



Validation of portable monochromatic X-ray fluorescence for plant elemental analysis using standard reference materials and field samples

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ABSTRACT

Monitoring metal(loid) contamination in plants across polluted landscapes requires analytical methods that are fast, quantitative, and cost-effective. Portable X-ray fluorescence offers these advantages, but its performance in plant matrices remains poorly validated. Here, we evaluate a first-generation portable monochromatic X-ray fluorescence analyzer (MXRF) using plant-based standard reference materials and field-collected plant samples from a reclaimed tailings pond. We assessed analytical performance and measurement-related factors and compared MXRF measurements with inductively coupled plasma mass spectrometry to identify matrix effects influencing inter-method agreement. Under optimized conditions, MXRF provided robust quantification of Cu, Mn, and Fe; acceptable performance for Zn, K, Ca, Se, and Re; and limited reliability for P, S, and Ti. Inter-method agreement was associated with controllable matrix effects, including sample mass-, homogeneity-, and concentration-dependent constraints. These findings identify analytical constraints and comprehensive quality-control standards for handheld MXRF plant elemental analysis, support its use for environmental plant monitoring workflows, and provide a validation template for evaluating future handheld MXRF systems.

1. Introduction

Accurate quantification of elemental concentrations in plant tissues is critical to a wide range of environmental, ecological, and agricultural studies. Portable X-ray fluorescence (pXRF) spectrometry has emerged as a powerful approach for rapid, multi-element sample analysis across diverse environmental matrices, offering a cost-effective and non-destructive alternative to conventional laboratory methods (Borges et al., 2020a; Faria et al., 2021; Li et al., 2026; Zhou et al., 2020). Modern pXRF units provide detection limits suitable for major nutrients in plant tissues (Arantes de Carvalho et al., 2018), enabling applications in pollution risk assessment (El Mellouki et al., 2025), crop nutrient management (Borges et al., 2020b), herbarium specimen screening (Purwadi et al., 2022), and

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trace element quantification in vegetation from mining-impacted sites (Rincheval et al., 2019). Advances in X-ray tube and detector miniaturization have brought pXRF performance close to that of benchtop XRF instruments and even Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Bueno Guerra et al., 2014; Sapkota et al., 2019).

A more recent technological development is the introduction of monochromatic X-ray fluorescence (MXRF) instruments capable of producing monochromatic spectra (Fleming et al., 2017; Guimarães et al., 2016; McIntosh et al., 2016; Zhang et al., 2025). The monochromatized source simplifies intensity-concentration relationships, reduces uncertainties associated with the energy distribution of polychromatic sources in fundamental parameter-based quantification algorithms, improves signal-to-noise ratio, and lowers detection limits (Wang et al., 2023). Recent studies have extended MXRF applications to plant materials using benchtop systems (Kahlon et al., 2026; Zhang et al., 2025), whereas the analytical performance of handheld MXRF for quantitative plant analysis remains largely unexplored. This gap is particularly important because plant material remains a challenging matrix for XRF analysis, and accurate application requires careful consideration of X-ray-matter interactions and proper calibration procedures (Towett et al., 2016). Without validation in a specific matrix, reliance on “internally consistent” measurements may lead to erroneous conclusions (Speakman and Shackley, 2013).

One of the main limitations of pXRF analysis in plant matrices arises from the dominance of light elements (C, N, H, O≈98%), which are largely transparent to X-rays. Consequently, absorption is lower than in denser matrices such as soils and is mainly influenced by foliar macroelements including K, Ca, S and Fe (Marguí et al., 2009). This makes quantitative analysis particularly sensitive to the physical characteristics of the plant material and measurement conditions. Specifically, the accuracy of pXRF in plant samples depends on numerous factors, including sample preparation, homogeneity, thickness, particle size, bulk density, moisture content, instrumental configuration, excitation energy, scan time, and X-ray penetration and escape depths (Sapkota et al., 2019; Towett et al., 2016; Zhou et al., 2022). These matrix-dependent effects also complicate calibration. Quantitative XRF calibration commonly relies on flat, homogeneous standard reference materials (SRMs), spanning narrow elemental concentration ranges (Arantes de Carvalho et al., 2018). Consequently, many studies rely on empirical calibrations using field-collected samples, which often lack the homogeneity in particle size, bulk density, and surface smoothness – conditions necessary for quality measurements (Guimarães et al., 2016; Khan et al., 2022).

Several studies have attempted to assess pXRF reliability in intact and powdered plant samples, recognizing challenges associated with particle size, low elemental concentrations, limited sample volumes, and heterogeneity in elemental distribution (Arantes de Carvalho et al., 2018; Ravansari et al., 2020; Ribeiro et al., 2021; Tadeu Costa Junior et al., 2020). Elemental allocation varies both among leaves and within a single leaf, introducing inconsistency even after washing, grinding, and homogenizing. Sample heterogeneity has also been recognized as a source of discrepancies when validating pXRF against ICP-OES-based analytical techniques (McLaren et al., 2012; Tadeu Costa Junior et al., 2020), as small analytical masses (≤ 0.5 g) in wet chemistry may not represent bulk composition. Thus, sample representation is critical when comparing analytical techniques, yet it is often overlooked. Although some studies perform replicate pXRF scans, they often omit subsampling for acid digestion, or report data without specifying biomass used in either method. Only a few studies include replicate acid digestions (e.g., Santos et al., 2017; Sapkota et al., 2019), and even in these cases, matched biomass between the two methods is unclear. Failure to control for sample representation may introduce systematic bias, particularly as instrumental sensitivity continues to improve. Together, the limited validation of handheld MXRF in plant matrices and the unresolved effects of sample representation when comparing MXRF with destructive analytical methods highlight the need for a validation framework that integrates SRMs with environmentally heterogeneous plant samples.

This study provides, to our knowledge, the first systematic validation of the first-generation handheld MXRF instrument evaluated here for plant elemental quantification and assesses its applicability to environmental monitoring of vegetation at metal(loid) contaminated sites. We systematically evaluated factors hypothesized to influence MXRF performance in plant matrices, including minimum biomass thresholds, particle size, sample heterogeneity, elemental concentration range, signal intensity, measurement time, replicate analysis, biomass matching between methods, and measurement configuration (e.g., sample cup vs. point analysis). The study was designed as a two-stage validation framework combining plant SRMs with environmentally relevant field-collected plant samples. Plant SRMs provided standardized matrices with certified elemental concentrations, enabling controlled evaluation of analytical performance and measurement-related factors, whereas field-collected samples allowed assessment under the greater matrix heterogeneity encountered in environmental applications. Together, these complementary stages were used to identify key sources of variability and establish practical guidelines and thresholds for robust multi-element analysis of plant tissues. Although the performance metrics established here are specific to the tested system and analytical conditions, the validation framework provides a transferable template for evaluating future handheld MXRF systems as they become available.

2. Materials and methods

The analytical workflow, including MXRF measurement configurations, SRM and field sample processing, and the MXRF-ICP-MS validation framework, is summarized in Fig. 1. Key technical terms are defined in Table S1.

2.1. Instrumentation and analytical parameters

Elemental quantification was conducted using a portable MXRF analyzer (Rocksand; X-ray Optical Systems, XOS Inc., USA) with a molybdenum X-ray tube (25–50 kV, 200 μ A) and a 25 mm silicon drift detector. Double-curved crystal optics generated monochromatic excitation beams at three energies (6.4, 17.4, and 34 keV), enabling detection of light to heavy elements. The instrument was operated in two configurations: *rotating sample cup* and direct *point* measurement. Two analytical modes were used: *screen* (real-time) and *quantify* (fixed settings). *Quantify* mode included two optimization settings: T1.5 (90 s total acquisition; 30 s per energy

level) and T6 (360 s total; 120 s per level). Thus, all three monochromatic excitation energies were applied sequentially under both acquisition settings. Unless stated otherwise, analyses used the rotating-cup configuration at T1.5, optimized for plant matrices.

Instrument footprints were evaluated using plant-based SRMs, including National Institute of Standards and Technology (NIST) 1573a (tomato leaves), 1570 (spinach leaves), 1515 (apple leaves), 1575a (pine needles), and 1547 (peach leaves). NIST 1568b (rice flour) was additionally included as a denser matrix to assess matrix density effects (Supplementary Material). Elements analyzed included Cu, Zn, Mn, Fe, K, P, S, and Ca, and were selected based on their presence and concentration ranges in SRMs. Sulfur was certified in only one SRM (rice flour) and Se was excluded due to low concentrations.

