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Development of a Methodology for Calcium, Iron, Potassium, Magnesium, Manganese, and Zinc Quantification in Teas Using X-ray Spectroscopy and Multivariate Calibration

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In this study an analytical methodology for food analyses combining X-ray spectroscopy (XRS) with partial least-squares (PLS) data treatment was developed. Fifteen tea samples were purchased at a local market, and XRS spectra were obtained without sample pretreatment. For comparison of the metal concentrations, the samples were also mineralized, and six elements were determined using flame atomic absorption spectrometry (Ca, Fe, Mg, and Mn), flame atomic emission spectrometry (K), and thermospray flame furnace atomic absorption spectrometry (Zn). The spectral information obtained from XRS and the metal concentrations found using the alternative techniques were employed to generate six PLS models. The Ca and Mn models required four latent variables (LV), Fe, five LV, K, two LV, and Mg and Zn, three LV. The limits of quantification for these models were 614, 134, 761, 140, 85, and 1 mg kg^{-1} for Ca, Fe, K, Mg, Mn, and Zn, respectively.

KEYWORDS: Tea; X-ray spectroscopy; partial least squares; direct solid sample analyses; atomic absorption spectrometry

INTRODUCTION

Food inspection is an important procedure to maintain and verify the quality control of products intended for final consumers. These analytes can have organic or inorganic constituents. For inorganic analyte determinations, some toxic elements (such as As, Cd, Cr, and Pb) and macro- (Ca, K, Mg, Na, P, and S) and micronutrients (Cu, Fe, Mn, and Zn) must be investigated (*1, 2*).

Elemental determinations can involve the use of several apparatus, for example, ovens or digestor blocks in dry and wet sample preparation, respectively. In these procedures, concentrated reagents (for example, H_2SO_4, HNO_3, $HClO_4$, and H_2O_2) are essential for organic material mineralization (*3*). Such procedures increase both the time and cost of the analytical sequence. In addition, the careful attention of the analyst is required, and errors (such as contamination or analyte losses) can be introduced during the analytical sequence (*4, 5*).

An alternative is a methodology that combines fast sample preparation, or even no sample pretreatment, good detectivity, and minimal generation of residues. Additionally, as for any analytical methodology, problems of contamination and systematic errors have to be reduced (*6*).

Direct X-ray fluorescence (XRF) is an option that can be considered for the performance of this task. However, this technique is often subjected to strong interelemental and matrix effects that affect concentration values (*7*). On the other hand, the use of X-ray spectroscopy (XRS) eliminates sample pretreatment, resulting in rapid measurements; it is nondestructive and presents good limits of detection. These combined features can offer suitable analytical alternatives for direct solid sample investigations. For instance, Szökefalvi-Nagy et al. (*8*) reported the analysis of paintings using a portable XRF spectrometer with radioisotope excitation to investigate unique and precious art and archaeology objects. Another XRF application field is related to the analysis of geological materials. Adams and Allen (*9*) proposed a methodology for the determination of iron, manganese, potassium, calcium, titanium, silicon, aluminum, magnesium, and sodium in certified geological material, combining XRF and partial least-squares regression (PLS), a chemometric tool. The proposed methodology presented better results than those obtained by univariate linear regression and multiple linear regression (MLR) analysis.

The XRF application can be extended to a great variety of samples, and the aim of this paper is to present an analytical methodology for metal determinations in teas, combining XRS with PLS data treatment (*10*). To illustrate this procedure, the tea samples were used with no pretreatment, and the limits of

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Table 1. Results (Milligrams per Kilogram) Found for the Calibration and Validation Sets for Fe, Mn, and Zn[a]

Calibration Set

tea	Fe mineral		Mn		Zn	
	minerald	pred	minerald	pred	minerald	pred
1	78 ± 20	49	127 ± 3	119	18 ± 2	15
2	345 ± 13	336	127 ± 3	74	17 ± 3	21
4	197 ± 33	290	72 ± 3	118	12 ± 2	15
5	161 ± 21	227	70 ± 3	63	24 ± 2	22
6	1000 ± 155	985	70 ± 2	176	25 ± 2	23
7	60 ± 10	54	72 ± 12	97	9 ± 2	9
11	175 ± 22	227	330 ± 20	307	23 ± 2	22
12	207 ± 29	235	82 ± 4	41	21 ± 5	21
14	366 ± 26	237	149 ± 3	114	17 ± 2	19
15	293 ± 31	252	1258 ± 42	1251	22 ± 2	22

Validation Set

tea	Fe		Mn		Zn	
	minerald	pred	minerald	pred	minerald	pred
3	280 ± 23	276	98 ± 3	75	19 ± 3	19
8	540 ± 67	664	118 ± 4	143	62 ± 3	24
9	60 ± 4	19	53 ± 6	136	7 ± 2	9
10	155 ± 33	243	111 ± 10	213	10 ± 2	13
13	239 ± 61	352	101 ± 4	84	14 ± 2	23

[a] The first values for each metal were obtained using AAS (Fe and Mn) and TS-FF-AAS (Zn) after the mineralization (mean ± SD) process. $n = 3$ for tea samples 1, 2, 4–9, and 11–14, and $n = 4$ for the others. minerald, mineralized; pred, predicted.

detection (LOD) and quantification (LOQ) with this XRS-PLS methodology were calculated. The proposed methodology can be easily applied for food or agricultural product quality control.

MATERIALS AND METHODS

Samples. Fifteen tea samples were purchased at a local market. These samples presented the following characteristics: two samples of *Camellia sinensis* (black tea, sample 1; and green tea, sample 15), three samples of *Cymbopogon citratus* (samples 2, 3, and 14), one sample combining *Cymbopogon citratus*, *Cichorium intybus*, and *Citrus limonum* (lime−lemon, sample 4), one *Matricaria recutita* (sample 5), one *Mentha piperita* (sample 6), two *Pyrus malus* (Apple) with *Cinnamomum zeylanicum* (samples 7 and 10), one *Melissa officinalis* with *Citrus aurantium bigaradia* (sample 8), one *Pyrus malus* (sample 9), one *Fragaria vesca* (strawberry, sample 11), and two *Peamus boldus* (samples 12 and 13).

