Rapid Chemical Analysis of Renewable Solid Biofuels by X-ray Fluorescence

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Table of Contents

Abbreviations

AAS	Atomic Absorption Spectroscopy
CCC	Concordance Correlation Coefficient
CHP	Combined Heat and Power
ED-XRF	Energy Dispersive X-Ray Fluorescence
FRW	Forest Residual Wood
HEC	High Elemental Concentrations
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
ISO	International Organisation for Standardisation
IQR	Interquartile Range
LA-ICP-MS	Laser Ablation Inductively Coupled Plasma Mass Spectrometry
LEC	Low Elemental Concentrations
LIBS	Laser Induced Breakdown Spectroscopy
LMM	Landscape Management Material
LOD	Limit of Detection
MAD	Median Absolute Deviation
NIR	Near Infrared
PCB	Polychlorinated Biphenyls
PCP	Pentachlorophenol
RSD	Relative Standard Deviation
TGA	Thermo-Gravimetric Analysis
TXRF	Total-Reflection X-ray Fluorescence
UV-VIS	Ultraviolet – Visible Spectrophotometry
WC	Wood Chips
WD-XRF	Wavelength Dispersive X-Ray Fluorescence
WW	Waste Wood
XRF	X-Ray Fluorescence

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Abstract

The chemical composition of solid biofuels is an important quality factor in the operation of biomass-fired heat and power plants (CHP), impacting economic efficiency, maintenance costs, and pollutant emissions (e.g., CO, NO_x, and particulate matter). Furthermore, the chemical composition during waste wood processing is also vital due to the legal limits of various elements (regulated in Germany by the Waste Wood Ordinance).

While fuel quality parameters are increasingly included in supply contracts, they have traditionally focused on physical aspects due to the high cost and time requirement for chemical analysis. Rapid analysers are expected to facilitate on-site quality assessment, measuring minor and trace elements upon fuel delivery to resolve this.

This thesis investigates the suitability of energy-dispersive X-ray fluorescence (ED-XRF) for detecting minor and trace elements in solid biofuels, identifying potential measurement errors, and the further potential of rapid analysis (not only for quality assurance).

The results confirm that ED-XRF is usable for rapidly determining elements such as Mg, Al, Si, P, K, Ca, Cr, Mn, Fe, Cu, Zn, and Pb. This was shown by the comparison with the reference approach using inductively coupled plasma optical emission spectroscopy (ICP-OES), which provided comparable analysis results. However, elements like S, Cl, Ti, and Ni require refined calibration, while Na, As, and Cd remain challenging to measure.

Furthermore, it has been shown that a certain amount of sample preparation is necessary, whereby grinding to ≤ 250 µm optimises homogeneity, reduces the grain-size-effect, and drying to < 10 % wt. minimises water-based measurement errors. As a result, the measurement procedure is extended because the samples should be slightly prepared and cannot be measured directly. However, the measurement time can be reduced to 60 seconds without significant accuracy loss, resulting in faster on-site analysis than external laboratory tests.

The empirical calibration of the ED-XRF analyser improved measurement accuracy for most elements (e.g., Na, P, Ca, Fe, Ni, Cu, Cd, Pb), but slightly reduced accuracy for others (Mg, S, Cl, K, Zn). While some limitations remain, ED-XRF presents a viable, efficient solution for rapid biofuel quality assessment.

Zusammenfassung

Die chemische Zusammensetzung biogener Festbrennstoffe ist ein wesentlicher Qualitätsfaktor für den Betrieb von Biomasse-Heizkraftwerken. Diese beeinflusst maßgeblich die Wirtschaftlichkeit, die Wartungskosten und die Emissionen von Schadstoffen (wie CO, NO_x und Feinstaub). Zudem ist die chemische Zusammensetzung bei der Altholzaufbereitung aufgrund gesetzlicher Grenzwerte verschiedener Elemente (in Deutschland durch die Altholzverordnung geregelt) von Bedeutung.

Während unterschiedliche Brennstoffeigenschaften zunehmend als Qualitätsparameter in Lieferverträgen berücksichtigt werden, konzentrieren sich Qualitätskontrollen aufgrund des hohen Zeit- und Kostenaufwands der Analytik derzeit primär auf physikalische Eigenschaften. In dieser Arbeit wurde die Eignung der energiedispersiven Röntgenfluoreszenz (ED-RFA) für die schnelle Analyse von Neben- und Spurenelementen in biogenen Festbrennstoffen untersucht. Neben der Evaluierung und Optimierung eines herkömmlichen Gerätes wurden mögliche Messfehler und das weitere Potenzial der Schnellanalyse (nicht nur für die Qualitätssicherung) betrachtet.

Die Ergebnisse zeigen, dass die ED-RFA für die schnelle Bestimmung von Elementen wie Mg, Al, Si, P, K, Ca, Cr, Mn, Fe, Cu, Zn und Pb geeignet ist. Dies wurde durch die Vergleichbarkeit der Messergebnisse der ED-RFA mit dem Referenzverfahren der optischen Emissionsspektroskopie mit induktiv gekoppeltem Plasma (ICP-OES) aufgezeigt. Die Ergebnisse der Elemente S, Cl, Ti und Ni zeigten jedoch den Bedarf einer verfeinerten Kalibrierung, während Na, As und Cd keine gute Vergleichbarkeit aufwiesen oder die Nachweisgrenzen des ED-RFA Gerätes nicht ausreichte.

Darüber hinaus zeigte sich, dass ein gewisses Maß an Probenvorbereitung erforderlich ist, wobei das Zerkleinern auf ≤ 250 µm die Homogenität optimierte sowie den Korngrößen-Effekt reduzierte und das Trocknen auf < 10 Gew.-% die wassergehaltsbedingten Messfehler minimierte. Die Messzeit konnte wiederum ohne Genauigkeitsverlust auf 60 Sekunden reduziert werden, was insgesamt zu einer schnelleren Vor-Ort-Analyse führt als Analyseaufträge bei externen Laboren.

Die empirische Kalibrierung des ED-RFA-Analysators verbesserte die Messgenauigkeit für die meisten Elemente (z. B. Na, P, Ca, Fe, Ni, Cu, Cd, Pb), verringerte jedoch leicht die Genauigkeit für andere Elemente (Mg, S, Cl, K, Zn). Trotz gewisser Einschränkungen zeigt die Arbeit, dass die ED-RFA eine effiziente und praxistaugliche Lösung für die schnelle Qualitätskontrolle biogener Festbrennstoffe darstellt.

List of Publications

a) Published in peer-reviewed Journals

F. ENDRISS, D. KUPTZ, H. HARTMANN, S. BRAUER, R. KIRCHHOF, A. KAPPLER, AND H. THORWARTH, "Analytical methods for the rapid determination of solid biofuel quality," *Chemie Ingenieur Technik*, vol. 95, pp. 1503–1525, 2023.

