Food Analytical Methods (2021) 14:545–551
https://doi.org/10.1007/s12161-020-01904-2

Minimal-Invasive Analytical Method and Data Fusion: an Alternative for Determination of Cu, K, Sr, and Zn in Cocoa Beans

Raimundo Rafael Gamela[1] · Edenir Rodrigues Pereira-Filho[1] · Fabíola Manhas Verbi Pereira[2,3]

Received: 15 October 2020 / Accepted: 21 October 2020 / Published online: 24 October 2020

Abstract

In the present study, a minimal-invasive analytical method for determination of Cu, K, Sr, and Zn in cocoa beans was performed using energy X-ray fluorescence (EDXRF) and laser-induced breakdown spectroscopy (LIBS) combined with multivariate calibration. Partial least squares (PLS) chemometric technique was applied to modeling the data, and inductively coupled plasma optical emission spectrometry (ICP OES) technique was the reference method for the chemical elements concentration levels, after microwave acid mineralization. The figures of merit estimated for Cu, Sr, Zn, and K showed good performance, with acceptable trueness values (85–120%). Data fusion strategy between EDXRF and LIBS data was used to enhance the predictive capability of K. In addition, lower standard error of cross-validation (SECV) (872 mg kg^{-1}) was obtained, showing better performance than those obtained by individual data.

Keywords Chemometrics · Partial least squares · Food samples · Nutrients · Spectroanalytical techniques · Direct solid analysis

Introduction

Elements mass fraction in food matrices have been commonly determined by different spectroanalytical techniques based on plasma, such as inductively coupled plasma optical emission spectrometry (ICP OES) (Villa et al. 2015; Mir-Marqués et al. 2015; Mir-Marqués et al. 2016; Costa et al. 2019a) and inductively coupled plasma-mass spectrometry (ICP-MS) (Chevallier et al. 2015; Mir-Marqués et al. 2016) due to its high sensitivity and multi-elemental capability.

However, these analytical instrumental techniques usually require a sample pre-treatment procedure employing acid mineralization with the help of oxidizing reagents (hydrogen peroxide, for instance). These procedures are most used in the sample preparation, presenting some drawbacks, such as risk of contamination of the samples, low analytical frequency, and use of concentrated acid, which can affect the analytical blank and the accuracy of the results (Korn et al. 2008; Ferreira et al. 2010). All these observations make less attractive the use of acid mineralization for the determination of macro- and micronutrients in food matrices.

Energy dispersive X-ray spectroscopy (EDXRF) is commonly used for metals determination in different matrices, since liquid to solid samples (Pereira et al. 2006; Gupta et al. 2013; Peruchi et al. 2014; Bull et al. 2017; Brito et al. 2017; Andrey et al. 2018; Byers et al. 2019). Aside from direct solid sample analysis, EDXRF is non-destructive, selective and allows simultaneous determination; also has higher frequency, it is simpler in design, and cost less (Kelsey et al. 2016; Oyedotun 2018; Oliveira et al. 2020), which makes it suitable to overcome the drawbacks described previously. EDXRF presents a simple spectrum with few spectral interference possibilities. Some difficulties can be observed to determine light elements, because mostly are transparent to X-rays and the X-ray absorption effect is relatively lower than those presented by heavy elements (Van Grieken and Markowicz 2001).

Another technique commonly used for direct solid analysis is laser-induced breakdown spectroscopy (LIBS). This is a versatile technique that presents several advantages, such as multi-elemental capability and direct solid analysis, and high analytical frequency where hundreds of spectra are collected in a short period of time (Markiewicz-Keszycka et al. 2017; Costa et al. 2019b; Machado et al. 2020).

✉ Fabíola Manhas Verbi Pereira
fabiola.verbi@unesp.br

[1] Group of Applied Instrumental Analysis, Department of Chemistry, Federal University of São Carlos, São Carlos, SP 13560-270, Brazil

[2] Group of Alternative Analytical Approaches (GAAA), Bioenergy Research Institute (IPBEN), Institute of Chemistry, São Paulo State University (UNESP), Araraquara, SP 14800-060, Brazil

[3] National Institute of Alternative Technologies for Detection Toxicological Assessment and Removal of Micropollutants and Radioactive Substances (INCT-DATREM), Araraquara, São Paulo State 14800-060, Brazil

Both techniques (EDXRF and LIBS) have been traditionally used in combination with routine univariate calibration strategies (Costa et al. 2019c). However, depending on complexity of the sample, this option is not always effective, being necessary other approaches to minimize matrix effect, and some examples are well described in the scientific literature.