Signal intensity was quantified as counts per second (cps) from raw spectra. Limits of detection (LOD) and quantification (LOQ)

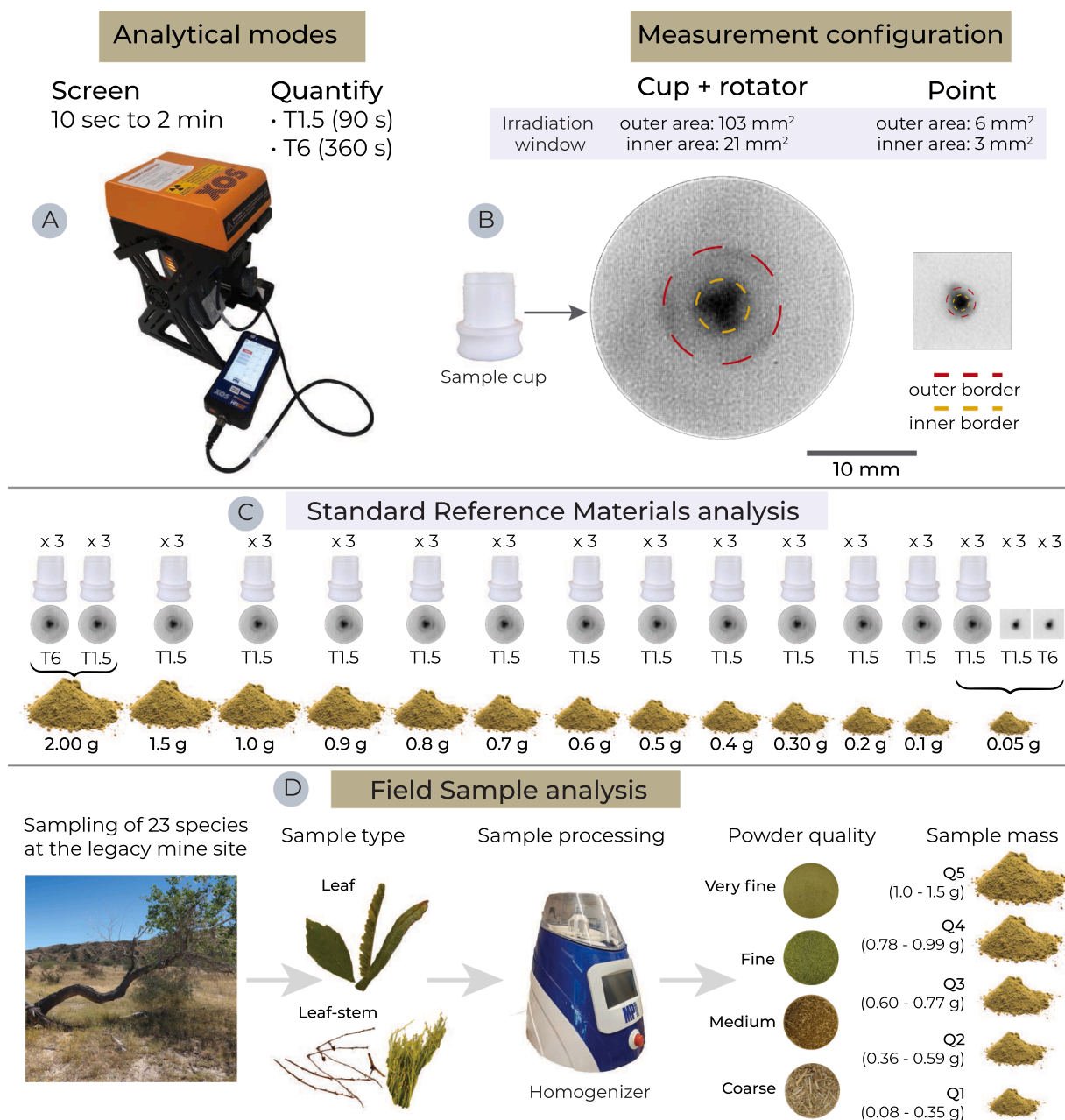


Fig. 1. Workflow of MXRF measurements and sample processing of SRMs and field-collected samples. A) Analytical modes (*screen*, *quantify*) and optimization settings (T1.5, T6). B) Irradiation footprint of two measurement configurations: *Cup + rotator* ($\varnothing$ 2.5 cm) and *Point* (no cup or rotator). Darker regions indicate higher irradiation intensity. The outer and inner boundaries represent the total irradiated area and the high-intensity region, respectively. C) SRM validation across decreasing sample masses and configurations. D) Workflow for field-collected samples: collection, tissue separation, homogenization, weighing, and classification by sample type, powder quality, and mass (five quantiles: Q1–Q5).

were estimated from repeated measurements of each SRM representing the lowest detectable concentration of a given element ($n = 10$). Following standard procedures (Guimarães et al., 2016; International Union of Pure and Applied Chemistry IUPAC, 2002), LOD and LOQ were calculated as $3 \times \text{SD}$ and $10 \times \text{SD}$, respectively, where SD is the standard deviation of the repeated measurements. Limits were calculated using plant-based SRMs for all elements except S, for which NIST 1568b (rice flour) was used as the only available SRM with a certified S concentration (Table 1).

2.2. MXRF analyses of NIST standard reference materials

All six plant-based SRMs were used to evaluate accuracy, precision, and effects of sample mass and measurement time. Settled bulk density was determined for each SRM from measured powder mass and volume after repeated tapping to constant volume (without mechanical pressing). Corresponding powder thickness was calculated for each sample mass using the measured bulk density and sample cup geometry (internal diameter: 25 mm). SRMs were grouped based on bulk density and corresponding powder thickness at fixed sample mass into a dense matrix (1568b) and light, leaf-based matrices (1515, 1547, 1570, 1573a, 1575a). These groupings were used to evaluate the influence of matrix density and sample thickness on MXRF measurements.

For the sample mass tests, SRM powders were loaded into sample cups sealed with 12 μm polypropylene film, across 13 masses (2.00, 1.50, 1.00, 0.90, 0.80, 0.70, 0.60, 0.50, 0.40, 0.30, 0.20, 0.10, and 0.05 g), each analyzed in triplicate for 90 s using plant setting. The largest mass (2.0 g) was additionally scanned for 360 s, while the smallest (0.05 g) was also analyzed using point measurements, with SRM powders placed directly on the irradiation window (separated only by polypropylene film) for 90 and 360 s.

To assess how element-specific uncertainty values change with measurement time, 2.0 g SRMs were measured at eight acquisition times: 10, 20, 30, 40, 50, and 60 s in *screen* mode, and 90 and 360 s in *quantify* mode.

Accuracy was evaluated as recovery $[(\text{MXRF}_{\text{mean}}/\text{SRM}_{\text{certified}}) \times 100\%]$; (Nedjimi, 2023)], where $\text{MXRF}_{\text{mean}}$ was the mean SRM value measured by MXRF across replicates and $\text{SRM}_{\text{certified}}$ was the NIST-certified value. Precision was assessed as coefficient of variation (CV) between triplicate scans of the same SRM sample and then averaged by element. SRM identity, sample mass, and precision effects on agreement between MXRF-measured and certified concentrations were further assessed using Partial Least Squares Regression (PLS-R; Section 2.6).

2.3. Field sample collection, preparation, and MXRF analyses

After SRM-based validation tests, we extended the analysis to field-collected samples to further investigate the influence of sample mass and assess matrix effects not represented in SRMs. Following a random sampling design, 75 plant samples from 23 species (up to six replicates per species) were collected from a reclaimed Cu-Mo sulfide-bearing mine tailings pond in central Arizona, USA (coordinates withheld per company policy). The $\sim 1 \text{ km}^2$ site received tailings between 1928 and 1959 and was regraded, capped with uncontaminated soil, and revegetated. This site exhibits a broad range of metal(loid) concentrations in soils and plants (Włodarczyk et al., 2025). Taxonomic identification was verified via voucher specimens deposited at the University of Arizona Herbarium (Table S2). Samples were washed (twice in deionized and once in Milli-Q water), air-dried, separated into *leaf* or *leaf-stem* material (when foliage mass was insufficient), oven-dried (70°C , 72 h) to eliminate moisture as a matrix factor, and homogenized using ceramic beads (TallPrep Lysing Matrix M, 4.5 mL tubes, MP Biomedicals, USA) in a FastPrep-24 5 G homogenizer (MP Biomedicals, USA). Powder quality was classified into four categories, based on particle size ranges identified in ImageJ: *very fine* ($<0.5 \text{ mm}$), *fine* (0.5–1.5 mm), *medium* (1.6–3.5 mm), and *coarse* (3.6–7 mm; Figure S1).

Samples were weighed (individual sample weights are provided in the Supplementary Dataset), transferred into a sample cup, sealed with polypropylene film, and scanned in triplicate (90 s), with vortex mixing between scans. Eleven elements were quantified: eight overlapped with SRM analysis (Cu, Zn, Mn, Fe, K, P, S, and Ca). K, P, S, and Ca represented essential plant nutrients, with S also relevant to sulfide oxidation in mining environments, while Cu, Zn, Mn, and Fe represented both plant nutrients and elements commonly associated with mining-impacted environments. Ti, Se, and Re were included for exploratory evaluation given their relevance to mining-related processes and environmental risk; Se and Re were also previously found at elevated concentrations in plants at the study site (Włodarczyk et al., 2025). Quality assurance and control (QA/QC) included NIST 1573a and 1570 – selected for

Table 1

Limits of detection (LOD) and quantification (LOQ) for MXRF analysis of plant samples estimated from repeated measurements of low-concentration SRMs. For each element, the plant-based SRM with the lowest concentration available for that element was measured repeatedly ($n = 10$). The SRM concentration, standard deviation (SD), LOD, and LOQ are reported in mg kg^{-1} .

Element	Low-concentration SRM	SRM concentration	SD	LOD	LOQ
Cu	NIST1575a	2.8	0.42	1.3	4.2
Zn	NIST1515	12.45	0.75	2.3	7.6
Mn	NIST1515	54.1	3.9	12	39
Fe	NIST1575a	46	3.1	9.0	31
K	NIST1575a	4170	106	317	1056
P	NIST1575a	1070	309	928	3094
S	NIST1568b	1200	171	512	1705
Ca	NIST1575a	2500	66	198	661
Se	NIST1570	0.11	0.1	0.28	0.9

their relatively high concentrations of target elements – and sucrose blanks every 20 scans.