DOI: https://doi.org/10.1002/cite.202200214 (Appendix I)

F. ENDRISS, B. BAUMGARTEN, P. HORN, M. SCHEUBER, AND H. THORWARTH, "Influence of milling on representative sample preparation for the analysis of trace elements in waste wood." *Biomass & Bioenergy*, vol. 168, 2023.

DOI: https://doi.org/10.1016/j.biombioe.2022.106679 (Appendix II)

F. ENDRISS, D. KUPTZ, D. WISSMANN, H. HARTMANN, E. DIETZ, A. KAPPLER, AND H. THORWARTH, "Impacts on X-ray fluorescence measurements for rapid determination of the chemical composition of renewable solid biofuels," *Renewable energy*, vol. 222, 2023.

DOI: https://doi.org/10.1016/j.renene.2023.119923 (Appendix III)

F. ENDRISS, D. KUPTZ, D. WISSMANN, H. HARTMANN, E. DIETZ, A. KAPPLER, AND H. THORWARTH, "Evaluation and optimisation of an X-Ray fluorescence analyser for rapid analysis of chemical elements in solid biofuels." *Energy & Fuels*, vol. 38, pp. 16426-16440, 2024.

DOI: https://doi.org/10.1021/acs.energyfuels.4c01771 (Appendix IV)

1 Introduction

Fossil fuels distinctly contribute to climate change by releasing long-stored CO_2 into the atmosphere. It is, therefore, essential to replace them as efficiently and expeditiously as possible with renewable energies [1]. While 44.0 % of gross electricity generation in Germany already comes from renewable energies (2022), their share in the heating sector is 17.4 % and in the transport sector 6.8 % [2].

There is a wide range of usable renewable energies (like wind energy, solar energy, hydropower, geothermal energy and bioenergy) with countless technologies to replace fossil fuels in the various sectors of electricity, heating and transport [3].

Solid biofuels represent Germany's primary renewable heat energy supply component, accounting for 65 % of the total (2022). However, only 4.4 % of renewable electricity generation comes from it [2]. The solid biofuels used for energy supply originate from various sources, all contributing to a climate-positive impact through the diverse utilisation of woody biomass.

Germany annually produces 4.788 million m³ of landscape management wood, with 1.155 million t_{db} thermally utilised in medium and large plants (< 1 MW) [2]. Additionally, sustainable forest management enhances carbon storage compared to unmanaged forests [4]. Furthermore, only 34 % of harvested trees are used for products, with the remaining 76 % (leaves, crown material, bark, sapwood, and sawdust) available for energy use (32.6 million m³ in Germany, 2020) [2].

Wood also substitutes fossil-based materials in construction and furniture, temporarily storing carbon [4]. At the end of the wood utilisation cycle, waste wood recycling supports the energy supply [5]. In 2020, Germany produced 16.254 million m³ of waste wood, with 6.116 million t_{db} used in medium and large combustion plants (> 1 MW) [2]. Advanced filtration ensures controlled pollutant separation, allowing for environmentally safe disposal or partial recycling (urban mining) [6].

This shows that energy wood is obtained in various areas with different qualities, which is available for thermo-chemical conversion and thus for the supply of thermal energy (Figure 1). Besides the positive aspects of wood fuels, various gaseous pollutants and particular matter are produced during thermal utilisation. These are decisively influenced by the quality of the fuel [7,8].

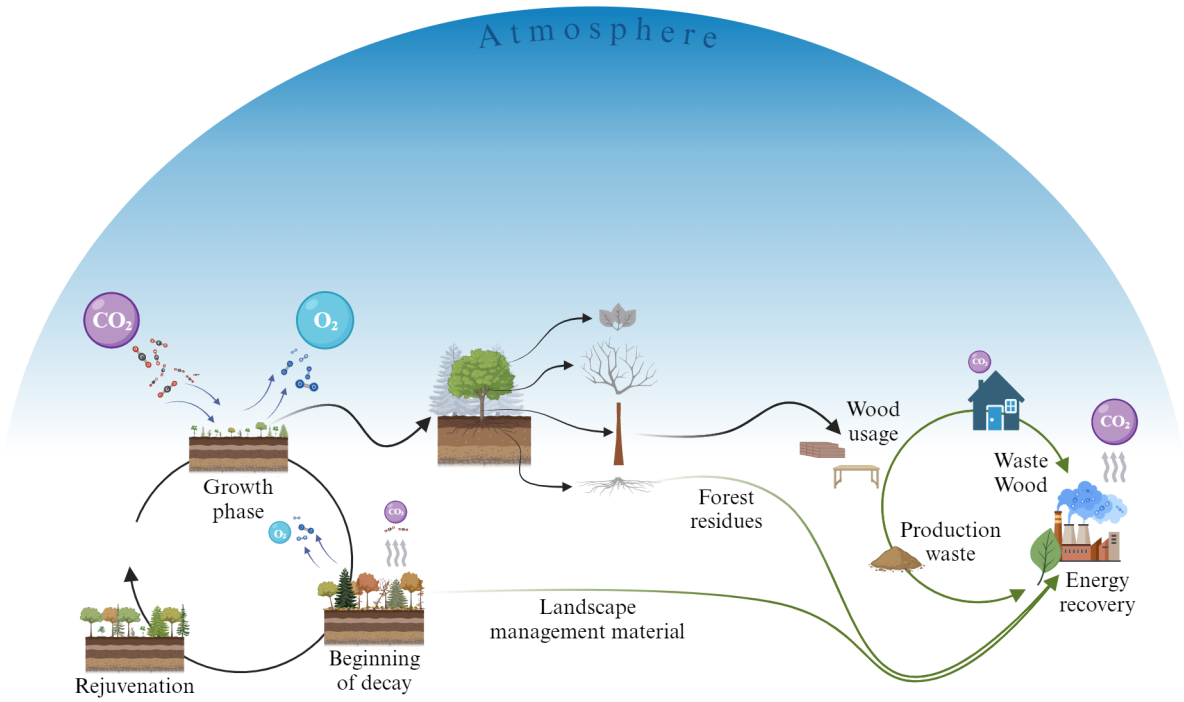

Figure 1: Visualisation of the relevance of wood as a fuel for CHP.

Several parameters can be used to evaluate fuel quality, influencing the CHP system and associated costs differently. The quality of solid biofuels is predominantly influenced by three key physical fuel properties: water content, ash content, and calorific value, each impacting various stages of the plant process [9–12].

Other relevant mechanical fuel properties, such as particle size distribution, particle shape or mechanical durability or the respective rapid determination techniques, such as image analysis [13] are considered in this work.