Therefore, the goal of this study was to evaluate multivariate calibration models employing direct solid sample analysis by EDXRF for the determination of Cu, K, Sr, and Zn in cocoa bean samples. Considering the potential information provided by EDXRF and LIBS, regarding the composition of cocoa beans, data fusion strategy was also evaluated to improve both analytical performance and predictive capability of the analytes.

Materials and Methods

Instrumentation

The measurements were carried out using a benchtop EDXRF spectrometer, Rigaku NEX QC$^+$ (Austin, TX, USA), equipped with an Ag target X-ray tube and Be detector window that can be operated at a maximum voltage of 50 kV with a resolution of 0.024 keV (2048 channels) and a 25% detector dead time. During the spectrum acquisition was considered Kα transitions for all elements under investigation.

A commercial LIBS, J 200 model from Applied Spectra (Freemont, USA), was used as complementary technique. The instrument is equipped with a Nd-YAG laser operating at 1064 nm. The instrument contains a high efficiency particulate air cleaner (HEPA) to purge the ablated particles, and the movement of the sample is automated with a XYZ stage. It also contains a 1280 × 1024 complementary metal-oxide semiconductor (CMOS) color-camera imaging system. An optical fiber bundle is coupled to a 6-channel charged-coupled device (CCD) spectrometer to convert the plasma emission light into spectra, with a spectral range of emission signals between 186 and 1042 nm resulting in 12,288 variables. The gate width is the time that spectrometer collects the emission signals, which is fixed at 1.05 ms. For the identification of elements emission lines, Aurora Software Package (also from Applied Spectra) was used. The additional operation conditions used were 2699 J cm^{-2} laser pulse fluence and 1.9 µs delay time, and the laser pulse energy was about 50 mJ (Gamela et al. 2020a).

Inductively coupled plasma optical emission spectrometer (ICP OES) model iCAP 7400 (Thermo Fisher, Madison, WI, USA) was used as reference method after microwave digestion. The measurements were performed using argon gas (99.999%, White Martins-Praxair, Sertãozinho, SP, Brazil), using both axial and radial viewing modes. The instrumental conditions and the emission lines used are shown in Table 1.

The digestion procedure was performed using a single reaction chamber oven (UltraWave^{TM}, Milestone, Sorisole, Italy). Before digestion process, a volume of 150 mL of water and 5.0 mL of concentrated HNO_3 were added into the single chamber reaction, which was pressurized with nitrogen gas (99.9%, White Martins-Praxair) until 40 bar.

Reagents and Solutions

Analytical-grade reagents and deionized water (Milli-Q system, 18.2 MΩ cm, Millipore, Bedford, MA) were used to prepare all solutions and standards. All glassware and vessels were soaked in a 10% v v^{-1} HNO_3 solution during 24 h. After that, a rinsing step with deionized water was performed, and the materials were left to dry in a clean hood before use. The multielementar solutions used for external calibration were prepared from dilution of 1000 mg L^{-1} of Cu, K, Sr, and Zn standard solutions (Qhemis, São Paulo, SP, Brazil) using dilute HNO_3, i.e., 1% v v^{-1} (Synth, Diadema, SP, Brazil), previously purified using a sub-boiling distillation system Distillacid™ BSB-939-IR (Berghof, Eningen, Germany).

Samples and Sample Preparation

Ten samples of cocoa bean were obtained in an area of the Cocoa Research Center—CEPEC, an entity linked to the Executive Committee of the Cacao Plan—CEPLAC of the Brazilian Ministry of Agriculture, Livestock and Supply (MAPA) located in Bahia State, Brazil.