2.4. ICP-MS analysis of field samples and SRMs

Following MXRF, all samples were analyzed with ICP-MS to obtain quantitative elemental concentrations and validate MXRF performance. Samples were split into three technical replicates (≤ 0.5 g, representing exactly one-third of the total homogenized sample mass) and digested (Stegink and Rader, 2024). Each batch included NIST 1547 and procedural blanks. Concentrations of Cu, Zn, Mn, Fe, K, P, S, Ca, Ti, Se and Re were quantified using an Agilent 7850 ICP-MS (Agilent Technologies; Santa Clara, CA). Each sample analysis consisted of an average of five blocks with 100 sweeps each. To mitigate potential polyatomic interferences, helium collision mode was applied for Mn, Fe, K, S, and Ti, while no-gas mode was used for Cu, Zn, P, Ca, Se, and Re. Analyses were performed in the Metal Isotopes Laboratory, Indiana University Bloomington.

All SRMs were also digested in triplicate and analyzed by ICP-MS to assess accuracy and analytical variance. Results were compared with certified values and served as the quality control reference for evaluating MXRF–ICP-MS agreement (Table S3).

2.5. Data processing and statistical analysis

MXRF outputs included spectra, element intensities (counts), concentrations, element-specific uncertainty values, and relative thickness (RT; also referred to as areal density in other studies). Data were processed in HD Data Viewer (v1.8.2844, XOS). Non-detection data points were coded as NA. For SRMs and field samples, mean, median, SD, and CV were calculated across replicates. For SRM MXRF datasets, residual normality was evaluated with Quantile-Quantile plots, density plots, and Shapiro-Wilk tests. Homogeneity of variance (measurement configurations: cup vs. point; optimization: 90 vs. 360 s) was assessed using Bartlett's and Levene's tests. One-way ANOVA, followed by Tukey HSD post-hoc pairwise comparisons, was applied when assumptions were met. For uncertainty tests, as assumptions were not met even after transformation, Spearman correlations were applied. For signal intensity, cps were computed by dividing raw counts by dwell time and min–max normalized (0–1) within element across SRMs. Relationships between RT and sample mass were modeled using asymptotic regressions, separately for dense and light SRMs (see Supplementary Material). Model performance for field samples (leaf and leaf-stem material analyzed separately) was evaluated using coefficient of determination (R^2), mean absolute error (MAE), root mean square error (RMSE), normalized root mean square error (NRMSE), residual prediction deviation (RPD), and intraclass correlation coefficient (ICC). All analyses were performed in R environment (v4.2.2, R core Team, 2022) and XLSTAT (Addinsoft, New York, USA).

2.6. Partial least squares regression (PLS-R) models

PLS-R models evaluated matrix effects on MXRF performance for SRMs and field datasets separately. The response variable was mean percent error, calculated as $[(MXRF_{\text{mean}} - \text{Reference}_{\text{mean}}) / \text{Reference}_{\text{mean}}] \times 100\%$, where the reference corresponded to replicate-averaged ICP-MS values (field samples) or certified SRM values (SRM samples). Separate models were fitted for each element. Each model was run three times with different random seeds to assess stability, using jackknife leave-one-out (LOO) cross-validation and automatic stopping criteria. For SRMs, the quantitative predictor was MXRF coefficient of variation ($CV(MXRF)$; i.e. MXRF precision), while *Sample mass* (13 levels, 0.05–2 g), and *SRM identity* were treated as qualitative predictors. For field samples, the quantitative predictor was MXRF uncertainty ($UNC(MXRF)$), and qualitative predictors included *Species*, plant *Form* (grass, forb, shrub, tree), *Sample Type* (leaf, leaf-stem), and *Powder Quality* (very fine, fine, medium, coarse). Additional qualitative predictors were generated by discretizing continuous variables into quantiles (Q1–Q5), including *sample mass*, $CV(MXRF)$, $CV(ICP)$, and ICP-MS concentrations ($CON(ICP)Q$). The rotating cup configuration and 90 s optimization were used in the models.

Model complexity was optimized using the LOO Q^2 method (Roy and Roy, 2008), with robustness and predictive relevance thresholds defined as small ($Q^2=0.02$), medium ($Q^2=0.15$), and large ($Q^2=0.35$) (Hair et al., 2021). Only models with at least medium predictive relevance were retained; models for Se and Re in field data did not meet this criterion. Variable Importance in Projection (VIP) scores ≥ 0.8 were considered influential (Kothawala et al., 2014). Significant standardized coefficients and VIPs were used to assess the direction and relative importance of individual predictors, respectively.

2.7. Agreement analysis between MXRF and ICP-MS

Based on PLS-R outputs, datasets were stratified into two subsets: i) optimal, representing samples with favorable and controllable characteristics expected to improve MXRF–ICP-MS agreement (i.e., qualitative predictors negatively associated with percent error; e.g., higher sample mass, greater powder homogeneity, low analytical variance), and ii) non-optimal, representing samples associated with weaker or less predictable agreement (i.e., predictors positively associated with percent error; e.g., low sample mass, poor powder quality, higher analytical variance). Species identity and plant form were excluded from stratification, except *Allionia incarnata*, retained as a proxy indicator of potential surface contamination. This species is known to exhibit foliar contamination due to adhesion of soil and dust particulates facilitated by sticky leaf exudates and glandular trichomes (Cunha Neto et al., 2020). For each element, optimal and non-optimal subsets were plotted separately, and regressions were performed to illustrate changes in MXRF–ICP-MS agreement after accounting for matrix effects.

Model quality for both field data stratification and sample mass prediction (SRM samples) was assessed using R^2 , MAE, RMSE, NRMSE, RPD, and ICC (Chang et al., 2001; Chen and Barnhart, 2008; McGladdery et al., 2018). Model fitness based on NRMSE was

categorized as excellent ($\text{NRMSE} < 10\%$), good ($10\% \leq \text{NRMSE} < 20\%$), common ($20\% \leq \text{NRMSE} < 30\%$), or poor ($\text{NRMSE} \geq 30\%$) (Peng et al., 2017). RPD values were interpreted as: accurate (>2), moderately predictive ($1.4-2$), or non-reliable (<1.4) (Antonangelo and Zhang, 2021), and ICC values indicated test-retest reliability as: excellent (>0.90), good ($0.75 < \text{ICC} \leq 0.90$), moderate ($0.50 \leq \text{ICC} \leq 0.75$), and poor (<0.50) (Koo and Li, 2016).

3. Results and discussion

3.1. Measurement characteristics and detection/quantification limits

MXRF irradiation footprints differed substantially between point and rotating-cup setups. The sample cup rotator increased the high-intensity irradiation area by seven times relative to point measurement (Fig. 1B). For the point configuration, the maximum-intensity footprint covered $\sim 3\text{mm}^2$ ($\sim 2\text{ mm}$ spot diameter), which was larger than $\sim 1\text{ mm}$ spot previously reported for this instrument (Fleming et al., 2017; Guimarães et al., 2016). This discrepancy likely reflects greater scatter and incidental beam irradiation under three alternating excitation energies. In the rotating-cup setup, the inner maximum-intensity irradiation area expanded to $\sim 5\text{ mm}$ diameter. These differences have practical implications: point configuration enables targeted analysis of small regions but is more sensitive to local heterogeneity, whereas cup mode averages over a larger area, reducing spatial variability at the expense of resolution.

Instrumental detection limits for the MXRF have been reported for aqueous, soil, and food tissue matrices, and are typically lower than those of conventional polychromatic pXRF instruments (Guimarães et al., 2016; McIntosh et al., 2016). Because formal LOD and LOQ values for plant matrices have not been established on the MXRF model used in this study, we calculated them using plant-based SRMs representing homogenous powdered matrices (Table 1) (Guimarães et al., 2016). For elements with established deficient and optimal concentration ranges in mature leaf tissues (Cu, Zn, and Mn), the calculated LODs were below or within these physiologically relevant concentration ranges, indicating that these elements were detectable at concentrations relevant to plant tissue analysis under the conditions used in this study (Kabata-Pendias, 2011).

3.2. SRM-based analytical performance across sample mass

To separate instrument- and matrix-driven error prior to summarizing recoveries, we first evaluated SRM-level effects using PLS-R models fitted across all SRMs and sample-mass tests (Fig. 2). NIST 1568b (rice flour) showed consistently high positive standardized coefficients for percent error, indicating systematic disagreement relative to certified values under the plant-optimized configuration. Because rice flour is denser and structurally distinct from foliage matrices and behaved as a consistent outlier in the multielement screening, it was excluded from subsequent SRM-based performance summaries, except where required to report S recoveries (Table 2). By contrast, NIST 1570 consistently showed the best agreement, indicating the importance of both matrix density and internal structure in MXRF accuracy.

Sample mass and MXRF replicate variability (CV; *i.e.* precision) emerged as dominant predictors of percent error. Very low sample mass (0.05 g) and elevated CV were major positive contributors to percent error across most elements, highlighting the importance of sufficient sample thickness and close evaluation of element-dependent precision for robust quantification. Higher CVs were consistently linked to reduced agreement, except for K, for which CV effect was indefinite (Fig. 2).

