A SOLID-SPIKING MATRIX MATCHED CALIBRATION STRATEGY FOR SIMULTANEOUS DETERMINATION OF CADMIUM AND CHROMIUM IN SEDIMENTS BY ISOTOPE DILUTION LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Appendix A. Supplementary data

Section S1. Preparation of the isotopically-enriched solid spike and the isotope-diluted blend samples and pellets.

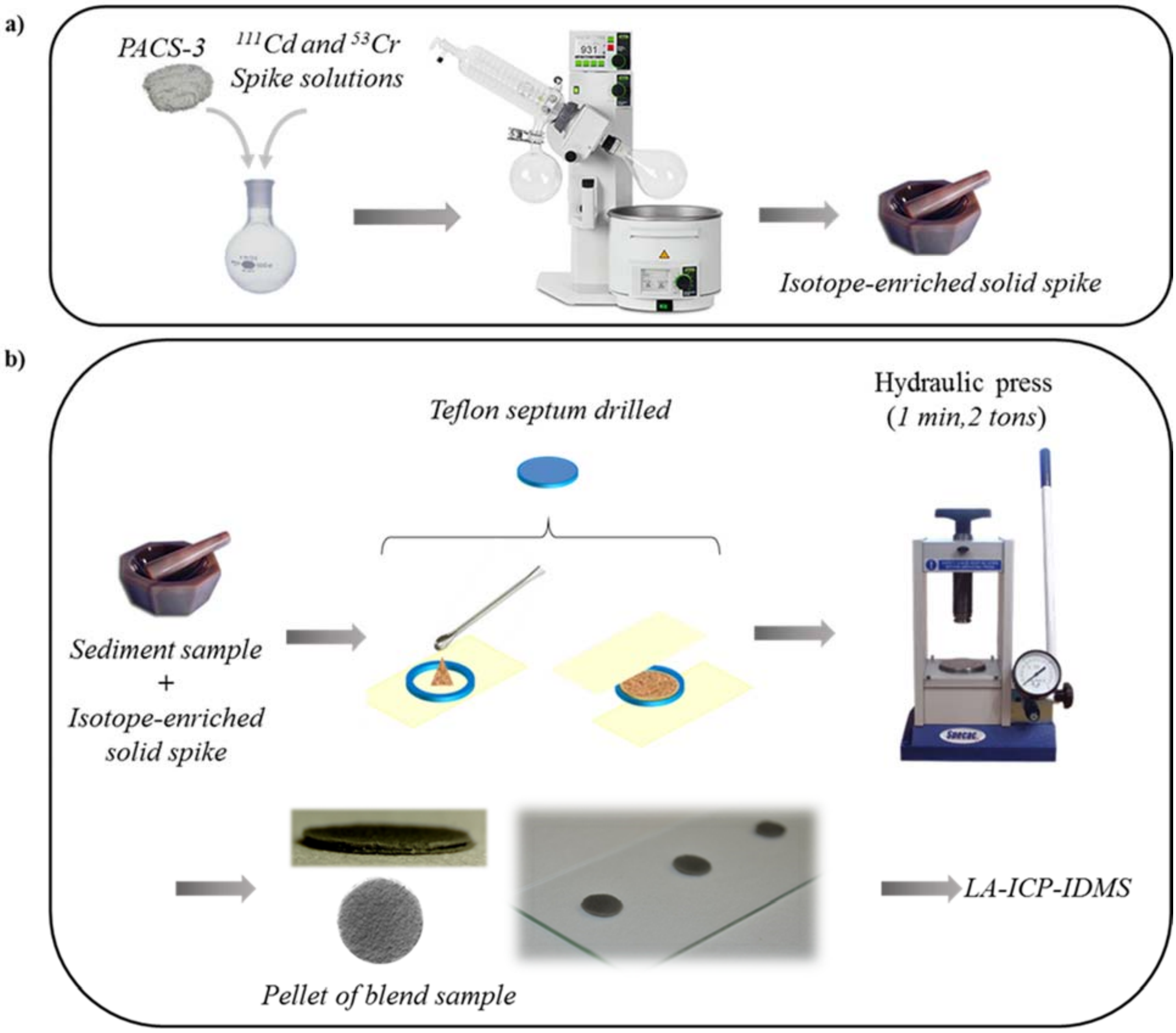


Figure S1. Operational processes for the preparation of: (a) the isotopically-enriched solid spike, (b) the isotope-diluted blend samples and pellets.

