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Evaluation and Optimization of an X-ray Fluorescence Analyzer for Rapid Analysis of Chemical Elements in Solid Biofuels

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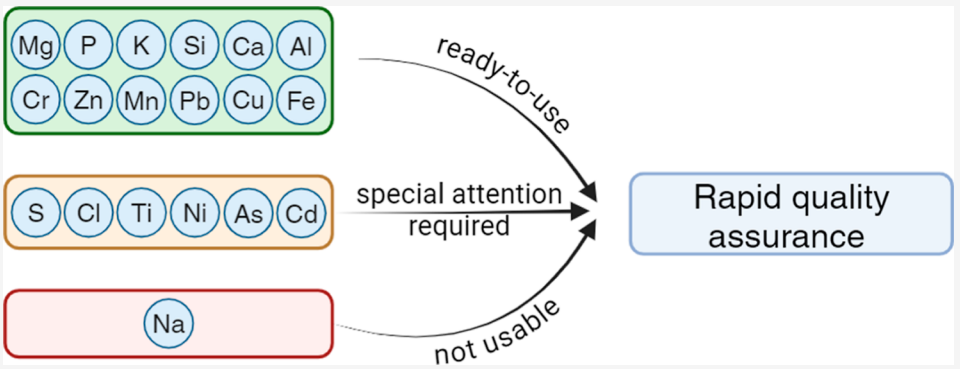

ABSTRACT: To optimize wood-fired heat (and power) plants, it is essential to rapidly determine the chemical composition of solid biofuels on-site shortly before combustion. However, the standard procedures for chemical analysis [inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry] are time-consuming, expensive and require highly trained personnel. Thus, they are unsuitable for online fuel analysis. Newly developed, rapid, on-site analysis methods might enhance analysis at the plant. Thereby, X-ray fluorescence (XRF) analysis is one of the most promising methods. So far, XRF has been evaluated in various fields like geology, coal, ash analysis, as well as biomass in general, but this method is still insufficiently investigated for the sector of solid biofuels. The aim of this work is to evaluate and optimize an XRF analyzer for the rapid determination of chemical elements in wood fuels. The XRF analyzer was calibrated using several wood chip samples. Measurements before and after calibration were compared with the reference method (ICP-OES). Results show that XRF can be recommended for analyzing the elements Mg, P, K, Ca, Si, Al, Cr, Mn, Fe, Zn and Pb, while S, Cl, Ti and Ni can potentially be determined with element-specific calibrations. Cu, As, and Cd could not be measured satisfactorily, as many measurements were below the limit of detection. Still, XRF might be used for threshold value monitoring (e.g., in the scope of the German Waste Wood Ordinance).

1. INTRODUCTION AND STATE OF THE ART

Wood combustion is essential for climate change mitigation by substituting fossil fuels such as coal, heating oil or natural gas. This is especially relevant for the heating sector, as wood combustion currently provides the highest share of renewable heat in many countries. For instance, in 2019, the primary energy consumption of heat from renewable energies in Germany derived 86.1% from the combustion of wood fuels.[1] As the overall availability of wood for bioenergy is limited, combustion must be performed as efficiently as possible.

For an optimized operation of wood-fired heat and power plants, it is essential to rapidly determine various physical fuel properties such as water content, ash content or the calorific value on-site. The chemical composition of wood fuels also provides important information about the fuels and their combustion behavior. These affect, for instance, the efficiency of plant operation or the production of air pollution such as gaseous emissions, total particulate matter emissions (TPM) and the emission of greenhouse gases. Furthermore, unsuitable chemical fuel qualities have an impact on the maintenance and servicing costs of the plant, e.g. due to slag formation or high-temperature corrosion in the boiler. Consequently, both physical and chemical fuel properties are increasingly used in delivery contracts, e.g. to avoid unsuitable fuels for the respective boilers or for transparent and fair pricing during fuel trading.[2,3]

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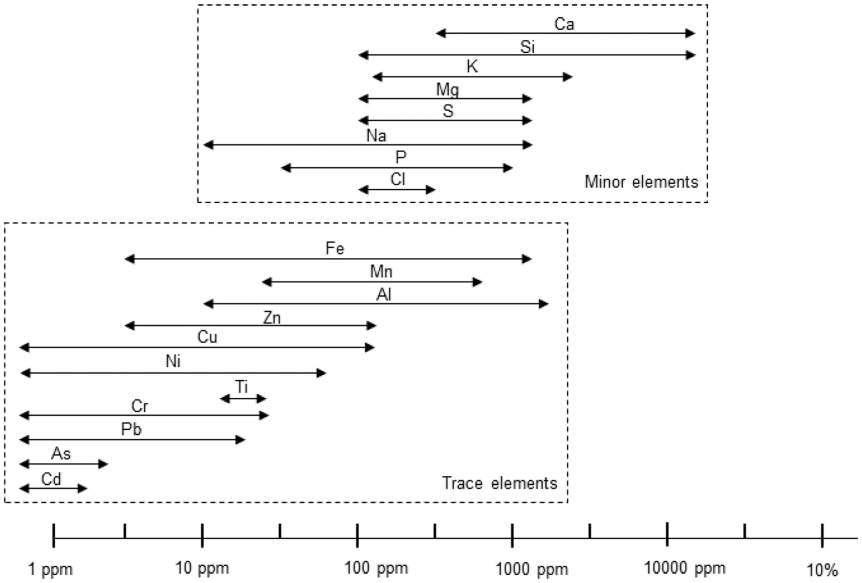

Figure 1. Range of minor and trace element concentrations (db = on dry basis) in solid biofuels which are investigated in this study (selected elements excluding N, F, Hg and V; data: ISO 17225-1[12]).

Wood fuels mainly consist of ≥95% of the "major" chemical elements carbon, hydrogen and oxygen that determine the energy content of the wood. The "minor" elements in wood fuels, such as potassium (K), calcium (Ca) or magnesium (Mg), are mainly responsible for ash formation and influence emission behavior. For example, potassium and sodium (Na) decrease the ash melting temperature[4] and increase TPM emissions, chloride increases high-temperature corrosion,[5,6] and nitrogen and sulfur are relevant for NO_x and SO_x emissions that are harmful to human health and the environment.[7] Heavy metals in solid biofuels are often labeled "trace elements". Although their overall concentrations are low in wood fuels, these elements can harm the environment and human organisms.[8−10] Moreover, they affect ash quality (and therefore ash recycling) as well as particulate emissions.[8,11] All 26 chemical elements relevant for wood fuel combustion are summarized in ISO 17225-1 with typical concentration ranges of selected minor and trace elements given in Figure 1. The elements that are not detectable with the XRF device used in this study (N and F) or which are present in solid biofuels in concentrations that are considered too low for XRF analysis (Hg) were excluded.

Ash content as well as minor and trace elements are usually higher in the bark or green biomass such as leaves and needles compared to bark-free wood. In the case of wood chips, a significant part of the ash content and the chemical fuel properties may also derive from impurities. In addition to metal parts, stones, and waste (coarse foreign matter), adhering humus and mineral soil (fine foreign matter) are included in this category. During combustion in a boiler, these impurities can lead to a deterioration of the combustion behavior. For example, an accumulation of silicon and heavy metals due to soil adhesion can decrease the ash melting temperature and increase the slag formation risk.[13,14] Furthermore, high ash contents due to high shares of impurities decrease the overall calorific value of the fuel.[15] Therefore, stable methods to determine fuel contamination with impurities on-site might help to improve plant efficiency strongly.[16]

Several fuel indices can help to quantify the effects of fuel quality on the combustion unit. For this purpose, typical correlations between different chemical elements and the combustion behavior of boilers, such as gaseous or TPM emissions, can be applied. Thus, estimations about the NO_x, HCl/SO_x emissions, aerosol formation, potassium release, ash melting behavior, and high-temperature corrosion directly from the chemical fuel quality are possible.[11,17−21]

There are different standardized methods to analyze chemical elements in wood fuels that are considered relevant for combustion according to ISO 17225-1.[12] In most cases, inductively coupled plasma-optical emission spectrometry (ICP-OES) according to ISO 16967 or ISO 16968 is used.[8,22,23] In ICP-OES analysis, the atoms and ions of the analyte are excited by temperatures (approximately 6000 K), usually using argon plasma. This leads to the different atoms and ions emitting photoelectric radiation (light emission) in characteristic wavelengths. Different types of detectors can be used to carry out individual or simultaneous measurements to determine the elements present in the sample. Qualitative and quantitative analyses can be realized with the measurement of the characteristic radiation and its intensity.[24−26]

