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Calibration strategies for the direct determination of Ca, K, and Mg in commercial samples of powdered milk and solid dietary supplements using laser-induced breakdown spectroscopy (LIBS)

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ABSTRACT

This study describes the application of laser-induced breakdown spectroscopy (LIBS) for the direct determination of Ca, K and Mg in powdered milk and solid dietary supplements. The following two calibration strategies were applied: (i) use of the samples to calculate calibration models (milk) and (ii) use of sample mixtures (supplements) to obtain a calibration curve. In both cases, reference values obtained from inductively coupled plasma optical emission spectroscopy (ICP OES) after acid digestion were used. The emission line selection from LIBS spectra was accomplished by analysing the regression coefficients of partial least squares (PLS) regression models, and wavelengths of 534.947, 766.490 and 285.213 nm were chosen for Ca, K and Mg, respectively. In the case of the determination of Ca in supplements, it was necessary to perform a dilution (10-fold) of the standards and samples to minimize matrix interference. The average accuracy for powdered milk ranged from 60% to 168% for Ca, 77% to 152% for K and 76% to 131% for Mg. In the case of dietary supplements, standard error of prediction (SEP) varied from 295 (Mg) to 3782 mg kg^{-1} (Ca). The proposed method presented an analytical frequency of around 60 samples per hour and the step of sample manipulation was drastically reduced, with no generation of toxic chemical residues.

1. Introduction

An equilibrated and healthy diet includes a large portion of chemical components essential for the proper physiological functions of the human body. Mineral elements, as Ca, K, Mg, and Na (macro elements), Cr, Cu, Fe, Mn, Se, and Zn (micro and trace elements) are generally found in a wide range of foods (Belitz, Grosch, & Schieberle, 2009). Calcium is involved in several processes, such as blood coagulation, muscular contraction and bone formation (Allgrove, 2003). Magnesium is a cofactor of enzymatic reactions (Barbagallo & Dominguez, 2007), and K participates in intracellular osmolality (Ekmekcioglu, Elmadfa, Meyer, & Moeslinger, 2016). A daily dose of these elements is important for the human body. On the other hand, this does not always occur, then fortified foods as powdered milk and solid dietary supplements can become an option, due to the special needs of some people, such as pregnancy and children with a restrictive diet. Powdered milk and solid dietary supplements contain a range of essential elements responsible for the health and child growth, being necessary a fast and reliable analytical method for quality control.

Traditional analytical techniques, such as inductively coupled plasma optical emission spectrometry (ICP OES), flame atomic absorption spectrometry (FAAS) and ICP-mass spectrometry (ICP-MS) have been applied for the quantification of several elements, but generally require a pre-treatment to convert the solid sample to an aqueous homogeneous solution. During the analytical sequence, errors can be introduced due to the manipulation that reduces analytical frequency and generate residues (Chinni, Cremers, & Multari, 2010). Other analytical strategies include analysis of samples as suspension using ICP OES or FAAS (Asfaw & Wibetoe, 2005; Sola-Larrañaga & Navarro-Blasco, 2009).

Analytical techniques such as laser-induced breakdown spectroscopy (LIBS) has been used in several applications related to food samples, like classification of red wine (Moncayo, Rosales, Izquierdo-Hornillos, Anzano, & Caceres, 2016), identification of meat species (Bilge, Velioglu, Sezer, Eseller, & Boyaci, 2016), and boron determination in

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meatballs (Hedwig et al., 2016). For those studies, LIBS advantages include: direct analysis with minimal or no sample preparation, high analytical frequency, the use of a small quantities of sample (typically <100 mg), and multielement capability (advantage if compared with FAAS) (Pasquini, Cortez, Silva, & Gonzaga, 2007). Spectra obtained from LIBS technique present several emission lines allowing a fast sample inspection and the application of chemometrics tools for calibration and classification purposes (Neiva, Chagas Jacinto, Mello de Alencar, Esteves, & Pereira-Filho, 2016). For calibration, several regression models, employing univariate or even, multivariate analysis are possible, using for instance partial least squares (PLS) (El Haddad, Canioni, & Bousquet, 2014; Hernández-García et al., 2017).

On the other hand, disadvantages related to method calibration are observed, because the ablation process involves some μg of samples and it is not available reference material with certified values concentration for masses in the range of μg or ng, for example (Andrade & Pereira-Filho, 2016; Andrade, Pereira-Filho, & Konieczynski, 2016; Augusto, Sperança, & Andrade, 2016). In addition, direct analysis presented some difficulties in solid analysis, such as the reproduction of the data related to the process of ablation, formation of the plasma, microheterogeneity and matrix effects. These issues can compromise quantitative analysis (Mukhono, Angeyo, Dehayem-Kamadjeu, & Kaduki, 2013).