For the five leaf-based SRMs measured in cups, recoveries at sample masses $\geq 0.3\text{ g}$ ranged from 94 to 105% for Cu, Zn, Mn, Fe, and 112–116% for K and Ca (Table 2). Recoveries remained stable above 0.3 g and gradually declined with decreasing mass, with a significant drop at 0.05 g (Fig. 3). Concentrations of P were largely overestimated, while S recoveries were unreliable due to single-

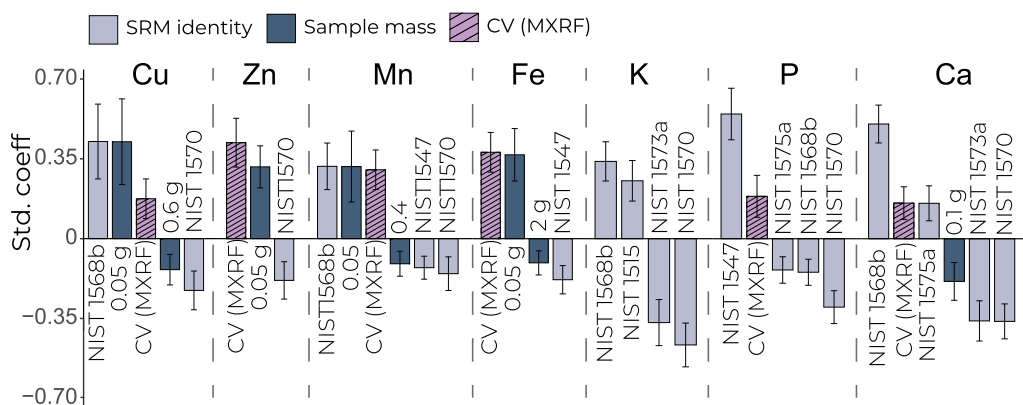


Fig. 2. Significant standardized coefficients from PLS-R models for six plant SRMs. Bars show predictor importance and direction (positive or negative) of association with percent error (MXRF vs. SRM certified concentration). Striped and solid bars indicate quantitative and qualitative variables, respectively.

Table 2

Accuracy (recovery) and precision (coefficient of variation, CV) of MXRF measurements for five plant SRMs (mean $\pm$ SD, mg kg⁻¹) across descending sample mass (SM). Different letters indicate significant differences between sample masses within a given measurement configuration for each element. NIST 1568 was excluded from analyses, except for S.

	Measurement configuration	SM (g)	Cu	Zn	Mn	Fe	K	P	S	Ca
Recovery	cup-T6	2	108 $\pm$ 7 ^{ab}	103 $\pm$ 4 ^{bc}	104 $\pm$ 3 ^{bc}	104 $\pm$ 8 ^{abc}	115 $\pm$ 6 ^a	171 $\pm$ 94 ^{ns}	105	116 $\pm$ 9 ^a
		2	107 $\pm$ 6 ^{ab}	103 $\pm$ 6 ^{bc}	105 $\pm$ 3 ^{abc}	101 $\pm$ 2 ^{abc}	115 $\pm$ 6 ^a	172 $\pm$ 41 ^{ns}	108	116 $\pm$ 9 ^a
		1.5	114 $\pm$ 13 ^a	105 $\pm$ 5 ^{ab}	102 $\pm$ 5 ^{bcd}	103 $\pm$ 9 ^{abc}	114 $\pm$ 6 ^{ab}	165 $\pm$ 38 ^{ns}	122	115 $\pm$ 8 ^{ab}
		1	107 $\pm$ 5 ^{ab}	104 $\pm$ 4 ^{abc}	105 $\pm$ 3 ^{abc}	100 $\pm$ 6 ^{abcd}	114 $\pm$ 7 ^{ab}	154 $\pm$ 28 ^{ns}	119	114 $\pm$ 9 ^{ab}
		0.9	104 $\pm$ 9 ^{ab}	104 $\pm$ 5 ^{abc}	101 $\pm$ 4 ^{bcd}	102 $\pm$ 7 ^{abc}	115 $\pm$ 6 ^a	140 $\pm$ 51 ^{ns}	105	115 $\pm$ 8 ^{ab}
		0.8	113 $\pm$ 12 ^a	103 $\pm$ 4 ^{bc}	105 $\pm$ 2 ^{abc}	102 $\pm$ 8 ^{abc}	114 $\pm$ 7 ^{ab}	159 $\pm$ 76 ^{ns}	109	115 $\pm$ 10 ^{ab}
		0.7	107 $\pm$ 9 ^{ab}	105 $\pm$ 4 ^{ab}	105 $\pm$ 2 ^{bc}	99 $\pm$ 8 ^{abcd}	113 $\pm$ 7 ^{ab}	160 $\pm$ 58 ^{ns}	97	114 $\pm$ 10 ^{ab}
		0.6	105 $\pm$ 5 ^{ab}	104 $\pm$ 4 ^{abc}	102 $\pm$ 2 ^{bcd}	99 $\pm$ 7 ^{abcd}	113 $\pm$ 6 ^{ab}	166 $\pm$ 53 ^{ns}	95	114 $\pm$ 10 ^{ab}
	cup-T1.5	0.5	97 $\pm$ 5 ^{abc}	104 $\pm$ 4 ^{abc}	102 $\pm$ 4 ^{bcd}	101 $\pm$ 9 ^{abc}	113 $\pm$ 7 ^{ab}	131 $\pm$ 45 ^{ns}	107	113 $\pm$ 10 ^{ab}
		0.4	100 $\pm$ 9 ^{ab}	105 $\pm$ 4 ^{abc}	102 $\pm$ 3 ^{bcd}	100 $\pm$ 9 ^{abcd}	112 $\pm$ 7 ^{ab}	146 $\pm$ 78 ^{ns}	111	113 $\pm$ 10 ^{ab}
		0.3	94 $\pm$ 14 ^{abc}	102 $\pm$ 6 ^{bc}	101 $\pm$ 3 ^{bcd}	98 $\pm$ 7 ^{abcd}	112 $\pm$ 7 ^{ab}	149 $\pm$ 58 ^{ns}	104	112 $\pm$ 9 ^{ab}
		0.2	88 $\pm$ 10 ^{bc}	98 $\pm$ 6 ^{bc}	97 $\pm$ 6 ^{cde}	93 $\pm$ 5 ^{bcd}	110 $\pm$ 6 ^{ab}	153 $\pm$ 24 ^{ns}	106	110 $\pm$ 9 ^{ab}
		0.1	88 $\pm$ 12 ^{bc}	90 $\pm$ 10 ^{cd}	90 $\pm$ 10 ^{de}	83 $\pm$ 10 ^{cd}	104 $\pm$ 8 ^{ab}	126 $\pm$ 18 ^{ns}	95	102 $\pm$ 9 ^{ab}
		0.05	59 $\pm$ 6 ^c	78 $\pm$ 7 ^d	78 $\pm$ 10 ^e	69 $\pm$ 15 ^d	92 $\pm$ 10 ^b	132 $\pm$ 18 ^{ns}	97	90 $\pm$ 11 ^b
		0.05	102 $\pm$ 9 ^{ab}	108 $\pm$ 4 ^{ab}	109 $\pm$ 4 ^{ab}	111 $\pm$ 16 ^{ab}	116 $\pm$ 7 ^a	116 $\pm$ 10 ^{ns}	95	117 $\pm$ 8 ^a
	point-T1.5	0.05	102 $\pm$ 21 ^{ab}	113 $\pm$ 5 ^a	115 $\pm$ 4 ^a	121 $\pm$ 24 ^a	118 $\pm$ 7 ^a	117 $\pm$ 14 ^{ns}	97	119 $\pm$ 8 ^a
	point-T6	0.05	5.5 $\pm$ 3.1 ^a	1.3 $\pm$ 0.5 ^c	2.0 $\pm$ 2.1 ^b	2.1 $\pm$ 2.2 ^{bc}	0.5 $\pm$ 0.5 ^d	27 $\pm$ 27 ^{ns}	4.5 $\pm$ 2.8	0.9 $\pm$ 0.7 ^{de}
	cup-T6	2	11 $\pm$ 4 ^a	3.5 $\pm$ 1.7 ^{bc}	2.6 $\pm$ 2.6 ^b	2.8 $\pm$ 1.8 ^{abc}	1.0 $\pm$ 0.6 ^{bcd}	21 $\pm$ 13 ^{ns}	9.2 $\pm$ 7.4	1.3 $\pm$ 1.1 ^{bcd}
		1.5	13 $\pm$ 11 ^a	3.3 $\pm$ 2.0 ^{bc}	4.3 $\pm$ 3.6 ^{ab}	2.2 $\pm$ 1.1 ^{abc}	1.4 $\pm$ 0.9 ^{bcd}	15 $\pm$ 14 ^{ns}	7.4 $\pm$ 3.8	0.8 $\pm$ 0.4 ^{cde}
		1	16 $\pm$ 11 ^a	2.9 $\pm$ 1.7 ^{bc}	3.4 $\pm$ 1.4 ^{ab}	3.1 $\pm$ 2.1 ^{abc}	1.0 $\pm$ 1.0 ^{cd}	17 $\pm$ 7.7 ^{ns}	5.5 $\pm$ 5.7	1.3 $\pm$ 0.7 ^{bcd}
		0.9	14 $\pm$ 5 ^a	2.6 $\pm$ 1.1 ^{bc}	3.6 $\pm$ 1.8 ^{ab}	4.1 $\pm$ 2.5 ^{abc}	0.8 $\pm$ 0.5 ^{bcd}	20 $\pm$ 17 ^{ns}	7.5 $\pm$ 8.0	0.7 $\pm$ 0.6 ^e
		0.8	6.6 $\pm$ 3.8 ^a	2.9 $\pm$ 2.1 ^{bc}	3.9 $\pm$ 2.8 ^{ab}	1.7 $\pm$ 1.6 ^c	1.0 $\pm$ 0.6 ^{cd}	25 $\pm$ 19 ^{ns}	10 $\pm$ 4.5	1.3 $\pm$ 0.6 ^{bcd}
		0.7	16 $\pm$ 13 ^a	2.4 $\pm$ 1.4 ^{bc}	3.9 $\pm$ 2.8 ^{ab}	3.1 $\pm$ 1.6 ^{abc}	1.5 $\pm$ 0.4 ^{abcd}	19 $\pm$ 21 ^{ns}	7.2 $\pm$ 2.2	1.1 $\pm$ 1.4 ^e
		0.6	12 $\pm$ 5 ^a	3.6 $\pm$ 3.1 ^{bc}	4.8 $\pm$ 1.9 ^{ab}	4.2 $\pm$ 2.1 ^{abc}	1.1 $\pm$ 1.0 ^{bcd}	22 $\pm$ 22 ^{ns}	6.7 $\pm$ 2.2	1.3 $\pm$ 1.1 ^{bcd}
		0.5	14 $\pm$ 7 ^a	3.3 $\pm$ 1.7 ^{bc}	3.2 $\pm$ 2.8 ^{ab}	4.1 $\pm$ 2.6 ^{abc}	1.1 $\pm$ 0.8 ^{bcd}	15 $\pm$ 7.1 ^{ns}	11 $\pm$ 5	1.2 $\pm$ 1.1 ^{cde}
CV	cup-T1.5	0.4	10 $\pm$ 8 ^a	3.7 $\pm$ 1.9 ^{bc}	4.9 $\pm$ 2.9 ^{ab}	2.9 $\pm$ 1.6 ^{abc}	1.4 $\pm$ 1.3 ^{bcd}	25 $\pm$ 13 ^{ns}	6.5 $\pm$ 5.7	1.5 $\pm$ 1.5 ^{bcd}
		0.3	15 $\pm$ 9 ^a	3.0 $\pm$ 2.0 ^{bc}	4.8 $\pm$ 3.2 ^{ab}	3.5 $\pm$ 2.4 ^{abc}	1.9 $\pm$ 1.6 ^{abcd}	14 $\pm$ 12 ^{ns}	10 $\pm$ 4	1.7 $\pm$ 1.8 ^{bcd}
		0.2	17 $\pm$ 10 ^a	4.7 $\pm$ 4.6 ^{abc}	5.0 $\pm$ 1.7 ^{ab}	4.4 $\pm$ 2.9 ^{abc}	2.3 $\pm$ 1.1 ^{abcd}	32 $\pm$ 25 ^{ns}	10 $\pm$ 7	2.4 $\pm$ 0.8 ^{abcde}
		0.1	25 $\pm$ 21 ^a	9.6 $\pm$ 7.4 ^{ab}	8.1 $\pm$ 5.1 ^{ab}	7.7 $\pm$ 3.5 ^{ab}	5.1 $\pm$ 4.4 ^{abc}	8.4 $\pm$ 6.3 ^{ns}	11 $\pm$ 10	5.8 $\pm$ 4.8 ^{abcd}
		0.05	19 $\pm$ 3 ^a	19 $\pm$ 10 ^a	13 $\pm$ 9 ^a	23 $\pm$ 21 ^a	14 $\pm$ 10 ^a	24 $\pm$ 9.8 ^{ns}	14 $\pm$ 5.9	15 $\pm$ 10 ^a
	point-T1.5	0.05	26 $\pm$ 11 ^a	8.2 $\pm$ 5.4 ^{abc}	7.8 $\pm$ 4.3 ^{ab}	14 $\pm$ 9 ^a	6.6 $\pm$ 4.0 ^{ab}	11 $\pm$ 4.8 ^{ns}	10 $\pm$ 5	7.1 $\pm$ 4.6 ^{ab}
	point-T6	0.05	17 $\pm$ 15 ^a	4.7 $\pm$ 4.2 ^{bc}	4.6 $\pm$ 2.6 ^{ab}	15 $\pm$ 22 ^{ab}	4.1 $\pm$ 2.7 ^{abc}	14 $\pm$ 8 ^{ns}	7.0 $\pm$ 3.5	5.1 $\pm$ 2.9 ^{abc}

