COFFEE SCIENCE
ISSN: 1984-3909

eISSN: 1984-3909
Coffee Science, e202386, 2025

Doi: https://doi.org/10.25186/.v20i.2386

Predictive modeling of nutrients in Conilon coffee leaves using portable X-ray fluorescence spectrometry

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Editor: Samuel Pereira de Carvalho
Received in April 11, 2025 and approved in July 2, 2025

ABSTRACT

Portable X-ray fluorescence (pXRF) can offer accurate assessment of total elemental contents in crop leaves rapidly without generating chemical waste, contributing to sustainable practices. The objective of this work was to create models capable of predicting nutrient contents in coffee leaves determined by ICP-OES from pXRF data. 1520 coffee leaf samples were collected across Conilon coffee farms in the State of Espirito Santo, Brazil, to compose 19 composite samples (80 leaves per sample). Leaf samples were subjected to macro and micronutrient analyses by wet chemistry and pXRF. pXRF analyses of leaf samples used two calibration methods: Mode 1 ("Soil") and Mode 2 ("Geochem"). Mode 1 was not capable of determining P contents. Nutrient contents determined by pXRF, in both modes, were higher than those determined by wet chemistry, except for Ca. High correlations were found between contents determined by wet chemistry and those determined by pXRF analysis, especially for mode 2 (r between 0.93 and 0.97), except for Zn (r = 0.65). With the calibration of linear equations, it was possible to predict P, K, Ca, Fe, and Mn contents in Conilon coffee leaves from pXRF data using mode 2 (R^2 between 0.89 and 0.95). Results showed that the prediction of ICP-OES contents in leaves using pXRF is an accurate, fast, and ecofriendly method.

Key words: pXRF; predictive modeling; plant nutrition; nutritional monitoring; *Coffea canephora*.

1 INTRODUCTION

The continuous search to understand the nutritional demand of plants is necessary for sustainable management through methods that enable a practical and accurate diagnosis of the nutritional status of crops (Tomkiewicz, Piskier, 2012; Partelli et al., 2016). The adequate measurement and interpretation of leaf analysis allows for a more efficient use of agricultural inputs, maintaining the balance among soils, plants, and the environment in agricultural systems. There are several methods available to determine plant nutrients in different mineral and organic matrices (Fauziah et al., 2024; Silva et al., 2023). The commonly performed wet-chemistry analyses destroy the samples through processes of extraction, digestion, or incineration. However, recently new methods have been developed wherein non-destructive radiation is used to measure different properties of samples, as is the case of the portable X-ray fluorescence (pXRF) spectrometry (Ribeiro; Silva; Guimarães, 2017; Silva et al., 2024).

X-ray fluorescence (XRF) spectrometry is an analytic technique that uses X-rays to excite electrons in internal orbitals, ejecting them (Silva et al., 2021). When other electrons fill the created gap, they release energy in the form of fluorescence, which is detected by the equipment and is used to determine the element from which the radiation was released from, and what is its estimated concentration in the analyzed sample (Weindorf; Bakr; Zhu, 2014). This technique is utilized to determine the elemental composition of samples without altering the sample's properties, so that samples can be reused in other analyses.

The portable version of the XRF technique (pXRF) is increasingly presenting promising results, allowing for the determination of the chemical composition of samples accurately, fast, and without generating chemical waste (Mancini et al., 2023; Gozukara et al., 2022). The main advantages of pXRF are its low operational cost, simplicity of sample preparation, and ease of use (Nogueira; Teixeira; Vasques, 2018; Reidinger; Ramsey; Hartley, 2012; Santos et al., 2013; Weindorf; Bakr; Zhu, 2014). Due to its operational simplicity, characteristics, and potential, the pXRF has been increasingly applied to several research areas, especially in soil and environmental assessments, including the assessment of parent material (Andrade et al., 2020a; Dijair et al., 2020; Di Raimo et al., 2022; Ferreira et al., 2021; Mensík et al., 2021; Pelegrino et al., 2021; Ribeiro; Silva; Guimarães, 2017; Rosin et al., 2022; Silva et al., 2020) and other applications relevant for agriculture, including plant tissue analysis (Benedet et al., 2021; Borges et al., 2020; Guerra et al., 2018; Khan et al., 2022; Ribeiro et al., 2021). Data obtained

from this technique has contributed to the evaluation of soil and sediment contamination by heavy metals, soil fertility and plant nutrition, soil salinity, and water analyses (Andrade et al., 2020b; Caporale et al., 2018; Costa et al., 2024; Pearson et al., 2017; Swanhart et al., 2014).

However, the application of pXRF to organic matrices, especially plant tissue, are still incipient. Analysis of leaf samples via pXRF can aid related studies, since the total elemental content of samples is an essential variable and is usually determined by acid digestion (Andrade et al., 2023; Borges et al., 2020; Silva et al., 2024; Towett, Shepherd, Lee Drake, 2016). Recently, new calibrations have been added to pXRF devices specific for the assessment of plant material, increasing the accuracy of analyses (Antonangelo; Zhang, 2021). Studies investigating different plant species, water content in the plant tissue, and other structural components (e.g., lignin and cellulose), have been implemented (Costa et al., 2023; Costa et al., 2024; Lima et al., 2024; McGladdery et al., 2018; Ribeiro et al., 2021; Silva et al., 2024). For instance, Antonangelo and Zhang (2021) predicted the nutrient contents of cover crops using pXRF data via the calibration mode "Soil Nutrient and Metal". The authors obtained highly accurate models for K, Ca, S, Cu, Fe, Zn, and Mn (R^2 between 0.82 and 0.99). Therefore, pXRF presents great potential for the assessment of plant samples (McGladdery et al., 2018; Ribeiro et al., 2021; Silva et al., 2024).