The goal of this study is to present a simple and fast method for the direct analysis of powdered samples of milk and solid dietary supplements using LIBS and determine the contents of three major constituents: Ca, Mg and K. Univariate and multivariate analysis strategies were tested and combined to build regression models. Some procedures, for instance sample dilution, were used to minimize matrix effects and achieve results with satisfactory accuracy, when solid samples are directly measured.

2. Materials and methods

2.1. Reagents, sample description and preparation for ICP OES determinations

All reagents were of analytical grade or higher purity. Deionized water (18.2 ΩM cm resistivity) produced by a Milli-Q® Plus Total Water System (Millipore Corp., Bedford, MA, USA) was used to prepare all of the solutions. Prior to use, all glassware and polypropylene flasks were washed with soap, soaked in 10% v/v HNO_3 for 24 h, rinsed with deionized water and dried to ensure that no contamination occurred. The multi-element standard solutions were prepared daily from 10,000 mg L^{-1} Ca along with 1000 mg L^{-1} K and Mg stock solutions (Qhemis, Jundiaí, SP, Brazil) and used for construction of the calibration curve.

Powdered samples of milk (M) and solid dietary supplements (S) were purchased at the local markets of São Carlos (São Paulo State, Brazil). Fifteen powdered milk samples (M1–M15), intended to be consumed by adults and children, and 8 samples of solid dietary supplements (S1–S8), intended only for children, were analysed without any prior treatment by LIBS. The selected samples were from different manufacturers and flavours (case of dietary supplements) to introduce a high sample variability in the calibration models proposed. In the case of powdered milk, skimmed, whole and with vegetable oils samples were selected. To establish regression models, concentrations of Ca, K and Mg, obtained with ICP OES (iCAP 6000, Thermo Scientific, Waltham, MA, USA), were used as reference values ($n = 3$), after acid digestion for mineralization of the samples. This instrument allows sequential analytical signal collection using both axial and radial views. Argon (99.996%, White Martins-Praxair, Sertãozinho, SP, Brazil) was used for all ICP OES measurements. ICP OES operational parameters and the emission lines used are shown in Table 1.

A microwave system (Speedwave Four, Berghof, Eningen, Germany) was employed to mineralize the samples for further ICP OES determinations. The microwave system was equipped with twelve high pressure TFM (a copolymer of tetrafluoroethylene and a small amount of the perfluoro(propyl vinyl ether)) vessels (100 mL, 230 °C and 70 bar), and the microwave heating program is shown in Table 2. In the case of powdered milk samples, 250 mg were mixed with 6 mL of HNO_3 (2 mol L^{-1}) (Synth, Diadema, SP, Brazil) and 3 mL of H_2O_2 (30% w/w) (Synth). This digestion mixture was already proposed by Bizzi et al. (2014). For solid dietary supplements only 6 mL of HNO_3 (2 mol L^{-1}) was employed and in both cases, no residues were observed in the resultant digested solution. The concentrated HNO_3 was previously purified using a sub-boiling distillation system Distillacid™ BSB-939-IR (Berghof, Eningen, Germany). After digestion, the final volume was adjusted to 14 mL with deionized water.

Table 1
ICP OES instrumental conditions to obtain reference values for Ca, K and Mg.

Parameters	Operational conditions
Integration time for low emission line (s)	5
Integration time for high emission line (s)	5
Sample introduction flow rate (mL min^{-1})	2.1
Sample flow rate during the analyses (mL min^{-1})	2.1
Pump stabilization time (s)	25
Radio frequency applied power (W)	1200
Auxiliary gas flow rate (L min^{-1})	0.25
Nebulization gas flow rate (L min^{-1})	0.83
Cooling gas flow rate (L min^{-1})	16
Lines for Ca, K and Mg on axial and radial view (nm)	Ca (II 317.9), K (I 691.1, I 766.4 and I 769.8) and Mg (II 279.5, II 280.2 and I 285.2)

I: Atomic.
II: Ionic.

2.2. LIBS system

A LIBS system (model J200, Applied Spectra, Fremont, California, USA) with Axiom 2.5 software was used to detect the emission lines of Ca, K and Mg in powdered samples of milk and solid dietary supplements. This instrument is equipped with an ablation chamber and a HEPA air cleaner to purge ablated solid particles. The laser (Nd:YAG) was operated at a fundamental wavelength of 1064 nm, and the maximum energy is 100 mJ in a single laser pulse with an 8 ns duration at a frequency of 10 Hz.

The plasma radiation emission was directly collected by an optical fibre coupled to a 6-channel CCD spectrometer with a spectral window ranging from 186 to 1042 nm. The spectral resolution varies from <0.1 nm in the ultraviolet to visible (UV–Vis) range up to 0.12 nm in the UV and near infrared (NIR) range. In the identification of the emission lines, Aurora software (also from Applied Spectra) was used. As solid samples without any sample preparation were used and in order to perform the measurements, 500 mg pellets were pressed at 10 tons using a hydraulic press. The pellets were introduced in the LIBS system and from 9 to 16 straight line scans, each with 9 mm of length, were applied, and the distance between the lines was 1 mm. Approximately 1000 spectra were recorded for each sample. The operational LIBS data collection parameters were previously optimized using a factorial

Table 2
Microwave heating program applied for sample mineralization.