^{ns}not statistically significant

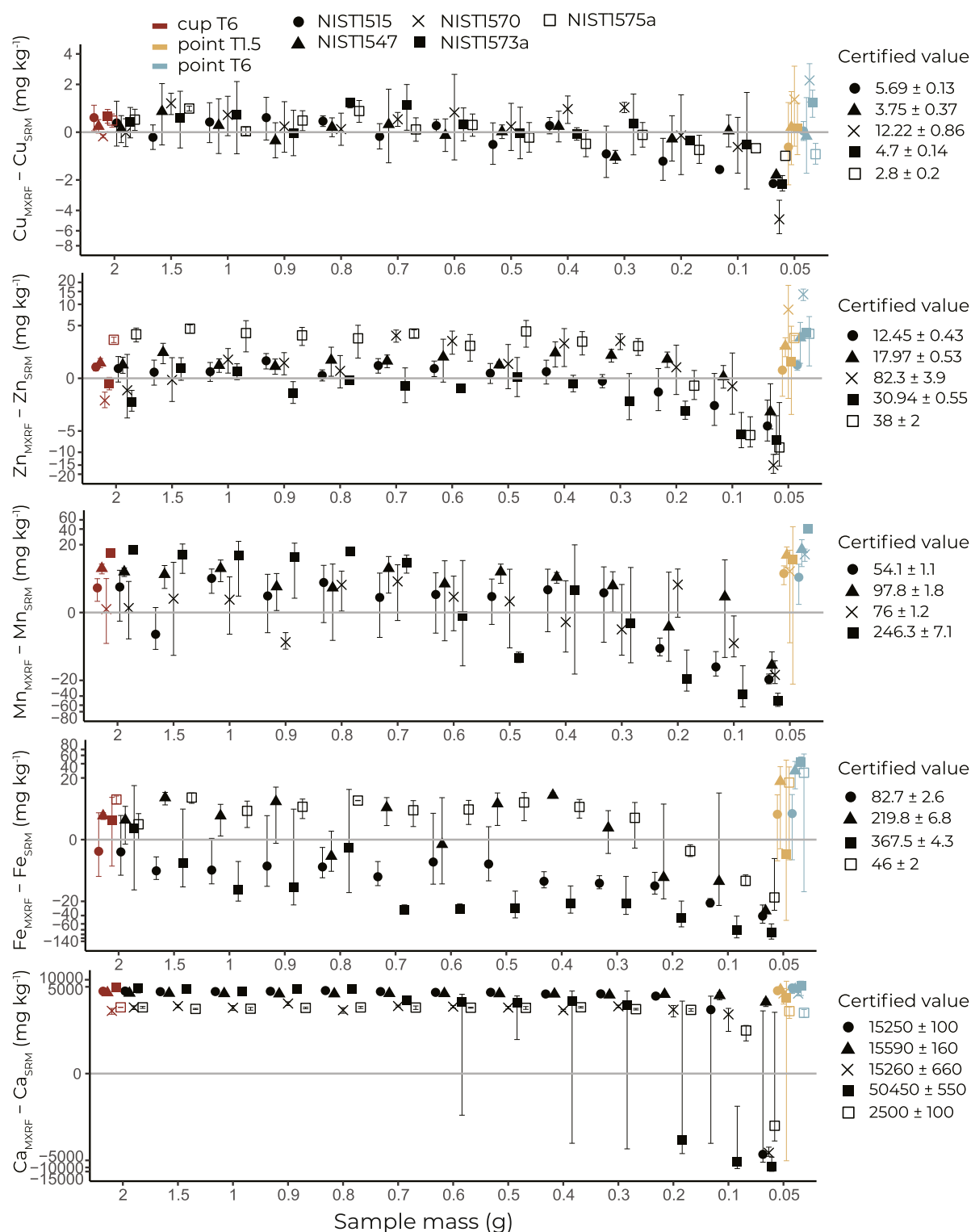


Fig. 3. Relative differences (mean $\pm$ SD; $n = 3$) between MXRF and certified concentrations for five SRMs across 13 sample masses. Colors indicate measurement configurations and acquisition times. The y-axis uses a pseudo-logarithmic scale combining logarithmic scaling at higher values with linear scaling near zero to preserve small differences.

SRM availability; both elements were thus excluded from further SRM-based interpretation. Only a few previous studies have explicitly tested the pXRF accuracy as a function of sample mass. Polychromatic pXRF studies show a significant decrease in concentration of internal standards below 1 g (Lima et al., 2024), whereas MXRF tests using algae SRMs reported little influence between 0.17–1 g (Guimarães et al., 2016). In contrast, foliage SRMs under the plant-optimized MXRF configuration displayed a clear sample mass dependency across the analyzed elements in the present work, indicating stricter thickness requirements for plant matrices than previously suggested for other biological matrices.

MXRF precision declined with decreasing mass, with a pronounced negative shift at ≤ 0.2 g (Table 2; Fig. 3). At ≥ 0.3 g, CV ranged 0.76–4.9% for Zn, Mn, Fe, K, and Ca, and 6.66–16% for Cu. Elevated Cu CV could be associated with its low concentrations in all SRMs relative to other elements, which can inflate CV estimates. Although $CV \leq 15\%$ is commonly considered acceptable in pXRF applications and is often used to determine optimal measurement time (Bueno Guerra et al., 2014; de Marchi Soares et al., 2021), MXRF demonstrated acceptable precision at sample masses ≥ 0.3 g for all elements except P. We therefore recommend that CV and recovery be evaluated jointly when defining minimum biomass thresholds, rather than relying on either metric independently.