Among the physical and mechanical quality parameters, the chemical composition of solid biofuels is distinctly responsible for fuel quality. The 26 chemical elements relevant to wood fuel combustion are comprehensively outlined in ISO 17225-1 [14], with Figure 2 presenting typical concentration. The concentration of elements depends mainly on the type of material (wood chips, forest residues, landscaping material, green waste, waste wood, etc.), impurities of anthropogenic origin such as metal splinters, paint, plastic and other waste, but also adhering humus, gravel and mineral soil [15,16].

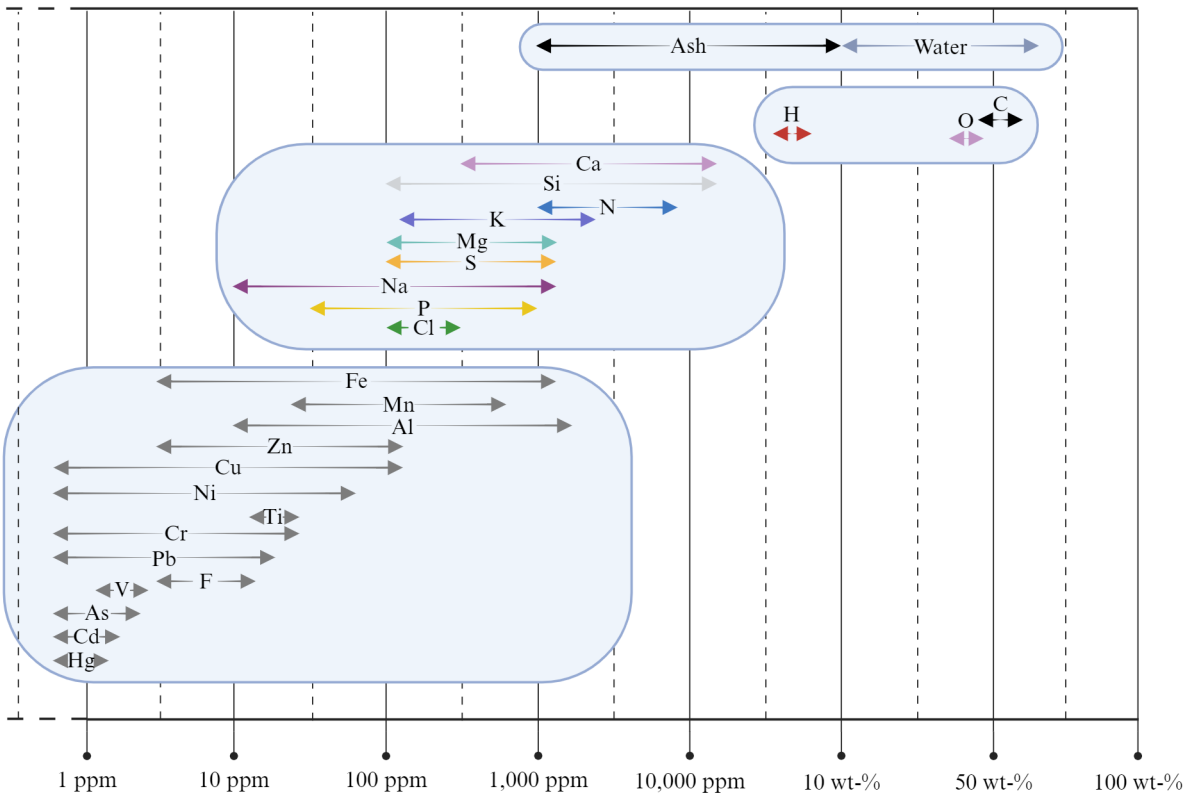

Figure 2: Expected concentrations of different fuel quality parameters in solid biofuels based on ISO 17255-1 [14].

Wood fuels comprise "major" elements – carbon, hydrogen, and oxygen – constituting ≥ 95 % of their composition. In thermo-chemical conversion processes, these factors primarily influence the calorific value and air demand while partially impacting particulate emissions.

Among the major compounds (C, H, and O), the fuel's minor- and trace elements also significantly impact the CHP process (Figure 3) and operation costs and can be used for quality assessment.

The minor elements can affect the ash melting behaviour, ash retention of pollutants, ash utilisation, particulate emissions, high-temperature corrosion, NO_x- und N_2O emissions, SO_x emissions, etc. [10–13].

Most of the trace elements in solid biofuels are heavy metals. Therefore, trace elements also impact particulate matter emissions, the toxicity of particulate matter and ash quality [17].

The impact of fuel quality on combustion units and pollutant emissions can be quantified using various fuel indices. This is achieved by calculating or setting ratios of different minor and trace elements [17–22].

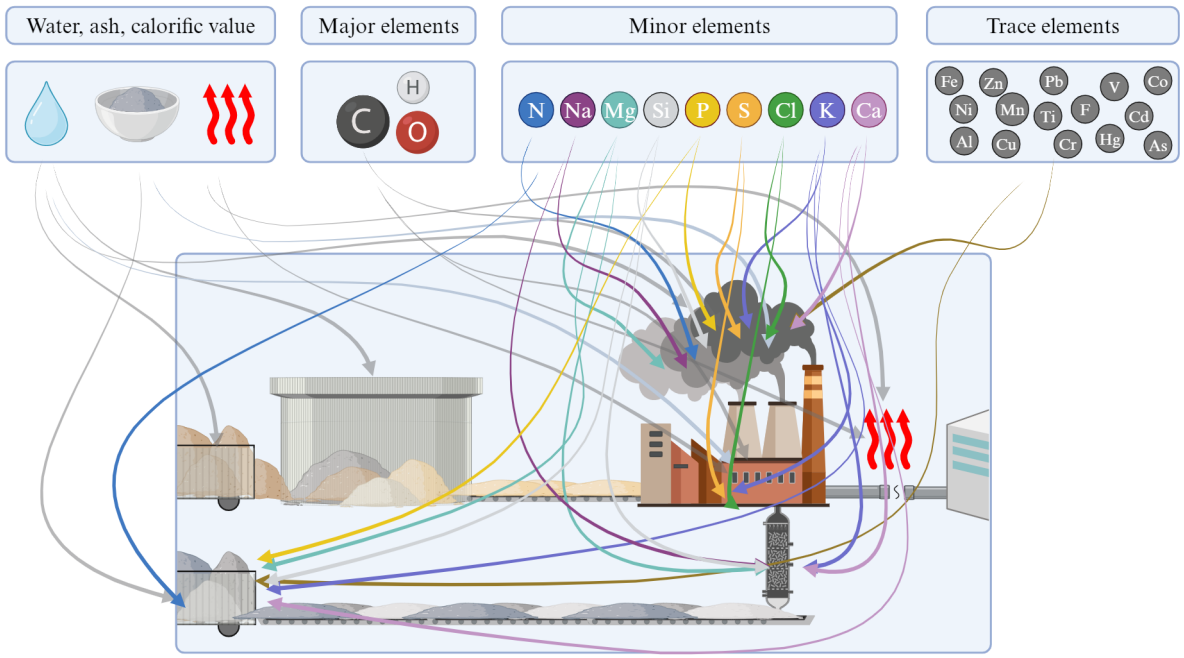

Figure 3: Visualisation of various influences of different quality parameters of solid biofuels on a CHP. Influences of the main parameters (water, ash content and calorific value), the main elements (C/H/N/O) and the minor and trace elements.

