



The use of a portable X-ray fluorescence spectrometer for measuring nickel in plants: sample preparation and validation

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Abstract X-ray fluorescence is a fast, cost-effective, and eco-friendly method for elemental analyses. Portable X-ray fluorescence spectrometers (pXRF) have proven instrumental in detecting metals across diverse matrices, including plants. However, sample preparation and measurement procedures need to be standardized for each instrument. This study examined sample preparation methods and predictive capabilities for nickel (Ni) concentrations in various plants using pXRF, employing empirical calibration based on inductively coupled plasma optical emission spectroscopy (ICP-OES) Ni data. The evaluation involved 300 plant samples of 14 species with variable of Ni accumulation. Various dwell times (30, 60, 90,

120, 300 s) and sample masses (0.5, 1.0, 1.5, 2.0 g) were tested. Calibration models were developed through empirical and correction factor approaches. The results showed that the use of 1.0 g of sample (0.14 g cm⁻²) and a dwell time of 60 s for the study conditions were appropriate for detection by pXRF. Ni concentrations determined by ICP-OES were highly correlated ($R^2=0.94$) with those measured by the pXRF instrument. Therefore, pXRF can provide reliable detection of Ni in plant samples, avoiding the digestion of samples and reducing the decision-making time in environmental management.

Keywords Calibration · Non-destructive method · Prediction · pXRF

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Introduction

X-ray fluorescence (XRF) is a cost-effective and efficient technique for analyzing plant elemental composition. Unlike spectroscopic methods such as inductively coupled plasma (ICP) and flame atomic absorption (FAA), XRF is fast, does not require sample digestion, does not generate chemical wastes, and has a relatively low cost of ownership. Besides, portable XRF (pXRF) instruments can optimize field investigations, allowing for in situ measurements. Such advantages have boosted the interest in the pXRF as a technique in the environmental field (Faria

et al., 2020; Horta et al., 2021; Lenormand et al., 2022; Ran et al., 2014).

Portable XRF instrumentation was initially conceived for qualitative, exploratory geochemical screening and mapping, representing a pivotal development in streamlining the timeline between sampling, obtaining results, and making decisions in environmental management (Lemière, 2022). Subsequent rapid progress and enhancements in both hardware and software have facilitated quantitative investigations across a diverse array of matrices, including soils, mining waste, sewage sludge, asphalt dust, rocks, microplastics, criminal evidence, archeological artifacts, works of art, recycling materials, wastewater, fertilizers, and plants (Andrade et al., 2021; Craddock, 1985; Lenormand et al., 2022; Lima et al., 2023; Pelegrino et al., 2022; Touzé et al., 2022; Turner, 2017; van der Ent et al., 2019).

Because pXRF analyses were initially established for rocks and soil analyses, some plant characteristics such as moisture, low density, and high concentration of organic compounds and light elements are still limiting factors for assessing plant mineral composition using pXRF (Costa et al., 2023; Lenormand et al., 2022; Ran et al., 2014; Zhou et al., 2020). Dwell time is ultimately related to the analysis error due to the counting statistics. However, when added to the other sample variations, the negative effects on elemental determination are significant (Zhou et al., 2020, 2022). Thus, calibration and validation of pXRF measurements for plant tissues against ICP data are still needed. Furthermore, inconsistencies have been reported in sample preparation, analytical rigor, and variations in equipment quality concerning detection limits, especially between light and heavy elements, with the latter exhibiting greater accuracy (Towett et al., 2015; Lemière, 2022; Touzé et al., 2022).

Studies using pXRF for elemental evaluation of plant samples began a few decades ago (Evans, 1970; Gladney et al., 1989; Reidingner et al., 2012). Current methodologies aim to explore various factors that may affect the accuracy of determinations. These factors encompass water content, the influence of protective film, critical X-ray penetration depth, sample thickness, measurement duration, and particle size (McLaren et al., 2012; Rincheval et al., 2019; Zhou et al., 2020). Moreover, high contents of carbon (C), hydrogen (H), oxygen (O),

and nitrogen (N) in plants may pose limitations for pXRF calibrations when utilizing Soil and Geochemical modes (Zhou et al., 2022). To address these challenges, it is imperative to establish standardized methodologies and model calibrations that can be applied across diverse instruments.