Before analysis by EDXRF, the samples were only grinded to reduce the particle size to improve the homogeneity of the analytes in the samples. Then, approximately 500 mg of each sample was placed into polypropylene cells and afterwards covered with Mylar® film of a 6-µm thickness (Premier Lab Supply, Port St. Lucie, FL, USA). The samples analyzed

Table 1 Instrumental parameters for ICP OES determinations

Parameter	ICP OES
Radio frequency applied power (kW)	1.2
Plasma gas flow rate (L min^{-1})	12.0
Auxiliary gas flow rate (L min^{-1})	0.5
Nebulizer gas flow rate (L min^{-1})	0.50
Analytes monitored	Emission line (λ/nm)
Cu	324.754 (I)
K	766.490 (I)
Sr	421.552 (II)
Zn	213.856 (I)

using EDXRF spectrometer were the same for LIBS. However, previously to LIBS analysis, the samples were pressed using 60 t in^{-1} to form pellets (~ 12 mm diameter) in order to make easier the data collection.

To evaluate the efficiency of the digestion procedure of the sample, four certified reference materials (CRMs) of baking chocolate (NIST 2384), whole milk powder (NIST 8435), apple leaves (NIST 1515), and spinach leaves (NIST 1570a), all from National Institute of Standard and Technology (Gaithersburg, MD, USA), were also digested using concentrated HNO_3.

Reference Method

The method used as reference was developed by Gamela et al. (2020b) and presents the following characteristics: a mass of 200 mg of cocoa beans was directly weighed in perfluoroalkoxy alkanes (PFA) vessels and, 5 mL of 3.75 mol L^{-1} HNO_3 and 1.75 mL of 30% v v^{-1} H_2O_2 were added. The samples were submitted to the following heating program (temperature in °C/ramp in min/hold in min): (i) 180/5/5, (ii) 210/5/10, and (iii) 230/5/10. After that, the vessel contents were transferred to volumetric flasks, and the solution was diluted to 25 mL with ultrapure water before analysis.

Acquisition of LIBS Spectra and Chemometric Tools

For LIBS, each sample was analyzed in triplicate using the conditions described in "Instrumentation." Approximately 600 spectra were collected, and all data treatment was performed using MATLAB® 2019a (The MathWorks Inc., Natick, MA, USA) laboratory-made routines, and an interface integrated MATLAB for first-order multivariate calibration (MVC1) (Olivieri et al. 2004). The collected spectra were normalized to minimize the microheterogeneity and signal fluctuation during the data acquisition (Castro and Pereira-Filho 2016). However, the normalization process was not necessary for EDXRF, since this technique has not shown this issue previously mentioned.

The samples were divided using Kennard and Stone algorithm into calibration and validation sets (Kennard and Stone 1969). A number of samples used in the calibration and validation sets were 7 and 3, respectively. After that, partial least squares regression (PLS) was used to model all data set, and appropriate number of latent variables was selected and predicted the concentration values in the sample test. This tool is considered first-order multivariate calibration, which minimizes the lack of selectivity. The mathematical algorithms are used to obtain information to predict the concentration in the samples, and the main advantage is the possibility to propose models in the presence of concomitants (Escandar et al. 2007; Olivieri 2015; Zhang et al. 2018).

The best results were considered those that present lowest standard error of cross-validation (SECV). In order to improve the capability of the prediction of the model, data fusion strategy was evaluated. Data fusion consists in the use of multiple sources of data to produce a single model (De Oliveira et al. 2019; Gamela et al. 2020c), and due to the versatile characteristic of LIBS, this technique was used as complementary.

Results and Discussions

Reference Method by ICP OES

For the evaluation of the proposed procedure, four different CRMs, such as apple and spinach leaves, baking chocolate, and whole milk powder, were submitted to the optimized conditions described in previous study by Gamela et al. (2020b), and the results are shown in Table 2. The results obtained using this procedure demonstrated that the concentrations of all analytes in CRM are in concordance with certified values according to Student's *t* test at 95% of confidence level. Moreover, the results obtained employing the total digestion of the samples with concentrated HNO_3 and with proposed procedure were also compared using a paired Student's *t* test at 95% of confidence level (Gamela et al. 2020b). The results showed that there is no significant difference between the reference method and proposed procedure.

Multivariate Calibration and Data Preprocessing

In this first step, univariate calibration was used to build regression models based on EDXRF data under the area of specific region of the element. However, this strategy presented unacceptable errors for all determined elements due to variability of matrix between the samples, what make this strategy inadequate to estimate the concentration values in the samples.

