



Article

Prediction of Foliar Nutrient Contents and Differentiation of Scion/Rootstock Combinations in Citrus via X-Ray Fluorescence Spectrometry

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Abstract: Citriculture has worldwide importance, and monitoring the nutritional status of plants through leaf analysis is essential. Recently, proximal sensing has supported this process, although there is a lack of studies conducted specifically for citrus. The objective of this study was to evaluate the application of portable X-ray fluorescence spectrometry (pXRF) combined with machine learning algorithms to predict the nutrient content (B, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn) of citrus leaves, using inductively coupled plasma optical emission spectrometry (ICP-OES) results as a reference. Additionally, the study aimed to differentiate 15 citrus scion/rootstock combinations via pXRF results and investigate the effect of the sample condition (fresh or dried leaves) on the accuracy of pXRF predictions. The samples were analyzed with pXRF both fresh and after drying and grinding. Subsequently, the samples underwent acid digestion and analysis via ICP-OES. Predictions using dried leaves yielded better results (R^2 from 0.71 to 0.96) than those using fresh leaves (R^2 from 0.35 to 0.87) for all analyzed elements. Predictions of scion/rootstock combinations were also more accurate with dry leaves (Overall accuracy = 0.64, kappa index = 0.62). The pXRF accurately predicted nutrient contents in citrus leaves and differentiated leaves from 15 scion/rootstock combinations. This can significantly reduce costs and time in the nutritional assessment of citrus crops.

Keywords: proximal sensing; machine learning; leaf nutrient analysis; pXRF; *Citrus* spp.



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1. Introduction

Citrus fruits, a group that includes oranges, lemons, mandarins, and grapefruits, originate from Southeast Asia but are now cultivated in various regions worldwide due to their nutritional value, flavor, and versatility [1,2]. Brazil stands out globally in the production of these fruits, particularly oranges, with a yield of 17 million tons during the 2022 season, establishing itself as the global leader in this segment [3]. For the 2024/25 season, the Citrus Defense Fund (Fundecitrus) projects a production of 232.38 million 40.8 kg boxes in the citrus belt of São Paulo and the Triângulo and Southwest regions of Minas Gerais, the world's largest orange-producing area [4]. Brazil is internationally recognized as the largest producer and leading exporter of sweet orange juice [5], with production distributed

across all regions of the country due to the crop's adaptability to diverse edaphoclimatic conditions [6,7].

To achieve higher productivity, proper crop nutritional management begins with an accurate assessment of the plant's nutritional status. While soil serves as the fundamental matrix for technical recommendations of amendments and fertilization, leaf analysis reflects the nutrients effectively absorbed and represents the best indicator of the plant's nutritional condition [2]. However, traditional methods of leaf analysis, such as ICP-OES, present challenges that may limit their large-scale application. These methods require skilled labor, significant sample preparation time (including oven drying and leaf grinding), and the use of chemical reagents and sophisticated equipment, which increase operational costs and can generate environmental waste [8]. Given these limitations, portable X-ray fluorescence spectrometry (pXRF) emerges as a promising alternative, enabling rapid and non-destructive analyses directly in the field or laboratory, reducing the time and costs associated with leaf nutritional characterization.

A recent and underexplored alternative is the use of a portable X-ray fluorescence spectrometer (pXRF). This device provides near-instantaneous results on the chemical element content of a sample (from Mg to U) without requiring chemical reagents or generating waste. Furthermore, this method is non-destructive to the samples [9]. While pXRF has been widely applied in recent soil studies [10–13], studies involving leaves remain scarce [14–17], particularly for citrus leaves, with limited research correlating pXRF results with those obtained through traditional methods.

pXRF operates by exciting atoms with high-energy radiation, prompting them to emit characteristic radiation, which enables the identification and quantification of specific chemical elements. The X-ray fluorescence (XRF) technique has been employed to develop a fast and reproducible method for assessing the origin and quality of Sicilian tomatoes, including the PGI “Pomodoro di Pachino” [18]. Additionally, it has been successfully applied to determine trace elements (As, Cu, Pb, and Zn) in deciduous leaves of beech (*Fagus sylvatica*), birch (*Betula* spp.), and oak (*Quercus* spp.) trees collected from three sites affected by metal mines in southwest England [19].

Despite the advantages of portable X-ray fluorescence spectrometry (pXRF), this approach has some limitations that must be considered. One of the main restrictions is the inability of pXRF to detect elements lighter than magnesium (Mg), such as carbon (C), nitrogen (N), and boron (B), which are essential for plant metabolism and frequently monitored in nutritional diagnostics [20,21]. Additionally, factors such as leaf moisture content can significantly influence the results, as the presence of water interferes with the interaction of X-rays with the elements in the sample, leading to the underestimation of nutrient concentrations. Although this effect is known, there are still few studies comparing analyses conducted on fresh and dried leaves, highlighting the need for more detailed investigations. Fresh leaf analysis could make field-based nutritional assessments more efficient by reducing the time required for diagnostics, but methodological adjustments are necessary to minimize the impact of moisture on the results [16]. In this context, the use of machine learning algorithms can help improve the accuracy of estimates by correcting variations caused by sample conditions, thereby enhancing the potential of pXRF for plant nutritional characterization.

The selection of the 15 scion/rootstock combinations in this study was based on their agricultural significance and widespread use in commercial citrus orchards in Brazil. These combinations are widely used for their influence on tree vigor, yield potential, disease resistance, and adaptability to diverse soil and climatic conditions. Given the scarcity of studies evaluating the influence of scion/rootstock combinations on leaf nutrient concentrations using pXRF, this study introduces an innovative approach by integrating

pXRF technology with machine learning algorithms to differentiate these combinations. By offering insights into how different combinations affect nutrient composition, this research contributes to enhancing citrus nutritional management and advancing precision agriculture practices.

Given the global importance of citrus cultivation and the absence of studies using pXRF for leaf analysis specifically focused on citrus plants, this study was conducted. The objectives were to apply pXRF data to (i) predict the nutrient contents (B, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn), as well as Na and Al determined via ICP-OES, using machine learning algorithms; (ii) predict 15 scion/rootstock combinations; and (iii) evaluate the effects of fresh versus dried citrus leaves analyzed via pXRF. We hypothesize that pXRF, combined with machine learning algorithms, provides a suitable alternative method for clean, rapid, and accurate prediction of the nutritional status of *Citrus* spp. and for differentiating scion/rootstock combinations.

2. Materials and Methods

2.1. Sample Collection

The study was conducted in a commercial orchard located in Perdões, Minas Gerais, Brazil (latitude 21°05'35.0" S and longitude 44°58'48.9" W), at an altitude of 848 m (Figure 1). The region is characterized by a Cwa climate, subtropical with dry winters and hot, rainy summers [22]. The orchard's soils are predominantly Red-Yellow Argisols [23], developed from granite-gneiss, as observed in the field. Soil samples collected at a depth of 0–20 cm were chemically characterized, yielding the following values: pH (H₂O) 6.1, exchangeable Ca 4.18 cmol_c dm⁻³, Mg 1.70 cmol_c dm⁻³, Na 11.00 mg dm⁻³, Al 0.10 cmol_c dm⁻³, H + Al 1.90 cmol_c dm⁻³, base saturation 6.39 cmol_c dm⁻³, potential cation exchange capacity (CEC) 8.29 cmol_c dm⁻³, effective CEC = 6.49 cmol_c dm⁻³, base saturation (V) 77.09%, aluminum saturation (m) 1.54%, available K 199.23 mg dm⁻³, P 21.00 mg dm⁻³, Zn 2.10 mg dm⁻³, Fe 38.30 mg dm⁻³, Mn 10.90 mg dm⁻³, Cu 0.13 mg dm⁻³, B 0.13 mg dm⁻³, S 3.30 mg dm⁻³, and soil organic matter 35 g kg⁻¹. The orchard is rainfed, and its pest, disease, and nutritional management follow the recommendations of [24,25].

