cakes	300	------	150
	Rice destined for the production of food for infants and young children	100		
Pb	Honey	100	200	80
	Food complement	3000		
	Fats and oils including milk fat	100		
	Meat (excluding offal) of bovine animals, sheep, pigs and poultry	100		
	offal of cattle, sheep, pigs and poultry	500		
	crustaceans	500		
	cephalopods	300		
	Cereals and dried vegetables	200		
	Sweet corn and fruits excluding cranberries, strawberry trees, currants and elderberries	100		
	blueberries, strawberry trees, currants and elderberries	200		
	Vegetables	100-300		
	Raw milk, thermally treated milk and milk for the manufacture of dairy products	20		
	Preparations for infants and young children: powder and liquid	50, 10		
	Foods for special medical purposes intended specifically for infants and young children: powder and liquid form	50, 30		
	Drinks for children and young children sold. Marketed liquid or to be reconstituted following the manufacturer's instructions, including fruit juices	30		

	Cereals excluding wheat and rice	100		
	Grains of wheat and rice			
	Wheat bran and wheat germ for direct consumption	200		
	Soybeans			
	Vegetables and fruits excluding root and tuber vegetables, leafy vegetables, fresh herbs, brassica vegetables, young stems, mushrooms and seaweed	50		
	Root and tuber vegetables (excluding celeries, chirivias, salsifies and rustica radishes), young stems (celery excluded).	100		
	Leafy vegetables, free herbs, vegetables of the Brassica genus, celery, celeriac, chirivias, salsifies, rustic radishes and the following mushrooms: mushrooms, oyster mushroom and shiitake mushroom	200		
	Milk chocolate with a total dry matter content of cocoa> 30	100		
	Chocolate with a total cocoa dry matter content <50; milk chocolate with a total dry matter content of	300		
Cd	cocoa ≥30%		100	30
	Chocolate with a total dry matter content of cocoa≥50%	500		
	Bivalve mollusks and cephalopods	1000		
	anchovy, swordfish and sardine fish	250		
	Melva fish	150		
	Food supplements composed exclusively of dried seaweed, products made from seaweed or dried bivalve mollusks	3000		
	Preparations for infants and continuation preparations:			
	Powdered preparations for infant formulated from proteins obtained from cow's milk	10		
	Prepared in liquid for lactating persons based on proteins obtained from cow's milk	5		
	Prepared powders for lactated elaborated from isolated soy proteins alone or mixed with milk protein			
	Prepared in liquid for lactating children prepared from isolated soy proteins alone or mixed with milk	20		
	protein	10		

Fig. S1. Influence of the supramolecular:acetic acid mixture ratio on the integrated emission signal of Cd II 214.439 nm. ICP-OES operating conditions: Q_g: 0.7 L min^{-1}; Q_l: 0.4 mL min^{-1}. Analyte concentration: 1 mg L^{-1}.

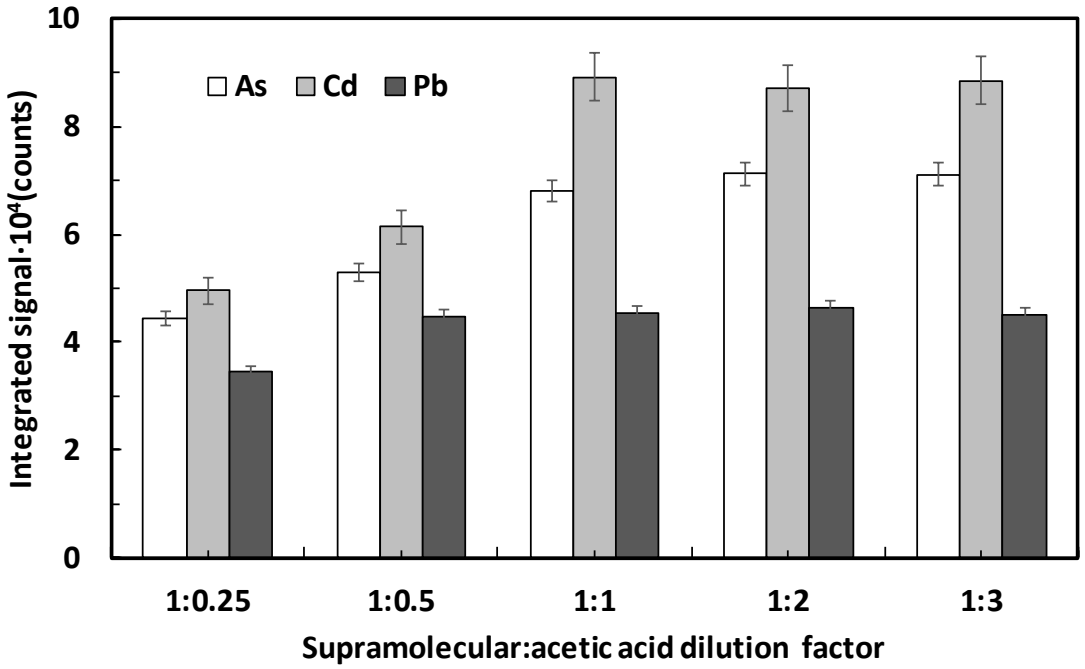

Fig. S2. Influence of the nebulizer gas flow rate on Cd II 214.439 nm integrated emission signal using a 1:1 supramolecular:acetic acid mixture at different Q_l.