At 0.05 g, point measurements improved accuracy compared to cups, but precision remained poor and was not recovered by changing analytical modes. The inaccuracy at extremely low mass likely reflects low signal intensity due to low thickness, air gaps within powder, and possible discontinuity of X-rays (Ribeiro et al., 2021; Sapkota et al., 2019). Extending measurement time from 90 s to 360 s at both the lowest (0.05 g) and the highest (2 g) sample mass did not significantly improve accuracy or precision for any element at any configuration (cup, point), though instrument-estimated uncertainty decreases with extended measurement time (Figure S2). This lack of improvement beyond 90 s is consistent with polychromatic pXRF studies, which show that quality is either already optimal at 90 s or does not improve further with extended measurement times (Acquah et al., 2022; Lima et al., 2024). However, some studies on plant matrices observed a notable increase in CV below 120 s when quantifying Cu and Mn (Tadeu Costa Junior et al., 2020). In contrast, our data suggest that MXRF maintains stable accuracy and precision across 90–360 s for all elements assessed here, suggesting limited benefit from longer acquisition times under these conditions.

Normalized cps mirrored mass-dependent trends (Fig. 4). Signal intensity peaked at 2 g with 360 s, remained high between 1–2 g at 90 s, then declined gradually with mass for Cu, Zn, Mn, and Fe, with a marked drop below 0.4 g and a sharp loss at 0.1–0.05 g in cups across all elements. Point mode at 0.05 g increased cps, especially for light elements (Ca, K), occasionally exceeding 2 g cup intensities. This pattern is consistent with shallower penetration depths and more consistent irradiation of a small, concentrated area. Importantly, higher cps at 0.05 g did not translate into acceptable precision, confirming that signal intensity and precision metrics diverge at very low mass.

Sample mass provides a practical operational proxy for sample thickness within a defined cup geometry and matrix, and both parameters can affect pXRF analytical performance in plant materials (Lima et al., 2024; Zhou et al., 2020). In our sample cups, loose powder thickness averaged ~ 1.8 cm at 2 g and ~ 0.9 cm at 1 g; however, NIST 1568b reached only ~ 0.5 cm at 1 g due to its higher density. Bulk-density measurements further supported this relationship, with relatively little variability among the five leaf-based SRMs ($0.35 - 0.38 \text{ g cm}^{-3}$), compared with NIST 1568b (0.92 g cm^{-3}). Using these densities and the fixed sample-cup geometry, corresponding settled powder thicknesses were calculated across the sample masses evaluated in this study (Table S5). The difference between loose and settled powder thickness further illustrates that absolute powder-layer thickness depends not only on sample mass

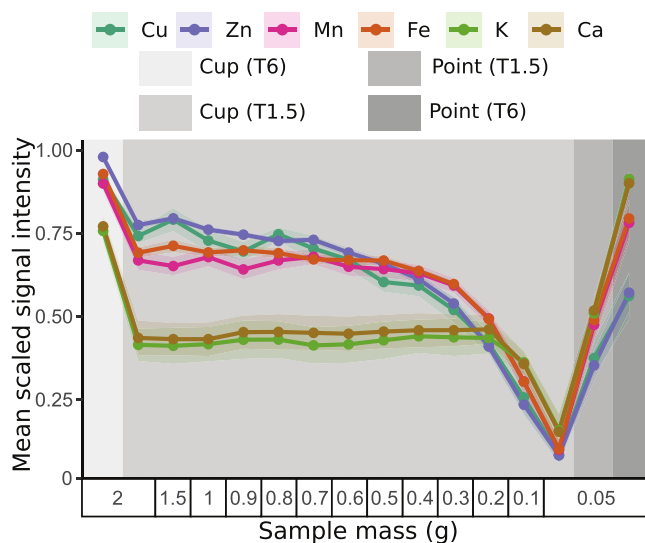


Fig. 4. Effect of sample mass on MXRF signal intensity. Elemental signal intensity was derived from raw counts and converted to counts per second (cps). Values were normalized and averaged across five SRMs. Points represent mean scaled cps; shaded areas indicate ± 1 SD. Grey shading indicates measurement configurations and acquisition times.

and matrix density, but also on powder packing. Thus, sample mass provides a reproducible operational parameter within a standardized cup geometry and similarly prepared matrices, while physical thickness remains dependent on matrix density and packing and is thus directly relevant to XRF analysis. Although a minimum thickness of ≥ 1 cm is often recommended to maintain pXRF analytical quality (Borges et al., 2020b; da Costa et al., 2024; Ribeiro et al., 2021), and some studies suggest ~ 3 cm as optimal (da Costa et al., 2023; Rincheval et al., 2019; Zhou et al., 2020), such thresholds can be impractical given that standard sample cups typically accommodate a maximum thickness of ~ 2 cm. Because sample thickness reflects the combined effects of biomass mass and matrix density, its analytical implications should be interpreted in the context of plant tissue type and preparation method rather than applied as a fixed universal criterion.

Overall, SRM-based evaluation demonstrates that MXRF accuracy is primarily affected by sample mass, CV values, SRM identity, and measurement configuration (cup vs. point), but not measurement time (90 vs. 360 s). Compared with recoveries reported for polychromatic pXRFs at 1 g of powder (a typical QA cup fill), our results show that the handheld MXRF evaluated here shows comparatively more favorable recoveries for Fe, Cu, Mn, and Zn at equivalent sample masses, whereas light elements exhibited more variable behavior. For P, K, Ca, and S, recovery patterns were inconsistent across studies and appeared to depend on the specific pXRF unit used (da Costa et al., 2023; McGladdery et al., 2018; Ribeiro et al., 2021; Rossi et al., 2025). At the manufacturer algorithm level, MXRF has also demonstrated superior Cu quantification relative to polychromatic units, under thin herbarium specimen measurements (Purwadi et al., 2024). Compared with a recent plant validation using a benchtop monochromatic XRF system, the handheld MXRF evaluated here showed similarly close agreement with certified values for Mn, Fe, Cu, and Zn, whereas K and Ca recoveries were less accurate (Zhang et al., 2025). Across the six elements common to both studies, the benchtop MXRF system generally underestimated SRM concentrations (average recoveries: 92.8–100.0%), while the handheld MXRF system evaluated here tended to overestimate them (101–116.9%) at the optimal 2-g sample mass (Table 2). These differences further demonstrate that both analytical performance and the direction of measurement bias may differ between benchtop and handheld MXRF systems. Accordingly, the performance thresholds and analytical recommendations established in this study should be considered specific to the handheld MXRF system and measurement conditions evaluated here and should not be generalized to other monochromatic XRF instruments.

3.3. Identification and causes of matrix effects in field-collected samples

PLS-R modeling of field samples identified multiple matrix effects significantly influencing percent error between MXRF and ICP-MS measurements. While these effects primarily reflect limitations of MXRF under the tested configuration, matrix-dependent biases can affect both techniques and must be considered when interpreting MXRF–ICP comparisons (Guimarães et al., 2016). Models achieved moderate to high predictive power for most elements, except for Se and Re, suggesting lower MXRF sensitivity of these

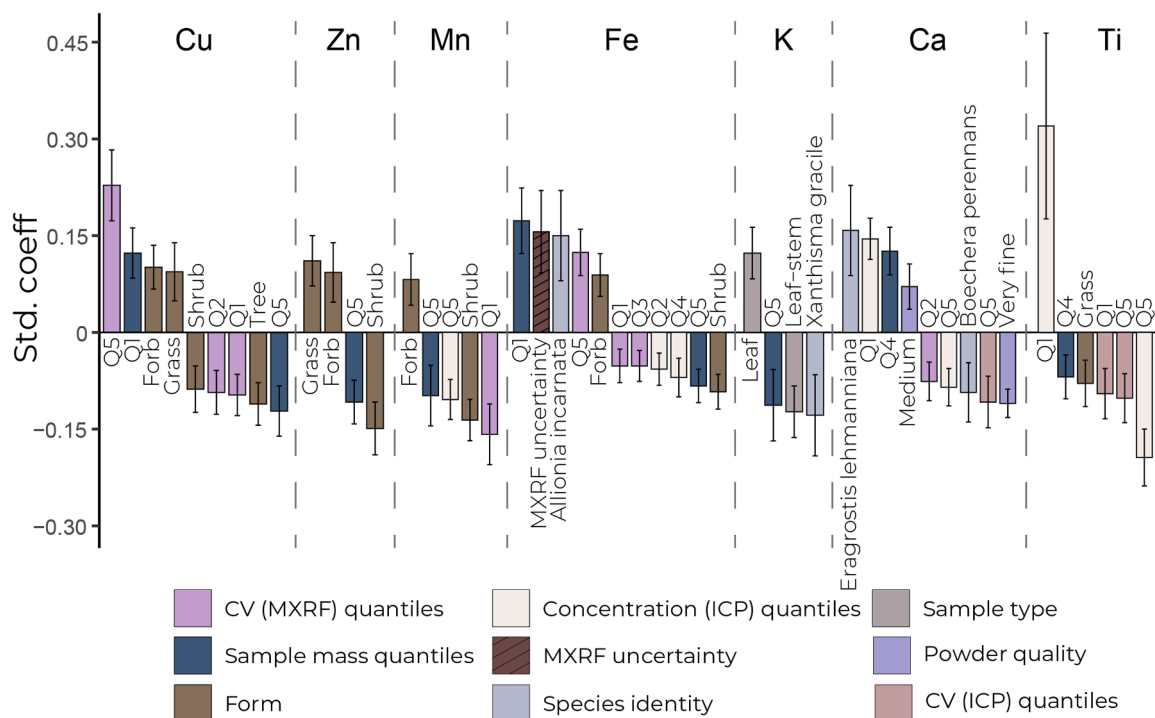


Fig. 5. Significant standardized coefficients from PLS-R models for field-collected samples. Bars indicate predictor importance and direction (positive or negative) of association with percent error (MXRF vs. ICP-MS). Striped and solid bars indicate quantitative and qualitative predictors, respectively.

elements to tested matrix effects.