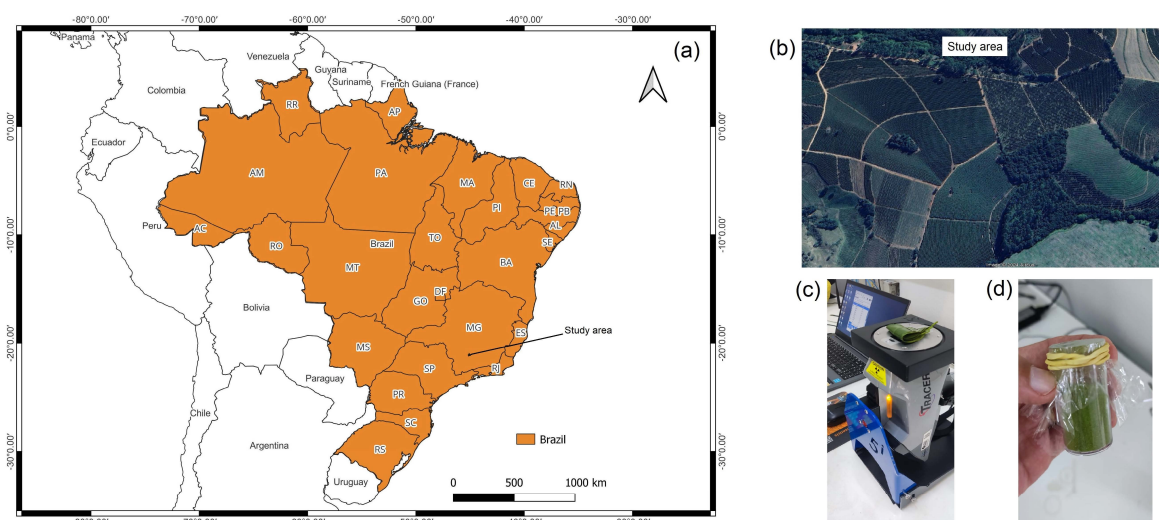


Figure 1. The study area location (a); an aerial photo of the site (Google Earth) (b); the pXRF equipment being used for the analysis of fresh leaves (c); and the ground, dried leaves ready for analysis via pXRF and acid digestion (d).

Fifteen scion/rootstock combinations of citrus (*Citrus* spp.) were evaluated, including 11 unique combinations and 2 cases of ‘Ponkan’ mandarin and ‘Natal’ orange grafted onto

Rangpur lime rootstock, differing in plant age. In total, 165 leaf samples were collected on 17 July 2023, 11 per combination. The combinations included the following:

Sweet orange (*Citrus sinensis* L. Osbeck) varieties Baianinha, Cara Cara, Natal (4 and 9 years), Pêra, Rubi, Folha Murcha; Tangor Piemonte [Clementine mandarin (*Citrus clementina* hort. ex. Tanaka) × Murcott tangor (*C. reticulata* Blanco × *C. sinensis* L. Osbeck)]; Ponkan mandarin (*Citrus reticulata* Blanco) (7 and 18 years), grafted onto Rangpur lime (*Citrus limonia* Osbeck); sweet orange varieties Rubi, Serra d'Água, and Westin and Tahiti acid lime (*Citrus latifolia* Tanaka), grafted onto Swingle citrumelo (*Citrus paradisi* × *Poncirus trifoliata* (L.) Raf.); Natal orange grafted onto Indio citrandarin [Sunki mandarin (*Citrus sunki* (Hayata) hort. ex Tanaka × *Poncirus trifoliata* (L.) Raf.).

These combinations are detailed in Table 1. The collected leaf samples were stored in labeled plastic bags and transported in a thermal box to the Plant Nutrition Laboratory at the Federal University of Lavras.

Table 1. Scion/rootstock combinations of citrus, planting information, and the symbols used in this study per combination.

Combination	Group	Scion	Rootstock	Planting Year	Age (Years)	Spacing (m)	Symbol
1	Orange	Baianinha	Rangpur lime	2016	7	5.5 × 2.5	BLC
2		Cara Cara	Rangpur lime	2016	7	5.5 × 2.5	CCLC
3		Folha Murcha	Rangpur lime and Swingle citrumelo	2010	13	6.0 × 3.0	MLCSW
4		Natal	Rangpur lime	2014	9	7.0 × 2.6	NLC14
5		Natal	Rangpur lime	2019	4	6.5 × 1.5	NLC19
6		Natal	Indio citrandarin	2019	4	6.5 × 1.5	NCI
7		Pêra	Rangpur lime	2014	9	7.0 × 2.6	PELC
8		Rubi	Rangpur lime	2020	3	6.5 × 1.5	RLC
9		Rubi	Swingle citrumelo	2020	3	6.5 × 1.5	RCSW
10		Serra d'água	Swingle citrumelo	2020	3	6.5 × 1.5	SCSW
11	Mandarin	Westin	Swingle citrumelo	2020	3	6.5 × 1.5	WCSW
12		Ponkan	Rangpur lime	2005	18	6.0 × 3.0	PKLC05
13		Ponkan	Rangpur lime	2016	7	5.8 × 2.6	PKLC16
14		Piemonte	Rangpur lime	2016	7	5.5 × 2.5	PILC
15	Acid lime	Tahiti	Swingle citrumelo	2020	3	6.5 × 3.0	TCSW

2.2. Laboratory Analyses

The 165 citrus leaf samples were analyzed in two conditions using a pXRF: intact, freshly collected, washed with distilled water using a laboratory wash bottle, and dried with paper towels (fresh leaves), representing field conditions, and after oven-drying at 65 °C until a constant weight was achieved, ground to 1 mm [26], and stored in plastic bags (dried leaves). A Tracer 5 g pXRF (Bruker Analytical Instrumentation, Billerica, MA, USA) was used, equipped with an Rh X-ray tube operating at 50 keV and 100 µA. Measurements were conducted in “Plants” mode in triplicate, with 60 s per reading, quantifying Al, Ca, Cl, Cr, Cu, Fe, K, Mg, Mn, P, Rb, S, Si, Sr, and Zn. The accuracy of the equipment for each element analyzed was conducted by the calculation of recovery values using three certified reference materials: NIST (National Institute of Standards and Technology) 1573a (tomato leaves), NIST 1547 (peach leaves), and CS-P provided by the pXRF manufacturer. The calculation of the recovery values (in %) (content determined by pXRF/certified content × 100) returned

the following results for NIST 1573a, NIST 1547, and CS-P, respectively: Al (118/485/-); Ca (18/82/90); Cl (75/183/-); Cr (-/-/-); Cu (125/181/-); Fe (122/174/-); K (74/89/88); Mg (-/-/-); Mn (113/129/98); P (60/79/83); S (64/66/83); Si (-/-/-); Sr (-/-/-); Zn (141/195/102). Dash symbol represents lack of that nutrient content in the reference material or no detection of that element by pXRF.

Fresh leaves were analyzed by stacking seven leaves per sample. Instrument performance was evaluated by recovery calculations using a certified reference material (CRM) provided by the pXRF manufacturer, reaching 85% for P, 91% for K, 89% for Ca, 87% for S, 97% for Mn, and 95% for Zn.

The same ground and dried samples analyzed via pXRF were also processed for conventional chemical analysis. Triplicate 0.5 g samples underwent nitric-perchloric digestion, followed by analysis using inductively coupled plasma optical emission spectrometry (ICP-OES) (Spectro Analytical Instruments Inc., Kleve, Germany). Concentrations of Al, B, Ca, Cu, Fe, K, Mg, Mn, Na, P, S, and Zn were quantified using a multielement calibration curve at specific wavelengths.

2.3. Statistical Analyses and Predictive Model Development

Outliers in the pXRF data for fresh and dried leaves were identified and removed using boxplots. Pearson correlations were calculated to compare pXRF and ICP results using the *corrplot* package [27] in R software (<https://www.r-project.org/>) [28].

The pXRF data were used to develop nutrient prediction models for citrus leaves. A subset of 70% of the data (116 samples) was used for training and the remaining 30% (49 samples) for external validation. Both datasets included all 15 scion/rootstock combinations.