Measuring metal concentrations in plants aids in prospecting species with potential for accumulating and remediating these contaminants in soils, as well as monitoring dangerous levels for human consumption of vegetables. Metal concentration in plant tissues can vary significantly, with plants displaying distinct adaptations to high metal concentrations in soils that range from avoidance (or exclusion) to hyperaccumulation (Krämer, 2010; Nascimento et al., 2022; Purwadi et al., 2022). Therefore, plant analysis via pXRF must ideally be able to measure metals in a wide range of concentrations. For instance, pXRF investigations in ultramafic areas and herbaria have identified hundreds of hyperaccumulators with a high range of metal concentrations (Gei et al., 2018; van der Ent et al., 2019), while metals of agricultural relevance (Fe, Mn, Cu, Zn) were properly assessed in varying concentrations for several crops (Costa et al., 2023; Costa Junior et al., 2020).

Nickel is a potentially toxic metal commonly reported to contaminate soil and water and is also much valued in the phytotechnology market (Nascimento et al., 2022; Nkrumah et al., 2017). Therefore, using plants to clean up Ni-polluted soils (phytoremediation) or mine Ni-rich substrates and soils using Ni hyperaccumulators (agromining) has increasingly gained attention (Tognacchini et al., 2020; Samojedny et al., 2023). In such scenarios, the fast analysis and in situ capability of pXRF to assess Ni concentrations in plants are fundamental to monitoring the success of these techniques in the field.

Considering the need for improving the predictive accuracy of pXRF data and standardization of methods for plant analyses, this study assessed sample preparation methods using an internal standard sample and predictive capabilities for Ni concentrations in a variety of plants using pXRF through empirical calibration of the data with inductively coupled plasma optical emission spectroscopy (ICP-OES) Ni measurements. We hypothesize that the use of pXRF is efficient and accurate for monitoring Ni contents in plants, considering different approaches to calibration and sample preparation.

Material and methods

Species selection

The plant species selected for the study had distinct patterns of Ni accumulation. The soils used were classified as Cambisol (France) and Leptosol (Brazil) according to the World Reference Base for soil resources (WRB/FAO, 2014). Between January and May 2023, 300 root and leaf samples represented 14 plant species grown in ultramafic and agricultural soils and tree trunks. The collection contained seven Ni hyperaccumulators (*Pfaffia sarcophylla*, *Lippia lupulina*, *Justicia lanstykii*, *Blepharidium guatemalense*, *Berkheya coddii*, *Bornmuellera emarginata*, and *Noccaea caerulescens*) and seven non-hyperaccumulators of the element (*Zea mays*, *Saccharum officinarum*, *Lactuca sativa*, *Brassica oleracea*, *Imperata cylindrica*, *Lupinus albus*, and *Calymperes palisotii*) (plants obtained in experiments by our research group). The Ni available concentrations in the soils where the plants were grown were determined through diethylenetriaminepentaacetic acid (DTPA) extraction (Lindsay and Norvell, 1978).

ICP-OES measurements

The plant samples were washed with running water and triple-washed with distilled water, dried in an oven at 65 °C for 48 h, and macerated in a Wiley-type mill ($\varnothing < 2.0$ mm). Subsequently, subsamples of 0.5 g of roots and leaves were digested with $\text{HNO}_3 + \text{H}_2\text{O}_2$ (3:1) in a microwave oven (Milestone-Ethos Easy) at 180 °C for 10 min, according to the manufacturer's protocol. The extracts were filtered ($\varnothing < 2.0$ μm), and the volume was topped up to 25 mL with ultrapure water in certified volumetric flasks and stored at 4 °C for later analysis.

The Ni concentration in the plants was determined by inductively coupled plasma optical emission spectrometry (ICP—OES Perkin Elmer 7000 DV). The analyses were carried out in duplicates and with blank tests. All the materials used in the analysis were properly washed, immersed for 24 h in the HNO_3 solution (10%), and then washed with distilled water. The NIST (National Institute of Standards and Technology) standard for certified metal concentration in plants (SRM 1570a—Trace Elements in Spinach Leaves) was used as a quality control. Nickel

recoveries in the certified sample ranged from 89.7 to 90.6%, which is considered satisfactory (Table S1).