Promising results have been obtained for species such as cocoa, oil palm, maize (Mellouki et al., 2025), and various kinds of plant tissues from native vegetation (McGladdery et al., 2018) and urban gardens (McStay et al., 2022), but few studies focused on specific crops. There is a need for studies exploring pXRF applied to perennial crops such as coffee, where the nutritional evaluation of plants must be frequent and directly impacts productivity (Gomes et al., 2016; Oliosi et al., 2020; Partelli et al., 2006; Partelli et al., 2006; Pires et al., 2022; Santos et al., 2021). Costa et al. (2024) is the only work that focused on the use of pXRF in coffee leaves, in which authors recommend further studies across different climatic conditions and management practices. Monitoring the nutritional status of coffee plants through fast and non-destructive analysis can significantly contribute for more efficient coffee management, increasing the value of productive systems, warranting deeper investigation of nutrient estimation methods that use pXRF data (Andrade et al., 2023; Costa et al., 2024; Singh; Sharma; Singh, 2022).

The objective of this study is to accurately predict macro and micronutrient contents in Conilon coffee leaves, using pXRF data obtained with different calibration modes ("Soil" and "Geochem") in tandem with predictive models. The central hypothesis is that the elemental contents determined by pXRF will correlate to those determined by acid digestion followed by inductively coupled plasma optical emission spectroscopy (ICP-OES), allowing for the robust modeling of nutrients in Conilon coffee leaves.

2 MATERIAL AND METHODS

2.1 Study area

The study area is located in the Coastal Tablelands in the north of the Espírito Santo state, spanning the municipalities São Mateus, Jaguaré, Boa Esperança, Pinheiros, Conceição da Barra and Montanha. According to the Köppen classification, the region has Aw climate, described as humid tropical weather with dry winter, having precipitation ranging from 1,000 and 1,400 mm and mean annual temperature of 23 °C (Alvares et al., 2014).

In each municipality, farms with Conilon coffee plants (*Coffea canephora*) were selected for this study in the upper parts of the landscapes, where Oxisols and Ultisols predominate. These soils are classified as Latossolos Amarelos and Argissolos Amarelos according to the Brazilian Soil Classification System (Santos et al., 2018), being typically very weathered, nutrient-poor, and kaolinitic, although not usually presenting high Fe contents due to their kaolinite-rich parent material (Andrade et al., 2020b).

2.2 Sampling of coffee leaves

Leaf sampling was conducted between March and July of 2018 in productive coffee plantations, in plants with ages between 2 and 16 years and different genotypes (Figure 1). Coffee plants, in general, were in the stage of grain filling and fruit maturation (Figure 2). There is no standard period to sample leaves, but the interpretations of results should change accordingly depending on the chosen sampling period. Plant density was between 2,500 to 4,400 plants per hectare and the mean productivity was 3.78 tons per hectare (varying from 1.5 to 6 tons per hectare). Most sampled crops were irrigated, fertilized, amended with lime, and subjected to phytosanitary control.

Leaf samples were collected across 19 coffee plots (Figures 1 and 2). In each plot, a composed sample consisting of 80 leaves was collected, following recommendations for coffee leaf analysis (Malavolta; Vitti; Oliveira, 1997). That is, a total of 1520 subsamples were collected and used to compose 19 samples. Sampling consisted of removing four leaves, including the petiole, from the third or fourth pair of leaves in productive branches located at roughly half of the plant's height. Leaf samples were then subjected to both wet-chemistry and pXRF analysis in order to develop predictive models for nutrient contents. Leaf samples were dried in a greenhouse with forced air circulation at 65 °C. Next, samples were ground in a Wiley mill and stored in plastic bags for posterior analyses.