Six machine learning algorithms were tested for nutrient prediction: projection pursuit regression (PPR), random forest (RF), support vector machine (SVM), extreme gradient boosting (XGB), cubist regression, and partial least squares (PLS). These algorithms have been widely used in the literature given their ability to deliver accurate predictions of multiple variables [29–31]. Also, it is well-known that different algorithms tend to produce variable results, which always requires tests of multiple algorithms to reach the best prediction model for each target variable of interest [32,33]. The nutrient concentrations (Al, B, Ca, Cu, Fe, K, Mg, Mn, Na, P, S, and Zn) obtained via ICP-OES were estimated based on pXRF results for fresh and dried leaves.

The accuracy of the predictions was assessed using the coefficient of determination (R^2), root mean square error (RMSE), and residual prediction deviation (RPD) between observed (ICP-OES) and predicted values for the validation subset. The best model for each nutrient was determined based on the lowest RMSE.

To evaluate the ability of pXRF data (from fresh and dried leaves) to differentiate the 15 citrus combinations, predictive models were developed using the C5.0, PLS, RF, SVM, XGB, and TreeBag algorithms. Similar to nutrient prediction, the modeling dataset (70%) was used to create models and the validation dataset (30%) to evaluate their accuracy through overall accuracy (OA) and kappa index (Equation (1)) calculations.

$$Kappa = (Po - Pe) / (1 - Pe) \quad (1)$$

where Po is the proportion of scion/rootstock combinations correctly classified and Pe is the probability of random agreement. Values of Kappa index range from -1 to 1 , with increasing accuracy as it becomes closer to 1 [34].

3. Results

3.1. Descriptive Statistics of Nutrients in Citrus Scion/Rootstock Combinations

The descriptive statistics for foliar macronutrient and micronutrient levels across different citrus scion and rootstock combinations are presented in Table 2. The results reveal greater variability in the concentrations of the micronutrients Zn and Cu, which exhibited high coefficients of variation, 36% and 59%, respectively.

Table 2. Descriptive statistics of data obtained via ICP-OES for 15 citrus scion/rootstock combinations and the adequacy classes per nutrient according to Quaggio et al. [25]. (Colors: black—adequate; orange—below adequate range; purple—above adequate range).

Element	Min ¹	Max ²	Mean	Adequacy Classes	STD ³	CV ⁴ (%)
P (g kg ^{−1})	1.0	2.9	1.7	1.2–1.6	0.1	17
K (g kg ^{−1})	8.7	25.3	16.2	10–15	0.6	16
Ca (g kg ^{−1})	23.8	61.1	37.3	35–50	1.3	14
Mg (g kg ^{−1})	0.9	5.9	2.8	3.5–5.0	0.2	18
S (g kg ^{−1})	1.6	5.1	3.0	2.0–3.0	0.2	13
Al (g kg ^{−1})	0.1	0.7	0.2	-	0.0	28
B (mg kg ^{−1})	42	233	101	50–150	11	21
Cu (mg kg ^{−1})	0	25	4	10–20	2	59
Fe (mg kg ^{−1})	94	359	170	50–150	12	20
Mn (mg kg ^{−1})	19	108	41	30–60	5	24
Zn (mg kg ^{−1})	12	144	30	35–70	7	36
Na (mg kg ^{−1})	89	306	193	-	9	14

¹ Min: minimum value; ² Max: maximum value; ³ STD: standard deviation; ⁴ CV: coefficient of variation. These nutrient levels were interpreted using the adequacy classes of nutrients defined by Quaggio et al. [25] for citrus.

The variability observed in micronutrient concentrations, especially zinc (Zn) and copper (Cu), can have significant implications for citrus productivity and quality. Zn plays a crucial role in the synthesis of auxins, hormones that regulate plant growth and development. Zn deficiencies can lead to reduced vegetative growth, lower fruit formation, and decreased productivity. On the other hand, excessive Zn levels can cause toxicity, leading to chlorosis and interference with the uptake of other essential nutrients [35,36]. Cu is essential for photosynthesis and lignin formation in plants. Inadequate Cu levels can compromise plant resistance to pathogens and negatively affect fruit quality. However, high Cu concentrations can be toxic to plants, causing symptoms such as chlorosis and leaf necrosis [37,38]. Therefore, proper management of Zn and Cu levels is essential to ensure nutritional balance, optimize productivity, and maintain citrus fruit quality.

The macronutrient and micronutrient levels per scion/rootstock combination (Table 3) highlight variability in nutrient levels among combinations. Furthermore, these levels can be interpreted using the classes defined by [25], which demonstrate variability in classification for the same nutrient across different scion/rootstock combinations.

Table 3. Average foliar macronutrient and micronutrient concentrations for the 15 citrus scion/rootstock combinations obtained via ICP-OES and their corresponding foliar nutrient adequacy ranges as defined by Quaggio et al. [25] (Colors: black—adequate; orange—below adequate range; purple—above adequate range).

Combination Scion/Rootstock ¹	P	K	Ca	Mg	S	B	Cu	Fe	Mn	Zn
	g kg ⁻¹				mg kg ⁻¹					
BLC	2.0	19	31	1.7	2.9	89	2	143	32	18
CCLC	1.9	13	41	3.6	3.6	137	4	238	28	22
MLCSW	1.4	14	39	2.8	3.6	172	7	162	68	85
NLC14	1.5	15	36	2.0	3.3	124	3	141	44	39
NLC19	1.3	17	39	1.7	3.0	100	4	193	50	38
NCI	1.5	18	42	2.3	2.8	145	5	190	51	25
PELC	1.2	18	41	2.1	3.8	120	6	147	54	51
RLC	1.7	22	29	2.7	2.7	61	5	182	31	18
RCSW	1.9	19	39	3.8	2.9	71	4	144	30	19
SCSW	2.3	20	42	4.9	3.0	94	4	201	38	20
WCSW	2.4	18	32	4.0	3.3	80	6	235	33	25
PKLC05	1.6	13	36	2.9	3.0	98	4	153	45	26
PKLC16	1.3	13	39	2.4	3.1	83	6	150	43	24
PILC	1.5	11	36	1.8	2.9	81	1	118	36	25
TCSW	1.6	16	37	3.6	1.9	59	3	153	26	16
Quaggio et al. [25]	1.2–1.6	10–15	35–50	3.5–5.0	2.0–3.0	50–150	10–20	50–150	30–60	35–70

¹ BLC: Baianinha–Rangpur lime, CCLC: Cara Cara–Rangpur lime, MLCSW: Folha Murcha–Rangpur lime and Swingle citrumelo, NLC14: Natal–Rangpur lime planted in 2014, NLC19: Natal–Rangpur lime planted in 2019, NCI: Natal–Índio citrandarin, PELC: Pêra–Rangpur lime, RLC: Rubi–Rangpur lime, RCSW: Rubi–Swingle citrumelo, SCSW: Serra d’água–Swingle citrumelo, WCSW: Westin–Swingle citrumelo, PKLC05: Ponkan–Rangpur lime planted in 2005, PKLC16: Ponkan–Rangpur lime planted in 2016, PILC: Piemonte–Rangpur lime, TCSW: Tahiti–Swingle citrumelo.

Considering the foliar macronutrient and micronutrient levels across the different scion/rootstock combinations, most combinations exhibited Mg, Cu, and Zn concentrations below the adequate ranges defined by [25]. Conversely, P, K, S, and Fe levels were predominantly higher than the adequate ranges. More importantly, since all the plants are healthy, i.e., plants were not presenting deficiency or toxicity symptoms, it is clear that nutrient contents tend to vary per scion/rootstock combination.

3.2. Comparison of pXRF Results in Fresh and Dried Leaves

Principal component analysis (PCA) of pXRF data obtained from fresh leaves (Figure 2) and dried leaves (Figure 3) demonstrated improved differentiation of scion/rootstock combinations when using dried leaves. In this case, PC1 and PC2 explained 47% of the data variability, compared to 39% for fresh leaves.