Other commonly used standard methods include inductively coupled plasma-mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS).[27,28] The typical analysis procedure at wood-fired heat and power plants is to sample the material on-site and analyze the different fuel properties using the above-named standardized methods in an external analytical laboratory. Only the water content according to ISO 18134-2 is usually determined on-site. In contrast, advanced analysis methods such as ICP-OES, ICP-MS, and AAS are often too time-consuming, complicated and expensive for regular fuel analysis performed at the plant. Thus, a relatively large time gap is to be expected when the chemical composition of fuels should be analyzed. Consequently, new and rapid on-site analysis methods have to be developed and evaluated if chemical fuel quality should be incorporated into the control unit of a heat and power plant to improve combustion behavior or for efficient fuel trades. One promising

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method for this is X-ray fluorescence (XRF) based analysis (see chapter 2), which is also described in ISO TS 16996.[29]

This study investigates whether XRF can be used to determine the essential minor and trace elements of ISO 17225-1 in solid biofuels. For this purpose, different samples from a wide range of origins (wood chips from natural wood such as stem wood and forest residues, waste wood (classification AI, AII, AI-III mixed, and AIV according to the German Waste Wood Ordinance), landscape maintenance materials and green waste from urban areas) were analyzed with a stationary XRF analyzer and with the reference method ICP-OES. The results of this first evaluation were used to calibrate the XRF analyzer. Afterward, the calibrated method was examined once more to test if an all over calibration is able to improve the measurement accuracy. Further considerations should clarify which accuracy of the element analysis is required for a rapid determination of the fuel quality at the heat (and power) plant in comparison to precise analyses performed in an analytical laboratory.

There are different useable physical principles for the rapid measurement of the chemical composition of wood fuels. Methods from optical spectroscopy are exceptionally functional. These differ mainly in the kind of excitation they use. For example, laser-based applications (LIBS, LA-ICP-MS, etc.), neutron activation analysis (INAA, PGNAA, etc.), or X-ray spectroscopy are possible.[30−32] This article deals with the XRF-based analysis of various renewable solid biofuel samples. The current state of the art in XRF analysis is given in this section.

XRF is based on the principle of emitting fluorescence radiation by exciting samples with high-energy electromagnetic radiation of 0.1 to 100 keV (kilo electronvolt). In contrast to ICP-OES, X-ray analysis methods detect and analyze wavelengths in the X-ray range and not in the optical range. The intensity of the fluorescence radiation depends on the number of element atoms in the sample. The energy of fluorescence radiation depends on the element atomic number.[24−26,33,34] Due to this, qualitative and quantitative element analyses are possible with XRF.[26] Furthermore, various studies have shown that the higher the atomic number of an element, the limit of detection (LOD) is lower because of the higher fluorescence radiation output.[26,33,35] In theory, with XRF approaches, 83 chemical elements are detectable.[24−26,33] However, the range of elements that can actually be detected depends on the excitation source and the fluorescence detector used.

Various factors have to be considered when measuring with XRF. For example, the sample preparation (particle size, water content), the sample itself (matrix effects) or the instrument measurement (measurement duration) have an impact on the analysis results.[36]

XRF analysis is often used for multielemental determinations in biomass as well as related materials.[35,37−55]

Andersen et al. (2013) investigated a wavelength dispersive WD-XRF (S8 Tiger, BrukerAXS) devise for minor and trace elements of certified reference materials (CRMs) biomass samples. They detected Na, Mg, Al, P, S, Cl, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Mo, Ba, and Pb in the biomass standards.[56]

A study by Riedel et al. (2014) investigated a stationary energy dispersive ED-XRF device (Spectro XEPOS plus) that is used for measuring different elements (As, Ca, Cl, Cr, Cu, Hg, Pb) in waste wood. The conclusion of this work demonstrates the possibility of XRF for identifying waste woods with high shares of heavy metals that is unsuitable for selected material or energetic uses. The study also evaluated a portable XRF (Niton XL3t 700) device concerning the ability to measure these elements in waste wood.[57]

Zimmermann et al. (2019) evaluated a portable ED-XRF instrument by Malvern Panalytical to investigate if the elements Mg, Al, Si, P, S, K, Ca, Mn, Fe, and Zn in wood fuels can be analyzed. This study provides promising results as most of the investigated elements have a high correlation (R^2 > 0.9) between the XRF measurement and ICP-OES as a reference approach.[16]

A study by Block et al. (2007) examined two hand-held XRF analysers [Alpha Analyzer (α-2000s) and Inspector (I-3000c)] concerning the usability of analyzing As in chemically treated wood. The analysers used in this study appeared promising for the analysis of arsenic in CCA-treated wood (chromate copper arsenate) with contamination ranging from 4 to 40 kg m^{-3} (db = on dry basis).[58]

Fellin et al. (2014) evaluate a hand-held XRF device (X-MET 5100, Oxford instruments) to determine various elements (As, Ba, Br, Cd, Cl, Cr, Cu, Hg, Pb, Sb, Sn, Ta, Ti) in waste wood. In this study, the minimum detection limit of elements lighter than Cl could not be determined. For elements up to potassium, elements in concentrations from tenths to hundreds of mg kg^{-1} could be measured. Elements with a higher atomic number in the periodic table could be determined up to concentrations of a few mg kg^{-1}.[59]

A bachelor thesis of Golubev (2015) investigated the analysis of N, Na, S, Cl, K, V, Cr, Mn, Co, Ni, Cu, Zn, As, Br, Cd, Sb, Hg, Tl, and Pb in wood chips using a hand-held XRF analyzer (Niton XL3t 980 GOLDD+, Thermo Fisher Scientific Inc.). This study showed that the XRF analyzer investigated can be used for quality control of solid biofuels. It was possible to identify with the analyzer the elements described in the EU biofuel standards (except N and Na).[60]

Additionally, a few studies examined the usability of XRF as an online sorting system for, among others, waste wood.[61,62]

Overall, few studies already investigate the possibility of measuring selected chemical elements with XRF devices in the larger field of solid biofuels with promising results.[63] Furthermore, analytical methods based on X-ray excitation can also do a structural and composition analysis of biomass, solid fuels, and related fields.[31,64−69]

Several studies have dealt with the specific calibration of different XRF analysers. Table 1 gives an overview of the target elements, the calibration approach and the degree of improvement.

Still, up to date, there has only been limited research on the rapid determination of the chemical composition of renewable solid biofuels using XRF in the literature. Moreover, individual elements tend to be selected and investigated. XRF is well studied for a wide range of different plant-based samples but not for rapid quality control of solid biofuels. Moreover, to our knowledge, none of these studies has investigated all relevant minor and trace elements of solid biofuels according to ISO 17225-1.

2. MATERIAL AND METHODS

Sampling, sample preparation, and analyses by ICP-OES and XRF, as well as the statistical evaluation, are illustrated in Figure 2. The samples used during this study derived from various origins to provide a wide range of typical woody (and, to some extent, nonwoody) biofuels (Section 2.1). In total, three sets of samples were used, one

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Table 1. Overview of Various Studies That Attempted to Improve the Measurements of an XRF Analyser Using Specific Calibrations

authors	set up	calibration method	matrix	targeted elements	results	ref.
Zielenkiewicz et al. (2012)[70]	hand-held ED-XRF	empirical calibration with standard materials	wood samples	Cu	$R > 0.8974$ (correlation of copper content in analyzed wood and average impulse counts)	70
Mejía-Piña et al. (2016)[71]	hand-held analyzer by Olympus Delta Premium-XRF	empirical calibration with CRMs	sediment samples (combine organic and inorganic matrices)	V, Cr, Fe, Co, Ni, Cu, Zn, W, Hg, As, Se, Pb, Bi, Rb, U, Sr, Y, Zr, Th, Mo, Ag, Cd, Sn, Sb, Mg, Al, Si, P, S, Cl, K, Ca, Ti and Mn	good correlations from Ni with $R > 0.761$ to Se with $R > 0.997$	71
Zimmermann et al. (2019)[16]	portable ED-XRF instrument by Malvern Panalytical	empirical calibration with reference method ICP-AES	wood fuels samples	Mg, Al, Si, P, S, K, Ca, Mn, Fe, and Zn	$R > 0.978$ (except Mg with $R > 0.875$)	16
Antonangelo and Zhang (2021)[72]	hand-held XRF- Bruker Tracer 5i (Bruker Corp., USA)	empirical calibrations with reference method ICP-AES and nitric acid digestion	forage plant samples	P, K, Ca, Mg, S, Cu, Fe, Zn, and Mn	successful calibration and highly reliable prediction of K, S, Zn, Mn, Ca, Fe, Mg. For P ($R^2 = 0.3$) and Cu ($R^2 = 0.14$) the predictions were not satisfying.	72
Acquah et al. (2022)[73]	hand-held XRF- Bruker Tracer 5i (Bruker Corp., USA)	empirical calibrations with reference method ICP-OES/MS and aqua regia digestion	fertilisers samples	Na, Mg, Al, P, S, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, C, Pb, Ti and Al	R^2 values greater or equal to 0.97 (excl. Fe with $R^2 = 0.255$ during validation)	73

for initial instrument evaluation using the factory setting of the XRF (fs, $n = 264$), one for instrument calibration ($n = 64$) and one for the final instrument validation using the specific calibration (sc, $n = 229$). Samples were handled as shown in Figure 2. Thereby, part of the samples derived from previous research projects of Technology and Support Center (TFZ, $n = 207$), some of them in cooperation with the Bavarian Forestry Research Institute (LWF) (see Section 2.2). For these samples, ICP-analysis was already performed before this study, whereas the new samples that were collected during this study ($n = 111$) were prepared for the ICP-OES measurement at HFR (Section 2.4). All samples were measured with the Spectro XEPOS XRF analyzer (Section 2.3) either at HFR or TFZ. Finally, all measurement results were evaluated statistically (Section 2.5).