Protocol for pXRF analyses

The pXRF analysis was carried out using an energy-dispersive spectrometer (EDXRF), S1 TITAN 800 model (Bruker, USA), equipped with a 4W Rh target tube (6–50 kV, 5–200 μA). Bruker XRF cylindrical sample cups (30.7-mm outer diameter \times 22.9-mm high) were covered with MYLAR® FILM—SCP SCIENCE (3.6 μm , with nearly no compositional interference and high X-ray transmission rate). The sample cup was placed in a test stand and analyzed according to Fu et al. (2024). Fluorescent X-rays generated are detected, identified, and quantified by the graphene window silicon drift detector (SDD) with a typical energy resolution < 145 eV at 450,000 counts per second.

The pXRF measurement protocol was established using a leaf sample of the Ni hyperaccumulator *Noccaea caerulescens* as an internal standard. The leaf sample was previously determined for Ni concentrations by ICP-OES in various French laboratories and showed a mean Ni concentration of 566 mg kg^{-1} . For pXRF analysis, the plant samples were dried at 65 °C, ground in a Wiley mill ($\varnothing < 2.0$ mm), macerated in an agate mortar, and sieved ($\varnothing < 300.0$ μm) to ensure homogeneity. The optimization of the method involved using the standard for testing five dwell times (30, 60, 90, 180, and 360 s) and four sample masses (0.5, 1.0, 1.5, and 2.0 g). Such treatments were replicated five times using the PLANT scanning mode (factory calibrated) of the pXRF equipment.

For calibration and validation of the data, 300 samples were divided into two groups: training and test and were analyzed in triplicate. The training dataset comprised 75% of the samples ($n = 240$) defined at random; from these samples, a linear regression modeling the relationship between the Ni concentrations measured by pXRF and ICP-OES was established. The test set was made up of the remaining 25% of random samples ($n = 60$) and was used to cross-validate the data. Cross-validation involves splitting the data into training and test sets, allowing the model to be trained on part of the data and evaluated on another part, providing a more robust estimate of performance on different subsets of data (Refaeilzadeh et al., 2009). For quality control of the

pXRF measurements, the internal standard sample (*N. caerulescens*) was employed to verify apparatus accuracy and assess analysis stability throughout measurements. Checks were performed at each 30 measurements, with the variation between readings being < 5%.

Data analysis

The data obtained was subjected to univariate statistical methods (frequency, minimum, maximum, mean, median, standard deviation, and coefficient of variation). The data on the effects of dwell time and sample mass on Ni concentrations were analyzed for criteria of homoscedasticity and normal distribution by the Shapiro–Wilk test ($p > 0.05$) and submitted to analysis of variance (ANOVA, $p \leq 0.05$). The effects of the treatments were evaluated using the Tukey test ($p \leq 0.05$). Empirical calibration was carried out using linear regression and the model validations were assessed by Pearson's correlation. Both graphical and

statistical procedures were executed utilizing Origin-Pro 2019 and SISVAR software (version 5.8).

Results and discussion

Nickel concentrations in the samples determined by ICP-OES

The average Ni concentrations in the species ranged widely from 2.9 to 14,960.0 mg kg⁻¹ (Table 1). As expected, the Ni hyperaccumulators had the highest Ni accumulation, which followed the order: *B. guatemalense* > *B. coddii* > *B. emarginata* > *P. sarcophylla* > *L. lupulina* > *J. lanstyakii* > *N. caerulescens* > *Z. mays* L. > *L. sativa* > *B. oleracea* > *L. Albus* > *I. cylindrica* > *C. palisotii* > *S. officinarum*. The frequencies of Ni concentration ranges (mg kg⁻¹) were as follows: 24% (0–100), 7% (101–200), 3% (201–300), 8% (301–400), 2% (401–500), 6% (501–600), 3% (601–2000), 17% (2001–4000), 12%

Table 1 Descriptive statistics and range of Ni concentrations in 14 plant species determined by inductively coupled plasma optical emission spectroscopy