Partial least squares (PLS) multivariate models were used to predict the concentration values of Cu, K, Sr, and Zn in cocoa bean samples. For modeling the data, the whole EDXRF spectra were used for the calculations and are shown in Fig. 1. The data were modeled using the calibration and validation samples, as described in "Acquisition of LIBS Spectra and Chemometric Tools" section. The reference concentration obtained from ICP OES was the y vector.

The MVC1 calculates important figures of merit, such as limit of detection (LOD), limit of quantification (LOQ), and SECV, which allows to evaluate the efficiency of the regression models (Olivieri et al. 2004). The obtained models presented good results using one latent variable (LV), where the

Table 2 Concentration values (mg kg^{-1}) of Cu, K, Sr, and Zn obtained in certified reference materials using diluted HNO_3 (mean ± standard deviation, *n* = 3)

Elements	Baking chocolate (NIST 2384)		Apple leaves (NIST 1515)		Spinach leaves (NIST 1570a)		Whole milk powder (NIST 8435)	
	Certified value	Microwave digestion	Certified value	Microwave digestion	Certified value	Microwave digestion	Certified value	Microwave digestion
Cu	840 ± 74	866.0 ± 0.2	15,250 ± 100	14,147 ± 126	15,270 ± 410	14,275 ± 52	9220 ± 490	9966 ± 445
K	8650 ± 400	7120 ± 17	16,080 ± 210	12,821 ± 198	29,030 ± 520	23,712 ± 433	13,630 ± 470	10,746 ± 139
Sr	*	____**	25 ± 1	24.9 ± 0.3	55.6 ± 0.8	54.6 ± 0.5	4.3 ± 0.5	4.3 ± 0.1
Zn	38 ± 2	37 ± 1	12.4 ± 0.5	13.01	82 ± 3	76 ± 1	28 ± 3	27 ± 0.5

[*] Value not informed

**Not determined

LOD and LOQ obtained were 1 and 3 mg kg^{-1} for Cu, 345 and 1036 mg kg^{-1} for K, 0.5 and 2 mg kg^{-1} for Sr, and 2 and 6 mg kg^{-1} for Zn. Moreover, the SECV was below the lowest concentration values in the validation samples for all determined elements. These values were 7 mg kg^{-1} for Cu, 1506 mg kg^{-1} for K, 4 mg kg^{-1} for Sr, and 7 mg kg^{-1} for Zn.

The predicted concentration values for these elements ranged from 16 to 17 mg kg^{-1} for Cu, 6602 to 8034 mg kg^{-1} for K, 8 to 12 mg kg^{-1} for Sr, and 36 to 38 mg kg^{-1} for Zn. Figure 2 shows the obtained trueness values for each element in all samples, which ranged from 85 to 106% for Cu, 94 to 100% for K, 109 to 120% for Sr, and 90 to 106% for Zn.

Other strategy evaluated was data fusion between EDXRF and LIBS combined with multivariate calibration to enhance the regression model for K. In this sense, the data fusion model was built using the specific selected spectra of the transition energy Kα (3.314 keV) of K from EDXRF, and the spectra of two emission lines of this element (K I 766.49 nm and K I 769.89 nm) from LIBS, as depicted in Fig. 3. After that, the data were autoscaled and the calibration model was calculated using PLS. However, due to lower sensitivity of the LIBS, the data fusion was not successful for Cu, Sr, and Zn.

The SECV value obtained for this element was 872 mg kg^{-1}. Figure 4 shows the SECV values obtained using single model EDXRF, and data fusion model employing EDXRF and LIBS simultaneously. The results obtained for K using data fusion strategy presented lower SECV when compared with those obtained by a single source (EDXRF), showing a good capability to predict the concentration values of this element. In addition, the obtained LOD and LOQ were 1899 mg kg^{-1} and 5697 mg kg^{-1}, respectively. The predicted concentration values found ranged from 6053 to 8339 mg kg^{-1}, and the trueness was 76 to 120% as depicted in Fig. 5.