Step	Power (W)	Temperature (°C)	Ramp time (min)	Hold time (min)
1	1260	120	5	5
2	1260	160	5	5
3	1260	230	5	10

Table 3
Solid calibration mixtures of solid dietary supplements (S) used in the univariate linear models for Ca, K and Mg.

Calibration solid mixture identification	Weight of each sample (g)					Analytes concentration (mg kg^{-1})		
	MC[a]	Mass1	Mass2	Mass3	Mass4	Ca	K	Mg
Blank	4.000	0.000	0.000	0.000	0.000	0	0	0
Standard 1	2.790	0.000	0.723	0.480	0.000	3900	2195	426
Standard 2	0.147	0.885	0.848	0.519	1.615	6330	7942	857
Standard 3	0.115	0.334	2.353	0.752	0.461	10,980	8060	1169
Standard 4	0.000	0.000	4.000	0.000	0.000	14,067	9128	1229
Standard 5	0.000	4.004	0.000	0.000	0.000	2890	10,318	1006
Standard 6	0.000	0.000	0.000	4.018	0.000	11,340	5720	1708
Standard 7	0.000	0.000	0.000	0.000	4.015	3121	2637	385

[a] Microcrystalline cellulose.

design, and the values selected were a delay time of 0.5 μs, a spot size of 50 μm, an energy of 50 mJ, a scan speed of 1 mm s^{-1} and a laser repetition rate of 10 Hz. Three pellets were prepared for each sample ($n = 3$) in order to evaluate the errors of the proposed method.

2.3. Calibration strategies

As previously mentioned, calibration using solid samples is a challenging task for any analytical method that performs direct measurements. In this case, two calibration strategies were investigated and implemented in this study.

To overcome some drawbacks of LIBS, the normalization of the data and instrumental parameters optimization (Klus et al., 2016; Pořízka et al., 2016) can be performed. In this sense, 12 types of normalization modes (Castro & Pereira-Filho, 2016) were tested in both cases (milk and solid dietary supplement). The goal of the normalization is to minimize problems related to sample microheterogeneity and signal fluctuation during data acquisition. In this sense, normalization by norm (Euclidean vector), signal area and height and carbon emission lines (used as internal standard) were evaluated for each type of sample.

For data set organization, Microsoft Excel™ was used. A critical step in the calibration is the selection of the most appropriate emission lines (free of spectral interference) to perform the calculations. A strategy used was in a first step, calculate PLS models using the entire peak profile (12,288 variables, from 186 to 1042 nm), the data set was mean-centred, and cross validation (leave-one-out, one by one sample) was used to identify the proper number of latent variables (LV). Reference concentrations obtained after microwave digestion and ICP OES determinations, were used as dependent variables (matrix Y). After inspecting the PLS regression vectors, those emission lines for Ca, K and Mg with high values and/or free of spectral interference were selected to calculate further univariate models using both signals, area and height.

Matlab (MathWorks, Natick, Massachusetts, USA) version 2010, was used for the normalization of the spectra and, both signals - area and height calculation, for the selected emission lines, and Pirouette Multivariate Data Analysis software, version 4.5 (Infometrix, Bothell, WA, USA), was used to calculate the PLS calibration models.

In the case of powdered milk, the 15 samples were pressed (10 tons in.$^{-1}$, 12 mm diameter) and 10 samples were applied to calculate univariate calibration models (Ca, K and Mg). The obtained models were tested on the remaining 5 samples.

For the solid dietary supplements, a calibration curve with the same matrix as the samples was constructed. In this case, microcrystalline cellulose (P.A., Synth) was used as a blank and mixed with different samples amount to build a calibration curve. This calibration curve was organized by mixing different proportions of the samples targeting a wide range of concentrations for the analytes under investigation. A calibration curve with 8 points was prepared by mixing 4 samples that presented the highest and lowest concentration values for Ca, K and Mg. The proportions of the samples in the mixture for each point and the final analytes concentration are shown in Table 3.

Only 500 mg of each mixture was used to prepare the pellets and 3 replicates were organized for each standard. The use of mixtures of

Table 4
Reference (ICP OES, $n = 3$), determined values (LIBS, $n = 3$), and accuracy for powered milk (M) and solid dietary supplements (S) (concentrations in mg kg^{-1}).