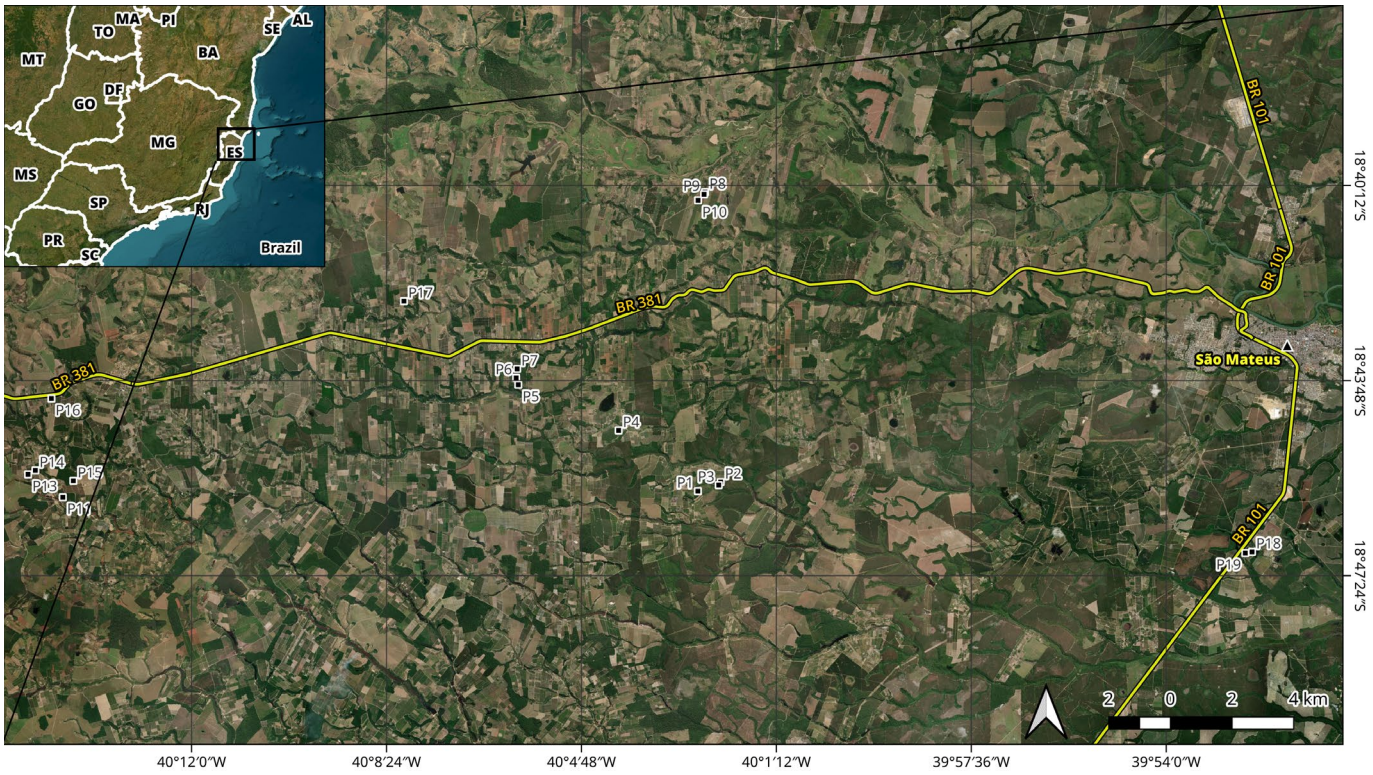

Figure 1: Geographic location of the sampled Conilon coffee plots across farms located near the São Mateus municipality, in the north of the Espírito Santo state, Brazil. 80 leaf samples were collected from each plot. Datum: WGS84.

Figure 2: Examples of productive farms where Conilon coffee plantations were sampled, located in the north of the Espírito Santo state, Brazil.

2.3 Wet chemistry analyses

Some macro (P, K, and Ca) and micronutrients (Fe, Mn, and Zn) were analyzed by wet chemistry methods (Carmo et al., 2000). These nutrients were selected for being the most commonly used in routine fertility analyses performed in Brazil. Samples (0.5 g) were transferred to glass tubes where 6.0 mL of acid solution was added (HNO_3:$HClO_4$, at the proportion 2:1 v/v). After digestion, the solutions were transferred to volumetric balloons, whose volumes were completed with ultrapure water. Macro and micronutrients were determined by ICP-OES (Optima 8300, Perkin Elmer).

2.4 pXRF analysis

Dry and grounded leaf samples were put inside Falcon tubes (15 mL) and slightly compressed manually for posterior analyses, following the methodology by Nogueira, Teixeira and Vasques (2018). Next, samples were analyzed by an Innov-X DP-6000 Delta Premium Handheld XRF Analyzer (Olympus, EUA), operated through the software "Innov-X Delta Advanced PC" (Figure 3). The device includes calibration settings provided by the manufacturer, namely "Soil" and "Geochem" modes, hereinafter referred to as modes 1 and 2, respectively. Each sample was scanned for 180 s in triplicates while slightly varying the position of the sample by laterally moving the sample holder.

N contents were not evaluated in this study, since pXRF cannot detect light elements such as Na, N, C, H, and Li, due to the stable electronic configurations and low fluorescent energies of these elements (Wang et al., 2015). Cu and Mg contents were excluded from this study because a large variability in measurements were found.

Figure 3: Portable X-ray fluorescence (pXRF) spectrometry device (Innov-X DP-6000 Delta Premium) analyzing ground Conilon coffee leaf samples collected in farms located in the north of the Espírito Santo state, Brazil.

2.5 Data analysis

A set of descriptive statistics were calculated for the contents of these elements determined by both wet chemistry and pXRF. Nutrient contents determined by pXRF using modes 1 and 2 were compared with contents obtained by wet chemistry through Student's t-test at 5% significance level. Pearson's correlation coefficients were calculated between nutrients determined by the studied analysis methods and pXRF calibration modes. Stepwise linear regression models were calibrated using pXRF data as input to predict nutrient contents determined by wet chemistry, and model accuracy was evaluated via leave-one-out cross validation. The accuracy of nutrient content predictions was quantified by comparing predicted and observed values using the coefficient of determination (R^2) and the root mean squared error (RMSE) (Equation 1):

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_i - m_i)^2} \quad (1)$$

where n: number of observations, yi: value estimated by models, mi: value measured by wet chemistry. Models with high R^2 and low RMSE were considered optimal to predict wet chemistry analysis.

3 RESULTS

3.1 Leaf nutrient contents by wet chemistry

From all studied elements, P presented the lowest variability among samples from the 19 studied farms, with a coefficient of variation (CV) of 13.2% (Table 1). The contents of K and Ca also presented low CV (16.6 and 18.4%, respectively), compared to micronutrients such as Fe, Mn, and Zn (between 69.2 and 90.3%). Additionally, while macronutrient contents presented similar variability among the 19 farms, a few farms presented very high contents of Fe, Mn, and Zn, resulting in the observed high CV (Figure 4).

3.2 Leaf nutrient contents by pXRF

Since some laboratories may only have calibrations for soil samples, analyses were also performed by pXRF in mode 1 ("Soil"), but these were not capable of detecting P contents due to its higher limit of detection (Table 2). Therefore, mode 1 cannot be recommended for the assessment of coffee leaf nutrients. Analyses performed using mode 2 ("Geochem"), however, were capable of quantifying P contents, therefore being more adequate for leaf analysis than mode 1. Maximum, minimum, and mean contents of K, Ca, and Fe determined by mode 2 presented wider amplitude than those obtained by mode 1, although both modes presented similar mean values. Mn contents determined by mode 2 were higher than those obtained from mode 1. Zn contents were also higher when determined by mode 2, but the difference compared to contents provided by mode 1 were small.

In comparison with nutrient contents determined by wet chemistry, results from mode 2 reported higher concentrations of P (Figure 5). Total contents of K, Fe, Mn, and Zn determined by pXRF in leaves using both modes 1 and 2 were higher than those obtained by wet chemistry (Table 3), especially those from mode 2. The exception was Ca, which was detected in higher concentrations when determined by wet chemistry analyses compared to when it was measured via pXRF.

3.3 Correlations between pXRF and wet chemistry results

Although analyses performed by pXRF in both modes presented higher nutrient contents (or lower, in case of Ca) compared to wet chemistry results, high correlation was found between both analysis methods (Table 3, Figure 6). Most strong and significant correlations were observed between wet chemistry and mode 2 results. All correlations calculated with mode 2 data presented r values above 0.93 for P, K, Ca, Fe,

and Mn. For Zn, only samples presenting contents above 40 mg kg^{-1} showed higher correlation with wet chemistry data (r=0.65 using mode 2 data). Therefore, mode 2 was considered more adequate to determine nutrient contents in coffee leaves.