Section S2. Corrections on signal intensities and isotope ratios

Corrections on intensities (dead time, background, normalization and isobaric interferences) and on isotope ratios (mass bias) were performed using an equation which resulted from the combination of the individual ones (Table S1). As an example the equation utilized to obtain the corrected isotope ratios for Cd is presented (Equation S1).

Table S1. Equations applied for corrections on intensities and isotope ratios.

Equations applied on intensities
Correction for dead time $I_{DTcorr} = I_{meas} / (1 - I_{meas} \cdot \tau(s))$
Correction for instrumental background $I_{BG\_corr} = I_{meas} - I_{BG}$
Correction for isobaric interferences on Cd $I_{int\ corr} = I_{meas} - (f_{int} \cdot I_{meas\ int})$; $f_{int} = R_{meas\ int}$
Normalization $I_{norm} = I_{corr} / I_{meas}{}^{28}Si$
Ecuations applied on isotope ratios
Correction for mass bias (bracketing approach) $K = [\ (R_{nat\text{-}theo} / R_{nat\text{-}meas})_1 + (R_{nat\text{-}theo} / R_{nat\text{-}meas})_2] / 2$; $R_{K\ corr} = K \cdot R_{meas}$

Parameter

I_{meas}: Measured intensity, *counts s^{-1}*.	*f_{int}:* correction factor.
τ: dead time, *s*.	*R:* isotope ratio.
BG: instrumental background.	*Norm:* normalized.
DT corr: corrected for dead time.	*K:* mass discrimination factor.
BG corr: corrected for instrumental background	*Nat:* natural isotopic composition.
Int: isobaric interference.	*K corr:* corrected for mass discrimination factor.

Equation S1

$$R_{corr} = \frac{R_{meas} \cdot \left(1 - \tau \cdot \left(\left(\frac{I_{meas}{}^{114}\mathrm{Cd}}{I_{meas}{}^{28}\mathrm{Si}}\right) - \left(\left(\frac{A_{nat}{}^{114}\mathrm{Sn}}{A_{nat}{}^{118}\mathrm{Sn}}\right) \cdot \left(\frac{I_{meas}{}^{118}\mathrm{Sn}}{I_{meas}{}^{28}\mathrm{Si}}\right)\right)\right)\right)}{\left(1 - \tau \cdot \left(\frac{I_{meas}{}^{111}\mathrm{Cd}}{I_{meas}{}^{28}\mathrm{Si}}\right)\right)} \cdot \left(\frac{\left(R_{nat}^{theo}\left({}^{114}Cd/{}^{111}Cd\right) \big/ R_{nat}^{exp-initial}\right) + \left(R_{nat}^{theo}\left({}^{114}Cd/{}^{111}Cd\right) \big/ R_{nat}^{exp-end}\right)}{2}\right)$$

Section S3. Isotope dilution equation

$$C_s = C_{sp} \frac{m_{sp}}{m_s} \frac{M_s}{M_{sp}} \frac{A_{sp}^b}{A_s^a} \left(\frac{R_m - R_{sp}}{1 - R_m R_s}\right) \qquad \text{(**Equation S2**)}$$

C_s: mass fraction of element in the sample.

C_{sp}: mass fraction of element in the spike.

m_{sp}: mass of spike.

m_s: mass of sample.

M_s: atomic weight of element in the sample.

M_{sp}: atomic weight of element in the spike.

$A^b{}_{sp}$: abundance of the most abundant isotope in the spike.

$A^a{}_s$: abundance of the most abundant isotope in the sample.

R_m: measured isotope ratio (a/b) in the blend.

R_{sp}: isotope ratio (a/b) in the spike.

R_s: isotope ratio (b/a) in the sample.

Section S4. Multivariate study of the laser ablation process

The variables included in the 8-trial Plackett–Burman experimental design were: (A) laser energy (50 – 80 %), (C) spot diameter (40 – 110 µm), (E) repetition rate (5 – 20 Hz) and (F) scan velocity (1 – 10 µm s^{-1}). Three dummy variables (B, D, G) were included to make the number of variables equal to 7. The variables were coded to simplify the study of potential interactions between them.

Table S2. Experimental design for the variables studied in the ablation process.