The correlations between elements detected by pXRF also varied between fresh and dried leaves. For instance, Mg levels in fresh leaves were directly correlated with S, Fe, Sr, and Cl. However, in dried leaves, Mg levels became inversely proportional to Fe and S. This indicates that drying the samples may alter the distribution of certain elements within the leaf tissue, possibly due to the removal of moisture interference and the redistribution of compounds. Importantly, significant variations were observed in elemental concentrations across different analysis conditions (pXRF on fresh leaves, pXRF on dried leaves, and ICP-OES) (Table 4). These differences emphasize the need for caution when interpreting results based on the analysis technique (pXRF vs. ICP) and leaf condition (fresh vs. dried) when using pXRF.

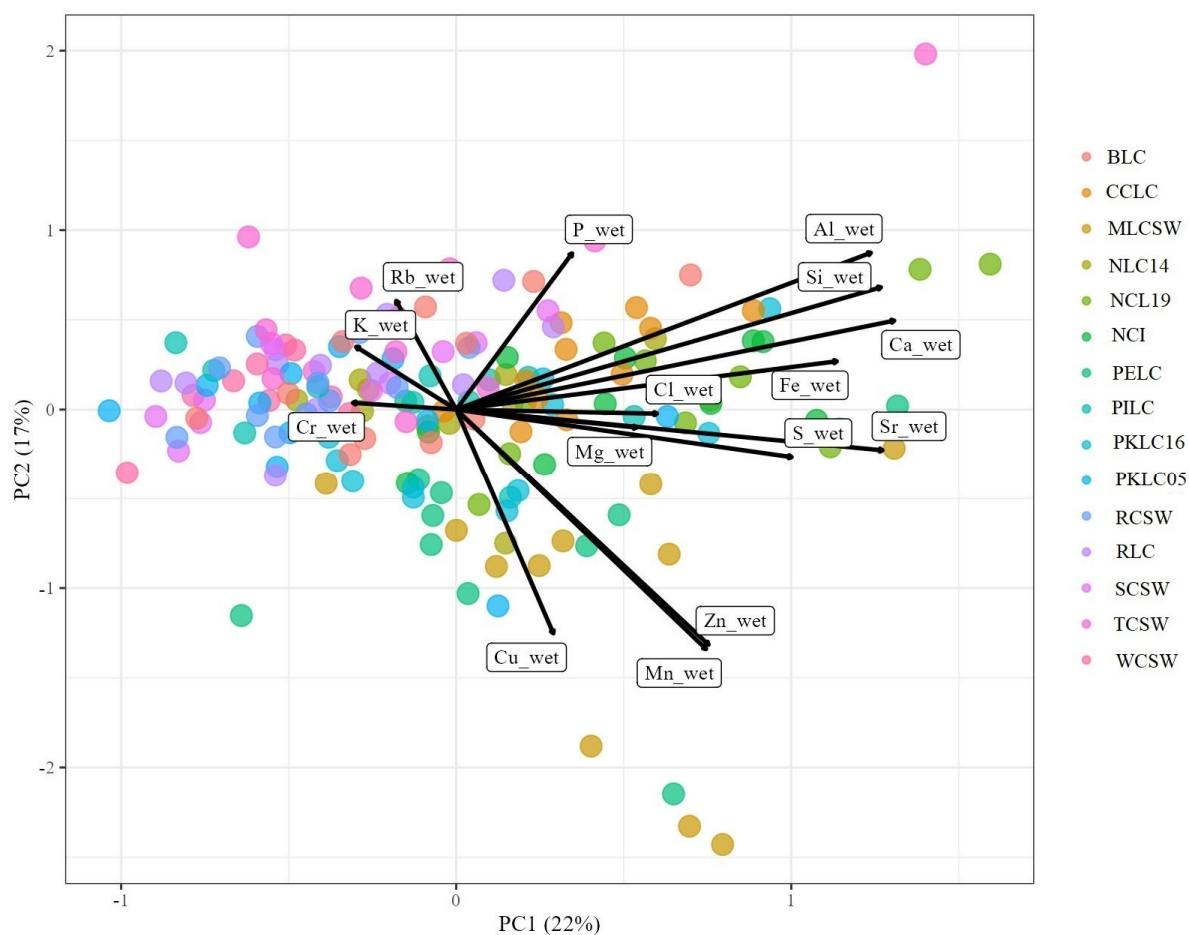


Figure 2. Principal component analysis (PCA) of 15 elements detected by pXRF for fresh leaves from 15 citrus scion/rootstock combinations. BLC: Baianinha–Rangpur lime, CCLC: Cara Cara–Rangpur lime, MLCSW: Folha Murcha–Rangpur lime and Swingle citrumelo, NLC14: Natal–Rangpur lime planted in 2014, NLC19: Natal–Rangpur lime planted in 2019, NCI: Natal–Índio citrandarin, PELC: Pêra–Rangpur lime, RLC: Rubi–Rangpur lime, RCSW: Rubi–Swingle citrumelo, SCSW: Serra d’água–Swingle citrumelo, WCSW: Westin–Swingle citrumelo, PKLC05: Ponkan–Rangpur lime planted in 2005, PKLC16: Ponkan–Rangpur lime planted in 2016, PILC: Piemonte–Rangpur lime, TCSW: Tahiti–Swingle citrumelo.

In the practical context, this means that using fresh leaves for field applications can provide a quick and low-cost alternative for nutritional screening but with lower accuracy compared to dried leaves. On the other hand, for calibration purposes and a more precise comparison of nutrient levels, dried leaves prove to be more reliable. Thus, the choice of the method should consider the balance between practicality and accuracy, depending on the objectives of the nutritional analysis.

Notable discrepancies were observed for Al, where ICP results were nearly 10 times lower than those from pXRF. Conversely, for Ca, K, P, and S, ICP values were significantly higher than those from pXRF. Comparing fresh and dried leaf results via pXRF, dried leaves showed much higher concentrations of Ca, Cl, Fe, K, Mn, P, S, Sr, and Zn—sometimes two to three times greater than fresh leaves. These findings underscore the need for careful interpretation.