Sample ID	Ca			K			Mg		
	Reference concentration (ICP OES)	Determined concentration (LIBS), I 534.945 nm	Accuracy (%)	Reference concentration (ICP OES)	Determined concentration (LIBS), I 766.490 nm	Accuracy (%)	Reference concentration (ICP OES)	Determined concentration (LIBS), I 285.235 nm	Accuracy (%)
Powdered milk (M), calibration dataset									
M2	4762 ± 136	4493 ± 573	94	7266 ± 1682	6309 ± 422	87	449 ± 10	480 ± 20	107
M3	2759 ± 142	4647 ± 564	168	4227 ± 1173	6438 ± 657	152	545 ± 61	582 ± 38	107
M4	13,482 ± 1100	17,298 ± 1001	128	13,707 ± 516	16,831 ± 2026	123	950 ± 75	963 ± 95	101
M5	4289 ± 117	4414 ± 478	103	6724 ± 1571	6206 ± 427	92	423 ± 9	457 ± 13	108
M6	24,178 ± 2494	23,721 ± 1326	98	14,148 ± 1753	13,305 ± 1170	94	1167 ± 61	1205 ± 59	103
M7	2586 ± 397	1547 ± 357	60	4113 ± 33	4104 ± 703	100	286 ± 69	265 ± 21	92
M9	5164 ± 549	5481 ± 362	106	5976 ± 187	5931 ± 684	99	391 ± 78	402 ± 12	103
M10	2970 ± 442	2575 ± 1230	87	4167 ± 58	3789 ± 522	91	415 ± 90	317 ± 37	76
M12	8880 ± 912	7835 ± 674	88	10,876 ± 1164	8370 ± 660	77	766 ± 54	619 ± 74	81
M14	11,345 ± 458	8404 ± 942	74	8473 ± 1537	8394 ± 1791	99	480 ± 13	582 ± 73	121
Powdered milk (M), validation dataset									
M1	13,032 ± 441	11,287 ± 2051	87	8727 ± 492	7931 ± 675	91	637 ± 24	667 ± 71	105
M8	4788 ± 520	4911 ± 1555	103	5969 ± 28	5034 ± 1209	84	375 ± 75	329 ± 43	88
M11	8997 ± 303	8849 ± 326	98	7086 ± 655	9480 ± 1326	134	495 ± 53	649 ± 25	131
M13	6787 ± 983	4202 ± 605	62	6548 ± 162	5965 ± 411	91	434 ± 72	369 ± 42	85
M15	12,480 ± 1349	8373 ± 732	67	7002 ± 260	7610 ± 600	109	487 ± 65	459 ± 30	94
Dietary supplement (S), prediction dataset									
S1	12,889 ± 206	5300 ± 1173	41	7581 ± 188	5351 ± 239	71	773 ± 17	487 ± 35	63
S2	4374 ± 377	2584 ± 511	60	10,318 ± 270	8436 ± 330	82	693 ± 63	291 ± 12	42
S3	2887 ± 119	1741 ± 521	60	2691 ± 279	1539 ± 485	57	1006 ± 59	778 ± 101	77
S4	10,319 ± 799	6575 ± 1537	64	5721 ± 101	10,041 ± 424	176	1451 ± 225	1546 ± 82	107
S5	11,340 ± 332	10,687 ± 1140	94	2638 ± 68	1664 ± 395	63	1708 ± 160	1655 ± 48	97
S6	3121 ± 125	4807 ± 630	154	3857 ± 145	6721 ± 344	174	385 ± 5	396 ± 13	103
S7	4267 ± 281	3615 ± 730	85	3566 ± 88	2352 ± 985	66	1031 ± 83	986 ± 397	96
S8	14,067 ± 506	9561 ± 1294	68	9128 ± 208	11,359 ± 1134	124	1229 ± 109	681 ± 22	55

samples to generate a calibration curve was a strategy to minimize interference from sample matrix under analysis (Gilon et al., 2011; Lei et al., 2011). Univariate models were established with these 8 calibration points (Table 3), and the predictive ability of the models was tested using 8 external samples (samples S1–S8, prediction dataset).

3. Results and discussion

3.1. ICP OES reference analytical method

As mentioned before, a digestion of all the samples (powered milk and solid dietary supplements) was performed and the solutions were analysed by ICP OES to obtain reference values for Ca, K and Mg. Table 1 presents the emission lines studied in ICP OES instrument in axial and radial views. The emission lines that presented concordant results between axial e radial views were selected and the average of the concentrations ($n = 3$) results was considered as reference values. Table 4 shows the reference values for these elements in powered milk (M) and solid dietary supplements (S).

The selected lines in ICP OES measurements were different for the powered milk and solid dietary supplements. To the mineralized milk were selected the lines: Ca II 317.9 nm, K I 691.1 nm and Mg II 279.5 nm. To the mineralized dietary supplements were selected the lines: Ca II 317.9 nm, K I 766.4 nm and I 769.8 nm and Mg II 279.5 nm, II 280.2 nm and I 285.2 nm.

3.2. Emission line selection in LIBS calibration and powdered milk analysis

To select the emission lines that present signals linearly proportional to the concentrations; firstly, PLS regression vectors were verified. In this evaluation, emission lines free of interferences for Ca, K and Mg were selected. More than 10 emission lines were investigated for each analyte. Fig. 1 shows the regression coefficients for Ca (Fig. 1a), K (Fig. 1b) and Mg (Fig. 1c). For each multivariate calibration models, the selected number of latent variables (LV) were 2, 1 and 2 for Ca, K and Mg, respectively.