Experiment	Variables							Normalized signal	
	A	B	C	D	E	F	G	^{114}Cd	^{52}Cr
1	80	+	110	-	20	1	-	$5.58\cdot10^{-6}$	$5.03\cdot10^{-4}$
2	50	+	110	+	5	10	-	$8.89\cdot10^{-6}$	$9.95\cdot10^{-4}$
3	50	-	110	+	20	1	+	$6.25\cdot10^{-6}$	$5.66\cdot10^{-4}$
4	80	-	40	+	20	10	-	$8.60\cdot10^{-6}$	$7.14\cdot10^{-4}$
5	50	+	40	-	20	10	+	$7.85\cdot10^{-6}$	$9.38\cdot10^{-4}$
6	80	-	110	-	5	10	+	$8.57\cdot10^{-6}$	$8.51\cdot10^{-4}$
7	80	+	40	+	5	1	+	$7.13\cdot10^{-6}$	$6.20\cdot10^{-4}$
8	50	-	40	-	5	1	-	$8.08\cdot10^{-6}$	$9.45\cdot10^{-4}$

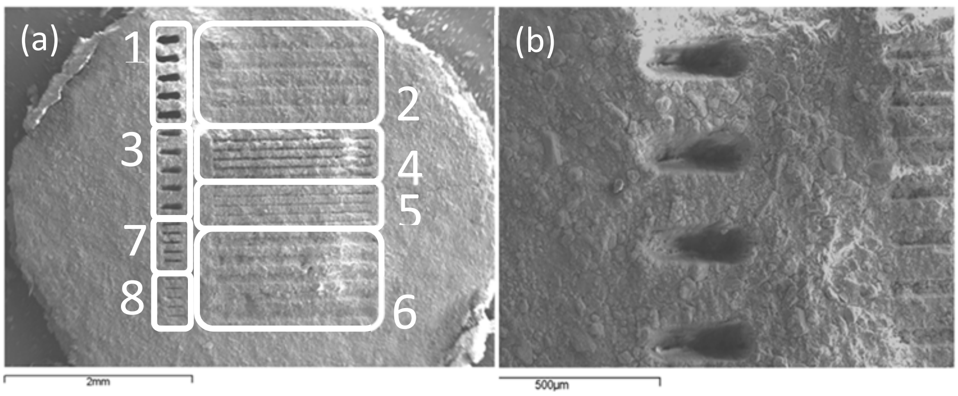


Figure S2. Scanning electron microscopy (SEM) images of: (a) the whole pellet submitted to the conditions of the experimental design (numbers correspond to the experiments); (b) detail of the ablation lines produced in experiment #1.

Section S5. Study of the minimum number of lines to be ablated per pellet

i) Solid spike

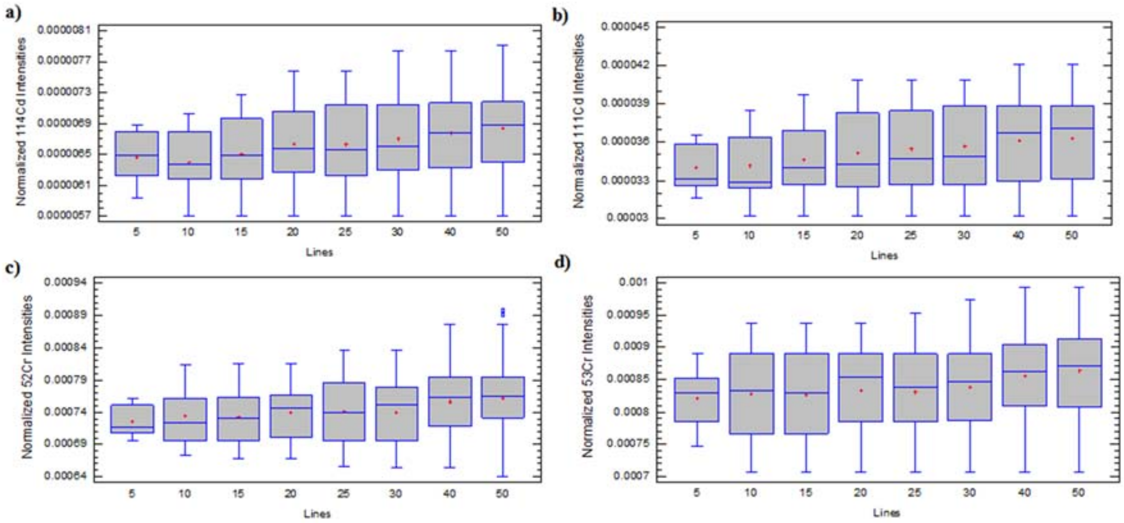


Figure S3. Box-and-Wisker plots (line groups from 5 to 50) obtained for the normalized signals of (a) ^{114}Cd, (b) ^{111}Cd, (c) ^{52}Cr and (d) ^{53}Cr measured from the solid spike synthetized using rotary evaporator.