Therefore, considering the essential species for human health, all analyzed samples presented high concentration

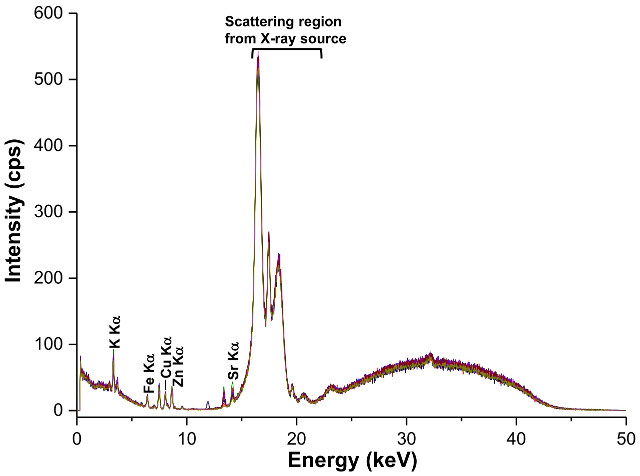

Fig. 1 Representative spectra obtained from cocoa bean sample using EDXRF

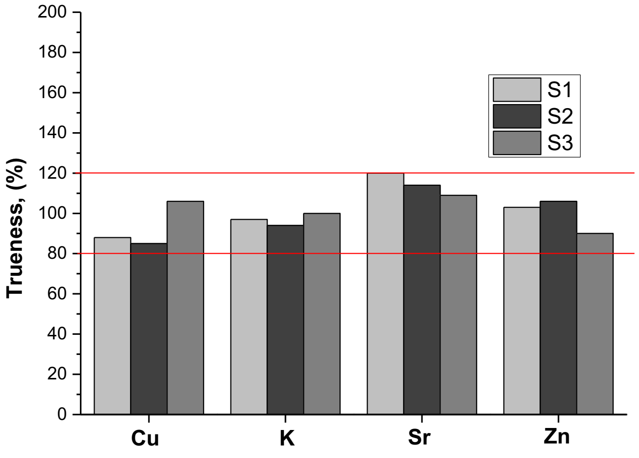

Fig. 2 Trueness values (%) obtained for (a) Cu, (b) K, (c) Sr, and (d) Zn using PLS

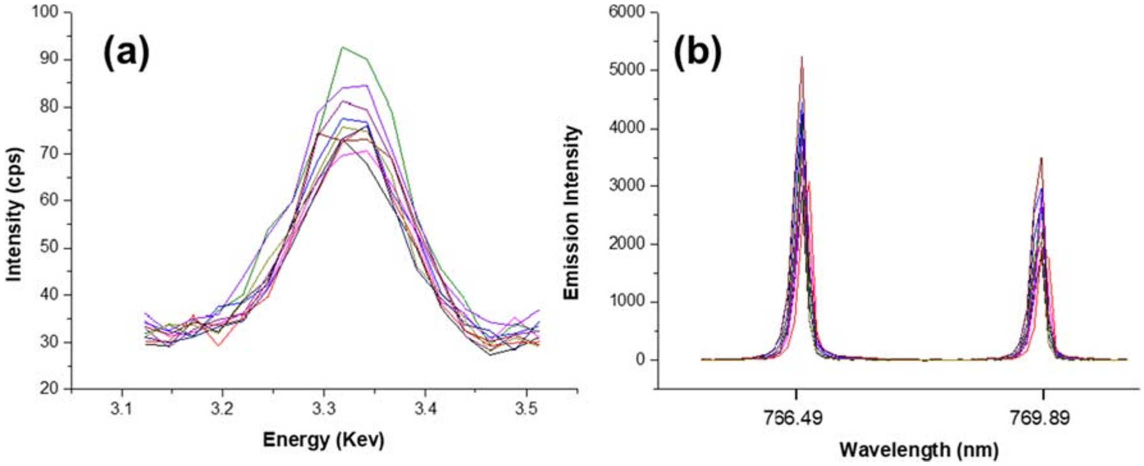

Fig. 3 The selected spectra of K from (**a**) EDXRF and (**b**) LIBS used for data fusion

values of K and can be considered good source of this nutrient. Regarding micronutrients, Zn were found in higher concentration values than Cu and Sr.