2.1. Samples. The samples used for the evaluation, calibration and validation of the XRF instrument came from various sources providing a wide range of different woody (and nonwoody) biofuels, as summarized in Table 2. To simulate a typical elemental concentration range of biofuels as described in ISO 17225-1, samples derived from both "natural" origin, i.e. directly from natural forest wood, and from different German biomass-fired heat (and power) plants. Samples had varying degrees of contamination (soil, gravel, and other impurities). The range of concentrations of selected chemical elements (analyzed with ICP-OES) of all samples is given in Figure 3.

New samples from forest wood originate from felling operations in a forest near Rottenburg am Neckar, Germany ($n = 40$). These consist of typical German wood species (European beech, Norway spruce, Scots pine, European larch and Black alder).

The other new samples were derived from different wood-fired heat (and power) plants in Germany ($n = 71$). These samples comprised of typical wood fuels such as wood chips from forest residues or landscape maintenance, waste wood (classification AI, AII, AI-III mixed, and AIV according to the German Waste Wood Ordinance), or green waste from parks and urban forestry. Thus, no clear species could be addressed to the samples. In addition, especially the samples collected at plants were contaminated differently with mineral impurities (soil, gravel, etc.) and other impurities (paint, coatings, metal, etc.).

After sample collection, samples were packed airtight in buckets and transferred to the University of Applied Sciences Rottenburg (HFR). The samples were prepared as described in Section 2.2. The sample preparation was achieved after a maximum of 1 day.

Another part of the samples was derived from previous projects from the Technology and Support Center (TFZ, $n = 207$), often in cooperation with the Bavarian State Forestry Institute (LWF). These also originated from a wide range of sources (pellets, wood chips from forest operations, etc.) and were contaminated to varying degrees with mineral impurities.

Overall, 264 samples were used for the initial instrument evaluation, 64 for calibration and 229 for the final validation. While the sample sets for calibration and validation share samples with the sample set for initial evaluation, no calibration sample was used for the final instrument validation.

2.2. Sample Preparation. All new samples ($n = 111$) collected by HFR were dried at 105 °C in a drying oven (UNP 700 Memmert Ltd.) until constant weight was reached. This step generated a sample which is as stable as possible, mostly eliminating the impact of the water content on the measurement. Afterward, the various thick wood pieces were coarsely broken to get them into the cutting mill (Pulverisette19 Fritsch Ltd.) with heavy metal-free inlet milling cassettes. The samples were milled in three steps, first to a grain size of 4, 1 mm, then 250 μm. In the study of Endriss et al. (2024) various impacts on XRF measurement of solid biofuels were investigated. Among other things, the influence of particle size was examined, with 250 μm proving to be the most appropriate particle size.[36] For this reason, this particle size is consistently evaluated in this study. This also avoids the particle size effect.

The dried and milled samples were prepared and measured with the XRF Analyzer XEPOS by SPECTRO Analytical Instruments GmbH (described in Section 2.3). Subsequently, the identical sample

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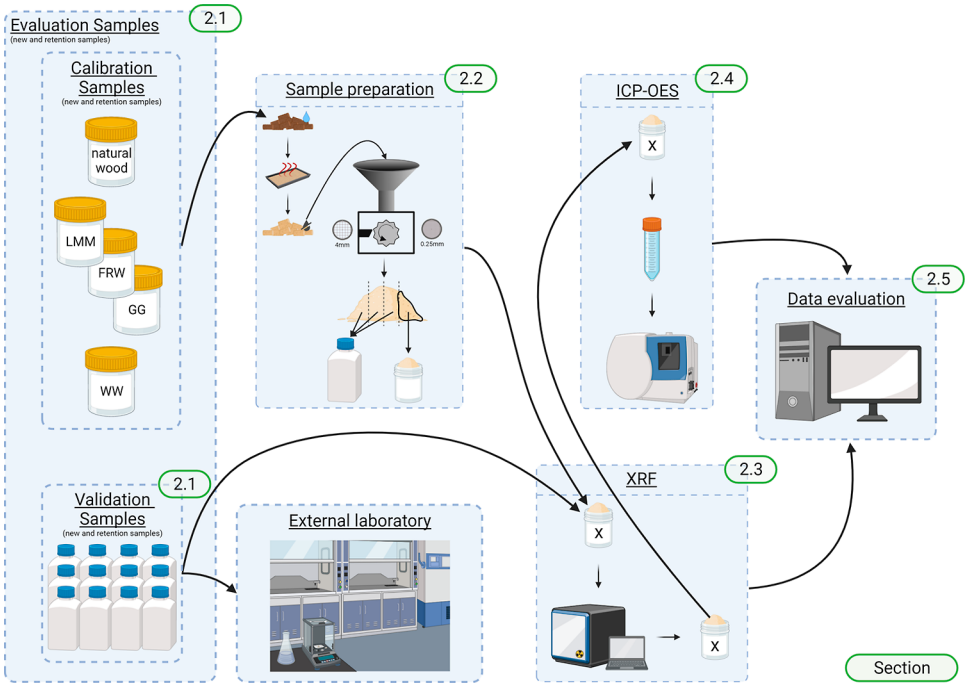

Figure 2. Sequence of sample preparation, analysis and statistical evaluation during this study.

Table 2. Sample Diversity and Origin for the Evaluation, Calibration and Validation Procedure (SW: Wood Chips from Stem Wood; Pellets: Wood Pellets with Undefined Woods Mixture; FRW: Wood Chips from Forest Residues; LMM: Wood Chips from Landscape Maintenance, NWF: Non-woody Biomasses Such as Straw; WW: Waste Wood) n_{sum} = 293 ([1] = New Samples, [2] = Retention Samples from Previous Projects)

samples	institute	SW	pellets	FRW	LMM	WW	NWF
evaluation	HFR[1]	22		13	19	7	
	TFZ[2]	47	51	53	23		29
calibration	HFR[1]	18		12	20	7	3
	TFZ[2]			2	2		
validation	HFR[1]	12		3	11		
	TFZ[2]	47	51	53	23		29

was prepared in the digestion procedure for the ICP-OES (described in Section 2.4). For each sample, n = 3 measurements were performed and the mean value was compared to decrease the impact of the heterogeneity of the biogenic materials.

Part of the samples (n = 207) originated from retained samples of TFZ (and LWF) from previous projects. In these cases, the chemical analyses were already carried out by external laboratories (e.g., LWF) according to standardized procedures.[27,28,74−76] As a consequence, some of the samples were dried (e.g., at ambient air temperature) and digested differently, i.e. they were digested using differing mixing ratios of nitric acid (HNO_3), hydrochloric acid (HCl) and hydrofluoric acid (HF) according to ISO 16967, ISO 16968 and the German "Handbook of Forest Analysis".[74] These samples were mainly used for evaluation (n = 203) and validation (n = 203) but also in part for the calibration of silicon (n = 4).

2.3. XRF Analysis Approaches. The used energy dispersive XRF analyzer XEPOS was manufactured by SPECTRO Analytical Instruments GmbH. The analyzer has a 50 W X-ray tube (max voltage 60 kV and max current of 2 mA) a binary-alloy cobalt−palladium anode, and fluorescence X-rays are detected by a silicon drift detector with <130 eV. The sample was measured in four subanalyses with different excitation for the determination of different elements (the elements mentioned in the following list refer only to the elements analyzed in this work and are not exhaustive):

- Pd-K excitation: 6 keV ≤ E ≤ 19 keV (Fe, Co, Ni, Cu, Zn, As, Pb)
- Bremsstrahlung-excitation: E > 19 keV (Cd)
- Co-excitation: 3 keV ≤ E ≤ 6 keV (K, Ca, Ti, Cr, Mn)
- Pd-L excitation: E < 3 keV (Na, Mg, Al, Si, P, S, Cl)

The samples were filled up to 10 mm level in a sample tube with a 4.0 μm membrane bottom (SpectroMembrane Prolene Thin-Film, chemplex Industries INC.). Typical impurities of the membrane can be Ca, P, Sb, Fe, Zn, Cu, Zr, Ti, Al in a ppm range. The measurement chamber was helium flushed. The measuring time were at 750 s per analysis, in which the sample rotated once every 30 s and excited in a radius of ∼10 mm.