Several emission lines were identified with the help of PLS regression coefficients and by means of these individual emission lines from LIBS data, univariate models were calculated using both types of signal information, i.e., the area and height. The lowest standard error of calibration (SEC) was the criteria to select the best lines to comprise the models (Pereira, Pereira-Filho, & Bueno, 2006). SEC values were calculated according to Eq. (1):

$$\mathrm{SEC} = \sqrt{\frac{(y_i - \hat{y}_i)^2}{n-1}} \tag{1}$$

where n is the number of samples and y_i and $\hat{y}_i$ are the reference (ICP OES) and the predicted analytes concentrations, respectively for data set of calibration.

Fig. 2 shows the emission lines selected for Ca I 534.947, K I 766.490 and Mg I 285.213 nm being atomic lines for all, denoted as (I).

The best results were obtained after signal normalization by individual norm and averaged (for Ca), only averaged (for K) and normalized by C I 247.856 nm and later the sum was calculated (for Mg). In the normalization by norm each spectrum was divided by its individual norm (||b||), see Eq. (2):

$$||b|| = \sqrt{signal_1^2 + signal_2^2 + \ldots + signal_n^2} \tag{2}$$

where $signal_n$ is the signal intensity for each emission line (from 186 to 1042 nm). After normalization by norm, each normalized spectrum has norm equals to 1, it means that all spectra have the same size. In the case of normalization by C I 247.856, each signal intensity is divided by C I 247.856 intensity. Later the C I 247.856 signal is equals to 1. After this first step the sum of spectra was calculated. Signals area and height were calculated after baseline offset correction and the proposed univariate models presented R^2 values ranging from 0.7965 (K) to 0.9216 (Ca) when area was considered.

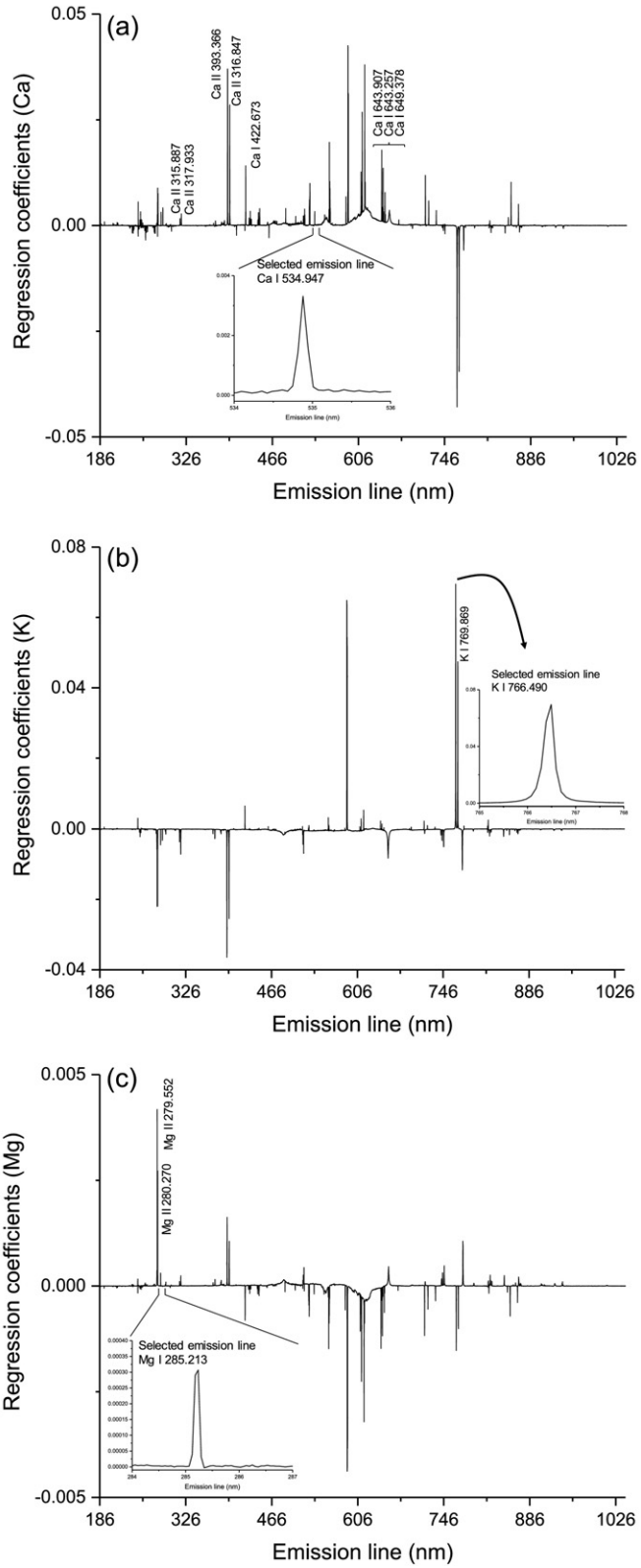

Fig. 1. Regression coefficients for PLS models calculated for Ca (a), K (b) and Mg (c).