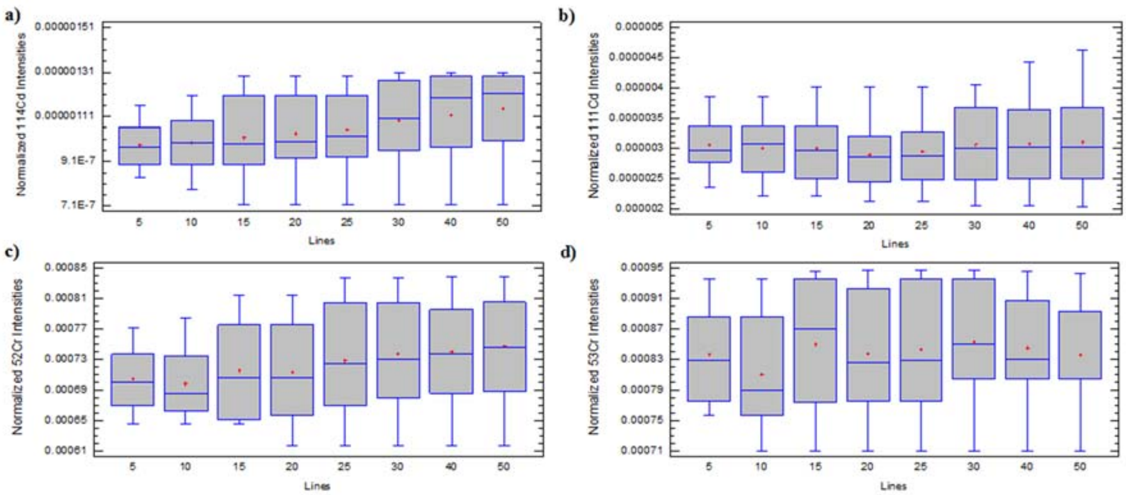
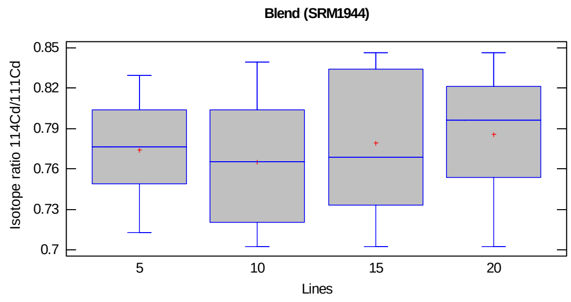


Figure S4. Box-and-Wisker plots (line groups from 5 to 50) obtained for the normalized signals of (a) ^{114}Cd, (b) ^{111}Cd, (c) ^{52}Cr and (d) ^{53}Cr measured from the solid spike synthetized using freeze-drier.

ii) Isotopically enriched blends prepared from reference sediments

a)



b)

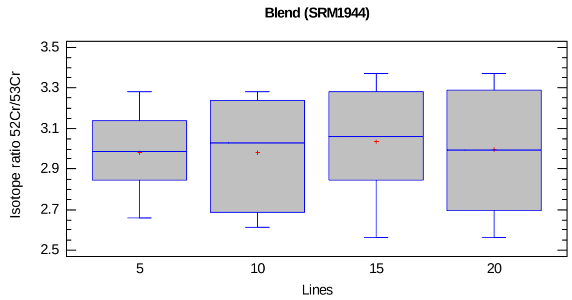
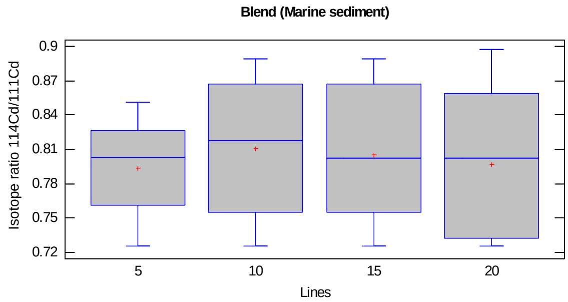