For low emissions, minimal wear, and energy-efficient wood combustion, it is beneficial to determine the different fuel properties before boiler input. This approach allows the rejection of poor-quality material, the pre-sorting and mixing of various qualities, and creating a more homogeneous overall fuel supply. Additionally, the process control can be adapted to the specific characteristics of the fuels by the necessary adjustments (air flow, grate cooling) [23]. Fuel costs constitute a significant proportion of the plant operation, and inferior fuel quality can exacerbate operational issues, leading to increased maintenance costs or operational downtimes. Therefore, physical (and sometimes chemical) fuel properties are integral to the pricing terms in supply contracts between plant operators and fuel suppliers [24,25].

Currently, the only typical approach in biomass-fired CHP involves measuring water content on-site. In instances where further analyses are deemed necessary, these are typically conducted by accredited external laboratories. These employ the use of time- and cost-intensive standardised analysis methods, including oven drying for water content (ISO 18134-1, 2, and 3 [26–28]), ash content determination by muffeloven (ISO 18122 [29]), calorific value with calorimeter (ISO 18125 [30]), minor elements and trace elements with ICP-OES (ISO 16967 or ISO 16968) [31–33], inductively coupled plasma mass spectrometry (ICP-MS) or atomic absorption spectroscopy (AAS) [34,35].

To benefit from the knowledge of the various quality parameters, it is essential to implement rapid measurement methods, especially chemical composition, that non-specialised employees can carry out on-site.

For the different quality parameters, a range of analytical methods is theoretically usable, which have been compiled and discussed in a review article by ENDRISS ET AL. (2024) [36] (Appendix I).

The review article concludes that among others like laser-induced breakdown spectroscopy (LIBS) [37–41], laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [42,43], X-ray fluorescence (XRF) based analysis is a promising approach for rapid analysis of the chemical composition of solid biofuels. Analysing solid biofuels with this method is also described in a technical specification ISO TS 16996 [44].

XRF operates on the principle of emitting fluorescence radiation by exciting samples with high-energy electromagnetic radiation ranging from 0.1 to 100 keV (kilo-electron volts). The energy of this fluorescence radiation primarily depends on the atomic number of the element, whereas the intensity depends on the number of element atoms in the sample [45–49]. This enables qualitative and quantitative elemental analyses [46]. Additionally, various studies have demonstrated that elements with higher atomic numbers show lower limits of detection (LOD) due to higher fluorescence radiation output (Kα-series) [46,47,50]. In theory, XRF methods can detect up to 83 chemical elements [45–48].

X-ray fluorescence spectroscopy includes various types, however, the most common approaches are wavelength dispersive spectrometers (WD-XRF) and energy dispersive spectrometers (ED-XRF) [47]. WD-XRF use crystal gratings to scan radiation wavelengths via Bragg reflection [51,52], whereas ED-XRF directly detects polychromatic fluorescence radiation with a semiconductor, enabling simultaneous multi-element analysis [45]. ED-XRF is more energy-efficient, simpler, and cheaper but has lower resolution and higher detection limits than WD-XRF, which offers superior resolution and sensitivity [48]. Other XRF-based technologies (e.g. total reflection XRF, etc.) appear to be more complex and specialised and, therefore, inappropriate for the requirements of the analytical task of this thesis [36].

In analytical processes (sampling, sample itself, sample preparation, measurements and data evaluation), potential sources of error arise at each stage. Sampling and data evaluation are not examined in this thesis, as sampling poses a significant challenge for future research, while data evaluation appears negligible [53,54]. In the case of XRF analysis, the sample matrix, the sample preparation, and the instrumental setup of the analyser affect the analytical result (Figure 4) [55,56].

XRF is considered a non-destructive analysing method, but samples may suffer radiation damage, affecting the sample [57]. Furthermore, interference caused by the sample matrix can affect the measurement results due to spectral interferences such as overlapping, enhancement

and absorption [58]. During sample preparation, the comminution affects the homogenisation of the sample [59] and the grain-size-effect (measured concentrations increase with decreasing particle sizes) [60,61], which can lead to measurement errors. Additionally, the sample's water content can significantly influence the measurability, especially in the case of light elements [62]. For the actual instrumental analysis, the measurement duration of a sample mainly influences the detection limits since the net counts increase. Thus, the detection limits decrease with longer measurement times [63–65]. However, a study on the measurement of forage samples by SAPKOTA ET AL (2019) showed no loss of accuracy when the measurement duration was reduced to 60s [63].