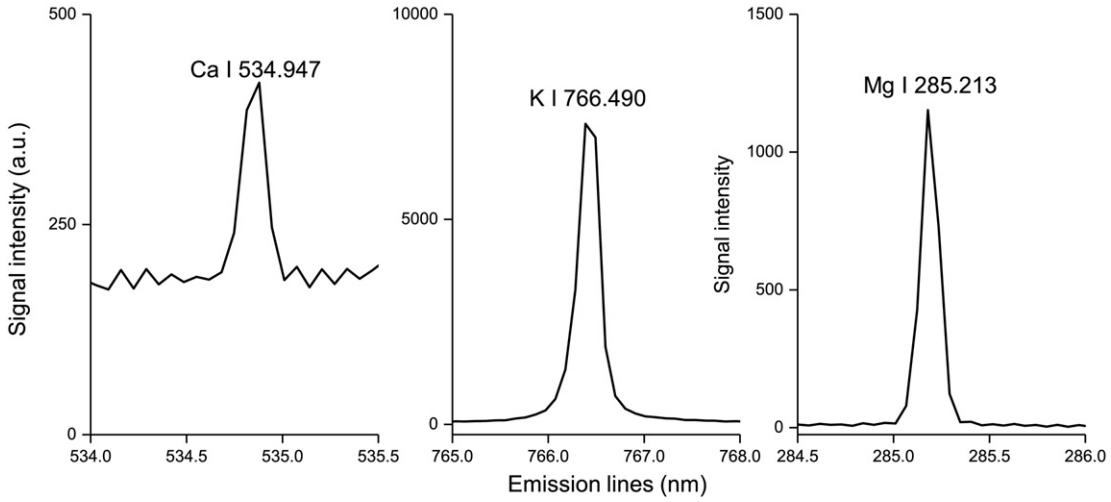

Fig. 2. Emission lines selected for Ca, K and Mg in LIBS univariate models.

The SEC values for Ca, K and Mg were 1895, 1825 and 85 mg kg^{-1}, respectively. In addition, all analytes presented good correlation, when reference and predicted values were compared, with R^2 values varying from 0.2681 (K in validation dataset) to 0.9616 (Ca in calibration dataset). The predicted concentrations and its standard deviation ($n = 3$) are presented in Table 4 and the analytical parameters are shown in Table 5.

The other normalizations presented approximately 5-fold higher SEC values. Surprisingly, normalizations using C emission lines presented suitable SEC value only for Mg, considering the content of C is higher than 90% in this type of samples. This calibration model can be used in the quality control of this type of sample. Fig. 3 shows the reference and predicted concentrations for milk samples for calibration (circles) and validation (squares) datasets. As 3 replicates were prepared average RSD values were 15% for Ca, 12% for K and 8% for Mg. Accuracy was calculated using Eq. (3):

$$\text{Accuracy} = \frac{\hat{y}_i}{y_i} \times 100 \quad (3)$$

where y_i and $\hat{y}_i$ are the reference (ICP OES) and the predicted analyte concentration, respectively.

Sample M2, for instance (see Table 4), presented a Ca reference (ICP OES) and predicted (LIBS) concentration of 4762 ± 136 and 4493 ± 573 mg kg^{-1}, respectively. The accuracy for this samples was 94% ($\frac{4493}{4762} \times 100 = 94\%$).

3.3. Analysis of solid dietary supplement samples

The same emission lines described for powdered milk were used for the solid dietary supplements. However, the strategy used in this part was to establish a calibration curve with external standards prepared by mixing different samples in different proportions with microcrystalline cellulose (see details in Table 3).

Initially, the mixtures described in Table 3 were used, and the concentrations varied from 0 (pure cellulose) to 14,067 for Ca, 0 to 10,318 for K and 0 to 1708 mg kg^{-1} for Mg.

In the case of Ca, several problems related with interference were observed, and the calibration ability of the model was highly compromised in all 12 normalization modes. To overcome this issue, dilution of the samples was performed (Jantzi et al., 2016). All pellets (mixtures for calibration, Table 3 and samples) were diluted 10-fold with microcrystalline cellulose, and the Ca concentration in the standards ranged from 0 to 1407 mg kg^{-1}. This approach was tested to reduce the influence of the matrix on the measurements and improve the predictive ability of the proposed calibration models.