The factory setting is a nonspecifically calibrated measurement method for biogenic material. The method is based on various NIST and IPE standards (NIST 1573a, 1570a FP, etc.) and the software definition of the main component "organic" ($C_6H_{10}O_5N$).

To compare the samples, the normalized net intensities were determined from the measured spectra by deconvolution. The intensities were also normalized on a Compton-scatter region in the spectra as internal standard. This approach corrects for matrix effects as described for example by Andermann, Kemp in "Scattered X-rays as Internal Standards in X-ray Emission Spectroscopy".[77] This procedure allows for a calibration valid for a wider matrix range and avoids to have different calibrations for different types of solid biofuels. To correct efficiently, two scatter regions with different energies were used. For the higher energies the Compton scatter range of the Pd-Kα (19.71−20.55 keV) was used, for the lower energies the Compton scatter of the Co Kα (6.75−6.83 keV). Table 3 lists the elements and the scatter regions used as internal standard. The selected lines represent the most sensitive lines for each of the analyzed elements and are also listed in ISO/TS 16996 solid biofuels—determination of elemental composition by XRF.[29] The calibration of the XRF is done by calculation of the Compton-normalized intensities versus the reference values obtained by ICP-OES for example.

2.4. ICP-OES Analysis Approaches. ICP-OES was used as the reference method for the element determination of solid biofuels. The "new" samples were prepared and measured according to ISO 16967 and ISO 16968.[27,28] Thereby, an identical sample material was used

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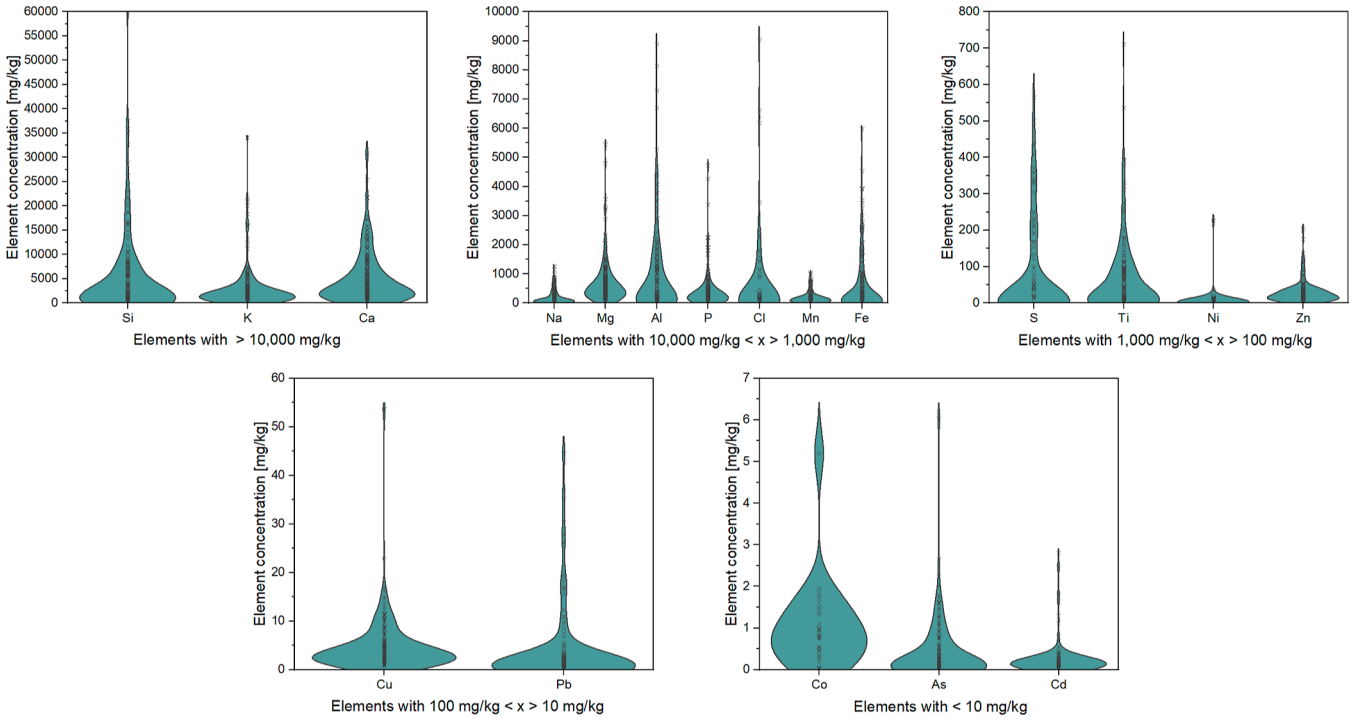

Figure 3. Concentrations of selected chemical elements (ICP-OES) in the different calibration samples (n = 64) and validation samples (n = 229). Combined presentation of all samples as violin plot with Kernel-smoothing.

Table 3. Elements, Fluorescence Lines, and the Scatter Regions Used as Internal Standard[a]

element	line	normalization to scatter region 6.75–6.83 keV	normalization to scatter region 19.71–20.55 keV
Al	K–$L_{2,3}$ ($K\alpha_{1,2}$)	x	
Si	K–$L_{2,3}$ ($K\alpha_{1,2}$)	x	
P	K–$L_{2,3}$ ($K\alpha_{1,2}$)	x	
S	K–$L_{2,3}$ ($K\alpha_{1,2}$)	x	
Cl	K–$L_{2,3}$ ($K\alpha_{1,2}$)	x	
K	K–$L_{2,3}$ ($K\alpha_{1,2}$)	x	
Ca	K–$L_{2,3}$ ($K\alpha_{1,2}$)	x	
Ti	*K–$L_{2,3}$($K\alpha_{1,2}$)*	x	
Cr	*K–$L_{2,3}$($K\alpha_{1,2}$)*	x	
Mn	K–$L_{2,3}$ ($K\alpha_{1,2}$)	x	
Fe	K–$L_{2,3}$ ($K\alpha_{1,2}$)		x
Ni	K–$L_{2,3}$ ($K\alpha_{1,2}$)		x
Cu	K–$L_{2,3}$ ($K\alpha_{1,2}$)		x
Zn	K–$L_{2,3}$ ($K\alpha_{1,2}$)		x
As	*K–$L_{2,3}$($K\alpha_{1,2}$)*		x
Cd	*K–$L_{2,3}$($K\alpha_{1,2}$)*		x
Pb	L_3–$M_{4,5}$ ($L\alpha_{1,2}$)		x

[a]Elements printed in italics are currently not considered but can be used additionally if required.

for the XRF measurement. The samples were microwave digested with Multiwave GO 3000 (Anton Paar Ltd.). Approx. 400 ± 1.0 mg of sample material was transferred in 50 mL Teflon vessels, and 2.5 mL of HNO_3 supra quality (69%) (Merck, Germany) and 7.5 mL of HCl supra quality (35%) (Roth, Germany) was added and digested at 190 °C for 20 min with a heat ramping by 12.6 °C min^{-1}. The solution was aliquoted to 50 mL with twice distilled water.

The ICP-OES was calibrated using a multielement ICP standard solution (ROTI Star, Carl Roth GmbH + Co. KG) for 28 elements in HNO_3 5% matrix. Dilution and calibration were performed at 0.001, 0.01, 0.1, 1, 10 ppm. Single standards for Ca and K were used for calibration at 25 ppm. For P and S at 0.1, 1, 10 ppm.

In addition, for higher concentrations, a second method was used with calibration to the standard "Multi-Element ICP Standard Solution IV" (ROTI Star, Carl Roth GmbH + Co. KG) for 26 elements in HNO 2% matrix. Dilution and calibration were performed at 1, 10, and 100 ppm. For P and S at 1, 10, and 50 ppm, respectively.

Different wavelengths were defined and read for the elements to be measured. The element-specific wavelengths were selected according to ISO 11885 "water quality—determination of selected elements by ICP-OES".[78] The total wavelength range analyzed is 162,911–771,160 nm.

The retained sample (from TFZ and LWF) were digested with differing mixing ratios of nitric acid (HNO_3), HCl and hydrofluoric acid (HF) according to ISO 16967, ISO 16968 and the German "Handbook of Forest Analysis".[74] All samples giving values for silicon were digested with the HF.

2.5. Data Evaluation. The statistical data evaluation was carried out with the following statistical approaches to evaluate the ability of the XRF device to measure different chemical elements in wood fuels. For the investigation of the correlation between XRF and ICP-OES measurement results, the results were check on normal distribution and subsequent a parametric Pearson correlation coefficients or nonparametric Spearman's coefficient (r) and the coefficient of determination (R^2) of linear regressions were used.[79]

The concordance correlation coefficient (CCC), according to Lin, was used to examine the correlation of the two measurement methods around the bisecting angle, with the interpretation following McBride (2005).[80] Thereby the factors <0.90 were related as "poor", 0.90 to 0.95 as "moderate", 0.95 to 0.99 as "substantial", and >0.99 as "almost perfect".