Species (n)	Ni (mg kg ⁻¹)	Substrate	Evaluated part	Ni soil ^a
<i>S. officinarum</i> (1)	2.9	Agricultural soil	Leaf	0.14
<i>C. palisotii</i> (3)	3.2–7.0	Bark	Phylloid	-
<i>I. cylindrica</i> (3)	6.0–9.3	Ultramafic soil	Leaf	42.0
<i>L. albus</i> (3)	8.2–13.0	Ultramafic soil	Leaf	42.0
<i>Z. mays</i> L. (132)	13.3–587.8	Ultramafic soil	Leaf and root	87.0–352.7
<i>B. oleracea</i> (3)	147.2–154.0	Ultramafic soil	Leaf	66.1–220.9
<i>L. sativa</i> (6)	166.9–224.5	Ultramafic soil	Leaf	66.1–220.9
<i>N. caerulescens</i> (3)	481.6–566.8	Ultramafic soil	Leaf	42.0
<i>P. sarcophylla</i> (3)	1044.0–3863.0	Ultramafic soil	Leaf	220.9
<i>B. coddii</i> (128)	1168.2–13,928.8	Ultramafic soil	Leaf and root	176.3
<i>J. lanstyakii</i> (1)	2221.5	Ultramafic soil	Leaf	220.9
<i>L. lupulina</i> (1)	3042.5	Ultramafic soil	Leaf	220.9
<i>B. emarginata</i> (12)	3337.0–5800.0	Ultramafic soil	Leaf	42.0
<i>B. guatemalense</i> (1)	14,960.0	Ultramafic soil	Leaf	66.1
Parameter	Value			
Minimum (mg kg ⁻¹)	2.9			
Maximum (mg kg ⁻¹)	14,960.0			
Median (mg kg ⁻¹)	1853.2			
Mean (mg kg ⁻¹)	3150.2			
Std. Dev. (mg kg ⁻¹)	3768.2			
CV (%)	119.6			

^aAvailable concentrations (mg kg⁻¹) extracted by diethylenetriaminepentaacetic acid (DTPA) (Lindsay & Norvell, 1978)

(4001–6000), 4% (6001–8000), 5% (8001–10,000), 4% (10,001–12,000), 5% (12,001–15,000).

The data's high amplitude, standard deviation, and coefficient of variation are desirable parameters in calibration studies as they allow for a greater range of linear regression estimation (Kalnicky & Singhvi, 2001). Additionally, high variation indicates different physiological characteristics regarding accumulation and tolerance between plants. For example, the lowest Ni concentrations were found in *S. officinarum*, a non-hyperaccumulator species cultivated with species grown in agricultural soil with a low available content of Ni (0.14 mg kg^{-1}), and in *C. palisotii*, a bryophyte collected in an environmentally preserved area that assimilates nutrients from particulate matter in the air and rainwater (Klos et al., 2018). Conversely, the highest Ni concentration was found in the Mexican woody hyperaccumulator *B. guatemalense*, grown in ultramafic soil with high Ni availability (66.1 mg kg^{-1}).

The substrate influenced the Ni concentration in some non-hyperaccumulator species such as *Z. mays* L., *L. sativa*, and *B. oleracea* grown on ultramafic soils and under the application of citric acid. This chelator increases Ni availability in the soil and plant uptake. Despite normally behaving as metal excluders, these species showed Ni concentrations much higher than when grown on “normal” agricultural

soils. Such high Ni accumulation can pose a risk to food safety, especially in leafy vegetables, due to their high transpiration and leaf mass that intensifies the absorption of water and metals by mass flow (Alfaro et al., 2021). Contrariwise, species *I. cylindrica* and *L. albus* showed low Ni concentrations in the leaves, even when grown in ultramafic soils. This can be attributed to protection strategies against Ni phytotoxicity through stabilizing the metal by the roots and, consequently, a low translocation factor (Ferraz et al., 2012; Tauqeer et al., 2019).

Effect of dwell time and sample mass on nickel pXRF measurements

The dwell time and sample mass significantly affected the Ni measurements (Fig. 1). The 30-s measurements showed Ni concentrations 35.0% lower than the other dwell times evaluated. The dwell time is directly related to the number of counts per second, usually maximized by longer times (Silva et al., 2021). Studies suggested dwell times between 30 and 200 s according to the characteristics of the equipment, type of element (light or heavy), concentration range investigated, and data quality requirements (Bull et al., 2017; McGarry et al., 2021; McGladdery et al., 2018; van der Ent et al., 2019; Zhou et al., 2020). Our data showed that 60 s was the ideal dwell time for