XRS Measurements. The XRS experiments were performed using benchtop X-ray fluorescence equipment, Shimadzu EDX 700 (Kyoto, Japan). This equipment is provided with a rhodium X-ray tube that can be operated at a maximum voltage of 50 kV. The measurements were performed in air, with a beam collimation of 3 mm, 25% of detector dead time, and the current was automatically adjusted during the spectrum acquisition. The Shimadzu EDX 700 has also the following characteristics: (1) X-ray generator, tube voltage from 5 to 50 kV, tube current from 1 to 1000 mA, and exposure area from 1 to 10 mm diameter; (2) detector, Si (Li), detection area of 10 mm^2 and resolution of <155 eV (Mn Kα, 1500 cps). For spectra acquisition, ≈200 mg of solid samples was put into Teflon cells. These cells have an orifice of 5 mm diameter that kept the samples compacted and were covered with a Mylar film (3 μm thickness).

Three irradiation times were tested, 100, 200, and 300 s, and two collimator diameters were evaluated (3 and 10 mm). In all cases the spectra were recorded from 0 to 40 keV, with a resolution of 0.02 keV, resulting in 2047 points per spectrum.

For data treatment and chemometrics applications, MatLab 6.5 (The MathWorks, Natick, MA) and PLS Toolbox (Eigenvector Research, Wenatchee, WA) were used.

Atomic Spectrometry Measurements. The tea samples were also mineralized in a digestor block (Quimis, São Paulo, Brazil), without

Table 2. Results (Milligrams per Kilogram) Found for the Calibration and Validation Sets for Ca, K, and Mg[a]

Calibration Set

tea	Ca		K		Mg	
	minerald	pred	minerald	pred	minerald	pred
1	3709 ± 355	3267	21531 ± 2391	16137	2620 ± 61	1750
2	4357 ± 474	4478	20646 ± 1764	22315	1818 ± 89	2516
4	3144 ± 360	4180	14476 ± 703	14154	1291 ± 64	1774
5	5599 ± 553	5446	24311 ± 2022	23561	3117 ± 208	2663
6	7500 ± 682	7133	22519 ± 2365	22417	2712 ± 156	2767
7	3125 ± 432	2902	6631 ± 713	6341	523 ± 44	843
11	7348 ± 564	7619	14848 ± 364	17692	3237 ± 146	2623
12	9717 ± 1254	9520	9753 ± 256	11797	2776 ± 256	2851
14	3832 ± 441	3752	19966 ± 1645	19850	1872 ± 139	2236
15	4767 ± 376	4928	13053 ± 508	13353	2281 ± 80	2400

Validation Set

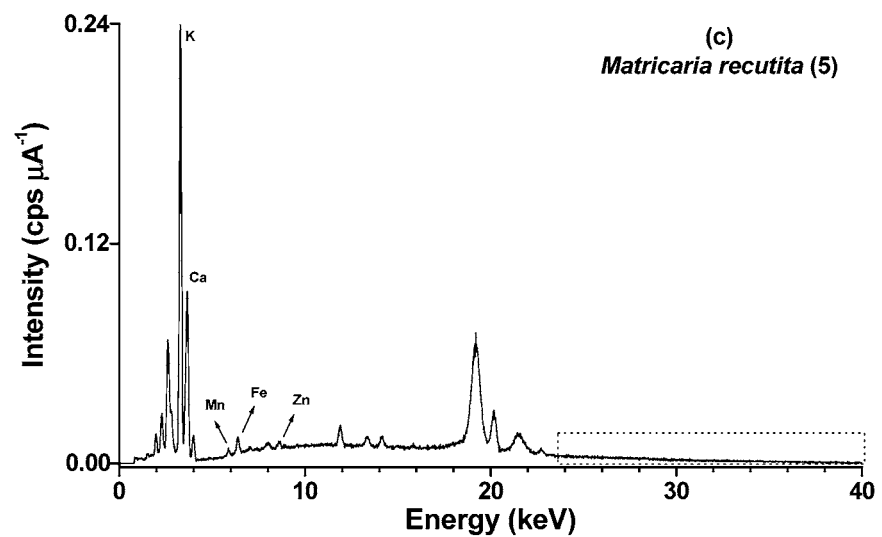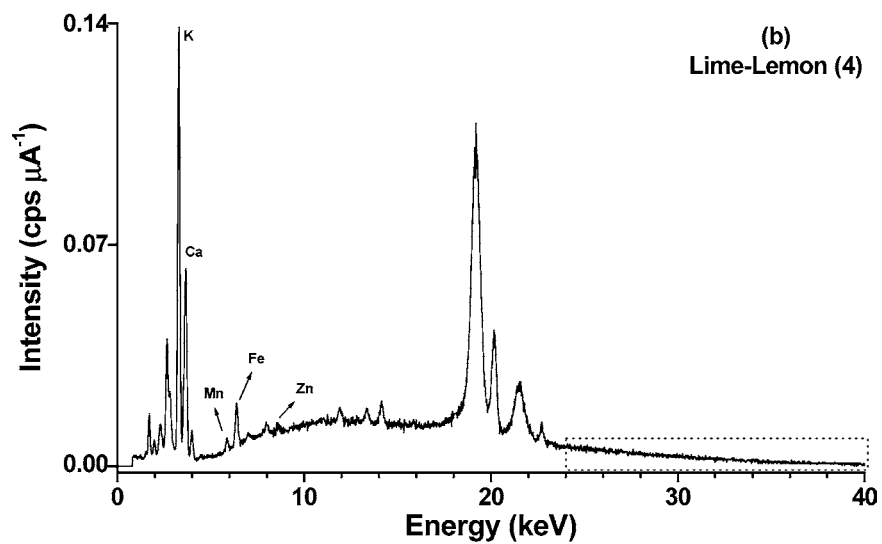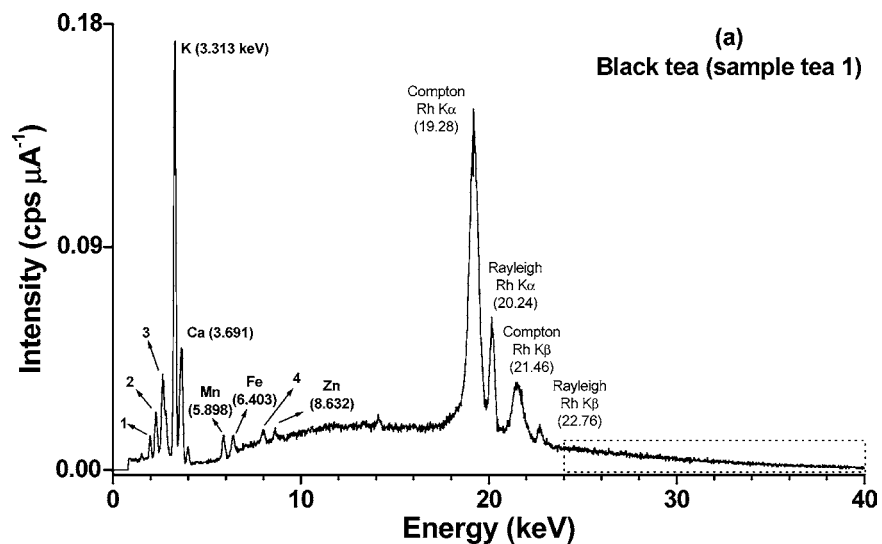| tea	Ca		K		Mg	
	minerald	pred	minerald	pred	minerald	pred
3	4243 ± 508	3797	20298 ± 1796	20306	2131 ± 115	2226
8	6931 ±487	6041	29585 ± 2939	25544	3856 ± 162	2874
9	1034 ± 237	1941	9318 ± 359	7067	774 ± 78	816
10	3069 ± 203	4821	8432 ± 524	9085	870 ± 40	1502
13	9692 ± 985	10747	11193 ± 403	13259	2250 ± 120	3109