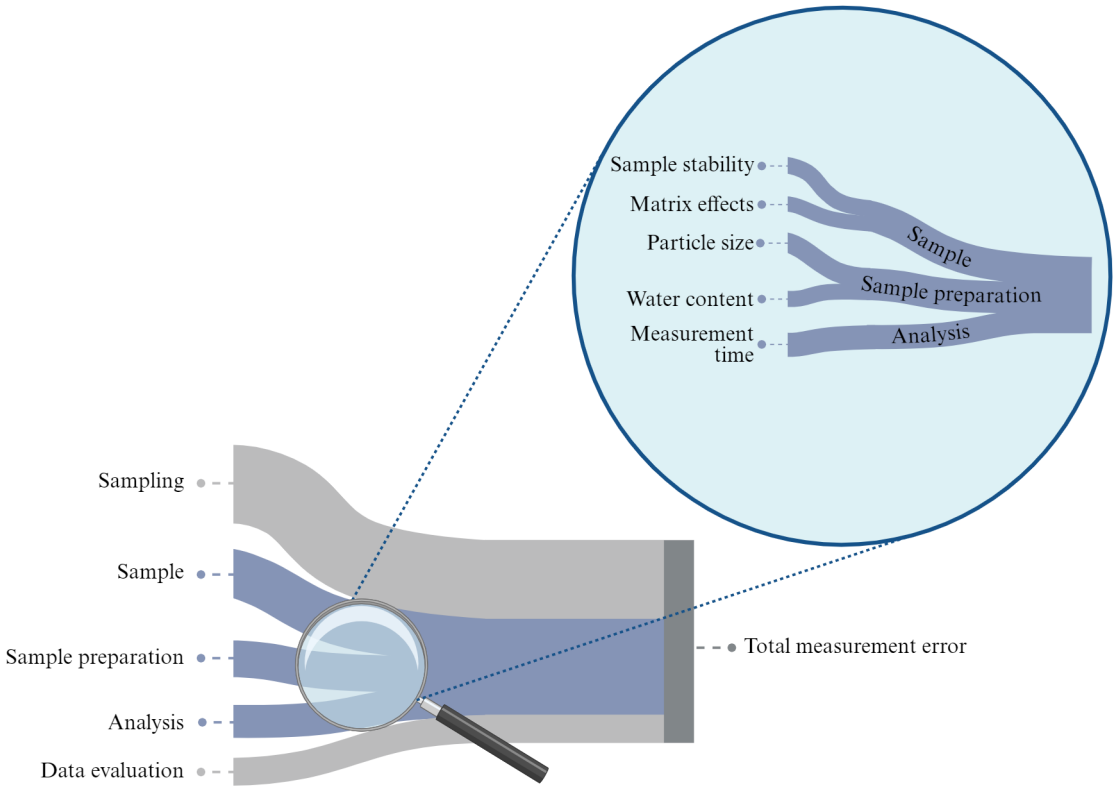

Figure 4: Visualisation of various typical parameters affecting the measurement of solid biofuels with an X-ray fluorescence analyser.

XRF analysis is usable for qualitative and quantitative analysis of chemical elements in various solid samples [46]. For instance, XRF is an often-used method for multi-elemental determinations of biomass (plant [66,67], wood [68,69], bio-based waste [70,71], algae/seaweeds [72,73], seeds [74]), or related fields (Biomass char [75–77], environmental samples [78], ash analysis [79]), coal [50], sewage sludge [80], and others [81–84].

Several studies have already been conducted on analysing various (often specific) components of solid biofuels using XRF.

RIEDEL ET AL. (2014) [85] investigated the feasibility of measuring As, Ca, Cl, Cr, Cu, and Pb in waste wood using a stationary and portable ED-XRF with promising results compared to ICP-MS. ZIMMERMANN ET AL. (2019) [61] and KUPTZ ET AL. (2020) [7] examined ED-XRF calibration for solid biofuels, finding high determination coefficients ($R^2 < 0.9$) for most elements but no holistic improvement across all aspects through the calibration. Other studies examined handheld ED-XRF devices for the analysis of specific components such as As in waste wood (BLOCK ET AL. (2007) [86]) or various relevant elements in solid biofuels such as FELLIN ET AL (2014) [87] or GOLUBEV (2015) [88] with good correlation but also with limitations at the detection limits. In other studies, WD-XRF solutions were also investigated for the rapid analysis of solid biofuels [89,90]. However, no study considers determining all relevant minor and trace elements in solid biofuels [7,61,85–88].

This doctoral thesis addresses the questions of why rapid analysis is essential, the suitability of XRF for the rapid analysis of the relevant minor and trace elements of solid biofuels, and the factors that must be considered for reliable measurement results. The precise objectives and individual research questions are elucidated in Chapter 2.

2 Objectives of the Thesis

Quality control in waste wood processors, biomass yards, fuel supply, and thermo-chemical conversion is beneficial for economic and ecological reasons. New rapid measurement techniques are required to simplify and accelerate the previous, time-consuming and cost-intensive standardised methods.

Therefore, the main objective of this work is to implement the ED-XRF measurements as a rapid method for determining the chemical composition of solid biofuels, thus enabling quality control of the fuels on-site.

Consequently, after consideration of the available methods and the relevance of rapid measurement technology (not only for rapid quality control), the ED-XRF approach is subjected to a detailed investigation. For this purpose, the impact of various factors on the ED-XRF measurements of solid biofuels is examined. Subsequently, a currently available analyser based on ED-XRF technology is evaluated, calibrated and validated compared to the current standardised reference method ICP-OES for solid biofuels.

To achieve this goal, the six following research questions are formulated:

- Is XRF analysis suitable for determining the chemical composition (minor and trace elements) in solid biofuels and, therefore, the rapid quality assessment during delivery?
- Do X-rays or the instrument have a noticeable effect on the sample during XRF measurements of solid biofuels?
- Do the elements in the matrices of different solid biofuel samples interfere with each other during XRF analysis?
- Does sample preparation, such as particle size and water content, affect the accuracy of XRF analysis of solid biofuels?
- Can the measurement time for XRF analysis be reduced without loss of accuracy?
- To what extent can calibration optimise XRF analysis of solid biofuels?

Four publications are discussed in this thesis to address the aim of the thesis and the research questions. The structure and overarching context of the dissertation and the associated publications are shown in Figure 5.