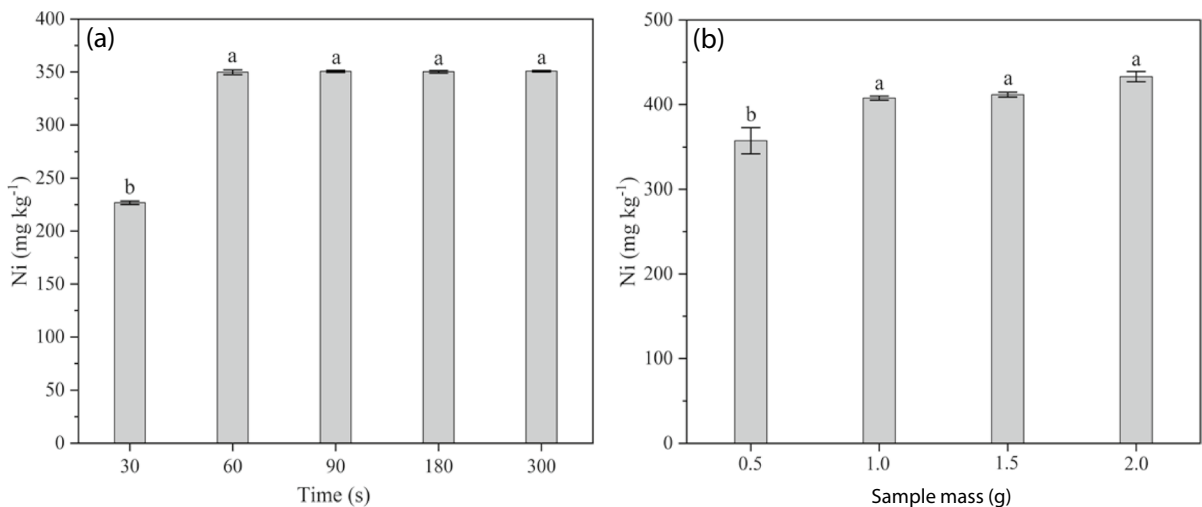


Fig. 1 Effects of dwell time (a) and sample mass (b) on Ni concentrations in leaves of *Noccaea caerulescens* measured by a portable X-ray fluorescence instru-

ment (pXRF). 0.5 g = 0.070 g cm^{-2} ; 1.0 g = 0.141 g cm^{-2} ; 1.5 g = 0.212 g cm^{-2} ; 2.0 g = 0.283 g cm^{-2} . Nickel content of the reference sample = 566 mg kg^{-1}

the samples and equipment utilized; increasing dwell time up to 360 s had no further effect in improving Ni measurement.

Regarding the sample mass, measurements with 0.5 g (0.070 g cm^{-2}) had a Ni concentration 15% lower than other treatments (Fig. 1). Also, variability between replicate measurements was relatively high (11%). Using a mass $\geq 1.0 \text{ g}$ (0.141 g cm^{-2}) combined with a dwell time $\geq 60 \text{ s}$ achieved a mean recovery of 72% of the Ni-certified value in the reference sample, generating a correction factor of 1.39. In addition, the Ni concentration variability between replicates was less than 1.0%. The underestimation of the Ni concentration in the sample with the lowest mass is probably due to the scattering of the X-ray signals due to the larger air space in the detection window (Touzé et al., 2022). Studies have shown that grinding or pressing the evaluated matrix increases the homogeneity of the sample and its compactness, reducing the air spaces in the detection window and showing higher metal concentrations in the smallest particle sizes (Silva et al., 2018, 2021).

Considering the trade-off between precision (maintaining a variation of less than 1.0% between replicates), accuracy (achieving over 70.0% approximation to the certified Ni concentration), and the objective of minimizing sample preparation via rapid drying and grinding, the recommended standard parameters for the study conditions include a particle diameter of $\leq 300.0 \mu\text{m}$, a dwell time of 60 s, and a mass sample of 1.0 g. The choice of these parameters resulted in a thickness of 1.7 cm (0.141 g cm^{-2}) of material in the pXRF sample cup. In this way, the degree of underestimation in pXRF-determined concentrations was constant, given that the sample mass per unit area remains fixed.

Model predictive capacity and validation

The models' predictive capacity needs validation to ensure the reliability, precision, and accuracy of predictions. Two methods for data calibration are regularly employed: (i) empirical calibration, involving linear regression between values measured by pXRF and those determined by the chemical method, and (ii) adjustments utilizing a correction factor derived from pXRF measurements on reference samples with certified concentrations for the assessed metal (Qu et al., 2022; Touzé et al., 2022). Both approaches were

considered in the present study. The calibration of pXRF data against ICP-OES measurements was conducted using a training set comprising 240 samples.

The linear regression showed a high coefficient of determination ($R^2 = 0.94$) (Fig. 2). The robustness of the model was supported by several factors, including the substantial number of samples, diverse preparation conditions, a wide concentration range, a minimal presence of outliers ($< 5.0\%$), and rigorous quality control measures applied to the analyses.