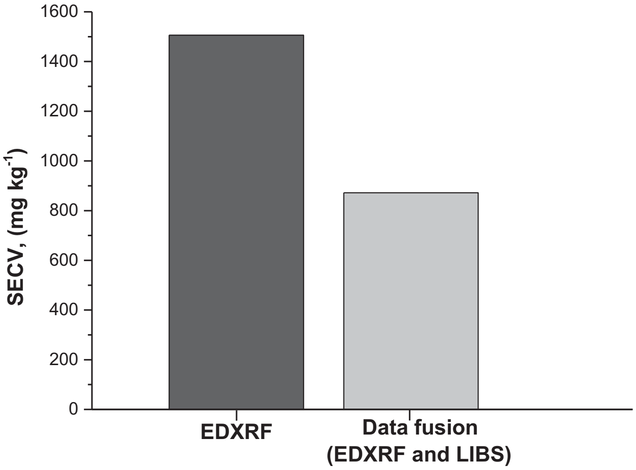

Fig. 4 The standard error of cross-validation (SECV) obtained for K using single EDXRF and data fusion model (EDXRF and LIBS)

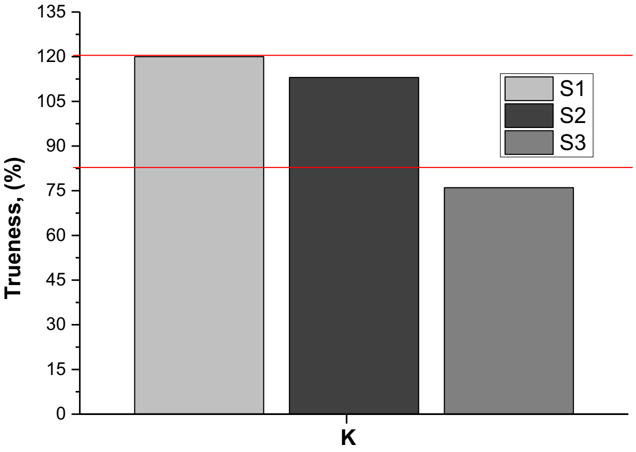

Fig. 5 Trueness values (%) obtained for K employing data fusion strategy and PLS

Conclusions

Multivariate calibration and EDXRF and LIBS data were able to predict the mineral content (Cu, Sr, and Zn) by means of direct solid analysis. Whole spectra and PLS were employed to calculate the calibration model, which showed simplicity and presented good results, as low SECV, LOD, LOQ, and acceptable trueness. Moreover, data fusion employing EDXRF and LIBS was used for the determination of K, and it demonstrated that with the use of this strategy and PLS for modeling, the SECV was improved. In this sense, the use of EDXRF and LIBS combined with multivariate calibration represents an alternative to minimize matrix effect.

Funding The authors acknowledge the financial support to CNPq/TWAS (158587/2017-0), CNPq (305637/2015-0, 307328/2019-8, and 465571/2014-0), and FAPESP (2019/24223-5, 2018/18212-8, 2019/01102-8, and 2014/50945-4). This study was financed in part by CAPES – Finance Code 001 and 88887136426/2017/00.

Compliance with Ethical Standards

Conflict of Interest Raimundo Rafael Gamela declares that he has no conflict of interest. Edenir Rodrigues Pereira-Filho declares that he has no conflict of interest. Fabíola Manhas Verbi Pereira declares that she has no conflict of interest.

Ethical Approval This article does not contain any studies involving human participants or animals performed by any of the authors.

Informed Consent Informed consent was obtained from all individual participants included in the study.

References

Andrey D, Dufrier JP, Perring L (2018) Analytical capabilities of energy dispersive X-ray fluorescence for the direct quantification of iron in cocoa powder and powdered cocoa drink. Spectrochim Acta B 148: 137–142. https://doi.org/10.1016/j.sab.2018.06.014

Brito GB, Teixeira LSG, Korn MGA (2017) Direct analysis of marine macroalgae for determination of macro minerals by energy dispersive X-ray fluorescence. Microchem J 134:35–40. https://doi.org/10.1016/j.microc.2017.05.001

Bull A, Brown MT, Turner A (2017) Novel use of field-portable-XRF for the direct analysis of trace elements in marine macroalgae. Environ Pollut 220:228–233. https://doi.org/10.1016/j.envpol.2016.09.049