For the purpose of examining the outliers and the deviation of the XRF from the ICP-OES, the percentage deviation was calculated and visualized as boxplots. Outliers were determined by Tukey's (1997) interquartile range (IQR), with outliers at 1.5 IQR and extreme outliers at 3 IQR.[81]

All elements are presented in ascending order of atomic number.

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Table 4. Number of Samples Measured with ICP-OES and XRF per Element and Their Usability for the Statistical Assessment (LOD: Limit of Detection; fs: Factory Settings Used during the Initial Evaluation, sc: Specific Calibration Used during Final Validation), Elements Presented in Ascending Order of Atomic Number

element	total measurements (n_{total})		values below LOD ($n_{<LOD}$)				extreme outlier during deviation analysis (n_{out})				useable values (n_{uv})			
	fs	sc	fs	%	sc	%	fs	%	sc	%	fs	%	sc	%
Na	264	229	196	74	203	89	36	14	4	2	32	12	22	10
Mg	264	229	0	0	10	4	1	0	0	0	263	100	219	96
Si	185	207	3	2	27	13	3	2	3	1	179	97	177	86
P	264	229	35	13	21	9	2	1	0	0	227	86	208	91
S	167	132	49	29	3	2	12	7	1	1	106	63	128	97
Cl	110	75	34	31	11	15	0	0	0	0	76	69	64	85
K	264	229	1	0	0	0	1	0	0	0	262	99	229	100
Ca	264	229	3	1	0	0	1	0	1	0	260	98	228	100
Al	264	229	51	19	24	10	5	2	16	7	208	79	189	83
Ti	182	147	31	17	13	9	47	26	0	0	104	57	134	91
Cr	170	135	83	49	69	51	0	0	2	1	87	51	64	47
Mn	264	229	40	15	37	16	2	1	0	0	222	84	192	84
Fe	261	226	70	27	3	1	0	0	3	1	191	73	220	97
Ni	170	135	67	39	92	68	49	29	4	3	54	32	39	29
Cu	230	195	19	8	30	15	0	0	3	2	211	92	162	83
Zn	230	195	0	0	1	1	4	2	0	0	226	98	194	99
As	230	195	186	81	146	75	8	3	0	0	36	16	49	25
Cd	230	195	230	100	161	83	0	0	28	14	0	0	6	3
Pb	230	195	102	44	73	37	0	0	4	2	128	56	118	61

3. RESULTS AND DISCUSSION

The ability to measure the chemical composition of solid biofuels using an XRF device is assessed in this study in comparison with ICP-OES as a standardized reference method. Generally, it has to be noted that ICP-OES cannot guarantee the "true value" of a sample as this method also provides a certain measurement error (usually 15 to 20%) depending on the chemical element analyzed. Still, as a frequently used and standardized reference method, it is seen as one of the best orientation options for a new analytical device. In addition, previous work[82] showed that the sum of ash-forming elements (i.e., the sum of oxides) measured with ICP-OES correlates well with the ash content (determined according to ISO 18122[75]), indicating that ICP-OES assesses the main share of chemical elements satisfactorily. Many round-robin tests with ICP-OES between laboratories further indicate a high reproducibility of this analysis method, suggesting that it is suitable as a reference method for evaluating XRF.

3.1. Accuracy of XRF Compared to ICP-OES. Table 4 shows the total number of measurements carried out with both devices (XRF, ICP-OES). The initial number of measurements (n_{total}) for the different elements varies from 110 to 264 as the reference analyses (ICP-OES) originate from several research projects, whereby not all elements were analyzed throughout. Especially for S and Cl, other standardized reference methods instead of ICP-OES were frequently used. The calibration was only carried out with values from the ICP-OES. S and Cl, which were determined with other standardized methods, can therefore be used for the initial evaluation of the factory setting. However, they should be taken with caution for the validation of the calibration. Furthermore, specific exclusion criteria (described below) decreased n_{total} to the number of useable measurements for the statistical evaluation (n_{uv} for "useable values").

The first exclusion criterion is the LOD. If a value was below the LOD, the sample was removed from the evaluation ($n_{<LOD}$) as it was not suitable anymore to compare with an exact value of the other method. Thus, in this study, only values > LOD detected by both systems are used for the comparison of the ICP-OES with XRF. Still, using values < LOD from an XRF device in practice may also be useful as a benchmark for evaluating fuels (e.g., threshold value monitoring for heavy metals, see Section 3.2).

The second criterion for exclusion is extreme outliers, i.e. a very high deviation between the XRF- and ICP-OES measurements of one sample while comparing the two measurement methods (n_{out}). Individual extreme values with a deviation of several thousand percent would otherwise not allow a precise statement about the main share of measurements. For this reason, the following statistical analysis excludes measured values with a deviation of IQR > 3.[81] An explanation for the extreme outliers could be measurement errors, as these occurred mainly for elements for which the XRF had measurement errors.

Nevertheless, the outliers cannot be excluded from consideration in every case since elements such as Na, Ti, and Ni consist of a substantial proportion of outliers. Therefore, the relative amount of measurements, which are to be regarded as extreme values, serves as a parameter for the evaluation of XRF as a measurement method for solid biofuels, and results are shown both with and without outliers.

Table 4 presents the number and the percentages of the total measurements, the share of values below the LOD, the number of measurements with extreme values (outliers) and the resulting number of useable values (n_{uv}) used for statistical analysis calculated as $n_{uv} = n_{total} - n_{<LOD} - n_{out}$.

After removing the excluded measurements, an individual number of useable values remained per element. The theoretical maximum of values for the initial evaluation was 264 (measurements with "factory settings"), while it was 229 for the final validation (measurements with "specific calibration"). The share of useable values (n_{uv}) was highest

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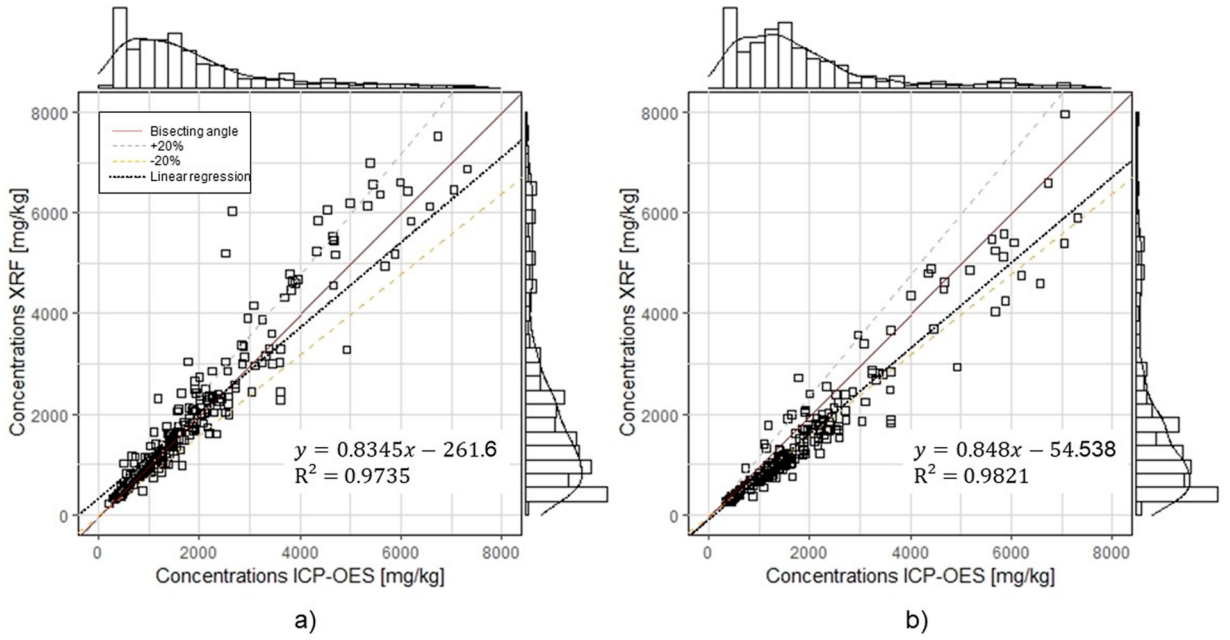

Figure 4. Linear regressions between XRF measurements and reference method ICP-OES for potassium before calibration (a) n = 262 and after calibration (b) n = 229 (all values on dry basis including outliers and values < LOD).