The underestimation of Ni concentrations by pXRF in comparison to ICP-OES can be linked to factors such as the low density of the plant matrix and the superior detection limit of ICP-OES (Zhou et al., 2020). Additionally, the accuracy of pXRF is influenced by interelemental spectral interferences, particularly the $K\alpha/K\beta$ interference (USEPA, 2007). Another aspect is the variability in detection limits (DL) among different equipment, primarily determined by the tube voltage and detector technology. Modern equipment employing Rh or Ag tubes operating at maximum capacity (50 kV and 200 μA) exhibits DL ranging from 5.0 to 100.0 mg kg^{-1} for elements with atomic numbers between 19 and 68, including Ni (Lemière, 2022; van der Ent et al., 2019).

However, it is noteworthy that the limit of quantification (LQ) tends to be, on average, three times higher than the LD, and utilizing samples with

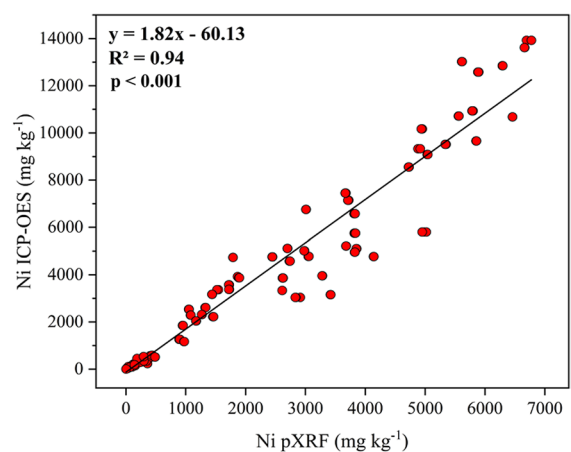


Fig. 2 Correlation between Ni concentrations determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) and portable X-ray fluorescence (pXRF) ($n = 240$)

extremely low concentrations may compromise the model’s accuracy. Consequently, it is imperative to establish the equipment’s sensitivity based on the lowest LD of the element with an acceptable recovery (USEPA, 2007). These limitations became evident during the cross-validation process (Fig. 3).

The empirical calibrations and those using correction factor adjustment showed strong correlations between the measured and predicted Ni concentrations ($r=0.98$) (Fig. 3a and c). However, the accuracy in the test set ($n=60$) for the values predicted by linear regression was negative for samples with

contents $< 100 \text{ mg kg}^{-1}$ (Fig. 3b). The average accuracy of the prediction, disregarding the negative values, was satisfactory (110%). Thus, the results suggest that empirical calibration is more appropriate for hyperaccumulator plants or species grown in metal-enriched soils with content $> 100.0 \text{ mg kg}^{-1}$. Calibration by adjusting the correction factor (1.39) showed an average accuracy of 96.0%, with greater precision for Ni concentrations close to the detection limit. Both calibration approaches were considered reliable due to the low dispersion of repeated measurements and the relatively high accuracy found.