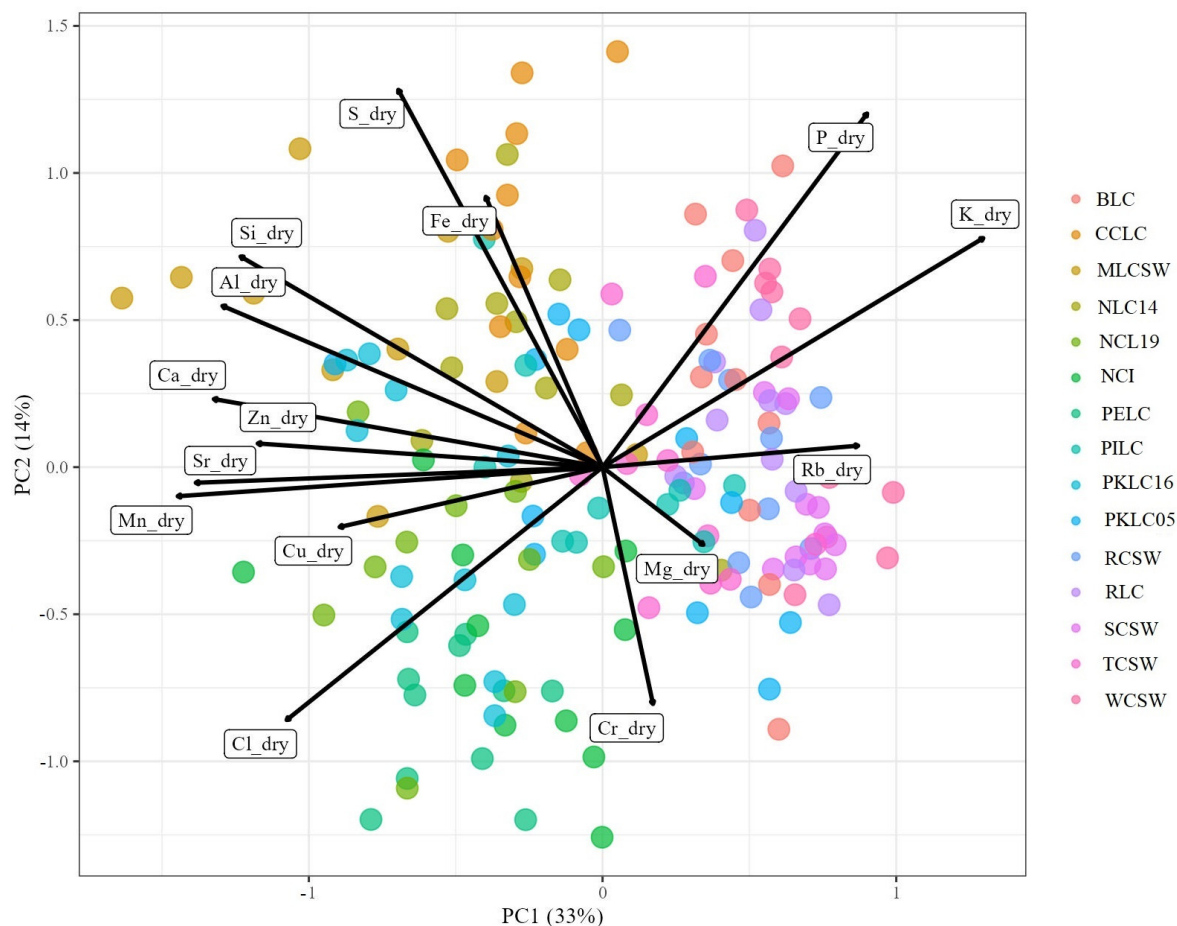


Figure 3. Principal component analysis (PCA) of 15 elements detected by pXRF for dried leaves from 15 citrus scion/rootstock combinations. BLC: Baianinha–Rangpur lime, CCLC: Cara Cara–Rangpur lime, MLCSW: Folha Murcha–Rangpur lime and Swingle citrumelo, NLC14: Natal–Rangpur lime planted in 2014, NLC19: Natal–Rangpur lime planted in 2019, NCI: Natal–Índio citrandarin, PELC: Pêra–Rangpur lime, RLC: Rubi–Rangpur lime, RCSW: Rubi–Swingle citrumelo, SCSW: Serra d’água–Swingle citrumelo, WCSW: Westin–Swingle citrumelo, PKLC05: Ponkan–Rangpur lime planted in 2005, PKLC16: Ponkan–Rangpur lime planted in 2016, PILC: Piemonte–Rangpur lime, TCSW: Tahiti–Swingle citrumelo.

Table 4. Elemental concentrations in citrus leaves analyzed via pXRF in fresh and dried conditions and via ICP-OES.

Method	Al (mg kg ^{−1})	Ca (g kg ^{−1})	Cl (mg kg ^{−1})	Cr (mg kg ^{−1})	Cu (mg kg ^{−1})	Fe (mg kg ^{−1})	K (g kg ^{−1})	Mg (g kg ^{−1})
pXRF Fresh	1520	13.584	61	3	5	112	4.589	1.817
pXRF Dry	1310	30.507	2633	2	7	217	12.484	0.159
ICP	192	37.325	--	--	4	170	16.240	2.821
Method	Mn (mg kg ^{−1})	P (g kg ^{−1})	Rb (mg kg ^{−1})	S (g kg ^{−1})	Si (g kg ^{−1})	Sr (mg kg ^{−1})	Zn (mg kg ^{−1})	
pXRF Fresh	14	0.342	4	0.729	1.013	113	14	
pXRF Dry	37	0.856	9	1.446	1.191	231	29	
ICP	41	1.680	--	3.045	--	--	30	

For Cr, Cu, Fe, Mn, Rb, and Zn, the concentrations obtained via pXRF (both fresh and dried) were more comparable to ICP results, indicating that these elements are less influenced by the leaf condition (fresh vs. dried) or the analysis method (pXRF vs. ICP).

Although the absolute values obtained differ across reading conditions, this does not preclude the use of pXRF to estimate ICP results through correlations. Measurements obtained via ICP-OES and pXRF in dried leaves exhibited stronger correlations compared to those in fresh leaves (Figure 4). Among the nutrients analyzed, only Zn showed a very strong correlation in fresh leaves (0.92), though it was still inferior to that observed for dried leaves (0.97).

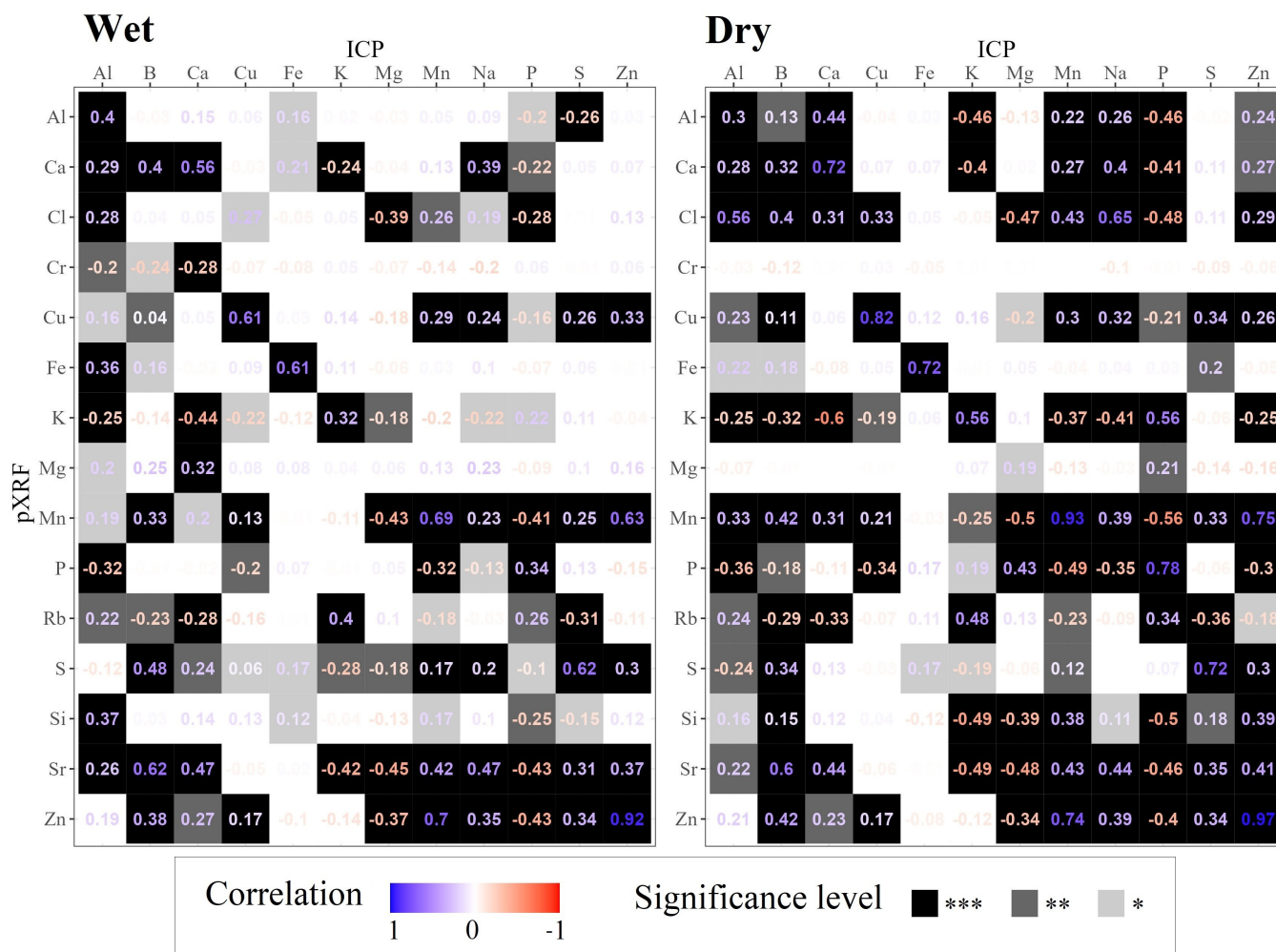


Figure 4. Correlations between nutrient contents in fresh and dried leaves of 15 citrus combinations of scion/rootstock obtained via pXRF and compared to ICP-OES results. Significance levels: * = 0.90; ** = 0.95; *** = 0.99.

pXRF measurements in dried leaves showed strong and positive correlations with ICP-OES results for Ca, P, S, Fe, and Cu ($0.70 < \rho \leq 0.90$) and very strong correlations for Zn and Mn ($\rho > 0.90$) (Figure 4). These results demonstrate that pXRF, a rapid and non-polluting method, provides consistent estimates for nutrient concentrations determined conventionally via ICP-OES, particularly for Ca, P, S, Fe, Cu, Zn, and Mn.