Byers HL, McHenry LJ, Grundl TJ (2019) XRF techniques to quantify heavy metals in vegetables at low detection limits. Food Chem 1: 100001. https://doi.org/10.1016/j.fochx.2018.100001

Chevallier E, Chekri R, Zinck J, Guérin T, Noël L (2015) Simultaneous determination of 31 elements in foodstuffs by ICP-MS after closed vessel microwave digestion: method validation based on the accuracy profile. Food Compos Anal 41:35–41. https://doi.org/10.1016/j.jfca.2014.12.024

Castro JP, Pereira-Filho ER (2016) Twelve different types of data normalization for the proposition of classification, univariate and multivariate regression models for the direct analyses of alloys by laser-induced breakdown spectroscopy (LIBS). J Anal At Spectrom 31: 2005–2014. https://doi.org/10.1039/C6JA00224B

Costa VC, Pinheiro FC, Amorim FAC, Silva EGP, Pereira-Filho ER (2019a) Multivariate optimization for the development of a sample preparation procedure and evaluation of calibration strategies for nutrient elements determination in handmade chocolate. Microchem J 150:104166. https://doi.org/10.1016/j.microc.2019.104166

Costa VC, Augusto AS, Castro JP, Machado RC, Andrade DF, Babos DV, Sperança MA, Gamela RR, Pereira-Filho ER (2019b) Laser induced-breakdown spectroscopy (LIBS): histórico, fundamentos, aplicações e potencialidades. Quim Nova 42:527–545. https://doi.org/10.21577/0100-4042.20170325

Costa VC, Amorim FAC, Babos DV, Pereira-Filho ER (2019c) Direct determination of Ca, K, Mg, Na, P, S, Fe and Zn in bivalve mollusks by wavelength dispersive X-ray fluorescence (WDXRF) and laser-induced breakdown spectroscopy (LIBS). Food Chem 273:91–98. https://doi.org/10.1016/j.foodchem.2018.02.016

De Oliveira DM, Fontes LM, Pasquini C (2019) Comparing laser induced breakdown spectroscopy, near infrared spectroscopy, and their integration for simultaneous multi-elemental determination of micro and macronutrients in vegetable samples. Anal Chim Acta 1062:28–36. https://doi.org/10.1016/j.aca.2019.02.043

Escandar GM, Olivieri AC, Faber NM, Goicoechea HC, de la Peña AM, Poppi RJ (2007) Second- and third-order multivariate calibration: data, algorithms and applications. Trends Anal Chem 26:752–765. https://doi.org/10.1016/j.trac.2007.04.006

Ferreira SLC, Miró M, da Silva EGP, Matos GD, dos Reis PS, Brandao GC, dos Santos WNL, Duarte AT, Vale MGR, Araujo RGO (2010) Slurry sampling—an analytical strategy for the determination of metals and metalloids by spectroanalytical techniques. Appl Spectrosc Rev 45:44–62. https://doi.org/10.1080/05704920903435474

Gamela RR, Costa VC, Babos DV, Araújo AS, Pereira-Filho ER (2020a) Direct determination of Ca, K, and Mg in cocoa beans by laser-induced breakdown spectroscopy (LIBS): evaluation of three univariate calibration strategies for matrix matching. Food Anal Methods. 13:1017–1026. https://doi.org/10.1007/s12161-020-01722-6

Gamela RR, Costa VC, De Mello ML, Romero JC, Amorim FAC, Pereira-Filho ER (2020b) Multivariate analysis: use of Doehlert design (DD) for optimization of a simple sample preparation procedure for the determination inorganic constituents in cocoa beans employing microwave acid digestion and ICP OES. J Braz Chem Soc. https://doi.org/10.21577/0103-5053.20200109

Gamela RR, Costa VC, Sperança MA, Pereira-Filho ER (2020c) Laser-induced breakdown spectroscopy (LIBS) and wavelength dispersive X-ray fluorescence (WDXRF) data fusion to predict the concentration of K, Mg and P in bean seed samples. Food Res Int 109037. https://doi.org/10.1016/j.foodres.2020.109037.