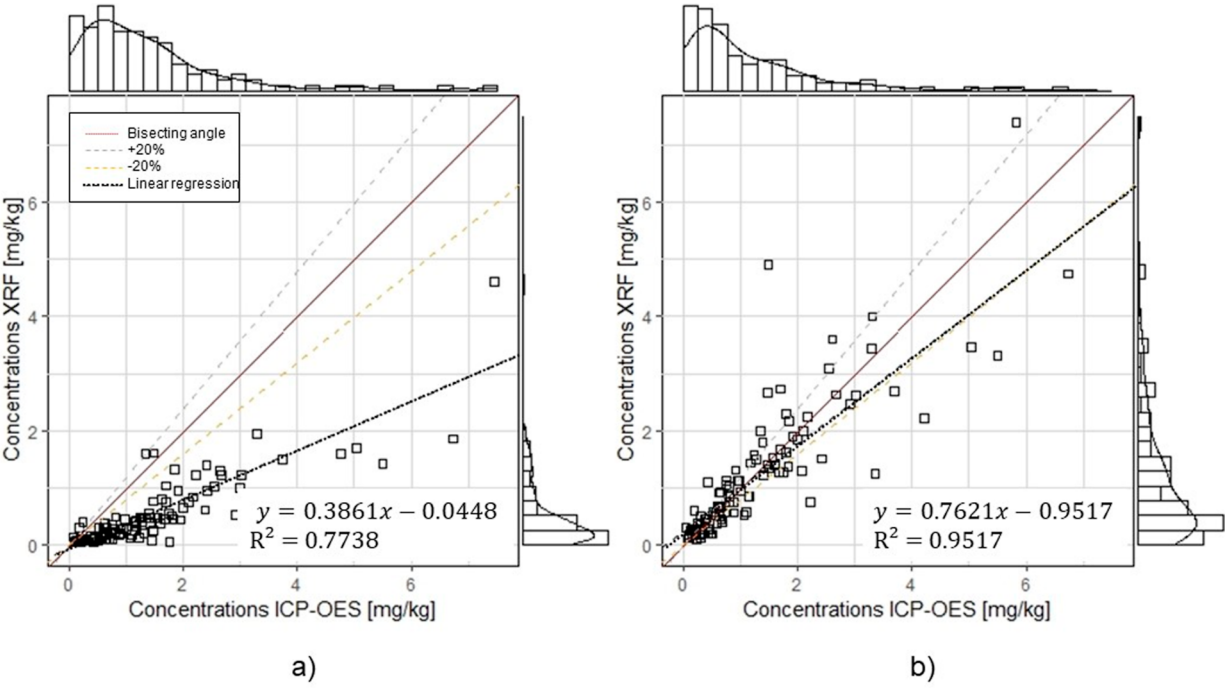

Figure 5. Linear regressions between XRF measurements and reference method ICP-OES for lead before calibration (a) n = 128 and after calibration (b) n = 118 (all values on dry basis including outliers and values < LOD).

for magnesium (fs: 263; sc: 219) and lowest for cadmium (fs: 0; sc: 6), respectively. The changing number of useable values has to be considered when evaluating the results.

Correlation diagrams may help to visualize the comparability of the measurement results of the rapid measurement technique XRF and the reference method ICP-OES, along with displaying the possibility of improving the accuracy of the measurement by calibration. Figures 4 and 5 show examples of high (potassium) and low (lead) correlations with the factory setting (i.e., the initial assessment of the instrument) and the effect of the calibration of the XRF instrument (final validation). The respective diagrams for all minor and trace elements that are particularly relevant to solid biofuel combustion according to ISO 17225-1 are listed in the "Supporting Information" (Figures S1−S4).

Figure 4 illustrates the correlations between the XRF measurements and the ICP-OES reference method for the element potassium. This is an example of elements that already provide satisfying results with the factory settings and would, therefore, not require calibration.

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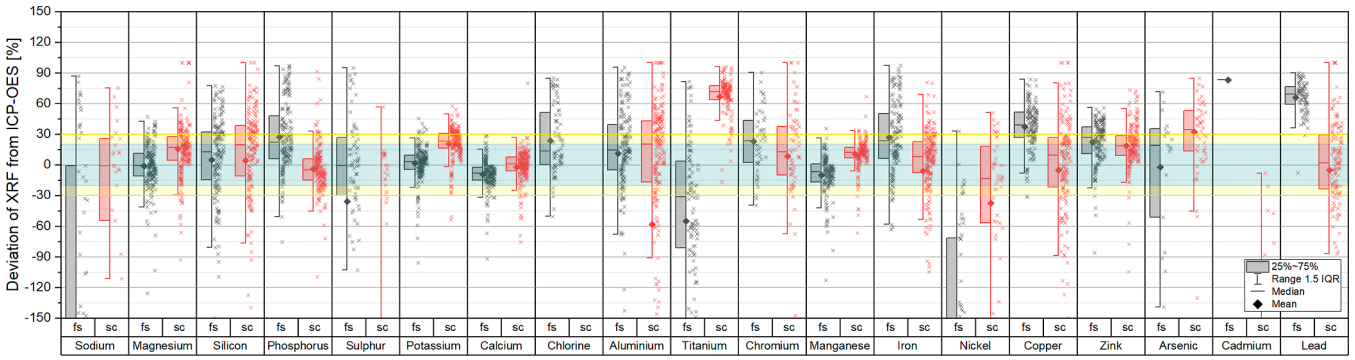

Figure 6. Deviation of the XRF measurements from the reference method ICP-OES in [%] with outliers for solid biofuels (n = Table 4; fs: factory settings used during the initial evaluation, sc: specific calibration used during final validation).

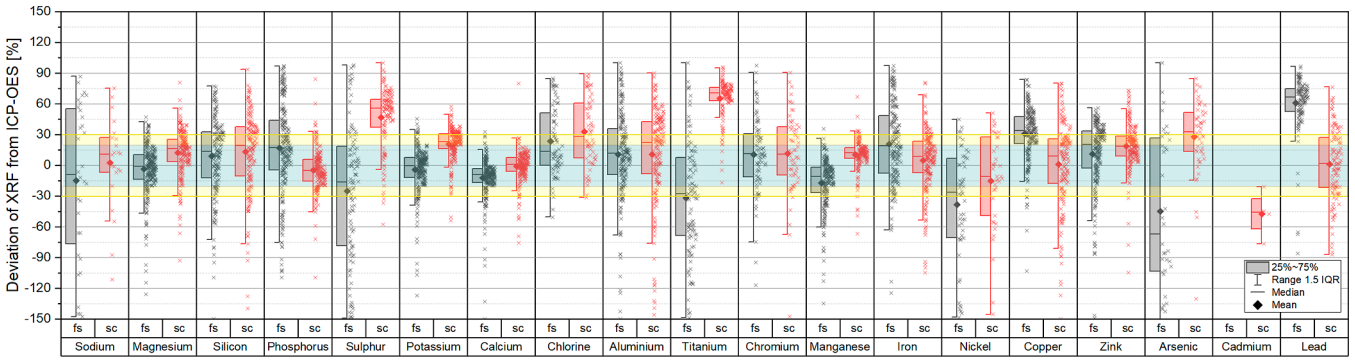

Figure 7. Deviation of the XRF measurements from the reference method ICP-OES in [%] without outliers for solid biofuels ($n \leq 229$; fs: factory settings used during the initial evaluation, sc: specific calibration used during final validation).

Table 5. Statistical Evaluation of the Usability of XRF for Different Essential Elements of Solid Biofuels with Comparison to ICP-OES as a Reference Method, Impact of Element Specific Calibration and Recommendation as a Rapid Determination Device per Element (N/A = Not Applicable Due to Low Number of Useable Values; ↑ = Trend towards Better Results, ↓ = Trend towards Worse Results)