Figure S5. Box-and-Wisker plots (line groups from 5 to 20) obtained for the isotope ratios of Cd (a) and Cr (b) measured from an isotopically enriched blend of reference sediment SRM 1944.

iii) Isotopically enriched blends prepared from sediment samples

a)



b)

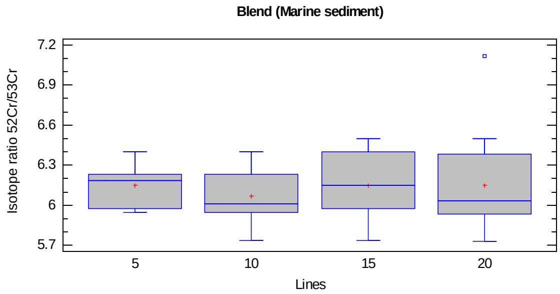


Figure S6. Box-and-Wisker plots (line groups from 5 to 20) obtained for the isotope ratios of Cd (a) and Cr (b) measured from an isotopically enriched blend of a sediment sample.

S6. Uncertainty estimation

The uncertainty associated to the isotope ratio measurements was determined taking into account the corrections performed on intensities (dead time, background, normalization and isobaric interferences) and on isotope ratios (mass bias). As it was mentioned in Section S1, a unique equation (Equation S1 for Cd) was applied which was obtained from the combination of the individual ones (Table S1). The uncertainty budgets associated to these corrections are shown in Table S3 (for Cd in PACS-3) and Table S4 (for Cr in SRM 1944).

Table S3. Uncertainty budget for the measured isotope ratios of Cd in PACS-3 corrected for dead time, isobaric interferences and mass discrimination.

Parameter	Unit	Value	Standard uncertainty	Index (%)*
R_{meas}	-	0.5467	0.0237	88.7
T	s	$35 \cdot 10^{-9}$	$707 \cdot 10^{-12}$	0.0
I_{meas} ($^{114}Cd/^{28}Si$)	cps	$13.875 \cdot 10^{-6}$	$417 \cdot 10^{-9}$	0.0
I_{meas} ($^{118}Sn/^{28}Si$)	cps	$229.0 \cdot 10^{-6}$	$10.9 \cdot 10^{-6}$	0.0
I_{meas} ($^{111}Cd/^{28}Si$)	cps	$26.68 \cdot 10^{-6}$	$2.48 \cdot 10^{-6}$	0.0
A_{nat} ^{111}Cd**	u	0.127950	$405 \cdot 10^{-6}$	0.0
A_{nat} ^{114}Cd**	u	0.287540	$60 \cdot 10^{-6}$	0.0
$R_{nat}^{exp\text{-}ini}$	-	2.1968	0.0561	8.0
$R_{nat}^{exp\text{-}end}$	-	2.2640	0.0377	3.2
$\mathbf{R_{corr}}$	-	0.551	0.0253	

** Represents the percentage contribution to the square sum of variances.*
*** To calculate $R_{nat}^{theo}(^{114}Cd/^{111}Cd)$.*

Table S4. Uncertainty budget for the measured isotope ratios of Cr in SRM 1944 corrected for dead time, isobaric interferences and mass discrimination.

Parameter	Unit	Value	Standard uncertainty	Index (%)*
R_{meas}	-	2.812	0.258	98.5
τ	s	$35 \cdot 10^{-9}$	$707 \cdot 10^{-12}$	0.0
I_{meas} ($^{52}Cr/^{28}Si$)	cps	201.8	38.0	0.0
I_{meas} ($^{53}Cr/^{28}Si$)	cps	63.33	5.93	0.0
A_{nat} ^{52}Cr**	u	0.8378950	$58.5 \cdot 10^{-6}$	0.0
A_{nat} ^{53}Cr**	u	0.0950060	$55.0 \cdot 10^{-6}$	0.0
$R_{nat}^{exp\text{-}ini}$	-	8.8470	0.0803	0.2
$R_{nat}^{exp\text{-}end}$	-	8.712	0.178	1.2
$\mathbf{R_{corr}}$	-	2.825	0.261	

** Represents the percentage contribution to the square sum of variances.*
*** To calculate $R_{nat}^{theo}(^{52}Cr/^{53}Cr)$.*