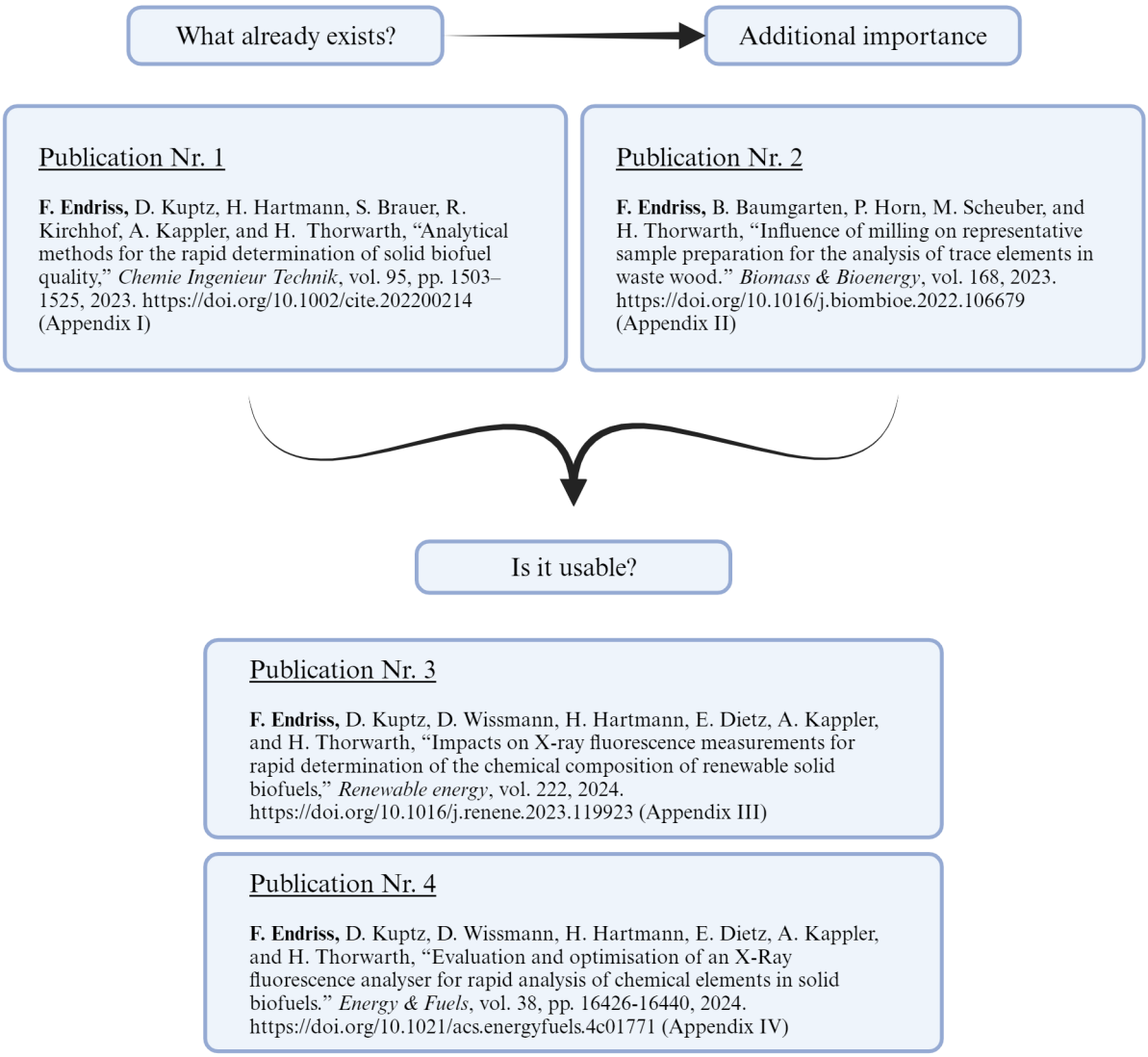

Figure 5: Thesis structure and publications.

3 Materials and Methods

A range of fuel samples is used to investigate the effect of fuel properties and the ED-XRF analyser's technical parameters on the analytical results' accuracy and quality and to evaluate, calibrate and validate the instrument. The selected fuel samples and their preparation procedures are described in Sections 3.1 and 3.2. In contrast, the technical specifications and analytical methodologies of the employed ED-XRF and ICP-OES instruments, along with the experimental procedures and statistical evaluation methods, are outlined in Sections 3.3 to 3.5. More detailed information on these aspects can be found in the corresponding publications (AII – AIV).

3.1 Samples

In all studies, a variety of woody fuels were used, originating from the municipal forest of Rottenburg am Neckar, Germany (e.g. bark-free stems of beech, spruce, pine, larch, alder, oak, ash-tree and bark of various tree species), from CHPs in Germany (e.g. wood chips, landscape management material, residual forest wood, green waste, waste wood of classification AI, AII, AI-III mixed, and AIV according to the German Waste Wood Ordinance), or from retained samples from the Technology and Support Center in the Center of Excellence for Renewable Resources in Straubing (e.g. chipping operations in the forest, biomass terminals, biomass heating plants, etc.) comprising, e.g. wood chips from stem wood, forest residues, roadside maintenance, urban forestry but also from wood pellets).

The wood samples from the forest of Rottenburg am Neckar, Germany, were stored openly at the university until use. In contrast, the samples from the CHP were collected according to ISO 21945 [91], packed in 20-litre airtight buckets, and sent to the Rottenburg University of Applied Sciences for further analysis.

3.2 Sample Preparation

Most of the samples were prepared for the analyses according to ISO 14780 [92]. Some were dried at 105°C in an oven (UNP 700 Memmert Ltd.) to minimise the influence of the water content on the measurements.

Subsequently, the materials were milled to various particle sizes (≤ 4 mm, ≤ 1 mm, and ≤ 250 µm) in a cutting mill (Pulverisette19 Fritsch Ltd.) with heavy metal-free inlet milling cassettes. For particle sizes ≤ 120 µm, the ≤ 250 µm samples were additionally milled in an ultra-centrifugal mill (ZM200 Retsch GmbH) with stainless steel inlets. After each

comminution step, a part of the sample was divided representatively in a riffle divider with 18 culverts.
Further special sample preparations were carried out (described in Appendix III) to investigate various impacts on the XRF measurement.

3.3 Analytical Devices

3.3.1 ICP-OES

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used as the minor and trace element analysis reference method. The samples, processed by the University of Applied Forest Sciences Rottenburg laboratory, were prepared and measured according to ISO 16967 [34] and ISO 16968 [35]. The materials were microwave-digested with Multiwave GO 3000 (Anton Paar Ltd.). Therefore, 400 ± 1.0 mg of sample material was transferred in 50 ml Teflon vessels, and 2.5 ml of nitric acid (HNO_3) supra quality (69 %) (Merck, Germany) and 7.5 ml of hydrochloric acid (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 device was calibrated using a multi-element ICP standard solution (ROTI Star, Carl Roth GmbH + Co. KG) for 28 elements in HNO_3 5 % matrix and the "Multi-Element ICP Standard Solution IV" (ROTI Star, Carl Roth GmbH + Co. KG) for 26 elements in HNO 2 % matrix.
The element-specific wavelengths were selected according to ISO 11885 [93]. The total wavelength range analysed is 162.911 – 771.160 nm.
The retained sample (from TFZ and LWF) were digested with differing mixing ratios of HNO_3, HCl, and hydrofluoric acid (HF) according to ISO 16967 [34], ISO 16968 [35] and the German "Handbook of Forest Analysis" [94].

3.3.2 ED-XRF

The rapid analysing method was the energy dispersive X-ray fluorescence analyser XEPOS manufactured by SPECTRO Analytical Instruments GmbH. The device has a 50 W X-ray tube (max voltage of 60 kV and max current of 2 mA) with a binary-alloy cobalt-palladium anode. The fluorescence X-rays are detected by a silicon drift detector with < 130 eV. Four sub-analyses with different excitations were carried out (the elements enumerated in the ensuing list pertain exclusively to the elements examined in this study and not be 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 material was filled to 10 mm in a sample tube with a 4.0 µm membrane bottom (SpectroMembrane Prolene Thin-Film, Chemplex Industries INC.). The measurement chamber was helium flushed, and the standard measuring time was 750 s per analysis. During a measurement, the sample rotated once every 30 s and excited in a radius of ~ 10 mm.

The factory setting uses a non-specific calibration method for biogenic material based on NIST and IPE standards (e.g., NIST 1573a, 1570a FP) and defines the main component as "organic" ($C_6H_{10}O_5N$). Normalised net intensities were determined from deconvoluted spectra and adjusted using Compton scatter regions as internal standards, correcting for matrix effects per ANDERMANN AND KEMP [95]. Two scatter regions—Pd-Kα (19.71 – 20.55 keV) and Co Kα (6.75 – 6.83 keV) – were used for correction. For Al K-$L_{2,3}$($K\alpha_{1,2}$) to Mn K-$L_{2,3}$($K\alpha_{1,2}$), the normalisation to scatter region (6.75 – 6.83 keV) was employed, and for Fe K-$L_{2,3}$($K\alpha_{1,2}$) to Pb L_3-$M_{4,5}$($L\alpha_{1,2}$) the normalisation to scatter region (19.71 – 20.55 keV) was utilised.