[a] The first values for each metal were obtained using AAS (Ca and Mg) and AES (K) after the mineralization (mean ± SD) process. mineral, mineralized; pred, predicted.

any control of sample particle size; that is, the samples were used as obtained in the local market. In this procedure, 200 mg of each tea sample was transferred to digestion glass tubes (25 cm length and 2 cm inner diameter). Two milliliters of concentrated HNO₃ (Merck, Darmstadt, Germany) was added to each tube and then heated to 100 °C for 2 h. During the heating process a small funnel was positioned over each tube entrance to allow acid reflux. After this period, the tubes were removed from the digestor block and, when the temperature had reached room temperature, 1 mL of H₂O₂ (Merck) was added to each tube. The tubes were again heated to 130 °C for 2 h. Finally, the samples were transferred to volumetric flasks; the volume was completed with deionized water, and the metal concentrations were determined. A cabbage powder (CRM 679, IRMM, Geel, Belgium) certified sample was used to verify the accuracy of the analytical sequence.

The mineralized solutions were analyzed using a Perkin-Elmer AAnalyst 300 atomic absorption spectrometer (Norwalk, CT), equipped with a deuterium lamp for background correction. Calcium, iron, magnesium, and manganese were determined in the atomic absorption (AA) mode (time average). Hollow cathode lamps (Perkin-Elmer) for Ca (422.7 nm), Fe (248.3 nm), Mg (285.2 nm), and Mn (279.5 nm) were employed as primary radiation sources. Potassium was determined in the atomic emission (AE) mode (time average); the emission line was 766.5 nm.

Due to the lower Zn content in the tea samples, these determinations were done using a thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) system (*11*) adapted to the same FAAS equipment. In these experiments, a Ni (99%) tube (Camacam, São Paulo, Brazil) was used as atomizer and positioned in an oxidizing air/acetylene flame. One hundred microliters of the mineralized samples was collected using an injector and introduced with the aid of a carrier stream into the Ni tube. In these measurements peak area signals at 213.9 nm were used to perform the determinations.

The concentrations of the analytical solutions (Merck) ranged from 1 to 5 mg L^{-1} for Ca and K, from 1 to 6 mg L^{-1} for Fe, from 0.1 to 0.5 mg L^{-1} for Mg, from 0.5 to 2.5 mg L^{-1} for Mn, and from 25 to 150 μg L^{-1} for Zn. For Ca, K, and Mg determinations, a La (Merck) solution (10% m/v, final concentration of 1%) was added to the samples and calibration solutions to avoid problems with concomitants. The other operating conditions (slits, flame compositions, and lamp currents) were those recommended by the manufacturer.
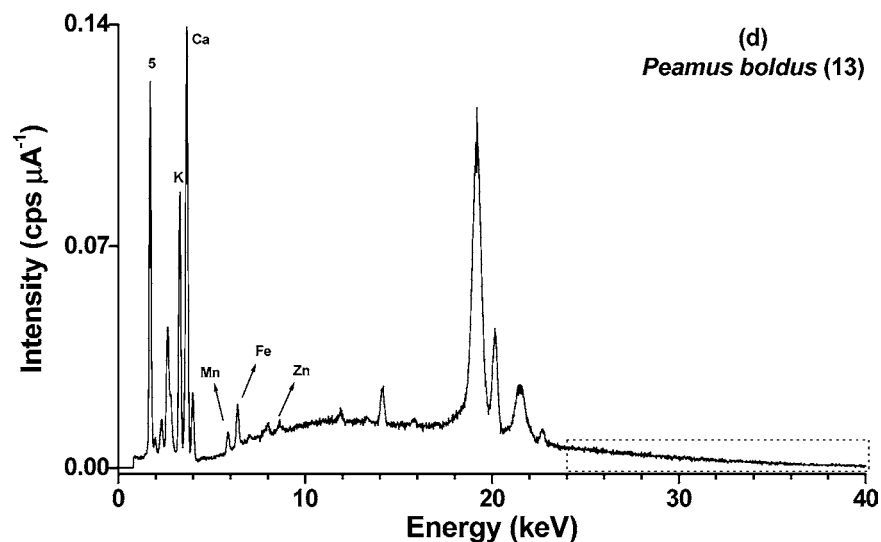
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(a)
Black tea (sample tea 1)