Univariate calibration (linear equation) was calculated for Ca, Mg and K and the normalization modes were tested again. For Ca and Mg normalization by norm presented the best results. In the case of K only average present good results. The univariate models using signal area presented R^2 values from 0.8639 for Mg to 0.9102 for Ca. These univariate models were tested in the 8 samples ($n = 3$) and the predicted values can be shown in Table 4. The RSD values average ranged from 10% for Mg to 19% for Ca. The accuracy of the measurements for Ca varied from 41 to 154%, and the R^2 obtained when reference (ICP OES

Table 5
Analytical parameters for powered milk and solid dietary supplements analysed by LIBS.

Sample dataset	Analyte	SEC (mg kg^{-1})	SEV, powdered milk or SEP, dietary supplement (mg kg^{-1})	R^2 (univariate regression model)	R^2 (reference × predicted)	
					Calibration	Validation
Powdered milk	Ca[a]	1895	2614	0.9216	0.9216	0.6336
	K[b]	1825	1548	0.7965	0.7965	0.2681
	Mg[c]	85	91	0.9087	0.9087	0.6770
Solid dietary supplements	Ca[a]	2137	3782	0.9102	–	0.6394
	K[b]	2027	2510	0.8665	–	0.5804
	Mg[c]	357	295	0.8639	–	0.8172

[a] 534.945 nm (I, atomic line).
[b] 766.490 nm (I, atomic line).
[c] 285.235 nm (I, atomic line).

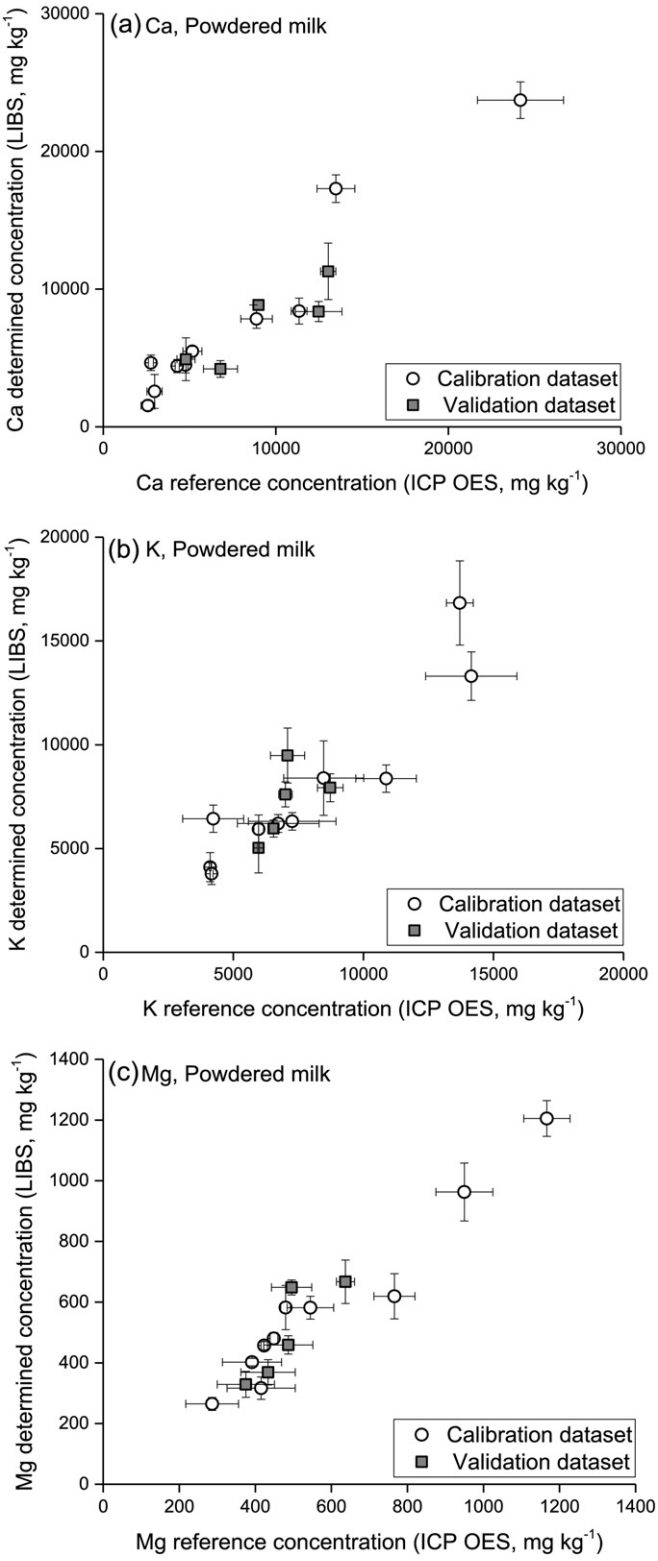

Fig. 3. Reference (ICP OES) and predicted (LIBS) concentrations (mg kg^{-1}) for powdered milk analysis for Ca (a), K (b) and Mg (c) determination.