Table 1: Descriptive statistics of nutrient contents obtained via Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (wet chemistry) from Conilon coffee leaves collected north of the Espírito Santo state, Brazil, in 19 coffee farms.

Nutrient	Max	Min	Mean	SD	CV (%)
P (g kg^{-1})	1.2	0.7	1.0 bB	0.1	13.2
K (g kg^{-1})	17.9	9.4	13.2 bB	2.4	18.4
Ca (g kg^{-1})	20.5	9.6	15.5 aA	2.6	16.6
Fe (mg kg^{-1})	290.0	29.7	60.8 bB	58.5	90.3
Mn (mg kg^{-1})	204.0	27.2	77.6 bB	53.7	69.2
Zn (mg kg^{-1})	26.0	4.1	7.0 bB	5.2	75.1

Max = Maximum value; Min = Minimum value; SD = Standard deviation; CV = Coefficient of variation.

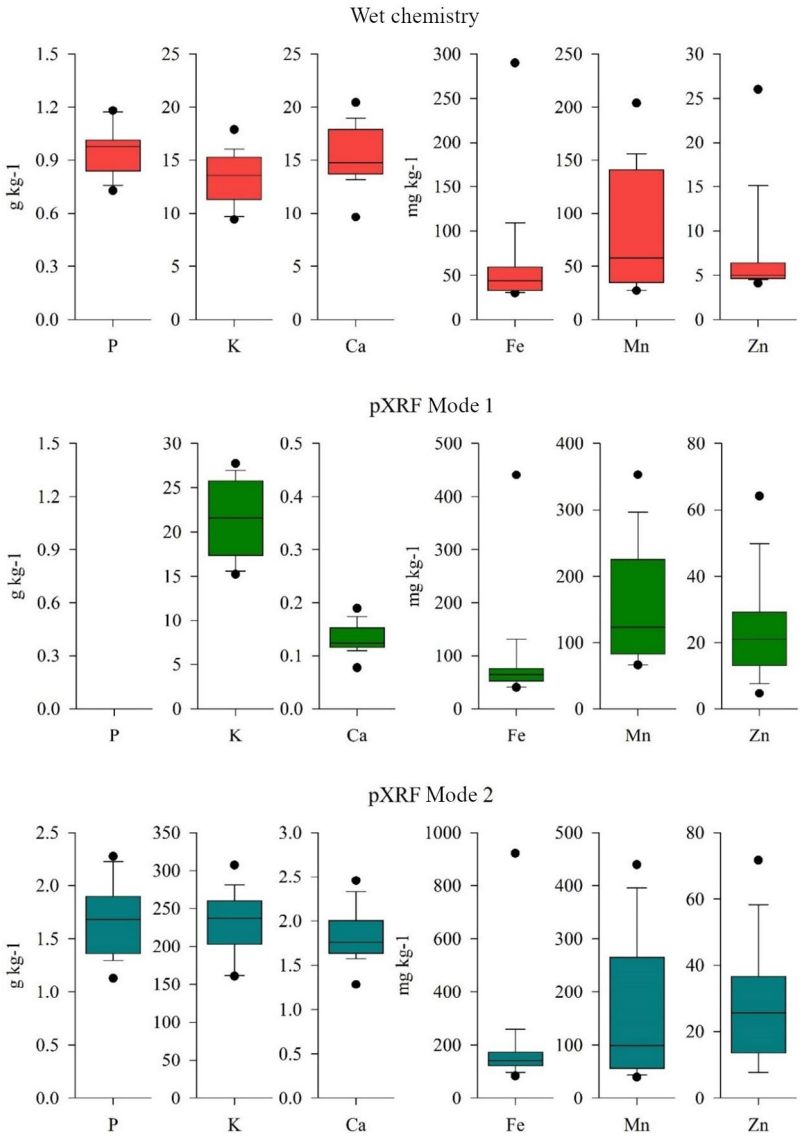

Figure 4: Boxplots of macro and micronutrient contents from Conilon coffee leaves obtained by wet chemistry (acid digestion) and by portable X-ray fluorescence (pXRF) spectrometry using two calibration settings (mode 1: “Soil”, model 2: “Geochem”). Coffee leaves were collected from 19 farms north of the Espírito Santo state, Brasil.

Table 2: Descriptive statistics of nutrient contents of Conilon coffee leaves obtained by pXRF analysis using Modes 1 ("Soil") and 2 ("Geochem"). The leaves were collected in the north of the Espírito Santo state, Brazil, across 19 coffee farms.

Nutrient	Mode 1					Mode 2				
	Max	Min	Mean	SD	CV	Max	Min	Mean	SD	CV
P (g kg^{-1})	NA	NA	NA	-	-	2.3	1.1	1.7	0.3	19.8
K (g kg^{-1})	27.7	15.2	21.4	4.2	19.7	307.2	160.9	231.4	39.9	17.2
Ca (g kg^{-1})	0.19	0.08	0.13	0.03	19.7	2.5	1.3	1.8	0.3	15.6
Fe (mg kg^{-1})	440.7	40.7	88.7	88.3	99.6	921.0	83.0	190.5	182.3	95.7
Mn (mg kg^{-1})	352.9	66.0	147.3	85.0	57.7	439.7	39.3	147.9	123.5	83.5
Zn (mg kg^{-1})	64.2	4.7	22.6	14.6	64.7	71.7	7.7	28.6	17.6	61.5

Mode 1 = "Soil"; Mode 2 = "Geochem"; Max = Maximum value; Min = Minimum value; SD = Standard deviation; CV = Coefficient of variation; and NA = undetermined.