K (3.313 keV)

Compton
Rh Kα
(19.28)

Rayleigh
Rh Kα
(20.24)

Compton
Rh Kβ
(21.46)

Rayleigh
Rh Kβ
(22.76)

Ca (3.691)

3

2

1

Mn
(5.898)

Fe
(6.403)

4

Zn
(8.632)

(b)
Lime-Lemon (4)

K

Ca

Mn

Fe

Zn

(c)
***Matricaria recutita* (5)**

K

Ca

Mn

Fe

Zn

Figure 1. XRS spectra for (**a**) black tea (tea sample 1), (**b**) lime–lemon (4), (**c**) *M. chamomilla* (5), and (**d**) *P. boldus* (13). The region marked with a dotted rectangle was used for LOD and LOQ calculation.

RESULTS AND DISCUSSION

Metal Determinations in the Mineralized Tea Samples. The metal concentrations (milligrams per kilogram) obtained after mineralization of the tea samples are summarized in **Tables 1** and **2** (mineralization column). Each tea was analyzed at least three times, authentic replicates, and these values are expressed as mean ± standard deviation (SD). In the case of the micronutrients (Fe, Mn, and Zn—**Table 1**) the concentrations ranged from 60 (samples 7 and 9) to 1000 mg kg^{-1} (sample 6) for Fe, from 53 (sample 9) to 1258 mg kg^{-1} (sample 15) for Mn, and from 7 (sample 9) to 62 mg kg^{-1} (sample 8) for Zn.

The highest concentrations were observed for Ca, K, and Mg (macronutrients—**Table 2**). These metals presented concentrations ranging from 1034 (sample 9) to 9717 mg kg^{-1} (sample 12) for Ca, from 6631 (sample 7) to 29585 mg kg^{-1} (sample 8) for K, and from 523 (sample 7) to 3856 mg kg^{-1} (sample 8) for Mg.

Iron and zinc were also determined in a certified reference sample (CRM 679) to verify the accuracy of the analytical sequence and to identify some contamination problems. The metal concentrations ($n = 6$ for both metals) obtained were 59 ± 6 mg kg^{-1} for Fe and 75 ± 5 mg kg^{-1} for Zn. The certified values are 55.0 ± 1.3 mg kg^{-1} for Fe and 79.7 ± 2.0 mg kg^{-1} for Zn. Both results were compared with their respective certified values using the unpaired *t* test, and no significant difference was observed with a confidence level of 95%. The repeatability for the metal determinations varied from 3 to 5%, and the intermediate precision was around 7 (samples 8 and 10) and 23% (sample 9) for Ca, 4 (sample 2) and 26% (samples 1 and 13) for Fe, 2 (sample 11) and 11% (samples 1, 6, and 7) for K, 2 (sample 1) and 10% (sample 9) for Mg, 2 (samples 1, 2 and 14) and 16% (sample 7) for Mn, and 4 (sample 8) and 26% (sample 12) for Zn. Some samples presented high SD values, probably due to the fact that the samples were used as obtained in the local market (see details under Samples and Atomic Spectrometry Measurements).

The LOD and LOQ were calculated using >20 blank signals for each metal. These limits were obtained by multiplying the SD of the blanks signals by 3 (for LOD) or by 10 (for LOQ), and the results were divided by the sensitivity for each metal from their respective calibration curves. This procedure was proposed by the Analytical Methods Committee (*12*, *13*). The LOD and LOQ were, respectively, 0.08 and 0.3 mg L^{-1} for

Ca, 0.1 and 0.4 mg L^{-1} for Fe and K, 0.02 and 0.06 mg L^{-1} for Mg, 0.06 and 0.2 mg L^{-1} for Mn, and 3 and 10 μg L^{-1} for Zn.

Acquisition of XRS Spectra. For the first measurements, the irradiation time was varied from 100 to 300 s. Over this range, no significant distinction in X-ray spectra was noted, and the shortest irradiation time (100 s) was then chosen for the subsequent experiments. In the experiments using different collimator sizes, it was observed that the smaller one (3 mm) led to more reliable and stable results. The larger collimator (10 mm) also provided information from the neighboring area, such as the cell material. The best XRS working conditions were an irradiation time of 100 s with the 3 mm collimator. Most teas were analyzed three or four times (authentic replicates), and a total of 54 XRS spectra were recorded.

Figure 1 illustrates some spectra for four representative tea samples. The first spectrum (**a**) is of black tea (sample 1), the second (**b**) is of lime–lemon tea (sample 4), the third (**c**) is the *M. recutita* tea, (sample 5), and the last one (**d**) is the *P. boldus* tea (sample 13).