3.4 Experimental Procedures

To analyse the influence of sample milling and outliers on the measurement results, two different milling methods were compared (whole sample and subsamples according to ISO 14780). The influence of single outliers of each sample's n = 16 measurements was also statistically evaluated.

Various tests were carried out to analyse different impacts on the XRF measurement of solid biofuels. Sample stability was assessed by measuring the same sample ten times (four materials), while interference effects were examined using retained samples from TFZ projects compared to reference methods. LEC (samples with low elemental concentration) and HEC (samples with high elemental concentration) were analysed for particle size, water content, and measuring time, with four samples per stage. Particle sizes were milled from 4 mm to 120 µm, water content was rehydrated from 0 % to 60 % in 10 % steps, and measurement durations were reduced from 750 s to 60 s in 60-second increments.

To evaluate and calibrate the XRF analyser, different types of samples were measured for evaluation (n = 264), calibration (n = 64) and validation (n = 229) using XRF and the standard method ICP-OES. Subsequently, the results of the two devices were statistically compared.

The experimental procedures are detailed in the appendices (AII – AIV).

3.5 Statistical Data Evaluation

The study by ENDRISS ET AL (2023) [56] assessed differences in waste wood classes using ANOVA and post-hoc tests, analysed element content variations in sample preparation with t-tests, evaluated normality with Shapiro-Wilk and Mann-Whitney tests, determined homogeneity via relative standard deviation, and addressed outliers using the 1.5 / 3.0 IQR rule by TUKEY (1997) [96].

The data evaluation for the investigations of the various impacts on the XRF measurements focused on individual element concentrations and cumulative concentrations of minor and trace elements per ISO 17225-1, using statistical methods including Shapiro-Wilk for homogeneity, Levene test for heteroscedasticity, coefficient of variation (VarC), ANOVA with paired t-tests, and non-parametric Kruskal-Wallis and Wilcox tests for statistical differences.

The statistical evaluation of the ability of an XRF device to measure chemical elements in wooden fuels included correlation analysis with Pearson or Spearman coefficients and linear regression (R^2), concordance correlation coefficient by LIN (1989) [97] for method agreement, outlier analysis using Tukey's IQR method, and visualisation of percentage deviations as boxplots.

4 Results and Discussion

The materials, techniques and processes previously referenced are utilised to show the heterogeneity of waste wood and the impact of outliers on measurement results (4.1), to examine various factors impacting ED-XRF analysis (4.2), and to evaluate, calibrate and validate an ED-XRF device (4.3). Furthermore, based on the findings of this thesis, a possible future direction for rapid analysis is outlined (4.4). The original publications are reprinted in the appendix (AII – AIV).

4.1 Heterogeneity of Solid Biofuels or Why Rapid Analysis is Important for More than Quality Control

Solid biofuels are highly heterogeneous materials [36]. This applies particularly to waste wood due to anthropogenic contamination such as metals, glass, paint, varnish, wood preservatives, etc. [5,98].

The heterogeneity of materials can complicate the homogenisation process for quality control analysis, thereby increasing the potential for errors in analytical procedures. Research in the field of waste analysis has demonstrated that sample preparation, after the sampling stage, constitutes the second most prevalent source of error in the analytical process [53,54,99].

However, it is crucial to carry out precise analyses when monitoring the quality of waste wood, as these determine whether the wood is suitable for use in a chipboard plant or for thermal utilisation in combined heat and power plants with advanced filter technologies.

The framework for this in Germany is the Waste Wood Ordinance (AltholzV). It specifies classifications from AI (natural, mechanically treated wood) - AIV (treated with wood preservative) and identical limit values for all classes of waste wood, for the following elements and compounds, As (2 mg kg-1 db), Pb (30 mg kg-1 db), Cd (2 mg kg-1 db), Cr (30 mg kg-1 db), Cu (20 mg kg-1 db), Hg (0.4 mg kg-1 db), Cl (600 mg kg-1 db), F (100 mg kg-1 db), PCP (3 mg kg-1 db) and PCB (5 mg kg-1 db) [100].

On this basis, the study by ENDRISS ET AL (2023) [56] primarily investigated the possibilities and limitations of the homogenisation process in sample preparation (two comminution processes: “fully milled” and “partially milled”) for waste wood and the effect of outliers on the measurement result.

Therefore, the heavy metals As, Cd, Cr, Cu and Pb were investigated. Ti and Ba were also examined as additional “homogenisation markers” because these are probably often represented

in waste wood AII – AIV due to painting and coatings [101,102]. Hg, F, PCP and PCB were not analysed in the study.

The results show that the homogeneity markers (Ti and Ba) have a distinctly higher variability as the waste wood class increases. This is mainly due to the markedly higher levels of impurities and the resulting inhomogeneity characteristic of the upper waste wood classes. Consequently, the increasing heterogeneity with higher waste wood classes underlines the growing challenge of obtaining a representative sample.

The elements listed in the AltholzV [100] (As, Cd, Cr, Cu, and Pb) can also be used as homogenisation markers. Typical sources of these elements are impurities, especially those present in the higher wood waste classes. For example, a study by HURON ET AL. (2017) showed that Cr and Cu mainly originate from the chemical treatment of the impregnated wood [103]. Arsenic and Cadmium are rarely used in modern wood preservatives or paints, which explains the generally low concentrations observed in the AIII and AIV waste wood categories [104,105]. However, Cadmium and Chromium are components of the cutting tools used in the mill for sample preparation. This may lead to measurement errors and a higher dispersion of the values.

Elevated lead concentrations in AIII and AIV waste wood are expected due to the historical use of lead-based paints, which, despite being banned today, still appear from old stocks. Additionally, lead compounds are occasionally found in wood preservatives [104].