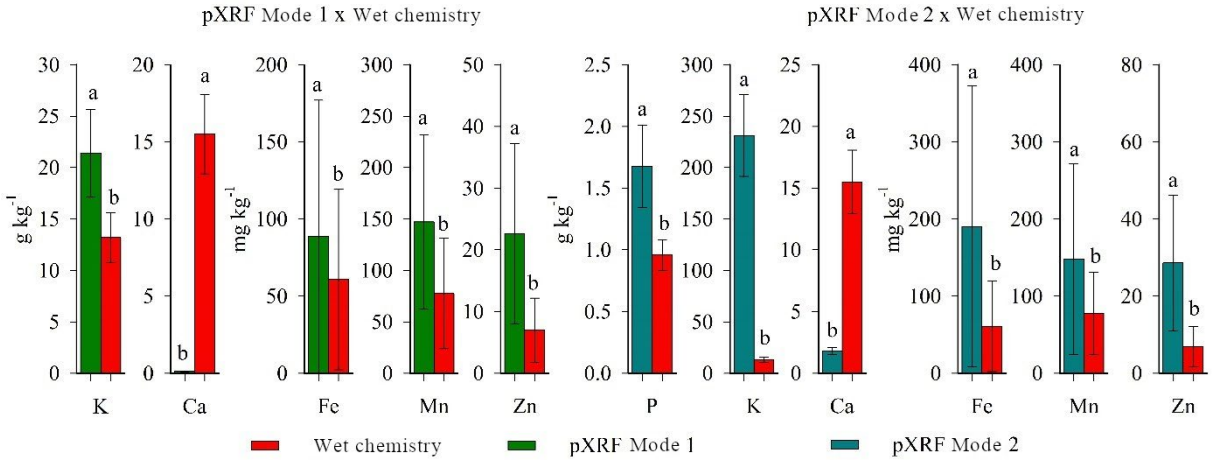

Figure 5: Student's t test performed to compare nutrient contents obtained by wet chemistry and by pXRF (modes 1 and 2) in Conilon coffee leaves collected north of the Espírito Santo state, Brazil, in 19 coffee farms. Different letters indicate statistically significant differences ($p < 0.05$).

Table 3: Correlation coefficients between nutrient contents determined by pXRF and by inductively coupled plasma optical emission spectroscopy (ICP-OES) in Conilon coffee leaves collected across 19 farms north of the Espírito Santo state, Brazil.

Nutrient	Mode 1 vs. wet chemistry	Mode 2 vs. wet chemistry
P	-	0.93**
K	0.90*	0.94**
Ca	0.97**	0.96**
Fe	0.98	0.97**
Mn	0.99	0.96**
Zn	0.54**	0.65**

Mode 1 = "Soil"; Mode 2 = "Geochem".

3.4 Predictions of leaf nutrient contents through predictive models

Using the correlation analysis as reference, it was possible to adjust models capable of predicting leaf nutrient contents (Tables 4 and 5). Mode 2 results were used for modeling, since mode 1 was not capable of detecting P contents and its results were less correlated to wet chemistry analyses when compared to results from mode 2 (Tables 2 and 3). The constructed linear models were accurate, presenting R^2 values between 0.89 and 0.94 and low RMSE for P, K, Ca, Fe, and Mn (Tables 5 and 6; Figure 7). The only exception was the Zn model, which could not achieve accurate predictions (R^2=0.33), although presenting low RMSE.