All examples presented Ca (Kα 3.691 keV), K (Kα 3.313 keV), Fe (Kα 6.403 keV), Mn (Kα 5.898 keV), and Zn (Kα 8.632 keV) signals. The teas presented also P (Kα 2.013 keV, peak 1 in **Figure 1a**), S (Kα 2.307 keV, peak 2), Cl (Kα 2.622 keV, peak 3), and Cu (Kα 8.046 keV, peak 4). Sample 13 (*P. boldus*, **Figure 1d**) presented a Si fluorescence line (Kα 1.740 keV, peak 5 in **Figure 1d**). In all tea spectra a high signal due to the Rh scattering region from 18 to 24 keV (see details in **Figure 1a**) was observed, because the matrices are essentially organic, not absorbing the incident X-rays. This region characterizes the Compton and Rayleigh X-ray scattering signal (*14*). The Compton lines are Rh Kα 19.28 and 20.24 keV and the Rayleigh lines are Rh Kβ 21.46 and 22.76 keV, respectively.

With metal concentrations and spectra for the teas obtained, the next step was to proceed with multivariate calibration to propose models for metal determinations using XRS. In this work, PLS was used.

Selection of Calibration and Validation Sample Sets. The first step for PLS application was the selection of the calibration and validation sample sets. To help in this selection a principal component analysis (PCA) (*15*) was done. The goal of PCA is to condense the original information (with a great number of variables) to a new data set with a smaller number of variables,
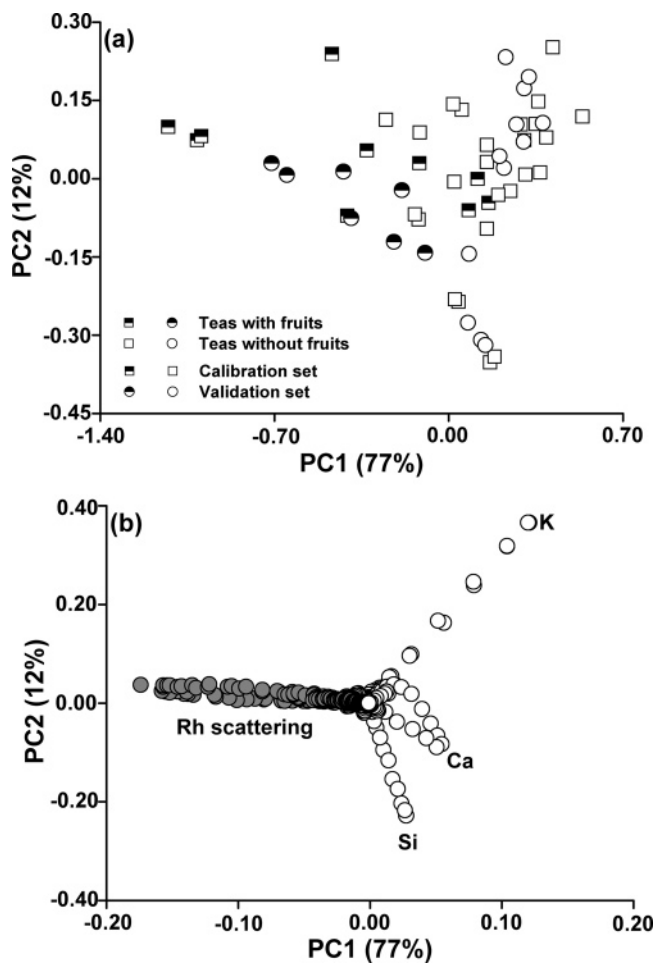
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Figure 2. Scores (**a**) and loadings (**b**) plots for the PCA. In the scores, the half-open and open symbols represent teas mainly composed by fruits and teas with no fruits, respectively. The squares and circles represent the calibration and validation sets, respectively. In the loadings plot, the gray circles represent Rh scattering.

called principal components (PC). In this process the initial information is not lost. This procedure is performed by linear combination of the original variables, where the information is projected into a smaller space, permitting better or easier data visualization. Using PCA, the original data set is decomposed into two new matrices according to the equation

$$\mathbf{X} = t_1 p_1' + t_2 p_2' + ... + t_n p_n' + \mathbf{E}$$

where $\mathbf{X}$ is an original data matrix, t_n are scores values for the a_n component, carrying information about samples, p_n are loadings values for the a_n component, carrying now information about variables, and $\mathbf{E}$ is the residual matrix (*16*).

In this case, a data matrix (**X**) with 54 rows (corresponding to the samples) and 2047 columns (corresponding to the energy scale, that is, from 0 to 40 keV, with 0.02 keV resolution) was organized (54 × 2047) and mean centered. Special attention was given to the spectral range from 18 to 24 keV that was included in this analysis.