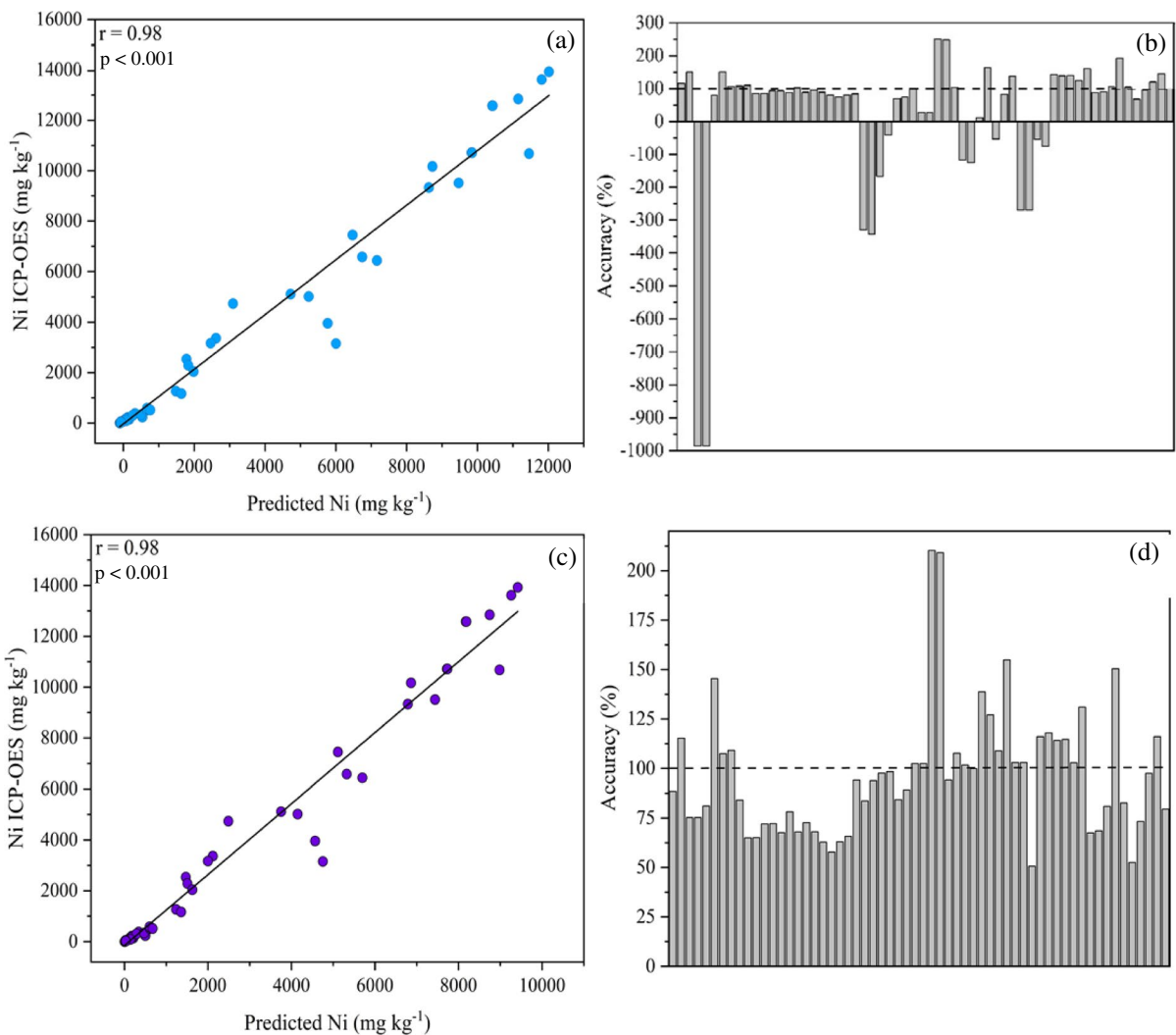


Fig. 3 a Cross-validation and (b) accuracy of Ni contents estimated by linear regression ($n=60$) (empirical approach). c Cross-validation and (d) accuracy of Ni contents estimated by the correction factor (1.39) ($n=60$)

Conclusions

This research introduced a calibration model allowing pXRF to quantify Ni concentrations in plants. The data support the potential of pXRF for reliable analyses of Ni in plant tissues and the need for method standardization. The ideal amount of plant used is related to the thickness of the material in the sampling cup. Using < 1.0 g of sample (0.14 g cm⁻²) and dwell time < 60 s for the study conditions led to decreased Ni detection by pXRF. Ni concentrations determined by ICP-OES were highly correlated ($R^2=0.94$) with those measured by the pXRF instrument. Both approaches tested were efficient for Ni determination ($r=0.98$), but the relatively high limit of quantification of pXRF in the empirical calibration model suggests that it is more suitable for use in hyperaccumulator plants or species grown in metal-enriched soils (> 100 mg kg⁻¹). Therefore, pXRF can provide fast, eco-friendly, and reliable detection of Ni in plant samples, avoiding the digestion of samples and reducing the decision-making time in environmental management. Furthermore, correlations of this study with new in situ measurements could further optimize the time it takes to obtain results with minimal sample preparation.

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Author contribution All the authors contributed to the study topic and research. Material preparation, data collection, and data analysis were carried out by Luiz Henrique Vieira Lima. The first version of the manuscript was written by Luiz Henrique Vieira Lima and revised and corrected by the other authors. All authors read and approved the final manuscript.

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Data availability Not applicable.

Declarations

Ethical approval All authors have read, understood, and have complied as applicable with the statement on “Ethical responsibilities of Authors” as found in the Instructions for Authors.

Competing interests The authors declare no competing interests.

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