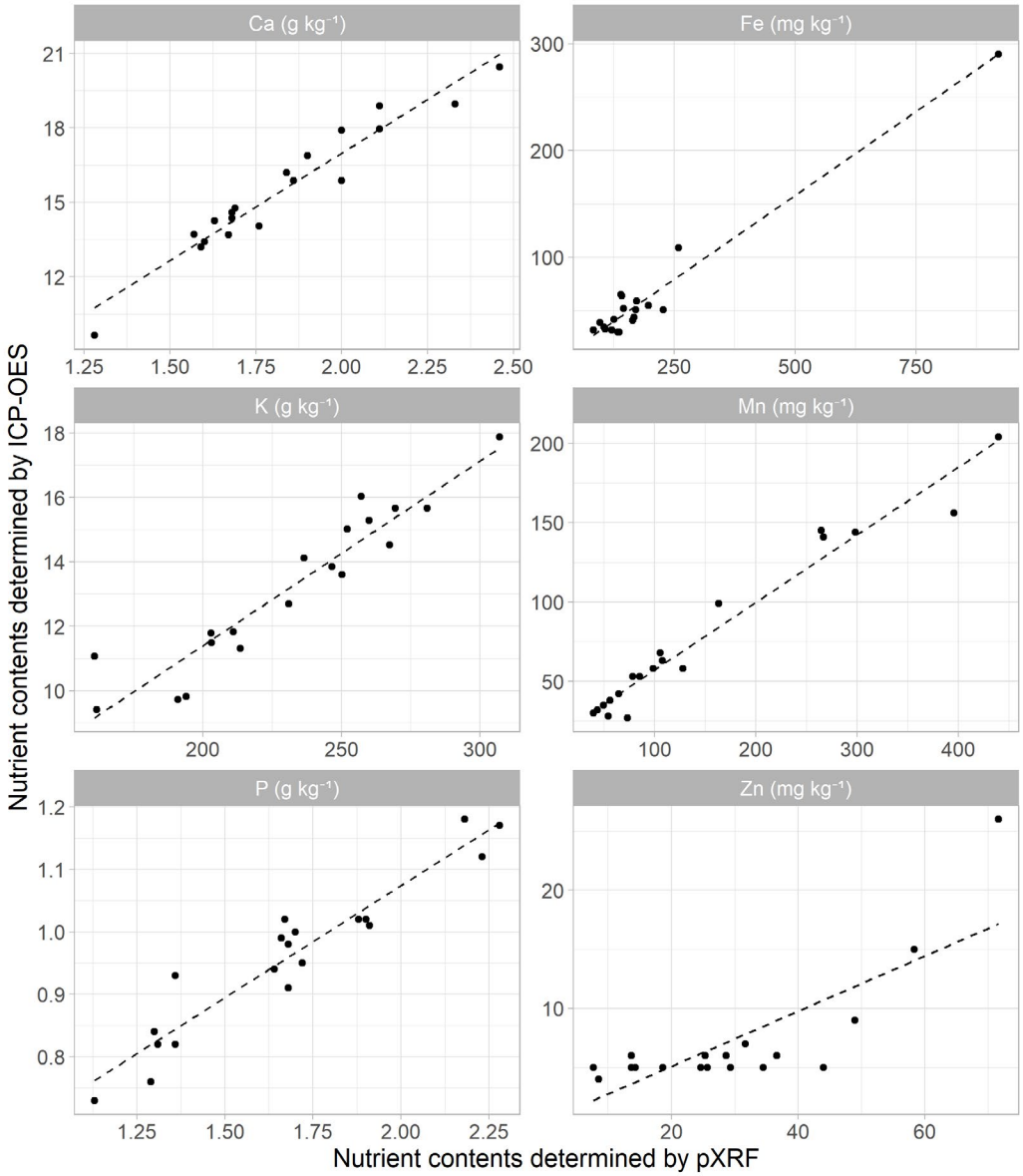

Figure 6: Scatter plots of nutrient contents determined by pXRF (mode 2) and inductively coupled plasma optical emission spectroscopy (ICP-OES) in Conilon coffee leaves collected across 19 farms in the north of the Espírito Santo state, Brazil.

Table 4: Linear models created to predict nutrient contents in Conilon coffee leaves determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) from portable X-ray fluorescence (pXRF) data (mode 2). The studied coffee leaves were collected across 19 farms located north of the Espírito Santo state, Brazil. wc = wet chemistry.

Nutrient	Model	R^2
P_{wc}	$P_{wc} = 0.361 \times P_{pXRF} + 0.3518$	0.90
K_{wc}	$K_{wc} = 0.0572 \times K_{pXRF} - 0.0611$	0.89
Ca_{wc}	$Ca_{wc} = 8.6784 \times Ca_{pXRF} - 0.3695$	0.93
Fe_{wc}	$Fe_{wc} = 0.3139 \times Fe_{pXRF} + 0.9317$	0.95
Mn_{wc}	$Mn_{wc} = 0.42571 \times Mn_{pXRF} + 14.61938$	0.94
Zn_{wc}	$Zn_{wc} = 0.23341 \times Zn_{pXRF} + 0.42613$	0.33

Table 5: Nutrient contents of coffee leaves determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) and predicted using portable X-ray fluorescence (pXRF) data through linear models. The studied coffee leaves were collected across 19 farms located in the north of the Espírito Santo state, Brazil.

Nutrient	ICP-OES[1]	Predicted[1]	Range (mininum-maximum)	RMSE[2]
P (g kg^{-1})	1.0 (± 0.1)	1.0 (± 0.1)	0.7-1.0	0
K (g kg^{-1})	13.2 (±2.4)	13.2 (±2.3)	9.4-17.9	0.8
Ca (g kg^{-1})	15.5 (±2.6)	15.5 (± 2.5)	9.6-20.5	0.7
Fe (mg kg^{-1})	61 (±59)	61 (± 57)	30-290	12
Mn (mg kg^{-1})	78 (±54)	78 (± 53)	27-204	11
Zn (mg kg^{-1})	7 (±5)	7 (± 4)	4-26	3

[1] Mean content determined by ICP-OES vs. predicted contents compared by the t test ($p<0.05$).
[2] Root mean squared error.

Table 6: Nutrient contents considered adequate in Conilon coffee leaves based on samples collected during the grain filling stage.

Nutrient	References					
	(Partelli et al., 2016)[1]		(Partelli et al., 2006)		(Gomes et al., 2016)[5]	(Santos et al., 2021)[6]
	Mean content	Sufficiency level[2]	Conventional management[3]	Organic farming[4]	Mean content	Mean content
P (g kg^{-1})	1.32	1.10 – 1.70	1.6	1.4	1.2 – 1.4	1.24 – 1.72
K (g kg^{-1})	15.9	12.5 – 20.5	16.7	18.5	14.7 – 16.9	8.54 – 14.17
Ca (g kg^{-1})	18.2	14.2 – 25.9	13.5	11.6	14.7 – 22.3	17.64 – 33.96
Fe (mg kg^{-1})	106	73 – 157	112	106	86.7 – 118.3	102.67 – 182.00
Mn (mg kg^{-1})	119	78 – 190	73.9	85	111.7 – 130.7	16.67 – 52.33
Zn (mg kg^{-1})	11.4	8.0 – 17.0	8.9	10.9	9.6 – 13.4	3.67 – 5.00

[1] High productivity (>6 tons ha^{-1}), north of the Espírito Santo state; [2] Sufficiency levels adjusted according to the Integrated System of Diagnosis and Recommendation; [3] High productivity (>3.6 tons ha^{-1} of enriched coffee), north of the Espírito Santo state; [4] High productivity (>2.4 tons ha^{-1} of enriched coffee), north of the Espírito Santo state; [5] Mean contents of seven highly productive genotypes (>6 tons ha^{-1}), north of the Espírito Santo state; [6] Mean contents of nine highly productive genotypes, north of the Espírito Santo state.

4 DISCUSSION

4.1 Nutritional assessment of coffee plants

Mean P and Fe contents in Conilon coffee leaves determined by wet chemistry were below the sufficiency levels reported by other studies conducted in the studied region (Tables 1 and 6) (Gomes et al., 2016; Partelli et al., 2006; Partelli et al., 2016; Santos et al., 2021). Mean K contents obtained from wet chemistry were lower than those of most studies used as reference, but were within the levels considered sufficient for coffee plants (adjusted according to the Integrated System of Diagnosis and Recommendations), as established by Partelli et al. (2016) and according to mean K contents of nine *Coffea canephora* genotypes reported by Santos et al. (2021). Mean Ca and Mn contents determined by wet chemistry were lower and higher than those reported by the literature depending on the study used as reference (Gomes et al., 2016; Partelli et al., 2006; Partelli et al., 2016; Santos et al., 2021), but both nutrients were found within sufficiency levels according to Partelli et al. (2016). Zn contents were within mean contents observed by Santos et al. (2021), but below mean contents reported by other reference studies (Gomes et al., 2016; Partelli et al., 2006), being under sufficiency levels defined by Partelli et al. (2016).