Figure 2 shows the scores (**Figure 2a**) and loadings (**Figure 2b**) plots. In the scores plot (**Figure 2a**) a separation between the tea samples mainly composed of fruits (half-open symbols) and without them (open symbols) is observed. According to the reference values (mineralized) presented in **Tables 1** and **2**, teas with mainly fruits (teas 4, 7, and 9−11—see Samples) presented, on average, metal concentrations 2 times lower than
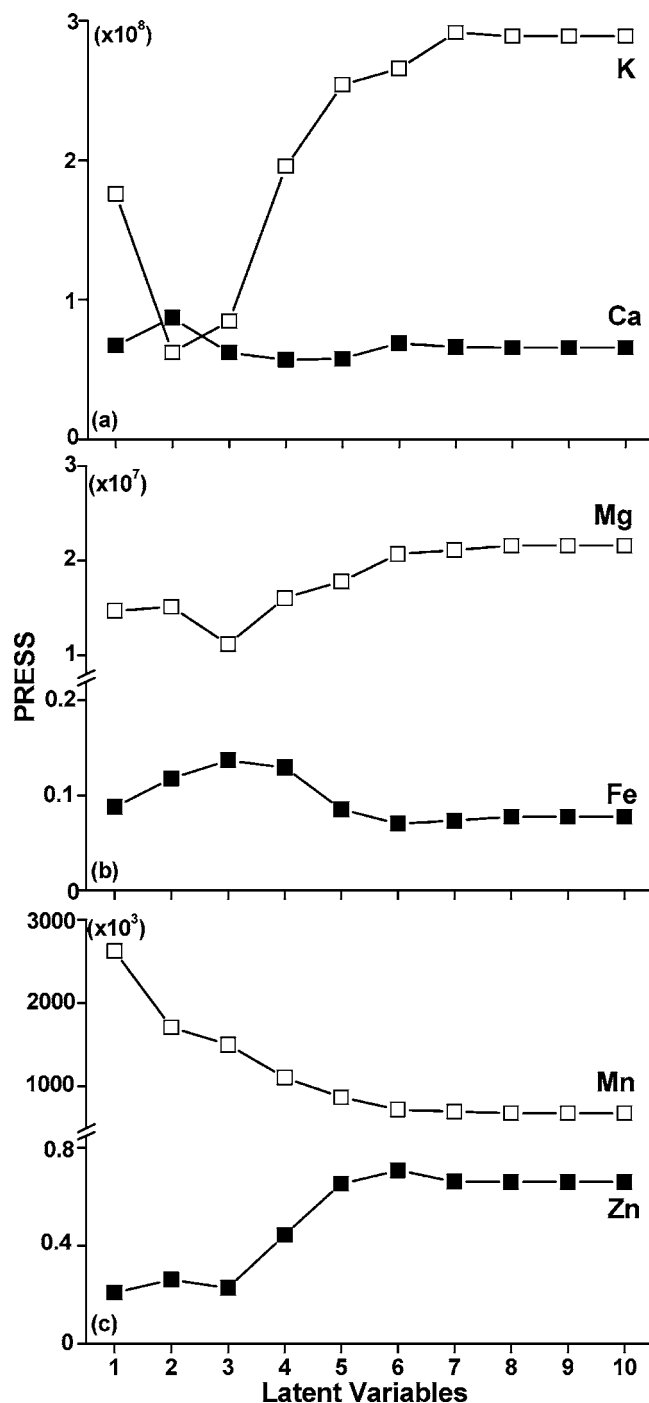

Figure 3. PRESS values for Ca and K (**a**), Fe and Mg (**b**), and Mn and Zn (**c**).

the teas without them. The loadings plots (**Figure 2b**) confirm the observation and was characterized mainly by Ca, K, Si (open circles), and Rh scattering (gray circles) signals. The sample separations were due to the high Ca, K, and Si XRS signals (open circles) in the teas without fruit. The teas with fruits were mainly related to the Rh scattering region (gray circles) due to the high organic content present in the fruits. The other regions of the XRS spectra were positioned in the coordinates 0 × 0 of the plot and do not present any influence on the PCA. In this analysis no potential outlier samples were observed when the leverage and residual values were analyzed.