Notably, the correlation between B (ICP) and Sr (pXRF) was 0.62 for fresh leaves and 0.60 for dried leaves. A similar pattern was observed for Na (ICP) and Cl (pXRF) in dried leaves, with a correlation of 0.65. These findings suggest that B and Na, though not directly quantifiable by pXRF, could be estimated using Sr and Cl as predictors, respectively. Moreover, the strong correlation between B (ICP) and Sr (pXRF) in fresh leaves (0.62) indicates that in-field scanning could be effective for estimating B concentrations in citrus leaves.

Additional correlations between ICP-OES and pXRF in fresh leaves, such as Cu (0.61), Fe (0.61), and Mn (0.69), suggest that proximal sensing analysis is promising. This approach is particularly advantageous due to its rapid results (within minutes) directly in the field, enabling faster decision-making and substantial savings in time, financial resources, and effort.

The differences in nutrient concentrations detected by pXRF in fresh and dried leaf samples, though variable, show notable correlations (Figure 5). For instance, the correlations for Ca (0.58), Cu (0.69), Fe (0.74), K (0.61), Mn (0.77), Sr (0.98), and Zn (0.95) demonstrate that despite differences in numerical values, these strong correlations allow for the development of correction factors to convert nutrient levels obtained in fresh leaves into values equivalent to dried leaves.

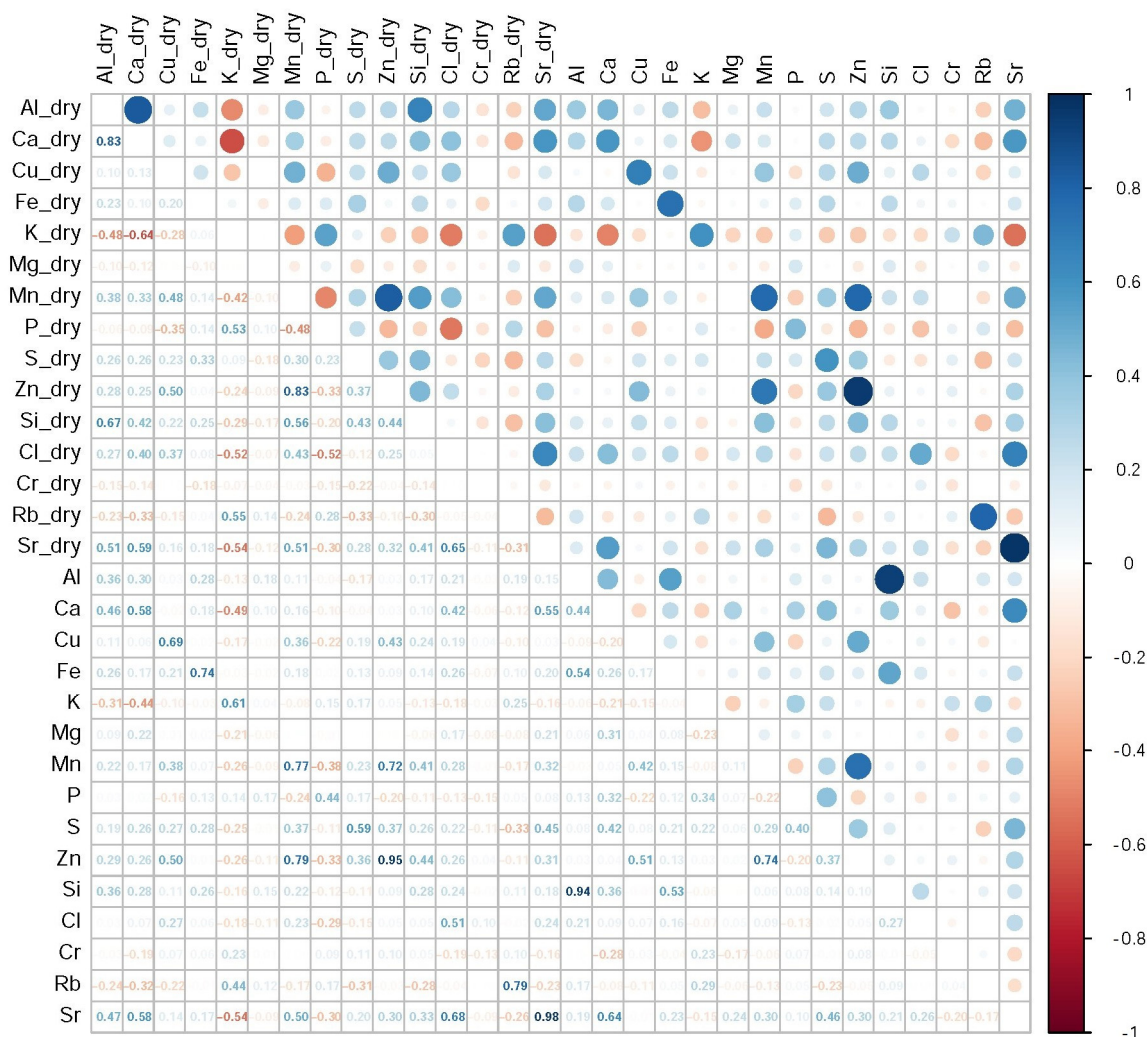


Figure 5. Correlation results between nutrient contents determined by pXRF in fresh (element symbol alone) and dried (“element_dry” notation) citrus leaves of 15 scion/rootstock combinations.

3.3. Prediction of Chemical Composition in Citrus Leaves via pXRF

Table 5 presents the validation results for the most accurate nutrient predictions, including Na (a beneficial element) and Al, in citrus leaves using pXRF under fresh and dried conditions. The best prediction models were chosen based on the lower RMSE value since it is the most popular model judging criterion and more sensitive to outliers than other indicators [39]. From 72 predictive models of elemental concentrations (6 algorithms $\times$ 12 elements), highly accurate models were achieved for all evaluated elements, with R^2

values ranging from 0.64 (Na) to 0.96 (Mn and Zn) for pXRF measurements on dried leaves. For fresh leaves, while the results were lower, the models still achieved adequate predictive performance ($R^2 > 0.60$) for B (0.78), Cu (0.63), Mn (0.77), and Zn (0.87).

Table 5. Best results for elemental concentration prediction in citrus leaves using pXRF on fresh and dried leaves.

