

SUPPLEMENTARY INFORMATION

Mesofluidic platform integrating restricted access-like sorptive microextraction as a front-end to inductively-coupled plasma atomic emission spectrometry for determination of trace level concentrations of lead and cadmium as contaminants in honey

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Table S1. Physicochemical characteristics of chelators and ion-exchangers explored as sorptive materials

Sorptive materials	Particle size distribution (μm)	Resin form (from manufacturer)	Ion exchange capacity (meq g^{-1})	Supplier
Chelex 100	38-75	Na^+ form	-----	Fluka
Dowex 50X8	75-150	H^+ form	-----	Fluka
Oasis MCX	30	H^+ form	1	Waters
Bond Elut Plexa PCX	40-55	H^+ form	0.60-1.20	Agilent

Table S2. Operating conditions for on-line ICP-AES detection

RF generator power (W)	1300
Frequency of RF generator (MHz)	40
Nebulizer flow rate (L min ⁻¹)	0.7
Coolant gas flow rate (L min ⁻¹)	15
Auxiliary gas flow rate (L min ⁻¹)	0.2
Carrier (2 % HNO ₃) flow rate (mL min ⁻¹)	1
Sample flush time (s)	0
Sample uptake delay (s)	0
View mode	axial
Analytical wavelengths Pb (nm)	220.353/217.00
Analytical wavelengths Cd (nm)	228.802/214.440

Table S3. Analytical sequence of the μ SPE-RAM type LOV procedure for preconcentration and determination of Cd and Pb in honey samples by ICP-AES.

Description	SP	LOV Position	Injection valve Position	Flow rate ($\mu\text{L s}^{-1}$)	Volume (μL)
System conditioning:					
a) Filling SP with carrier	Aspirate	---	Inject	200	2500
b) Filling the transfer line (to discharge beads)	Dispense	4	Inject	200	1500
Sorbent conditioning:					
a) Beads loading	Aspirate	6	Inject	200	200
	Aspirate	1	Inject	8	50
	Dispense	4	Inject	8	350
	Dispense	3	Inject	100	250
b) Conditioning	Aspirate	6	Inject	100	
b ₁) 3.0 mol L ⁻¹ HNO ₃	Aspirate	5	Inject	100	200
b ₂) Acetic acid/acetate buffer (pH 4.5)	Dispense	4	Inject	20	350
	Dispense	4	Inject	20	350
					550
Cleaning					
a) HC cleaning	Aspirate carrier	---	Inject	300	4700
	Dispense	3	Inject	300	5000
b) Sample tube cleaning	Aspirate carrier	---	Inject	300	200
	Aspirate	6	Inject	100	200

	Aspirate	2	Inject	100	500
	Dispense	3	Inject	100	900
Sample loading	Aspirate carrier	---	Inject	100	300
	Aspirate	6	Inject	100	300
	Aspirate	2	Inject	100	4000
	Aspirate	6	Inject	100	300
	Dispense	4	Inject	20	4900
Rinse with buffer					
Elution	Aspirate carrier	---	Inject	100	500
	Aspirate	6	Inject	100	100
	Aspirate	5	Inject	100	200
	Aspirate	6	Inject	100	100
	Dispense	4	Load	14	900
ICP-OES activation and signal recording	Stop flow	---	Inject	...	...
Beads disposal	Aspirate carrier	---	Inject	100	400
	Dispense	4	Inject	100	200
	Aspirate	6	Inject	100	200
	Aspirate	4	Inject	200	1000
	Dispense	3	Inject	200	1400
Cleaning of HC	Aspirate carrier	---	Inject	300	5000
	Dispense	3	Inject	300	5000

Table S4. Full fractional design for multivariate screening of critical variables in the elution stage of Pb and Cd for the μ SPE-LOV procedure.

Run	Eluent concentration (mol L ⁻¹)		Eluent flow rate (μ L s ⁻¹)		Eluent volume (μ L)		Absolute recovery (%)	
	Uncoded	Coded	Uncoded	Coded	Uncoded	Coded	Cd	Pb
1	3	1	20	1	600	1	82	63.5
2	3	1	20	1	100	-1	75.6	59.1
3	3	1	8	-1	600	1	74.5	76.0
4	3	1	8	-1	100	-1	70.8	67.5
5	1	-1	20	1	600	1	69.5	50.0
6	1	-1	20	1	100	-1	72.7	36.9
7	1	-1	8	-1	600	1	76.4	54.0
8	1	-1	8	-1	100	-1	71.5	44.6
9	2	0	14	0	350	0	79.6	53.7
10	2	0	14	0	350	0	81.4	66.2
11	2	0	14	0	350	0	77.9	67.6

Figure S1. Absolute recoveries of Pb and Cd at trace level concentrations (15 and 5 ng/mL, respectively) using distinct copolymeric-based sorptive materials.