Gupta DRS, Ghosh R, Mitra AK (2013) Chemical composition of soil evolving from municipal solid waste using energy dispersive X-ray fluorescence. X-Ray Spectrom 42:268–275. https://doi.org/10.1002/xrs.2478

Kelsey EY, Cynthia AE, Kip VH, Jacob E, Trevor G (2016) A review of the handheld X-ray fluorescence spectrometer as a tool for field geologic investigations on Earth and in planetary surface exploration. Appl Geochem 72:77–87. https://doi.org/10.1016/j.apgeochem.2016.07.003

Kennard RW, Stone LA (1969) Computer aided design of experiments. Technometrics 11:137–148

Korn MGA, Morte ESB, Dos Santos DCMB et al (2008) Sample preparation for the determination of metals in food samples using spectroanalytical methods - a review. Appl Spectrosc Rev 43:67–92. https://doi.org/10.1080/05704920701723980

Machado RC, Andrade DF, Babos DV, Castro JP, Costa VC, Sperança MA, Garcia JA, Gamela RR, Pereira-Filho ER (2020) Solid sampling: advantages and challenges for chemical element determination-a critical review. J Anal At Spectrom 35:54–77. https://doi.org/10.1039/C9JA00306A

Markiewicz-Keszycka M, Cama-Moncunill X, Casado-Gavalda MP, Dixit Y, Cama-Moncunill R, Cullen PJ, Sullivan C (2017) Laser induced-breakdown spectroscopy (LIBS) for food analysis: a review. Trends Food Sci Tech 65:80–93. https://doi.org/10.1016/j.tifs.2017.05.005

Mir-Marqués A, González-Masó A, Cervera ML, De GM (2015) Mineral profile of Spanish commercial baby food. Food Chem 172:238–244. https://doi.org/10.1016/j.foodchem.2014.09.074

Mir-Marqués A, Cervera ML, De GM (2016) Mineral analysis of human diets by spectrometry methods. Trends Anal Chem 82:457–467. https://doi.org/10.1016/j.trac.2016.07.007

Oliveira LB, Dos Santos WPC, Teixeira LSG, Korn MGA (2020) Direct analysis of cocoa powder, chocolate powder, and powdered chocolate drink for multi-element determination by energy dispersive X-ray fluorescence spectrometry. Food Anal Methods 13:195–202. https://doi.org/10.1007/s12161-019-01565-w

Olivieri AC (2015) Practical guidelines for reporting results in single- and multi-component analytical calibration: a tutorial. Anal Chim Acta 868:10–22. https://doi.org/10.1016/j.aca.2015.01.017

Olivieri AC, Goicoechea HC, Iñón FA (2004) MVC1: an integrated MatLab toolbox for first-order multivariate calibration. Chemom Intell Lab Syst 73:189–197. https://doi.org/10.1016/j.chemolab.2004.03.004

Oyedotun TDT (2018) X-ray fluorescence (XRF) in the investigation of the composition of earth materials: a review and an overview. Geol Ecol landsc 2:148–154. https://doi.org/10.1080/24749508.2018.1452459

Pereira FMV, Pereira-Filho ER, Bueno MIMS (2006) Development of a methodology for calcium, iron, potassium, magnesium, manganese, and zinc quantification in teas using X-ray spectroscopy and multivariate calibration. J Agric Food Chem 54:5723–5730. https://doi.org/10.1021/jf0603782

Peruchi LC, Nunes LC, De Carvalho GGA, Guerra MBB, De Almeida E, Rufini IA, Santos D Jr, Krug FJ (2014) Determination of inorganic nutrients in wheat flour by laser-induced breakdown spectroscopy and energy dispersive X-ray fluorescence spectrometry.

Spectrochim Acta B 100:129–136. https://doi.org/10.1016/j.sab.2014.08.025

Van Grieken R, Markowicz A (eds) (2001) Handbook of X-ray spectrometry. CRC press

Villa JEL, Pereira CD, Cadore S (2015) A novel, rapid and simple acid extraction for multielemental determination in chocolate bars. Microchem J 121:199–204. https://doi.org/10.1016/j.microc.2015.03.008

Zhang T, Tang H, Li H (2018) Chemometrics in laser-induced breakdown spectroscopy. J Chemom 32:2983. https://doi.org/10.1002/cem.2983