In the selection of calibration and validation sets, teas were chosen from both groups, with and without fruits. For the calibration (squares in **Figure 2a**) the following tea samples
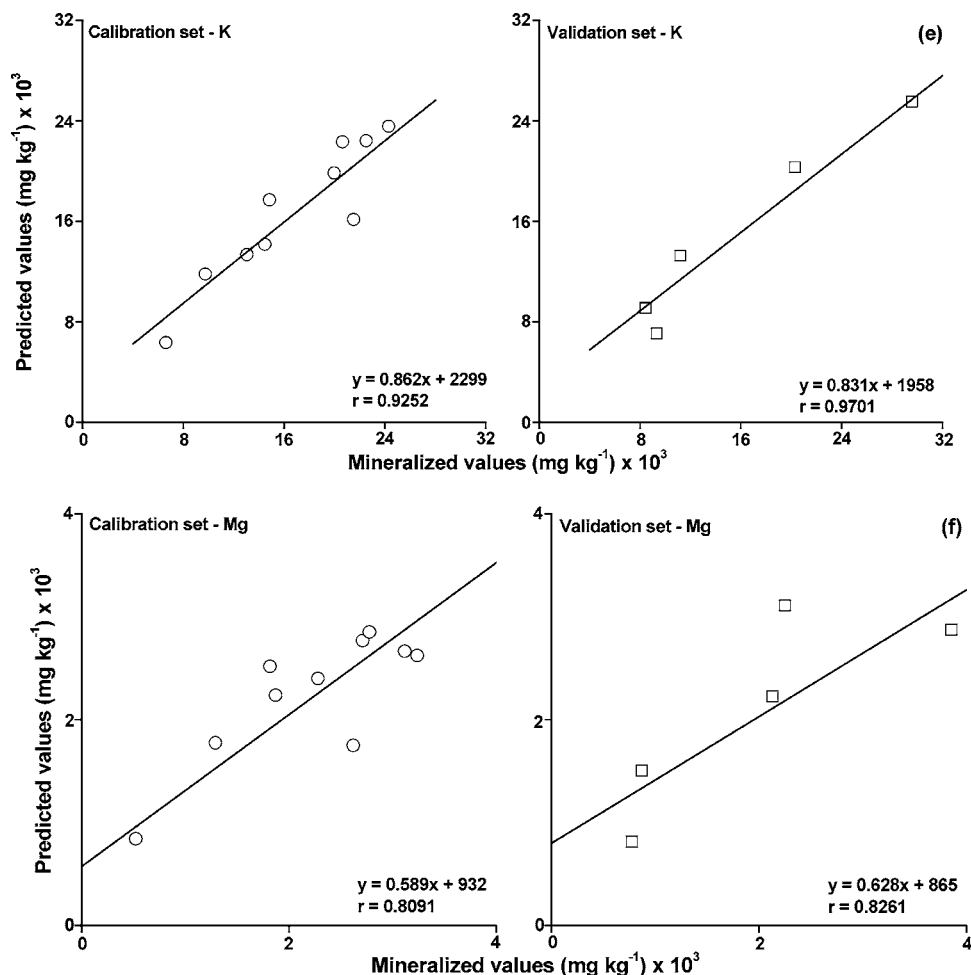
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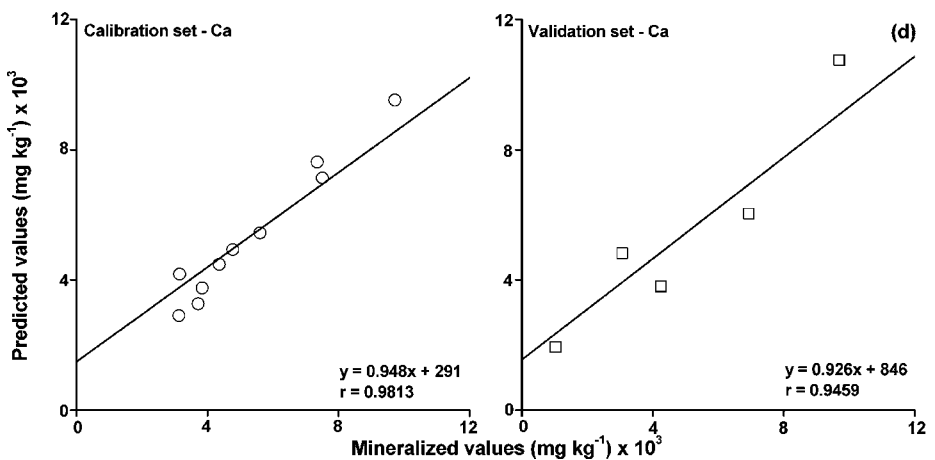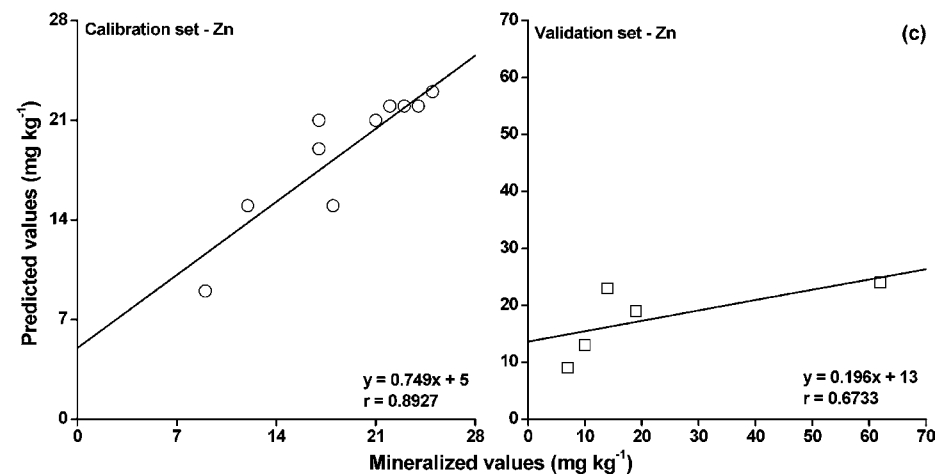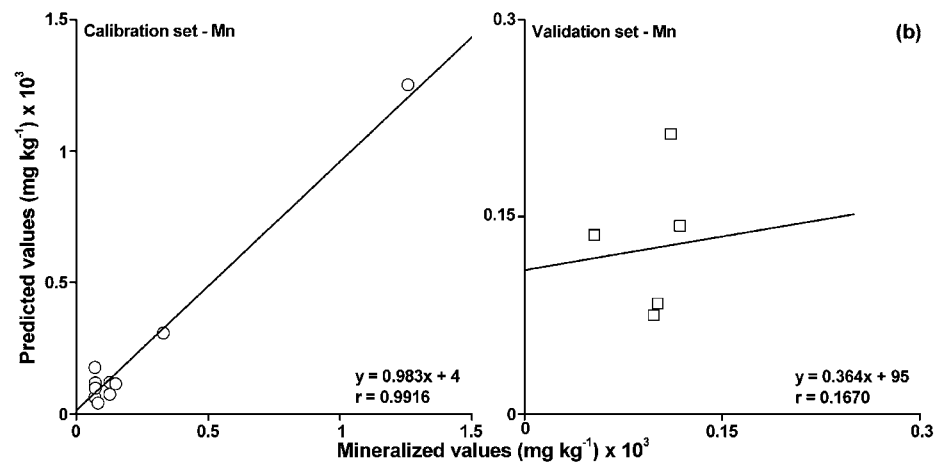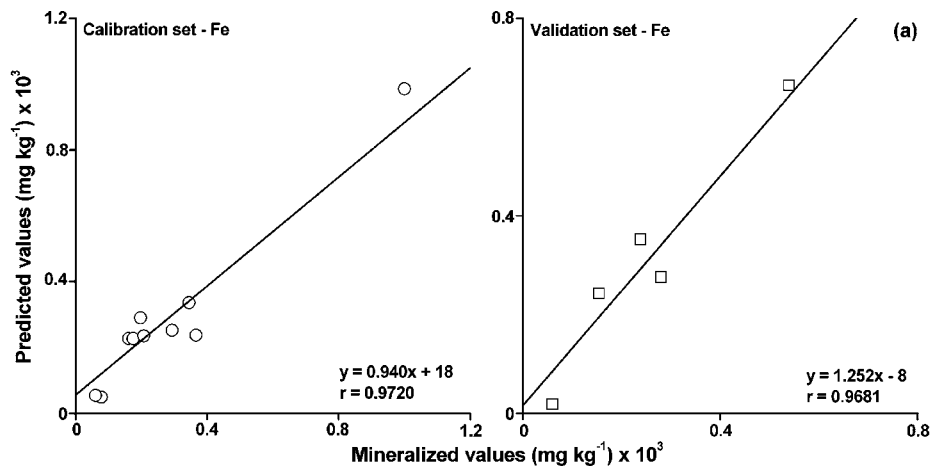
Figure 4. Mineralized versus XRS-PLS values (mg kg^{-1}) for Fe (**a**), Mn (**b**), Zn (**c**), Ca (**d**), K (**e**), and Mg (**f**).

were selected: 1, 2, 4−7, 11, 12, 14, and 15, and for the validation (circles in **Figure 2a**) samples 3, 8, 9, 10, and 13 were chosen. For the PLS models, the data from spectra and the metal concentrations were not pretreated. In addition, the average spectra for each tea were used.