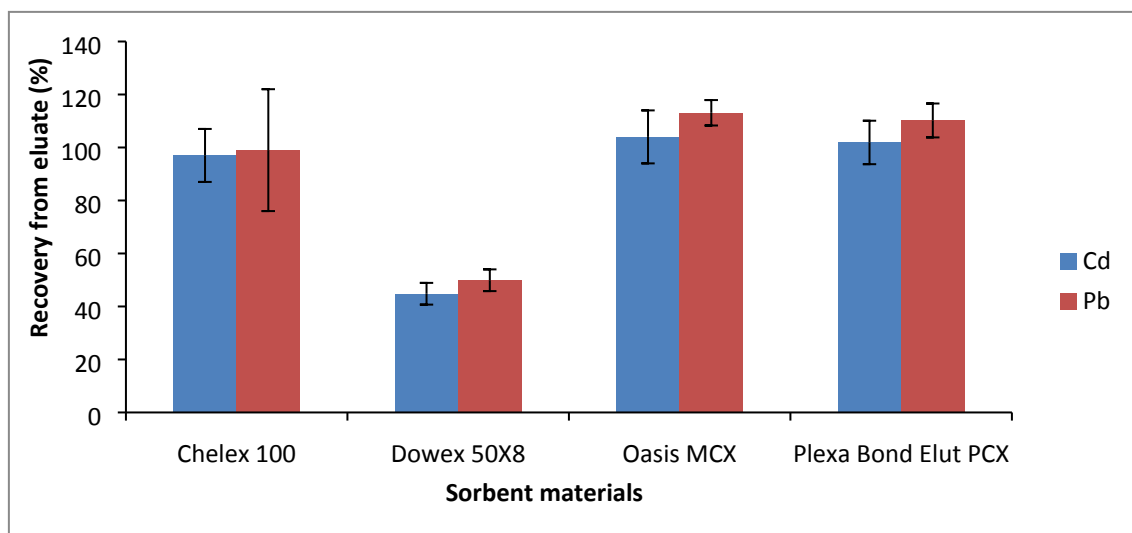
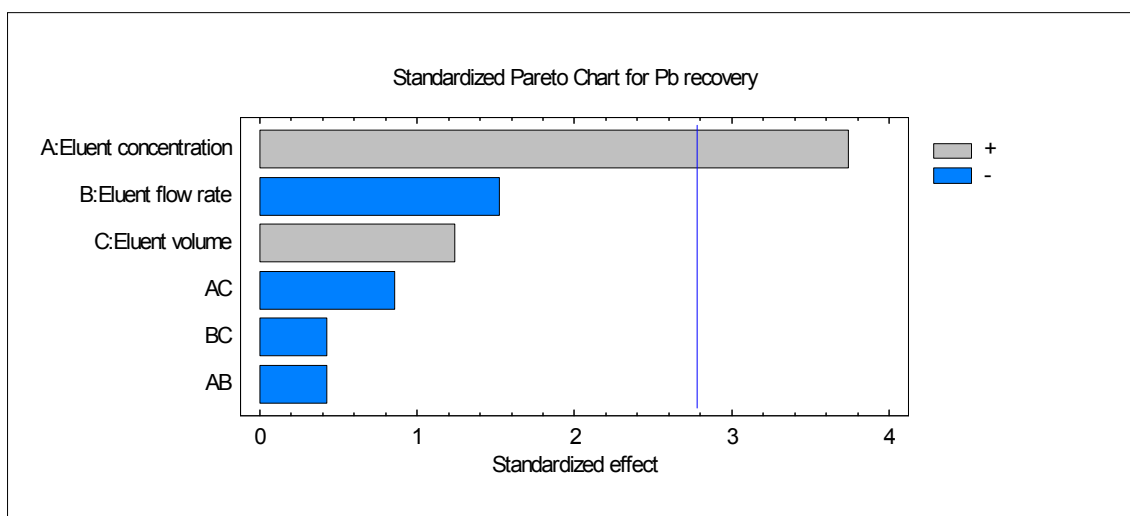


Figure S2. a) Pareto charts of standardized effects for Pb ($\alpha=0.05$). b) Pareto charts of standardized effects for Cd ($\alpha=0.05$). Variables: (A) Eluent concentration; (B) Eluent flow rate; (C) Eluent volume. Eluent flow rate: 1.0-3.0 mol L⁻¹; eluent flow rate: 8-20 μ L s⁻¹; eluent volume: 100-600 μ L.

a)



b)

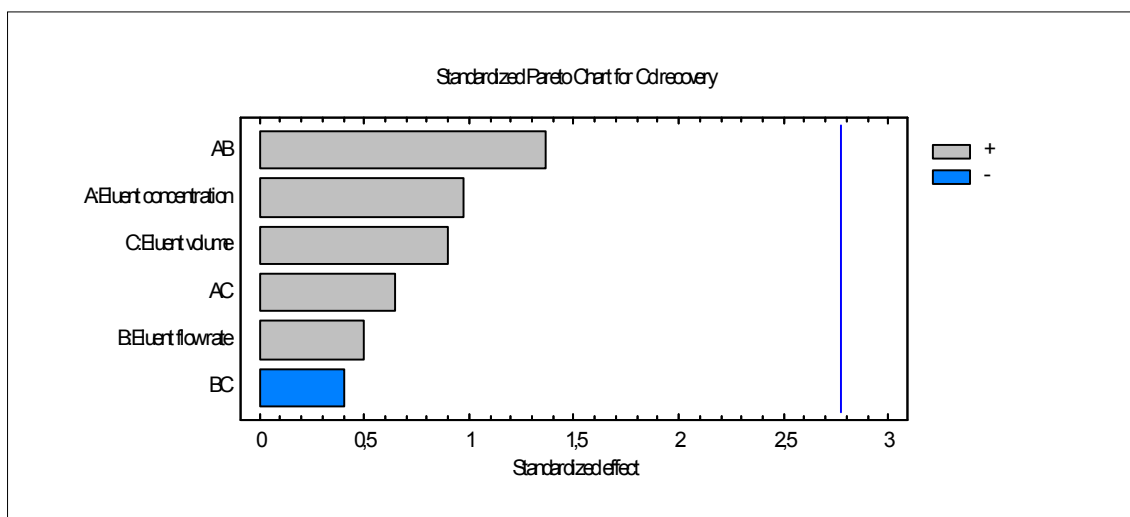


Figure S3. Smoothed readouts for on-line analysis of lead in five honey samples (H1-H5) at two spike concentration levels and calibration standards. Sample 2 (H2) is contaminated by Pb at a level above MAC. Note that the calibration graph in Table 1 refers to raw (unsmoothed) data as obtained by ICP-AES.