Consistent with SRM results, sample mass was among the strongest predictors. The lowest mass quantile (0.08–0.35 g) was positively associated with percent error, whereas the highest (1.0–1.5 g) was negatively associated (Fig. 5; Table S4). For P and Ca, mass effects were weaker, likely because their low-energy lines have lower measurement depth, show stronger sensitivity to particle size in plant matrices, and are more affected by pXRF film/air conditions (Towett et al., 2016). This is particularly relevant as the MXRF setup employs triple film (beam window, stand window, cup). Because of shallower X-ray penetration, particle size becomes more important, as evident in the strong effect of powder quality on percent error for these elements: coarse powders increased error, while medium grade and very fine powders shifted to a significant negative association for P and Ca, respectively (Table S4; Figure S1). This observation is consistent with reports from polychromatic pXRF for P and Ca (Sapkota et al., 2019), but contradictory for Fe and K, for which the particle size was not important in our study.

MXRF CV (i.e. precision & homogeneity) remained a key predictor of inter-method agreement for most elements with the optimal precision generally recorded at $CV \leq 6.7\%$ (for Cu, Zn, Mn, Fe, S, and Ca; Table S4; Table S6). ICP-MS replicate variance also influenced agreement, reflecting shared sensitivity to sample homogeneity and analytical precision of wet-chemistry measurements. For S, higher ICP-MS CV was associated with improved agreement, whereas the opposite relationship was observed for Ti. These patterns warrant cautious interpretation. For S, elevated ICP-MS CV values likely reflect spatial heterogeneity in elemental distribution (e.g., uneven allocation between leaves and stems combined with coarser particle size effects), which increases replicate variability and may shift ICP-MS means toward MXRF estimates. In contrast, for Ti, the inclusion of a soil-contamination species (*A. incarnata*) elevated Ti concentrations and likely reduced relative ICP-MS variability, thereby affecting percent error at higher concentration ranges. Because MXRF accuracy for Ti remained strongly concentration-dependent, ICP-MS CV emerged as a key predictor of intra-method agreement. Taken together, MXRF CV (partly reflecting within-sample homogeneity) and ICP-MS CV (directly capturing it) highlight the central role of sample heterogeneity in shaping cross-method agreement, consistent with prior studies (Guimarães et al., 2016; Khan et al., 2022; McLaren et al., 2012; Tadeu Costa Junior et al., 2020).

Elemental concentration strongly influenced agreement for most elements (Fig. 5; Table S4). Higher concentrations (above LOQ) consistently improved agreement, whereas the lowest concentration ranges were associated with poorer agreement (Table 1; Table S4; Table S6). This is consistent with the known concentration-dependent pXRF error profile, where bias/relative (percent) error inflates at low concentrations, especially near/below the LOQ (Konstantakopoulou et al., 2025; McIntosh et al., 2016; Vázquez et al., 2005). Potential sources of ICP-MS analytical bias may also contribute to inter-method discrepancies; however, their contribution was not independently quantified in our study. At low concentrations, excessive dilution reduces sensitivity and can shift values below detection or quantification limits. Conversely, insufficient dilution (i.e. high dissolved solids) can lead to signal suppression and larger errors, emphasizing the need for carefully chosen dilution factors. At high concentrations, additional challenges including ionization suppression, ion beam defocusing, cone deposition, and polyatomic overlaps can further compromise signal stability (Henderson et al., 2019; McCurdy and Proper, 2014; Zhang et al., 2023). These issues are particularly relevant for metallophytes, where deficiencies of some elements and extreme enrichments of others can co-occur within the same plant tissue (Murawska-Włodarczyk et al., 2024; Stefanowicz et al., 2016). Thus, applying a uniform dilution factor across a wide concentration range is problematic, and ICP-MS measurements should not be treated as error-free reference values when evaluating pXRF performance (Fleming et al., 2020). In our study, ICP-MS analysis of SRMs showed several anomalies of high triplicate variance (CV), including Zn in NIST 1547, S in NIST 1568b, and P and Ca in NIST 1515 and 1570, as well as greater bias at low Se concentrations (Table S3), further illustrating that ICP-MS measurements can also exhibit variability under some conditions.

Species identity influenced MXRF-ICP-MS agreement primarily through interactions with elemental concentration, matrix heterogeneity, and contamination. Across elements, species effects were most pronounced for Zn, with 13 species with VIP scores > 0.8 , whereas P and S showed comparatively weak species dependence (3–4 species with $VIP > 0.8$). Although these differences may partly reflect species-specific elemental allocation patterns that influence within-sample variability (Babst-Kostecka et al., 2018; Dietrich et al., 2021), they are more likely explained by concentration constraints. In this dataset, foliar Zn concentrations were frequently low - consistent with nutrient deficiencies common at legacy mine sites and only the highest concentration quantile exceeded the LOQ, resulting in improved inter-method agreement in PLS-R models. This indicates that MXRF performance for Zn is limited at low concentrations and becomes increasingly sensitive to species-related matrix heterogeneity under such conditions. Robust characterization of Zn-specific matrix effects would therefore require experiments conducted within a single, controlled plant matrix. Similar species- or crop-dependent effects on pXRF-ICP agreement have been reported previously, although without consensus on their mechanistic basis (Borges et al., 2020b; McLaren et al., 2012). Plant form further modulated agreement in an element-dependent manner (Babst-Kostecka et al., 2020). Measurements performed on shrub and tree material generally exhibited more consistent agreement than those on grasses and forbs. This difference is likely attributed to matrix homogeneity rather than concentration per se. Shrub and tree samples consisted predominantly of leaf-only material, whereas grasses and some forbs often required leaf-stem mixtures, increasing variability in density, particle size, and elemental distribution. Such heterogeneity likely contributed to the more variable agreement observed for grasses and forbs, particularly for elements sensitive to particle size and low-energy X-ray attenuation. Consistent with this interpretation, sample type (leaf vs. leaf-stem) showed a clear positive effect on agreement only for Zn, while its influence on other elements was weak or non-significant, indicating that tissue mixing represents a secondary matrix effect relative to sample mass, overall homogeneity, and concentration.

Contamination further modified inter-method agreement. The soil-contaminated *A. incarnata* was a prominent source of disagreement for most elements, with the strongest effect observed for Fe (Fig. 5; Table S4). In contrast, this species was associated with improved agreement for Ti, likely because soil-derived inputs elevated Ti concentrations into a range where MXRF accuracy improves. Nevertheless, soil contamination can adversely affect MXRF measurements by introducing speckle-driven heterogeneity and

altering effective sample density, thereby violating assumptions embedded in fundamental-parameter calculations optimized for plant matrices.

MXRF-reported uncertainty was also identified as a significant predictor of inter-method agreement, with higher uncertainty associated with reduced agreement for Fe and P. This relationship suggests that instrument-reported uncertainty metrics can serve as a practical indicator of compromised measurement quality. Because MXRF uncertainty decreases with increasing measurement time (Figure S2), these findings further imply that longer acquisition times beyond 90 s may be required for Fe and P in heterogeneous plant field samples, even though SRM-based analyses did not indicate systematic gains beyond this duration for any element.

3.4. Improvement of intra-method agreement after matrix effects segmentation

PLS-R-guided stratification into optimal and non-optimal subsets significantly improved MXRF-ICP-MS agreement for most elements (Fig. 6; Table 3). The observed improvement was associated with the controllable matrix effects identified by the PLS-R models. Selenium and Re were not evaluated using this approach because their PLS-R models did not reach sufficient predictive relevance; nevertheless, their unstratified agreement with ICP-MS was satisfactory under the tested configuration. For Zn, improvements were