PLS Models. In all PLS models, the total spectral (2047 variables) region (matrix **X**, independent variables) was used. To help the selection of the proper number of LV, some parameters such as the predictive residual error sum of squares (PRESS), root mean square errors for calibration (RMSEC), and **X** and **Y** explained variances were observed and carefully evaluated. **Figure 3** shows the PRESS values obtained for the PLS models.

Figure 3a shows the PRESS values for Ca and K, and these metals needed 4 and 2 LV, respectively, in their models. The RMSEC values were 404 for Ca and 2122 mg kg^{-1} for K. The explained variances in **X** and **Y** were, respectively, 99 and 100% for Ca and 98 and 99% for K.

For Fe and Mg models (**Figure 3b**), 5 and 3 LV, respectively, were necessary. The RMSEC values were 60 (Fe) and 482 mg kg^{-1} (Mg), and the explained variances for **X** and **Y** were, respectively, 99 and 98% for Fe and 99 and 96% for Mg. In the last two models, Mn and Zn needed 4 and 3 LV, respectively (**Figure 3c**). The RMSEC values were 45 (Mn) and 2 mg kg^{-1} (Zn), and the explained variances for **X** and **Y** were 99% for both metals.

The predicted values for Fe, Mn, Zn (**Table 1**), Ca, K, and Mg (**Table 2**) are shown, together with those obtained by wet analysis (mineralized values).

For Fe, the correlation coefficients (CC) for the calibration and validation sets were 0.9270 and 0.9681, respectively, and the root mean square errors for prediction (RMSEP) was 87 mg kg^{-1}. In the case of Mn and Zn, the CC for the calibration and validation set were, respectively, 0.9916 and 0.1670 for Mn and 0.8927 and 0.6733 for Zn. The RMSEP values for these metals were 61 (Mn) and 18 mg kg^{-1} (Zn).

For the macronutrients (**Table 2**), Ca, K, and Mg presented the following CC: 0.9813 and 0.9459 (Ca−calibration and validation sets, respectively), 0.9252 and 0.9701 (K−calibration and validation sets, respectively), and 0.8091 and 0.8261 (Mg−calibration and validation sets, respectively). The RMSEP values were 1095, 2284 and 650 mg kg^{-1} for Ca, K, and Mg, respectively. **Figure 4** shows the other parameters when the reference (mineralized values) and predicted metal concentrations were evaluated (slope of the adjusted curve and interception value on the y-axis).

Limits of Detection and Quantification. For LOD and LOQ calculations, it is necessary to estimate the standard deviation of a blank. As expected, a tea sample with no metals is not easily available. In this case, an alternative approach was to select, from the tea sample spectra, a spectral region containing only signal noise.

The region from 24.02 to 40.92 keV was selected (846 variables). This region is highlighted in **Figure 1** (the rectangle with dotted lines), and the regression coefficients for this region presented negligible values for all models.

For standard deviation estimation, a matrix was arranged with 54 samples (tea samples) and 846 variables. Then, the standard

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deviation and variance values for each column were calculated. Finally, the average variance and the final standard deviation were obtained. This procedure was adapted from that of Sena et al. (*17*).

The next step was the calculation of the sensitivity [intensity (cps μA^{-1}/(mg kg^{-1})]. These values were obtained by inversing the regression coefficient norm (*18*, *19*). The corresponding values obtained for Fe, Mn, and Zn were 1.47×10^{-4}, 2.33×10^{-4}, and 1.92×10^{-2}, respectively. The LOD and LOQ are defined as 3 and 10 times the SD divided by the sensitivity, respectively. In this way, the values for LOD and LOQ obtained were, respectively, 40 and 134 mg kg^{-1} for Fe, 25 and 85 mg kg^{-1} for Mn, and 0.3 and 1 mg kg^{-1} for Zn. The LOD values are lower than the micronutrient concentrations observed in the tea samples (**Table 1**). In the case of Fe and Mn, samples with concentrations lower than the LOQ were observed. This statement can explain the bad prediction for samples 4, 6, 9, and 10 in the Mn model. For Fe, sample 9 presented mineralized and predicted values lower than the LOQ and sample 10 presented a mineralized value too close to the LOQ.

With regard to macronutrients, the sensitivities were 3.21×10^{-5}, 2.59×10^{-5}, and 1.41×10^{-4} for Ca, K, and Mg, respectively. The limits obtained were 184 (LOD) and 614 mg kg^{-1} (LOQ) for Ca, 228 (LOD) and 761 (LOQ) mg kg^{-1} for K, and 42 (LOD) and 140 mg kg^{-1} (LOQ) for Mg. For these last three metals the LOD and LOQ were lower than the sample concentrations observed in **Table 2**. The average relative errors observed for these three metals varied from 7% (in the calibration set) to 36% (in the validation set).

This study permits several conclusions. It is possible to achieve Ca, K, and Mg concentrations using PLS models in combination with XRS. Also, the tea samples can be used for metal evaluation without pretreatment or sample preparation. In the case of micronutrients (Fe, Mn, and Zn) it was possible to access their concentrations, and these values can be used in semiquantitative metal analyses. It is important to point out that the cost of the proposed methodology is ≈10 times lower than that of the conventional methodology, which employs sample mineralization and metal determinations using atomic spectrometry (absorption or emission). The PLS models can be improved using additional tea samples. It was possible to calculate the figures of merit from the PLS models, resulting in innovative analytical methodology involving XRS. In addition, because there is no need to mineralize the samples, the methodology used in this study can be adapted to other substrates for food or agricultural product quality control.

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