Element	Algorithm ¹	MAE	R ²	RMSE	RPD	Algorithm	MAE	R ²	RMSE	RPD
Fresh Leaves						Dry Leaves				
Al	Cubist	53.88	0.52	38.46	1.36	Cubist	29.60	0.84	22.44	2.47
B	PLS	20.17	0.78	15.59	2.05	Cubist	18.09	0.81	14.17	2.29
Ca	PPR	4160.17	0.58	3315.39	1.54	PLS	3380.15	0.76	2879.25	1.89
Cu	SVM	1.48	0.63	1.23	1.66	SVM	0.87	0.88	0.74	2.81
Fe	Cubist	33.05	0.55	25.97	1.50	SVM	23.66	0.77	18.97	2.10
K	Cubist	2966.99	0.43	2424.43	1.33	Cubist	2259.60	0.71	1447.02	1.74
Mg	RF	705.30	0.58	557.04	1.49	Cubist	532.19	0.74	393.16	1.98
Mn	Cubist	7.44	0.77	5.77	2.07	Cubist	3.00	0.96	2.24	5.13
Na	RF	39.00	0.35	33.14	1.24	Cubist	29.06	0.64	23.73	1.66
P	RF	286.22	0.61	222.74	1.53	Cubist	158.56	0.87	122.28	2.76
S	PPR	394.47	0.54	327.54	1.47	PPR	269.45	0.80	216.47	2.16
Zn	PLS	5.56	0.87	4.16	2.67	PLS	2.96	0.96	2.11	5.01

¹ PLS—partial least square, PPR—projection pursuit regression, SVM—support vector machine, RF—random forest.

The inclusion of multiple element concentrations obtained via pXRF was critical for these predictions. For example, B, which cannot be directly detected by pXRF, was accurately predicted based on correlated elements, achieving an R^2 of 0.81 and an RMSE of 18.09 for dried leaves.

The Cubist algorithm performed best for predicting multiple elements, particularly in dried leaves. For fresh leaves, Cubist provided the highest predictive performance for four elements (Al, Fe, K, and Mn), followed by RF (three elements: Mg, Na, and P), PLS and PPR (two each), and SVM (one). For dried leaves, Cubist was the top-performing algorithm for seven elements (Al, B, K, Mg, Mn, Na, and P), followed by SVM and PLS (two each) and PPR (one). This demonstrates the importance of testing multiple algorithms to optimize predictions, as their predictive capabilities vary.

3.4. Prediction of Citrus Scion/Rootstock Combinations Using pXRF Data

Predictions of citrus scion/rootstock combinations based on pXRF data showed high accuracy, especially for dried leaves (Table 6). The overall accuracy (OA) reached 91%, with a kappa index of 0.90 for PLS, RF, and SVM on dried leaves.

Table 6. Overall accuracy (OA) and kappa index for predicting citrus scion/rootstock combinations based on pXRF data from fresh and dried leaves.

Algorithm ¹	Fresh Leaves		Dry Leaves	
	OA (%)	Kappa	OA (%)	Kappa
C5.0	38	0.33	80	0.79
PLS	53	0.50	91	0.90
RF	53	0.50	91	0.90
SVM	64	0.62	91	0.90
XGB	33	0.29	07	0.00
TreeBAG	51	0.48	78	0.76

¹ PLS—partial least square, SVM—support vector machine, RF—random forest.

Since the citrus plants of the different scion/rootstock combinations were cultivated under similar management and soil conditions, the chemical element concentrations ob-

tained via pXRF, especially in dried leaves, combined with machine learning techniques, effectively differentiated these varieties. This differentiation likely reflects the distinct nutrient accumulation patterns specific to each combination. This approach could prove useful for identifying varieties in cases of field uncertainty.

4. Discussion

Considering the concentration of elements delivered by ICP-OES for the 15 scion/rootstock combinations of the main citrus varieties (Table 3), the highest CV values were found for micronutrients, mainly Cu (59%) and Zn (36%). Similar high variability in these micronutrients for citrus has also been reported in the literature [40,41], these authors suggest that this variability can be explained by imbalances in these micronutrients, whether due to deficiency or excess, which may be influenced by the crop protection products used and the topography of the studied area. For macronutrients, CV values were low.

Interestingly, Cu and Zn mean contents were below the adequate range of contents; the same occurred for Mg. The same happened when analyzing nutrient concentrations per scion/rootstock combination (Table 4). Since the management practices were uniform and the plants were grown in the same soil class, these results suggest that different scion/rootstock combinations exhibit varying nutrient uptake efficiencies, leading to variable nutrient accumulation in foliar tissues [42]. Although recent studies have explored alternative methodologies for assessing citrus nutritional status [43], there remains a lack of research on nutrient sufficiency ranges tailored to specific citrus varieties.

By evaluating the PCA (Figures 2 and 3) based on pXRF for fresh and dried leaves, there is a clear greater dispersion of data in PCA using dried leaf results. These findings highlight the potential of using pXRF to differentiate scion/rootstock combinations more effectively with dried leaf samples while also illustrating the impact of leaf moisture, which complicates data differentiation, similar to reports for eucalyptus [8] and blueberry [16].

The correlations between pXRF results of fresh and dried leaves in relation to ICP-OES indicate that the relationships between elements detected by pXRF are strongly influenced by the condition of the leaves (fresh or dried), which should be taken into account when utilizing this equipment under varying conditions [14,44].

Numerous studies have highlighted the negative effects of moisture on pXRF results for leaves and other materials [14,16,42]. While this underscores a limitation of the equipment for fresh leaf analysis, it does not preclude the development of predictive models for nutrient content using fresh leaves, although such models may exhibit weaker correlations with ICP results. While discrepancies between pXRF and ICP results are documented in the literature [45,46], there is limited information on the effects of fresh and dried citrus leaf analysis on pXRF outcomes. A more in-depth understanding of these differences is essential, as some pXRF limitations must be acknowledged. Sample preparation, including analyses of fresh leaves (minimal preparation) and drying and grinding samples, can modify pXRF measurements' accuracy, as variations in moisture, particle size, and surface homogeneity can affect X-ray interactions [43]. Also, discrepancies between pXRF and ICP results may arise due to factors such as differences in detection limits, matrix effects, and elemental interferences [47,48]. To overcome this limitation, it has been advised to analyze all samples under the same conditions as an attempt to reduce the power of these influencing factors [43]. Also, correction factors could be calibrated to convert fresh to dried leaf results, which could be tested per crop or even species/variety.

In particular, the observed underestimation (recovery rate below 100%) of certain elements by pXRF may be attributed to the attenuation of X-rays in fresh leaves due to their higher water content, leading to lower detected intensities. The elements used as

explanatory variables with lower atomic numbers, P and S, were more affected by matrix effects, resulting in underestimated concentrations (74 and 71% in average, respectively).

For other crops, relationships between pXRF and ICP data as well as between fresh and dried leaf analyses via pXRF have been shown to vary per element and species/variety [14,16]. Differences between fresh and dried leaf results in pXRF are primarily attributed to the effects of moisture and particle size, which can disperse primary and secondary X-rays during the equipment–sample interaction [43].

The stronger correlations between dry leaves and ICP results align with those of [49], who noted that pXRF measurements are influenced by the water content in foliar samples. These correlations observed for dried leaves can be attributed to their lower water content and the greater homogeneity of ground material, which is also used in ICP-OES analysis. In contrast, the water content in fresh leaves scatters X-rays, leading to underestimated values in pXRF readings. Furthermore, the uneven nutrient distribution in fresh leaves is another factor that can impact results [15]. Variations in leaf thickness and water storage in fresh samples also contribute to measurement discrepancies [49].

Ref. [50] similarly observed strong correlations between pXRF and ICP results for Fe and Cu in dried samples of plants, animals, and fungi. Ref. [51] reported very strong correlations for Mn determined via ICP and pXRF in fresh (0.87) and dried (0.86) leaves from soybeans, beans, coffee, eucalyptus, guava, maize, and mangoes. These authors also observed a strong correlation (0.64) for S concentrations obtained through ICP and pXRF, comparable to the findings of this study (0.72). Ref. [15], studying 28 plant species across diverse Brazilian regions, reported very strong correlations for P, K, Ca, S, Fe, Zn, Mn, and Cu, concluding that foliar macronutrient and micronutrient concentrations could be quantified using pXRF in dried and ground leaf samples.

The reasonable correlations between pXRF results of fresh leaves and ICP-OES may help the rapid evaluation of these nutrient contents even in the field. Supporting these findings, ref. [52] demonstrated that pXRF could approximate Mn, Fe, Cu, and Zn concentrations in agreement with ICP measurements.