Element	r		R^2		Lin's CCC		Average		Values below 20% deviation				Values below 30% deviation				Values below 20% & 30% combined		Trend	Code
	fs	sc	fs	sc	fs	sc	fs	sc	fs	%	sc	%	fs	%	sc	%	fs	sc	fs→sc	
Na	0.78	0.38	0.61	0.15	0.76	0.35	✓	✓	5	15.6	10	45.5	6	18.8	13	59.1	x	x	⇧	- -
Mg	0.93	0.87	0.87	0.76	0.90	0.86	✓	✓	190	72.2	127	58.0	223	84.8	169	77.2	✓	✓	⇩	+ +
Si	0.92	0.90	0.85	0.82	0.91	0.89	✓	✓	61	34.1	56	31.6	97	54.2	84	47.5	x	x	o	+
P	0.95	0.93	0.90	0.87	0.93	0.92	o	✓	83	36.6	152	73.1	115	50.7	185	88.9	x	✓	⇧	+ +
S	0.89	0.81	0.78	0.66	0.84	0.59	o	x	31	29.2	19	14.8	40	37.7	23	18.0	x	x	⇩	O
Cl	0.98	0.55	0.97	0.31	0.97	0.27	o	x	36	47.4	24	37.5	45	59.2	31	48.4	x	x	⇩	O
K	0.98	0.99	0.96	0.98	0.97	0.97	✓	✓	207	78.7	75	32.8	229	87.1	162	70.7	✓	x	⇩	+ +
Ca	0.97	0.96	0.94	0.91	0.97	0.96	✓	✓	207	79.6	203	89.0	230	88.5	216	94.7	✓	✓	⇧	+ +
Al	0.97	0.97	0.95	0.94	0.97	0.95	✓	✓	90	43.3	55	29.1	123	59.1	87	46.0	x	x	o	+
Ti	0.97	0.89	0.94	0.80	0.82	0.51	x	x	26	25.0	4	3.0	41	39.4	9	6.7	x	x	o	O
Cr	0.97	0.89	0.94	0.79	0.97	0.89	✓	✓	40	46.0	26	40.6	58	66.7	38	59.4	x	x	o	+
Mn	0.99	1.00	0.98	0.99	0.97	0.99	✓	✓	145	65.3	149	77.6	168	75.7	179	93.2	✓	✓	o	+ +
Fe	0.97	0.96	0.93	0.92	0.96	0.96	o	✓	73	38.2	122	55.5	102	53.4	167	75.9	x	✓	⇧	+ +
Ni	0.95	0.93	0.90	0.86	0.86	0.86	x	✓	18	33.3	15	38.5	26	48.1	20	51.3	x	x	⇧	O
Cu	0.84	0.79	0.70	0.62	0.70	0.77	x	✓	43	20.4	59	36.4	83	39.3	101	62.3	x	x	⇧	+
Zn	0.95	0.98	0.90	0.95	0.94	0.96	✓	✓	81	35.8	100	51.5	131	58.0	146	75.3	x	✓	⇩	+ +
As	0.86	0.91	0.74	0.82	0.51	0.81	x	o	5	13.9	15	30.6	7	19.4	20	40.8	x	x	o	-
Cd	N/A	0.99	N/A	0.99	N/A	N/A	x	x	N/A	N/A	1	16.7	N/A	N/A	2	33.3	x	x	⇧	-
Pb	0.94	0.98	0.88	0.96	0.65	0.95	x	✓	2	1.6	44	37.3	4	3.1	72	61.0	x	x	⇧	+

++	XRF highly recommended
+	XRF recommended
O	Presumably recommended with special calibration
-	Currently not sufficiently recommended, but may be usable for limited monitoring
- -	Currently not sufficiently recommended

		R^2	r	CCC	Average	Values below % deviation
xx	poor	$R^2 < 0.6$	r < 0.6	CCC < 0.9	Mean out of 30% corridor	>25% of 20% & >50% of 30%
xx	moderate	$R^2 < 0.8 > 0.6$	r < 0.8 > 0.6	CCC < 0.9 > 0.95	Mean into 30% corridor	>25% of 20% & >75% of 30%
xx	substantial	$R^2 > 0.8$	r > 0.8	CCC > 0.95	Mean into 20% corridor	>50% of 20% & >75% of 30%

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Figure 5 demonstrates the effects of calibration on the trace element lead. This element exemplary shows a strong improvement in the correlation between XRF and ICP-OES results after the calibration.

Thus, results indicate that a specific calibration does not always have a positive effect but can also result in a decline in the measurability of some elements. For a more concise visualization of the correlation results, the percentage deviation of the XRF results from the ICP-OES results is presented in Figures 6 and 7. As described above, extreme outliers (n_{otl}) cannot be excluded in general. Therefore, Figure 6 visualizes the deviation of the XRF measured values from the ICP-OES measurements in percentage, including outliers, while Figure 7 shows the results without the extreme values.

Figure 6 shows that for some elements, due to the extreme outliers, the entire element has a high deviation between the XRF measurements and the ICP-OES results. After adjustment (Figure 7), it appears that many elements measured with XRF agree better with the reference for selected elements (e.g., Al and Ni).

Some elements already performed well with the factory settings, i.e. before calibration, as the highest share of the results were within a 15 to 20% deviation from the reference method that can be considered the typical measurement precision of the ICP-OES (Mg, Si, K, Ca, Al, Cl, Mn, and As), while other elements revealed a small deviation from the reference only after calibration (P, Cr, Fe, Cu, Zn, and Pb). For a detailed consideration of the different statistical evaluations of the results, Table 5 presents several statistical parameters for the interpretation of the results and the final evaluation of the XRF device as a rapid measurement method for solid biofuels. Thereby, the coefficients r and R^2 reveal the correlation of the reference with the rapid measurement method. High values > 0.9 suggest the possibility of precise measurement. The CCC indicates the correlation of the values around the angle bisector[83] and, thus, the conformity of the XRF and ICP-OES results. Furthermore, the amount of values within a 20% percentage deviation from XRF to ICP-OES indicates the measurability of the individual elements.

Although the results of the various evaluation methods are not always consistent, considering all relevant parameters (values < LOD, share of extreme values, CCC, mean value of the deviation from XRF to ICP-OES, percentage of measured values outside 20% deviation), it is possible to come to conclusions about the measurability of various elements.

According to the measurements of this study, the elements Mg, P, K, and Ca showed highly similar results when measured with XRF compared to the reference method (before and after calibration). All correlation factors (r, R^2, CCC) were high, the mean values were within the 20% deviation of ICP-OES, and additionally, most of the individual values were located within the 20% or 30% deviation corridor (>70% either before or after calibration). Mn, Fe and Zn also achieved high correlations but have slightly more values outside the 20% deviation range. However, these elements are also highly recommended to be measured with XRF. Other studies in this area have shown equally good correlations and measurability for these elements.[16,60]

For the elements Si, Al, Cr, and Pb, good measurability was achieved. Similar to the previous elements, these have good correlations, and the mean value is within the 20% deviation corridor. However, there is a higher scattering of the values, so the main share of the values was not in the optimal deviation range compared to the ICP-OES values. Nevertheless, the data show that the XRF provides satisfactory measurement results and that the device can be used to analyze these elements in solid biofuels.

In addition to the elements that can be measured well, e.g. Ti showed a high correlation and good linear regressions between the rapid measurement device and the reference method even before calibration (Table 5). A good correlation between the values, even if not around the bisector, indicates a high ability for calibration.

While some elements such as Ni, Cu, and Pb benefited strongly from the calibration, other elements such as S and Cl considerably reduced their measurability after calibration. For S and Cl, this may be due to the fact that these two elements were not determined with the ICP-OES, but according to the standard procedure. This should be taken into account for future calibrations. This effect is slightly visible for K. Thus, these two elements should not be categorically excluded from measurements with XRF but should be calibrated and compared with a consistent reference method in future evaluations.

Na and Cd provided almost no values above LOD. The remaining useable values had no recognizable correlation to the reference method. Because of this, these two elements are already classified as not measurable. However, the XRF results of Cd could be used for limit value monitoring if the limit value is clearly above the LOD. Furthermore, XRF might be able to measure higher Cd concentrations reliably (in the limit value range). For Cd, this should be part of further research and should be investigated, e.g. with spiked samples with sufficiently high element concentrations. For Na, almost all measurement results were below the LOD or consisted of extreme values. No correlation between XRF and ICP-OES was discernible, which precludes the measurability of Na at this stage. The results for Na are comparable to other studies, which were also not able to measure Na with XRF.[60]

The column “trend” presented in Table 5 indicates whether the calibration resulted in an improvement or a deterioration of the measurability. It shows that a holistic calibration with different sample types from various areas (stem wood, landscape maintenance material, waste wood, forest residues, etc.) did not improve the factory-set method for all elements. For some elements, the results even deteriorated compared to the noncalibrated process. These results are in general comparable with findings from a study by Zimmermann et al. 2019.[16]

The results imply that an overall improvement of the XRF measurement of all essential minor and trace elements in solid biofuels according to ISO 17225-1 by a calibration over a wide range of different fuels is not to be expected for each element. Should not all elements or fuel types be required for a given task (i.e., only a specific element or a group of elements such as the trace elements are required or only a category of fuels such as waste wood), a specific calibration to these elements or the respective materials could provide a more accurate result. This should be the subject of further research.