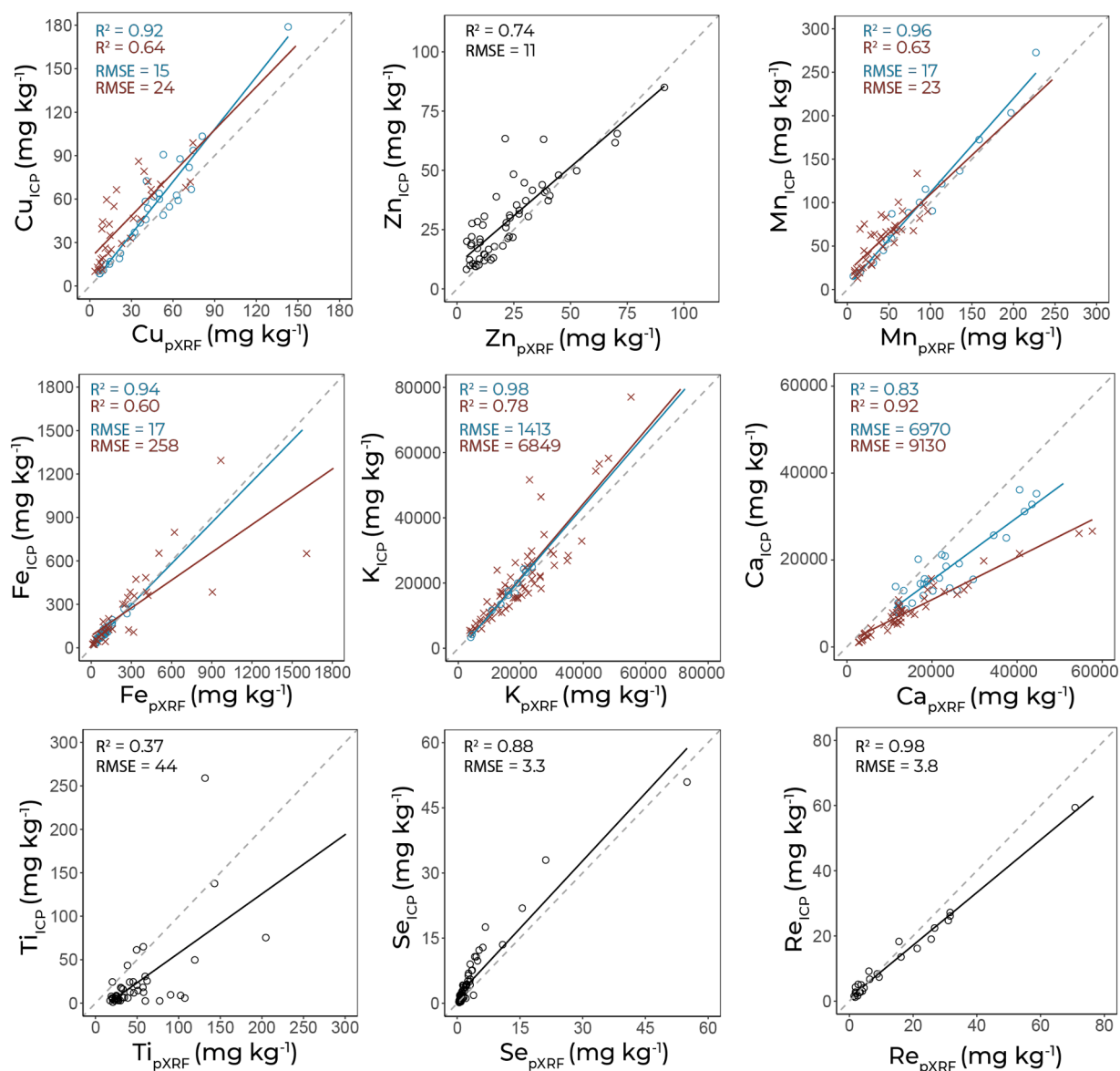


Fig. 6. MXRF vs. ICP-MS elemental concentrations. Blue circles: samples with optimal parameters (VIPs > 0.8 and negative associations of standardized coefficients with percent error as identified from PLS-R models); red crosses: samples with non-optimal parameters. Grey dashed line indicates a 1:1 relationship. All regressions were significant ($p \leq 0.001$). Zn, Ti, Se, and Re include the unfiltered dataset.

Table 3

Validation of agreement between ICP-MS and MXRF concentrations tested on data subsets defined by PLS-R based on associations with percent error between two methods, distinguishing optimal (best agreement) and non-optimal (moderate/poor agreement) subsets. Performance metrics are provided for each subset. No filtering for Zn, Ca, Se and Re. MAE and RMSE are given in mg kg⁻¹.

Element	n	Filtering	R ²	MAE	RMSE	NRMSE	RPD	ICC
Cu	30	Optimal	0.92***	10	15	0.28	2.5	0.91***
	31	Non-optimal	0.64***	19	24	0.54	1.1	0.60***
Zn	57	None	0.74***	7.6	11	0.38	1.5	0.82***
	16	Optimal	0.97***	12	17	0.17	4.1	0.97***
Mn	38	Non-optimal	0.64***	17	23	0.40	1.2	0.68***
	38	Optimal	0.94***	14	17	0.15	3.5	0.96***
Fe	37	Non-optimal	0.60***	124	258	0.84	1.6	0.77***
	11	Optimal	0.98***	1111	1413	0.09	5.2	0.98***
K	64	Non-optimal	0.79***	4571	6849	0.33	2.1	0.86***
	29	Optimal	0.83***	5890	6970	0.40	1.2	0.76***
Ca	46	Non-optimal	0.92***	6559	9130	1.10	0.7	0.63***
	49	None	0.36***	32	44	1.90	1.0	0.41***
Se	65	None	0.88***	2.1	3.3	0.64	2.5	0.91***
Re	25	None	0.98***	2.7	3.8	0.32	3.5	0.93***

R² and ICC significance levels: $p \leq 0.05$ (*), $p \leq 0.01$ (**), and $p \leq 0.001$ (***)

difficult to isolate because error patterns were dominated by species identity, which was intentionally excluded from stratification. For Ti, stratification resulted in only marginal gains and was therefore not shown.

Taken together, the SRM-based evaluation (Fig. 2; Fig. 3; Table 2) and the MXRF–ICP-MS agreement observed for the optimal field performance subsets (Fig. 6; Table 3) under the plant-optimized MXRF configuration indicate: i) robust performance for Cu, Mn, and Fe; ii) moderate performance for Zn, K, Ca, Se, and Re; and iii) weak performance for P, S, and Ti. Reduced performance for light elements such as P and S is well documented and reflects attenuation of low-energy fluorescence in air and through film interfaces, highlighting the need for vacuum or light-element-optimized acquisition (Tadeu Costa Junior et al., 2020; Towett et al., 2016). For P, S, and Ti, poor performance was also associated with low elemental concentrations, consistent with the concentration-dependent error observed across the field dataset. For Ti, performance was further complicated by soil-derived Ti in contaminated samples, likely reflecting a mixed plant–mineral matrix analyzed under the plant-optimized MXRF configuration. ICP-MS measurements can also be affected by matrix-related factors, including spectral interferences from Pⁿ⁺ and Sⁿ⁺ species and concentration-dependent biases, which may further complicate direct method-to-method comparisons (Tan and Horlick, 1987); however, their contribution to inter-method disagreement was not independently quantified in this study. Elemental sensitivity in XRF also depends on excitation energy, with the highest sensitivity generally achieved when the excitation energy is close to the absorption edge of the element of interest (Zhang et al., 2025). In this study, all three monochromatic excitation energies were used to support analysis across a broad elemental range. Because these excitation energies were not independently varied, their individual effects on elemental sensitivity could not be evaluated experimentally. Targeted manipulation of excitation energy, including restriction to the low-energy range or use of the dedicated light-element mode available on this instrument, will thus be an important direction for future optimization of P and S measurements by MXRF.

Despite relatively large mean absolute and root mean square errors for S and Ti, MXRF measurements for these elements may still be suitable for relative comparisons, given the high precision observed for SRM materials. For Zn, targeted validation using a single, controlled plant matrix would be required to disentangle species-driven heterogeneity from other matrix effects. More broadly, MXRF validation performance is expected to improve when restricted to concentrations above LOQ and when validated using standards that span relevant concentration ranges. For elements lacking adequate plant SRMs (S, Ti, Se, Re), development of spiked cellulose-based standards with concentrations above the LOQ would strengthen MXRF validation frameworks.

4. Conclusions

This study demonstrates that the performance of the handheld MXRF system evaluated here in plant matrices is strongly element- and matrix-dependent. Under the optimized sample preparation and measurement conditions, the system provided robust quantitative performance for Cu, Mn, and Fe; acceptable performance for Zn, K, Ca, Se, and Re; and poor quantitative reliability for P, S, and Ti. For Ca, relative comparisons remain informative, despite limitations in absolute concentrations. Selenium and Re showed acceptable agreement with ICP-MS, but further validation with internally spiked standards is still required. Zinc performance varied among plant species, emphasizing the need for species-specific interpretation. More broadly, where absolute accuracy is limited, MXRF is best suited for relative comparisons and trend analysis within the operational constraints identified in this study.

Based on the experimental conditions evaluated in this study, we recommend the following quality-control and measurement practices for plant elemental analysis using the handheld MXRF system and analytical configuration evaluated here:

- Fine grounding of plant material to < 0.5 mm particle size
- Avoiding mixed tissue matrices (e.g., leaves with stems)
- ≥ 1 g of powder in a 10 mL sample cup (~0.9 cm thickness) or point measurement for ≤ 0.3 g

- ≥ 90 s measurement time (30 s per energy level)
- Exclusion of soil-contaminated samples
- Quality control with triplicates; concentrations $\geq$ LOQ, and $CV \leq 10\%$; if CV exceeds threshold, re-measure after improved homogenization and with increased measurement time.

Future work should evaluate the applicability of handheld MXRF across a broader range of plant matrices and environmental conditions. In particular, in addition to integrating relative thickness corrections for variable-density tissues (e.g., woody vs. foliar tissues), additional work should systematically evaluate the effects of variable moisture content in fresh plant materials and evaluate MXRF acquisition modes optimized for light elements (K, P, S, Ca). Development of high-concentration plant standards, particularly for elements underrepresented in existing SRMs (e.g., S, Ti, Se, Re), would further strengthen validation and better reflect the concentration ranges encountered under field conditions.

Finally, comparisons with ICP-MS should account for uncertainty associated with both analytical methods. Although ICP-MS provides an established reference approach for elemental quantification, its measurements may also be influenced by factors such as concentration range, sample preparation, dilution, and matrix effects. Accounting for these sources of uncertainty will be important when interpreting inter-method differences and when developing calibration relationships or correction factors for handheld MXRF measurements.

CRedit authorship contribution statement

Tomasz Włodarczyk: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Shelby Rader:** Writing – review & editing, Resources, Investigation. **Antony van der Ent:** Writing – review & editing, Investigation. **Raina M. Maier:** Writing – review & editing, Funding acquisition. **Alicja Babst-Kostecka:** Writing – review & editing, Supervision, Resources, Investigation, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.eti.2026.105229](https://doi.org/10.1016/j.eti.2026.105229).

Data availability

Data will be made available on request.

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