The differences found between wet chemistry and reference studies can be explained by the variability of genotypes, soil types, sampling period, management strategies, and local climatic conditions, which greatly affects the nutritional status of coffee plants and requires the development of specific sufficiency levels for each set of conditions (Barros et al., 2022; Gomes et al., 2016; Oliosi et al., 2020; Partelli et al., 2006; Partelli et al., 2016; Santos et al., 2021). However, as mentioned by Pires at al. (2022), low contents of some nutrients found in this study require attention and correction through the application of fertilizers and amendments, since highly productive coffee plantations require substantial quantities of available nutrients to reach an adequate nutritional status. Out of the 19 studied coffee farms, only three presented P contents within sufficiency levels recommended for the studied region (Table 6) (Partelli et al., 2016). Additionally, only one sample

for Fe, five samples for Mn, and two samples for Zn were within adequate levels. Conversely, one of the studied farms presented contents of Fe, Mn, and Zn above sufficiency levels. This strengthens the need for more precise management of coffee plantations to ensure that plants have adequate levels of available nutrients to maintain high productivity.

4.2 Using pXRF to assess the nutritional status of coffee leaves

Leaf nutrient contents determined by pXRF differed from those determined by wet chemistry in both scanning modes 1 and 2 ("Soil" and "Geochem") (Tables 1 and 2; Figure 5). Total P contents (mode 1) and total contents of K, Fe, Mn, and Zn (modes 1 and 2) were higher compared to wet chemistry results, while Ca contents were lower. These dissimilarities between pXRF and conventional laboratory analyses have also been reported by other authors (Costa Júnior et al., 2020; Silva et al., 2024). Borges et al. (2020) obtained higher contents of macro and micronutrients via pXRF analysis compared to wet chemistry when assessing nutrient contents in 614 leaf samples from 28 plant species. The authors argue that these results were expected, since pXRF determines the total elemental content of samples, while wet chemistry analyses measure only contents extractable by acid solutions. Besides, wet chemistry methods are influenced by the utilized digestion and dilution procedures performed prior to the determination of concentrations by ICP-OES. Still, the opposite trend has also been reported by Andrade et al. (2023), who observed lower nutrient contents when assessing leaves with a pXRF compared to wet chemistry when analyzing 923 samples of eucalyptus leaves. Silva et al. (2024) assessed

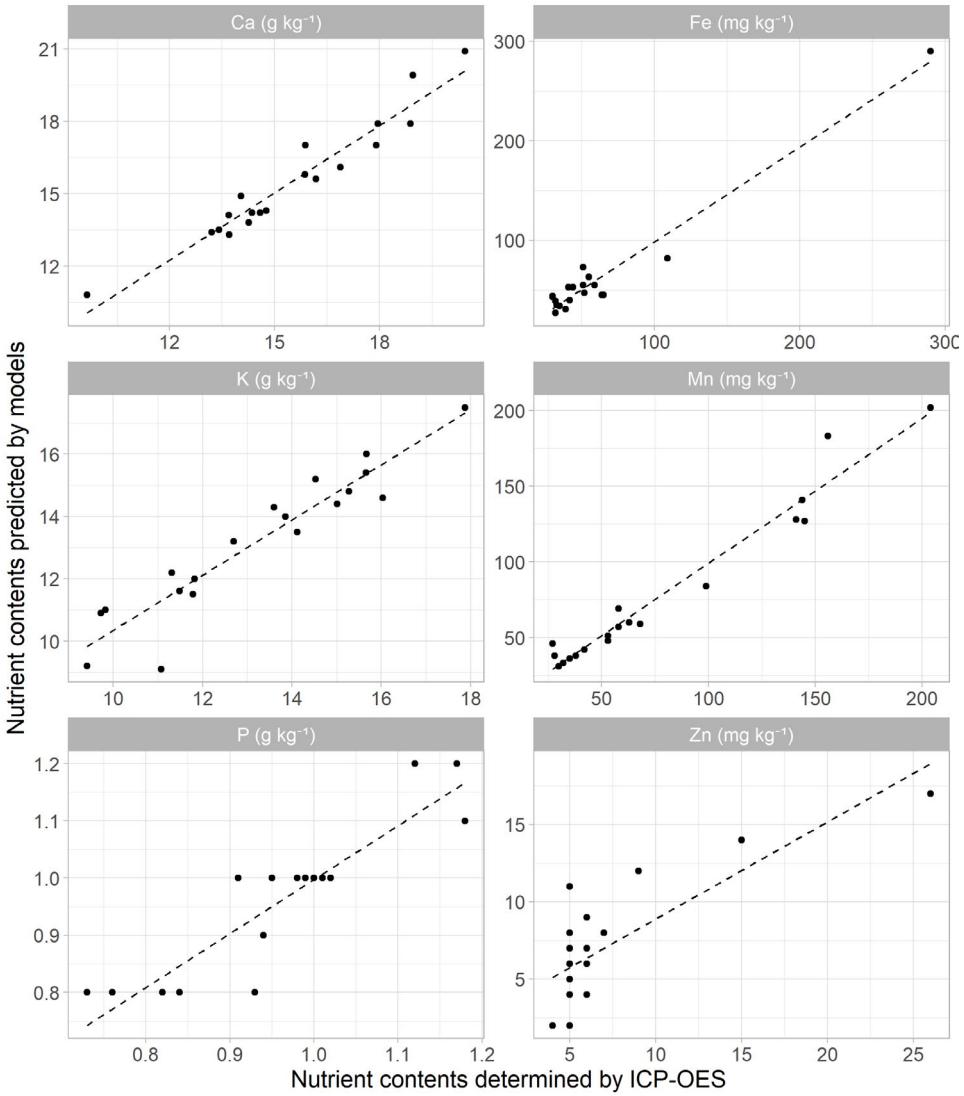

Figure 7: Scatter plot of leaf nutrient contents determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) and predictions performed by linear models using portable X-ray fluorescence (pXRF). Coffee leaves were sampled across 19 farms located in the north of the Espírito Santo state, Brazil.

nutrient contents in leaves of three blueberry varieties and observed that pXRF measurements could be higher or lower than wet chemistry results depending on the assessed element and plant variety, but results from both methods were highly correlated. The irregular distribution of nutrients in leaf samples helps explain these variations in elemental contents (Costa Júnior et al., 2020).