3.2. Required Accuracy in Practice. Overall, whenever the results of this study or other studies focusing on XRF analysis are considered, the fundamental question arises about how precise the results of XRF have to be for practical application. This study aims to implement XRF for quality assessment during fuel delivery or in sorting areas at biomass terminals as well as for adjusting the combustion process at

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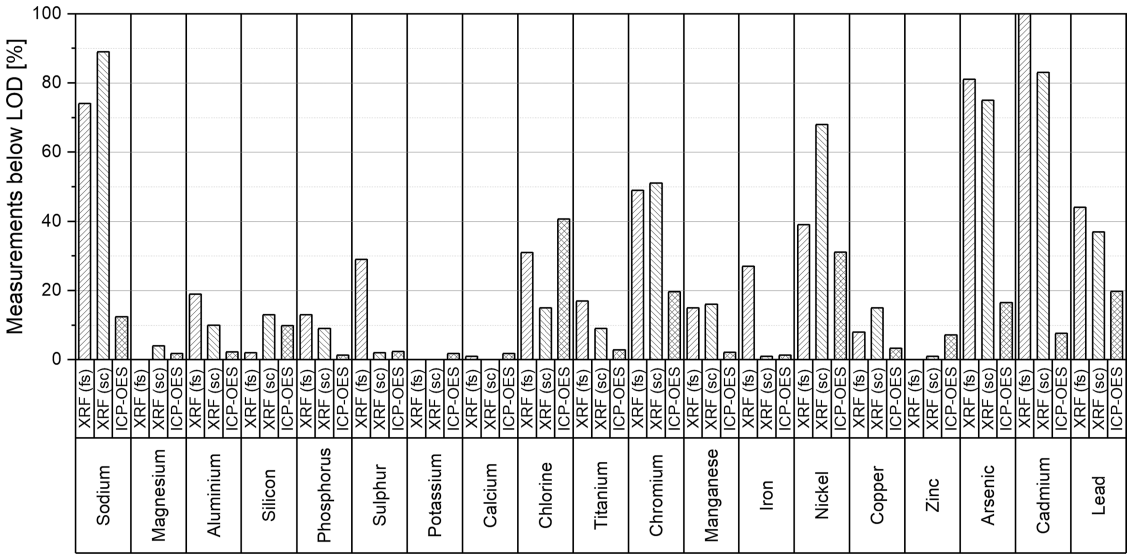

Figure 8. Measurements below the LOD in [%] (n = 229; values of XRF relate to "after calibration").

heat and power plants. Therefore, no laboratory-precise analyses might be required. For instance, many values (especially for trace elements) were frequently below or near the LOD. Thereby, the result "<LOD" might be sufficient for limit value monitoring.

Both the conventional reference method ICP-OES and the rapid analysis method XRF have varying LODs for each element. The LODs of the XRF instrument used in this work after calibration tended to be slightly higher than those of the ICP-OES device. Figure 8 shows the percentage of individual element values of all samples below the LOD for the two approaches.

Considering the LODs, it becomes apparent that, in most cases, even the calibrated XRF device generated more values below the LOD than ICP-OES. Especially for trace elements, ICP-OES had better detection capabilities.

In particular for Na, Cr, Ni, As, and Cd, the majority of the measured values were below the detection limit. This indicates that XRF is rather unsuitable for the measurement of the absolute concentrations of these elements in solid biofuels. Nevertheless, XRF could be useful for limit value monitoring purposes, e. g. for heavy metal thresholds according to the German Waste Wood Ordinance. If the LODs are substantially below (i.e., ten times, which, according to the experience of various working groups in this field, is considered reliable but should still be confirmed in future work by an empirical study) the legal limits and if these can be determined reliably, XRF might be useable for limit monitoring.

For example, the detection limit of XRF for arsenic is 0.1 mg/kg, whereas the limit value according to the German Waste Wood Ordinance is 2 mg/kg,[84] i.e. it is 20 times higher. This shows that XRF is suitable for limit value monitoring, even if the absolute value for As cannot be determined exactly because it is below the LOD. However, in the case of this element, the fact that the measurable values of arsenic in this study (around 2 mg/kg) also did not provide satisfactory results argues against a recommendation for limit value monitoring. Considering that there were only very few As values above the LOD, no good conclusion can be stated for the measurability of samples that are high in As. This should possibly be specifically evaluated with spiked samples in future work. In addition, a specific calibration for arsenic could significantly improve the results due to the high correlation between the XRF and ICP-OES values (r = 0.91).

The individual elements that can be analyzed by XRF provide the heating plant or biomass yard operator with different information about the quality of the fuels. In combustion or biomass CHP, different elements have various effects. Other elements are restricted by limit values that can be assessed on-site at the biomass yard or heating plant. In addition, different fuel indices can be used to calculate different economic and environmental consequences.[11,17−21] Table 6 summarizes the useable knowledge for plant operators through chemical analysis of the fuels.

4. CONCLUSION

The results of this study reveal varying precisions of the XRF device for the elements investigated, which are relevant for solid biofuels according to ISO 17225-1. While the analysis of some elements yielded very good (Mg, P, K and Ca) or satisfactory (Si, Al, Cr, Mn, Fe, Zn, Pb) results compared to the reference method, other elements such as S, Cl, Ti and Ni can possibly be determined with calibrations specifically designed for these elements. Cu, As, and Cd could not be measured satisfactorily with the XRF device used in this article, as many of the values were below the LOD. However, since the LOD of the XRF device was generally low for all three elements, it could potentially be used for limit value monitoring, e.g. in the scope of the German Waste Wood Ordinance. This should be evaluated in future work using spiked samples.

For Na, most measurements were below the LOD or consisted of extreme values. No correlation between the values could be recognized. No recommendation for measuring Na with XRF can be given at the time of publication. However, the LOD could be improved by using various approaches (e.g., tablet pressing of the material instead of powder filling or using other applications such as WD-XRF instead of ED-XRF). However, this makes the process more complex, time-consuming and cost-intensive.

Furthermore, the calibration with a high share of very different samples (stem wood, landscape maintenance material,

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Table 6. Useable Knowledge for Biomass Farm and CHP Plant Operators through the Various Minor and Trace Elements of Solid Biofuels (Excluding N)[11,16−18] (Usability from "-" to "++"; ? = Presumably Measurable with Specific Calibration; LM = Presumably Useable for Limit Value Monitoring)

minor elements		
elements	useable knowledge	measurability
Na	ash melting behavior, ash utilization, particle emissions	-
Si	ash melting, ash utilization, particle emissions	+
P	ash retention of pollutants, ash utilization, particle emissions	++
S	SO_x emissions, high-temperature corrosion, particle emissions	?
Cl	emissions of HCl and organohalogen compounds (e.g., PCDD/F), high-temperature chlorine corrosion, particulate emissions	?
K	ash melting behavior, ash utilization, high-temperature corrosion, particle emissions	++
Ca	ash melting behavior, ash retention of pollutants, ash utilization, Particulate emissions	++
Trace Elements		
Mg	ash melting behavior, ash retention of pollutants, ash utilization, particle emissions	++
Al−Pb	limit value monitoring (LM) (e.g., German AltholzV), particular matter, toxicity, fly ash, assessment of mineral contamination (Al, Fe, and Mn)	Al → +
		Ti → o
		Cr → +
		Mn → ++
		Fe → ++
		Ni → o
		Cu → +
		Zn → ++
		As → LM
		Cd → LM
		Pb → +

waste wood, forest residue wood, etc.) does not overall improve the measurement precision compared to the factory setting. For some elements, the results even deteriorated compared to the noncalibrated method. Assortment-specific calibration could improve this issue and should be considered in future projects.

According to the evaluation, there are always compromises to be made during the calibration of the XRF device. All elements cannot be improved equally based on the results of this study. However, if not all elements are needed for a task, a specific calibration for the required elements or materials might lead to more accurate results. Thus, the required elements should be identified and the instrument explicitly calibrated. Then, it is expected that significant improvements can be achieved.

Automated online processes for quality control in power plants are currently part of the research. Until these are ready for the market, a stationary XRF device as a batch control is a useful and more cost-effective option for the elements investigated in this study.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.4c01771.

Correlation between XRF and ICP-OES for all relevant elements (PDF)

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Notes

The authors declare the following competing financial interest(s): Declaration of interest: Dirk Wissmann is an employee of the manufacturer of the analyser and contributed to the manuscript. But neither the structure nor the results were biased in any way.

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■ ABBREVIATIONS

AAS	atomic absorption spectroscopy
CAA	chromated copper arsenate
CHP	combined heat and power
ED-XRF	energy dispersive X-ray fluorescence
FRW	forest residue wood
GHG	green house gases
HFR	University of Applied Forest Sciences Rottenburg
ICP-MS	inductively coupled plasma-mass spectrometry
ICP-OES	inductively coupled plasma-optical emission spectrometry
INAA	instrumental neutron activation analysis
IQR	inter quartile range
LA-ICP-MS	laser ablation-inductively coupled plasma-mass spectrometry
LIBS	laser-induced breakdown spectroscopy
LMM	landscape maintenance material

LOD	limit of detection
LWF	Bavarian State Institute of Forestry
NWB	non-woody biomass
PGNAA	prompt gamma neutron activation analysis
RSD	relative standard deviation
SDD	silicon drift detector
SW	stem wood
TFZ	Technology and Support Center in the Center of Excellence for Renewable Resources
TPM	total particular matter
WC	wood chips
WD-XRF	wave dispersive X-ray fluorescence
WW	waste wood
XRF	X-ray fluorescence

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