Also, efforts should be driven to correlate pXRF results of fresh leaves into those of dry leaves, which was attempted in this study, in order to facilitate the diagnosis of plant nutritional status during the field work. This approach could effectively eliminate the undesirable effects of variable water content in fresh samples [16,51].

Still regarding the pXRF results for fresh and dried leaves and the ones delivered by ICP, caution is needed on the differences these varying conditions of analyses cause on the final results. For instance, for Ca contents, the results by pXRF on fresh leaves are approximately 2.5 times lower than the results of dried leaves and 3 times lower than the results of ICP. Thus, when evaluating fresh leaves, attention is needed to interpret the results correctly; otherwise, drastic misunderstandings may occur when inferring about the possible deficiency of nutrients in citrus leaves. The same differences in results from pXRF analyzing dry and fresh plant material and their comparisons with ICP results have been reported [14,16], but none were performed specifically for citrus.

Regarding the predictions of nutrient contents in citrus leaves based on pXRF data, accurate predictions were reached for all elements evaluated, including B and Mg. This represents a significant improvement over previous studies, which reported less satisfactory results for Mg and B in other crops [8,15,16]. Notably, this study represents the first attempt to predict Na concentrations, which, although not essential, is beneficial for certain species (a beneficial element) [53]. It is important to highlight the better predictions when utilizing dried leaves instead of fresh leaves. High R^2 values coupled with low RMSE values for all nutrients were achieved, especially for Zn, which reached $R^2 = 0.96$. Also, the predictions were affected by the machine learning algorithm, which suggests that

prediction models should be created using these different methods to widen the possibilities to increase the chances to obtain the best model per nutrient of interest. Variations in the prediction capability per machine learning method have been reported worldwide for different purposes [54–56].

The superior performance of Cubist for specific elements, particularly in dried leaves, can be attributed to its ability to capture complex interactions between predictors [57,58], which is crucial for elements that have non-linear relationships with the measured variables. Thus, the element content benefits from Cubist's flexibility in modeling such complexity. On the other hand, less powerful algorithms like SVM or PPR may struggle with capturing these intricate patterns, particularly for elements with less uniform distribution across the leaves.

The second best performance was achieved by the partial least squares (PLS) algorithm. PLS is particularly effective when there is high collinearity among predictor variables, a common characteristic in pXRF data. Since this method reduces data dimensionality by extracting latent components that maximize the covariance between independent and dependent variables [59,60], it can effectively capture linear relationships between the target elements and the explanatory variables.

Support vector machines (SVM) also showed good predictive performance for some elements, particularly in dried leaves. This can be attributed to its ability to handle complex, high-dimensional relationships by using kernel functions to map non-linear patterns [61]. However, its performance may be limited when dealing with highly noisy data or when the number of predictors is very large, as it requires careful tuning of hyperparameters to avoid overfitting [62]. Similarly, random forest (RF) performed well for some elements in fresh leaves, benefiting from its ensemble approach, which reduces overfitting and improves robustness in heterogeneous datasets [63].

The poor performance of the projection pursuit regression (PPR) algorithm may be attributed to its limitations in handling high-dimensional and highly collinear data, such as pXRF spectra. PPR relies on identifying projection directions to model nonlinear relationships, but it may struggle to capture complex interactions between variables, especially when the underlying patterns are not easily represented by smooth transformations [64,65]. Additionally, PPR is more sensitive to noise and data heterogeneity compared to more robust algorithms like Cubist regression. Its performance also depends on the choice of basis functions and the number of projection terms, which, if suboptimal, can lead to inadequate model fitting [62].

For the predictions of the citrus scion/rootstock combinations based on pXRF data, the values of OA (91%) and kappa index (0.90) using the results from dried leaves represent “almost perfect” accuracy [34]. For fresh leaves, the best predictive performance was achieved using SVM, with OA = 64% and kappa = 0.62, indicating “substantial” accuracy per [34].

The results obtained in this study both for foliar nutrient content prediction and for the 15 scion/rootstock combinations stress the high potential of using pXRF data for accelerating the characterization of citrus leaves. While still in its early stages, this method warrants further testing in different crops. However, the results obtained for citrus, involving some of the main varieties cultivated in the region, underscore the potential of using leaf chemical composition to differentiate varieties. Furthermore, these findings highlight possible variations in nutrient absorption and accumulation among varieties, which could be further investigated regarding their relationship to fruit quality or specific characteristics.

Despite the promising results obtained with the use of pXRF in the nutritional analysis of citrus leaves, some limitations and challenges of this methodology must be considered.

The variability observed between pXRF and ICP methods for certain chemical elements indicates that the choice of technique and sample condition (fresh or dried) can significantly influence the results, requiring caution when interpreting the data. Additionally, although the predictive models showed high accuracy for dried leaves, the lower precision for fresh leaves suggests the need for methodological improvements to enhance the reliability of the estimates. The correlations between nutrient and micronutrient concentrations were not uniformly high for all elements, which may indicate the influence of additional factors that still need to be better understood. Therefore, it is essential that future studies assess the practical application of these predictive models on new samples, covering a greater diversity of scion/rootstock combinations and environmental conditions, in order to validate and refine this approach.

The findings of this study indicate that the methodology based on pXRF, combined with machine learning algorithms, can be a promising tool for nutritional analysis in citrus. However, its applicability may extend to other crops, especially those where foliar nutritional assessment is essential for proper fertilization management. Adapting this approach to different species will require specific calibrations, considering variations in leaf morphology and the distribution of chemical elements within tissues. Additionally, integrating this methodology into existing agricultural management systems, such as digital agriculture platforms and remote sensors, could enhance nutritional monitoring and facilitate real-time decision-making.

It is recommended to investigate the applicability of pXRF at different phenological stages of plants, assess its efficiency under varying environmental conditions, and test combinations of this technique with other rapid analysis methods. It would also be relevant to explore the development of more robust predictive models, incorporating climatic and soil data to improve nutritional management recommendations.

5. Conclusions

The different citrus scion/rootstock combinations exhibited varying nutrient concentrations in their leaves despite identical fertilization management, soil class, and the absence of nutrient deficiencies or toxicities in all sampled plants. This suggests that nutrient accumulation varies according to the citrus scion/rootstock combination.

For certain chemical elements (Al, Ca, Cl, Fe, K, Mn, P, S, Sr, and Zn), results obtained via pXRF (fresh and dried citrus leaves) and ICP showed significant variability. This highlights the need for caution when interpreting data based on the technique used (pXRF or ICP) and the sample condition (fresh or dried via pXRF). For other elements, such as Cr, Cu, Fe, Mn, Rb, and Zn, the results were more consistent across methods.

Using predictive models based on data from the primary scion/rootstock combinations in Brazil, it was possible to estimate nutrient concentrations (in addition to Al) in citrus leaves with high accuracy (R^2 ranging from 0.71 to 0.96), particularly for dried leaves analyzed via pXRF. Predictions for fresh leaves were less reliable (R^2 ranging from 0.35 to 0.87).

The scion/rootstock combinations were predicted with high accuracy (OA = 0.91, kappa = 0.90), especially using dried leaves. Predictions for fresh leaves were less accurate (OA = 0.64, kappa = 0.62). Thus, pXRF demonstrates significant potential for aiding in the nutritional characterization of citrus leaves and identifying scion/rootstock combinations, reducing both costs and time required for this evaluation.

From a practical perspective, these results can significantly contribute to precision agriculture and citrus nutritional management. The ability to differentiate varieties and rootstocks based on the chemical composition of leaves can assist in selecting more efficient combinations for nutrient absorption and utilization, optimizing fertilization, and reducing

waste. Additionally, the application of pXRF in the field, especially on fresh leaves, can provide rapid diagnostics for real-time nutritional adjustments, although with lower accuracy compared to dried leaves.

For future studies, it is recommended to assess the practical application of these predictive models on new samples collected from various scion/rootstock combinations. The integration of pXRF with other technologies, such as remote sensing and artificial intelligence-based recommendation systems, can further expand its use in advanced nutritional management strategies.

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