Supplementary Information

Combination of Multi-Energy Calibration (MEC) and Laser-Induced Breakdown Spectroscopy (LIBS) for Dietary Supplements Analysis and Determination of Ca, Mg and K

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Table S1. Microwave heating program applied for sample mineralization

Step	Power / W	Temperature / ºC	Ramp time / min	Holding time / min
1	1260	120	5	5
2	1260	160	5	5
3	1260	230	5	10

Table S2. ICP OES instrumental conditions to obtain reference values for Ca, K and Mg

Parameter	Operational condition
Integration time for low emission line / s	15
Integration time for high emission line / s	5
Sample introduction flow rate / (mL min^{-1})	4.2
Sample flow rate during the analyses / (mL min^{-1})	2.1
Pump stabilization time / s	5
Radio frequency applied power / W	1150
Auxiliary gas flow rate / (L min^{-1})	0.5
Nebulization gas flow rate / (L min^{-1})	0.5
Cooling gas flow rate / (L min^{-1})	12
Lines for Ca, K and Mg on axial and radial view / nm	Ca (II 393.366), K (I 769.896) and Mg (II 280.270)

I and II: atomic and ionic emission lines, respectively.

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Table S3. Figures of merit for the LIBS analysis using one-point gravimetric standard addition calibration (OP GSA)

	Ca				K				Mg			
Sample	λ / nm	RSD / %	Trueness / %	Ratio[a]	λ / nm	RSD / %	Trueness / %	Ratio[a]	λ / nm	RSD / %	Trueness / %	Ratio[a]
S1	λ1(393.36)	29	94	16	λ1(766.49)	46	196	–	λ2 (383.829)	9	45	–
S2		13	87	24		–141	–211	–		51	28	–
S3		3	110	64		8	111	44		82	24	–
S4		4	99	41		–43	–320	–		6	46	–
S5		15	83	87		19	105	6		14	52	–
S6		3	82	83		36	194	–		12	26	–
S1	λ3 (317.93)	29	34	–	λ2(769.896)	31	116	–	λ3 (383.23)	14	35	–
S2		17	42	–		–161	–170	–		35	23	–
S3		7	39	–		12	97	–		21	32	–
S4		14	35	–		–46	–322	–		16	40	–
S5		17	36	–		21	92	–		7	56	–
S6		3	32	–		39	206	–		22	23	–
S1	λ4 (373.687)	20	27	–	–	–	–	–	λ4 (279.55)	4	107	8919
S2		14	49	–		–	–	–		415	49	2
S3		7	46	–		–	–	–		6	87	539
S4		5	83	–		–	–	–		6	82	462
S5		20	45	–		–	–	–		6	98	612
S6		3	31	–		–	–	–		8	108	340
S1	λ6 (370.603)	21	26	–	–	–	–	–	λ6 (279.79)	4	107	–
S2		14	47	–		–	–	–		322	52	–
S3		11	50	–		–	–	–		6	87	–
S4		30	49	–		–	–	–		6	82	–
S5		10	43	–		–	–	–		6	97	–
S6		6	34	–		–	–	–		11	107	–
S1	λ7 (422.673)	23	71	–	–	–	–	–	λ8 (285.21)	4	124	–
S2		14	98	–		–	–	–		–195	–1	–
S3		4	134	–		–	–	–		7	78	–
S4		4	135	–		–	–	–		7	62	–
S5		9	68	–		–	–	–		7	62	–
S6		4	95	–		–	–	–		9	66	–

[a]Ratio of $F_{calculated}$ / $F_{tabulated}$. RSD: relative standard deviation.

Calculation of the uncertainty

In this part of the Supplementary Information, we will use an example to explain how to calculate the uncertainty slope of the linear model and how to propagate this value to the final results.

The first step is the organization of the matrices. In this example, we will use replicate number 2 for sample S1 and for Ca determination. As five emission lines were used (see Figure 2a for more details), an **X** matrix containing five rows and two columns is need. The first column contains the Ca signal intensity for the five emission lines for pellet 2 (sample + stock mixture, see Figure 1), and is used to calculate the slope (b_1), and the second column "ones" to calculate the intercept (b_0). The coefficients (b_1 and b_0) are calculated according to:

$$b = (X^t X)^{-1} \times X^t y \qquad \text{(S1)}$$

where y is the Ca signal intensity for pellet 1 (sample + cellulose, see Figure 1).
The error for each coefficient is calculated according to:

$$\text{error} = \sqrt{(MS_{residue}(X^t X)^{-1})} \qquad \text{(S2)}$$

where $MS_{residue}$ is the mean of squares of the residues.
The uncertainty for the coefficients will be:

$$\text{uncertainties} = \text{error} \times t \qquad \text{(S3)}$$

where t value was selected with 95% of confidence.
In the specific case of the above-mentioned sample, the slope (b_1) value was 0.503 and the uncertainty was 0.037.
The relative uncertainty was calculated according to:

$$\text{Relative uncertainty} = \frac{0.0369}{0.5028} = 0.0735 \qquad \text{(S4)}$$

These calculations should be applied to all the replicates and the propagated relative uncertainty was calculated using the equation S5.

$$\text{relative } \sigma = \sqrt{\text{relative } \sigma 1^2 + \text{relative } \sigma 2^2 + \text{relative } \sigma 3^2} \qquad \text{(S5)}$$

where relative σ is the propagated relative uncertainty.
These calculations were repeated for all samples and the final results are presented in Table 2.