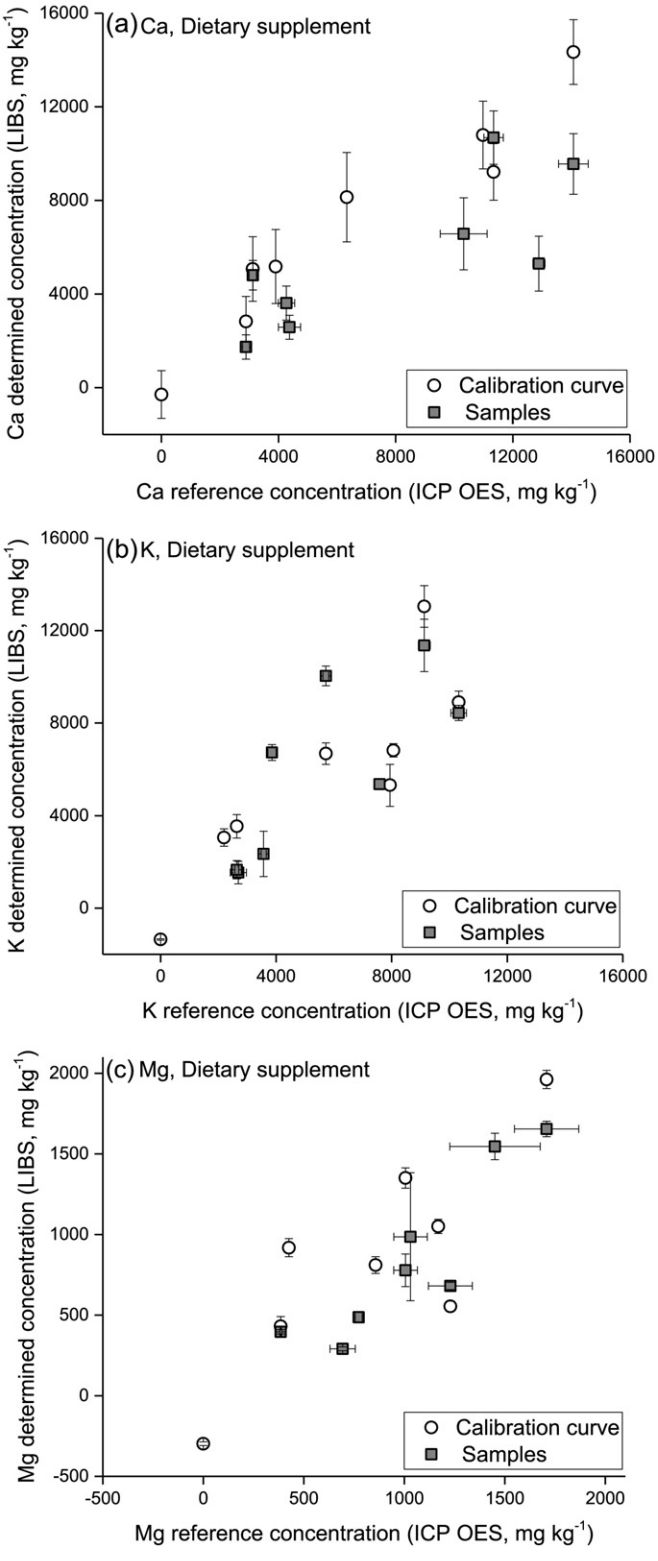

Fig. 4. Reference (ICP OES) and predicted (LIBS) concentrations (mg kg^{-1}) for solid dietary supplement analysis for Ca (a), K (b) and Mg (c) determination.

concentrations) and predicted (LIBS) values were compared was 0.6394. The SEC values ranged from 357 (for Mg) to 2137 mg kg^{-1} (for Ca).

Good concordance was observed for Ca, with the SE of prediction (SEP) equal to 3782 mg kg^{-1}. Accuracy varied from 57 to 176% for K and 42 to 107% for Mg. The SEP values were 2510 and 295 mg kg^{1} for K and Mg, respectively and were calculated according to Eq. (4):

$$SEP = \sqrt{\frac{(y_i - \hat{y}_i)^2}{n-1}} \quad (4)$$

where n is the number of samples and y_i and $\hat{y}_i$ are the reference (ICP OES) and the predicted analyte concentration for data set of prediction, respectively.

Fig. 4 shows the reference and predicted concentrations for solid dietary supplement samples (squares) and calibration (circles) curve.

The analytical frequency of the proposed method is around 60 samples per hour, without chemical toxic waste generated by using solvents and/or acids. The limits of quantification for the proposed LIBS method was calculated considering microcrystalline cellulose as blank and the values ranged from 49 (Mg) to 1955 (Ca) mg kg^{-1}.

4. Conclusions

The proposed method is suitable, fast and can be implemented for the direct determination of Ca, K, and Mg in solid food samples. In the case of Ca, limitations from matrix interference were minimized after dilution of the material using cellulose, case of the supplement samples. It was also concluded that the normalization process of the raw data plays an important role in the quality of the results.

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