In the present study pXRF results from both scanning modes 1 and 2 ("Soil" and "Geochem") followed distributions similar to those of wet chemistry data, resulting in similar coefficients of variation (Tables 1 and 2), which could be observed in the boxplots (Figure 4). It was clear that one of the samples presented anomalous values of Fe, Mn, and Zn contents when analyzed via both wet chemistry and pXRF. The utilization of pXRF data to develop predictive models for leaf nutrient contents is a promising strategy, but requires further testing (Singh; Sharma; Singh, 2022), specifically on how to identify problematic nutrients that present high variability and how to adequately model these nutrients.

4.3 pXRF data and predictive modeling applied to leaf nutrient predictions

pXRF analysis determines the total elemental contents of samples, which can be highly correlated with nutrient contents measured by the wet chemistry analysis of leaves. In this study, contents provided by pXRF (modes 1 and 2) were higher (P, K, Fe, and Mn) or lower (Ca) than those obtained through wet chemistry, but presented strong correlation with each other, especially results from mode 2 (Tables 1, 2, and 3). This is due to mode 2 being calibrated for materials with a broader range of elemental contents (Andrade et al., 2023; Silva et al., 2024). High correlations between contents obtained by conventional laboratory analysis and pXRF were also reported by other studies which evaluated the applicability of pXRF to the assessment of other types of plant tissue (Borges et al., 2020; Costa Júnior et al., 2020; Costa et al., 2023; Guerra et al., 2018; Silva et al., 2024). McGladdery et al. (2018) studied 25 species of shrubs and grasses and found that correlations for their studied nutrients (K, Cu, Cd, Fe, Mn, Pb, and Zn) were stronger between wet chemistry results and pXRF data from leaves that were dried and ground leaf samples, while data from green leaves (field moisture) and unground dry leaves presented weaker correlations with wet chemistry. Variations between correlation coefficients were also reported by Silva et al. (2024) in blueberry samples.

The strong correlations observed for P, K, Ca, Fe, and Mn in this study using two pXRF scanning modes strengthen the potential of this methodology to aid in the nutritional assessment of plants, especially of coffee plants. The high correlation coefficients showed that, despite wet chemistry and pXRF measuring different quantities (fraction extractable by acid vs. total contents), results from both methods follow similar distributions and vary together (Figure 6), also shown by the boxplots (Figure 4). Differences in distribution explain the weaker correlation observed for Zn, since pXRF analysis could determine Zn contents up to 40 mg kg^{-1}, while wet chemistry only extracted up to 10 mg kg^{-1} from leaf samples, which resulted in very different data distributions.

The high correlation between pXRF and wet chemistry data reveals the compatibility between both methods and facilitates the modeling of wet chemistry data using data from pXRF. The observed strong correlations indicate a linear relationship between data from the two methods and explain the high accuracy obtained from prediction models for P, K, Ca, Fe, and Mg (R^2 between 0.89 and 0.94) and low RMSE values (Tables 4 and 5; Figure 7). Using pXRF to assess elemental contents in plants, Reidinger, Ramsey, and Hartley (2012) were able to create accurate models for P and Si in dried and ground leaves of plant of the *Poaceae* family. Borges et al. (2020) evaluated the contents of macronutrients (P, K, Ca, Mg, and S) and micronutrients (Cu, Fe, Zn, and Mn) in plants of several species and observed strong correlations between wet chemistry and pXRF results. In eucalyptus leaves, nutrient contents presented strong correlations for all elements, except Mg, while in sugar cane leaves, nutrient contents were weakly correlated, except for S. In a study about micronutrients in ground barley, Zn contents obtained by pXRF analysis presented strong correlation with those from wet chemistry, while Fe and Cu presented moderate correlations (Khan et al., 2022). Guerra et al. (2018) assessed fresh sugar cane leaves and found high correlation coefficients for Ca, K, S, and Si.

Results obtained in this study strengthen the potential of pXRF data applied to leaf assessment. The use of proximal sensing to estimate leaf nutritional status reduces the number of samples that undergo wet chemistry analysis, decreasing the long-term cost of frequent nutrient assessment. Inexpensive methods can incentivize large coffee farm to monitor their plants more frequently, adjusting management according to plant needs. Lower costs make leaf analysis more accessible to smaller farms, better informing small producers about the nutritional needs of their coffee crops. Rapid methods such as pXRF analysis can also contribute to increasing data available for research, facilitating agronomical studies that involve plant tissue analysis. Future research should focus on nutrient analysis in different relevant crops and management strategies that utilize predictive models of leaf nutrient contents.

5 CONCLUSIONS

Strong correlations were found between pXRF and wet chemistry results for all studied nutrients (r>0.9), except for Zn (r<0.65). Mode 2 is recommended for Conilon leaf analysis due to higher correlation with wet chemistry and its capability

of detecting P in leaf samples. Except for Zn, predictive models of nutrient contents were accurate and can be used to reduce the number of samples sent for laboratory analysis, providing low-cost and rapid monitoring of the nutrient status of Conilon coffee leaves.

6 ACKNOWLEDGEMENTS

The authors would like to thank the coffee farmers of the northern region of the Espírito Santo state, who allowed the use of their coffee plants in this study, and the institutions UFES, EMBRAPA Solos and CAPES for the financial support to collect and analyze the studied samples.

7 AUTHOR CONTRIBUTIONS

Conceptual Idea: Pires, I.F.; Fontana, A.; Partelli, F.L.; Teixeira, W.G.; Methodology deisgn: Pires, I.F.; Fontana, A.; Maestá, B.C.; Mendonça, H.M.; Partelli, F.L.; Teixeira, W.G.; Data collection: Pires, I.F.; Fontana, A.; Maestá, B.C.; Mendonça, H.M.; Partelli, F.L.; Teixeira, W.G.; Data analysis and interpretation: Pires, I.F.; Fontana, A.; Maestá, B.C.; Mendonça, H.M.; Teixeira, W.G.; and Writing and editing: Pires, I.F.; Benedet, L.; Mancini, M.; Curi, N.

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