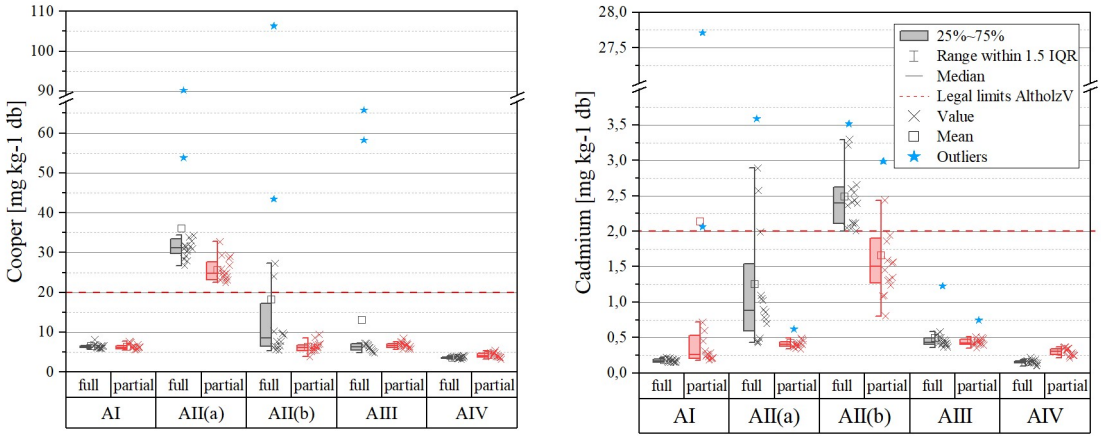

Figure 6: Disparate measured values with outliers per waste wood batch (n = 16) for copper and cadmium. The limit value stipulated by the Waste Wood Ordinance (AltholzV) is illustrated as a red dotted line.

Partly, the measured values of the various elements scatter in themselves (n = 16) in some cases by up to ~ 15 x 10^4 % (for Cd-AI 0.18 [mg kg-1 db] – 27.7 [mg kg-1 db]), which means an outlier deviation from the average of ~ 8.8 x 10^3 % (Figure 6). Furthermore, the examination of the relative standard deviations (RSD) of the samples reveals that the sample preparation

does not achieve satisfactory homogenisation for the majority of elements when the RSD 10 % benchmark proposed by BEARNTHALER ET AL. (2006) [59] is employed.

The increasing trend for the waste wood classes, as found for the homogenisation markers, cannot be seen for the elements of the Waste Wood Ordinance. This demonstrates the difficulty of preparing representative samples of highly heterogeneous materials such as waste wood.

Concerning the results of the "homogenisation markers" and the heavy metals, it should be noted that the fluctuations in the results are not exclusively due to the heterogeneity of the samples. Other factors that can lead to certain fluctuations are, for example, sample handling or the measuring instrument used, ICP-OES, which (like any other measuring instrument) can have certain measurement uncertainties [59,106]. However, given the high level of fluctuation and outliers observed, the ICP-OES measurement error (with RSDs of 10 – 20 % [7]) appears to be a negligible parameter but should be mentioned for completeness.

Following the AltholzV [100], category AI wood must be free from paints, coatings and preservatives. However, visual inspections and analysis data indicate that samples classified as AI show deviations from the established standard and display elevated arsenic concentrations. Class AIV wood shows the lowest concentrations of heavy metals in most cases. In contrast, class AIII wood generally falls within the legal limits for all heavy metals except lead. In contrast, AII samples frequently show a broad range of values, often exceeding the legal limits considerably.

It has, therefore, been suggested that the classification of the materials is at least partially incorrect. This supports the assumption that visual sorting (as described in the AltholzV [100]) is not reasonable or correct, which is also shown by a study by SCHILD AND COOL (2021) [107]. Such misclassification may result in pollutants inadvertently entering the circular economy or in waste wood that could still be utilised for recycling being removed from the circular economy prematurely [101,108,109]. This demonstrates the necessity of examining the fuel at the point of delivery or identifying pollutants precisely at the waste wood processing facility.

Individual outliers can attain remarkably high values, especially with heterogeneous materials like waste wood. Outliers in this study are defined according to the interquartile ranges according to TUKEY (1997), where outliers are set at an interquartile range (IQR) of 1.5 and extreme outliers at IQR 3.0 [96]. The high variability of the measurements, especially for waste wood, is probably due to the presence of foreign objects (e.g. a small circuit board in the A3 sample corresponds to Cu Spikes). Additionally, objects like glass or metal can damage the chromium steel blades used for milling, potentially contaminating samples and affecting chromium and cadmium measurements.

These factors contribute to the emergence of isolated outliers with exceedingly high concentrations. However, most results remain consistent, as evidenced by the reduction in RSD following the removal of outliers. In this work, it is shown that only for one sample (AI, "partial" for cadmium) did the outlier affect the assessment of whether an element exceeded the legal limits (Figure 6).

However, it is also noteworthy that most laboratories do not analyse four subsamples with four replicates each (n = 16), as was done in this study. The ISO 16968 [35] standard does not stipulate a minimum number of measurements (but refers to ISO 5725-2 and ISO 21748). Whereas the Waste Wood Ordinance (AltholzV) applicable in Germany, describes in Annex IV to §6 'Specifications for the analysis of wood chips and wood shavings for the production of wood-based materials' according to point 1.4 that at least two parallel determinations must be carried out for each test parameter [100].

The findings of ENDRISS ET AL. (2023) demonstrate that the minimum two measurements are inadequate in providing reliable information regarding the contamination status of a waste wood batch.

The lower the number of measurements for each test parameter, the higher the influence of outliers on the final results. Consequently, the optimal methodology involves taking an appropriate number of measurements to attenuate the effect of outliers effectively. This ensures that outliers are included in the results without compromising the overall representativeness of the sample or can then be adjusted using the appropriate statistical methods for handling outliers (like IQR according to Tukey (1997) [96] for identification; Winsorized Mean [110], Median Absolute Deviation (MAD) [111], Bootstrap [112], etc. for mitigated integration).

Nevertheless, standardised methods such as ICP-OES, which are used for solid biofuels, are unsuitable for carrying out many measurements of the relevant elements in a short time. A study by GROSS ET AL. (2024) shows the time differences between the TXRF and the ICP-OES/ICP-MS measurement of a graphite material. Therefore, the time required for sample preparation for TXRF analysis was 22 minutes for 15 samples, whereas for ICP-OES/ICP-MS, the time was 122 minutes [113]. There are no detailed records for the times used to analyse solid biofuels with XRF and ICP-OES, but they are probably much further apart.

Therefore, methods such as **X-ray fluorescence analysis** are required to perform a more significant number of measurements in less time.

4.2 Impacts and Sources of Error in ED-XRF Analysis During Measurements of Solid Biofuels

The necessity for rapid measurement techniques for on-site quality control of solid biofuels has been demonstrated, and XRF has been identified as a promising method for rapid analysis of the chemical composition of solid biofuels. As a next step, the suitability of XRF for the analytical task must now be verified.

Therefore, in a first step, the study by ENDRISS ET AL (2024) [114] investigated various impacts and sources of error that can arise during XRF measurement of solid biofuels.

These are distributed over the entire analysis procedure (excluding sampling and data evaluation). The sample itself (sample stability, matrix effects), the sample preparation (water content, particle size) and the actual analysis (measurement time) each have a particular potential source of error. It is essential to quantify them to avoid measurement failures or include them in interpreting the measurement results.

The study considered all minor (Na, Mg, Si, P, S, Cl, K, and Ca) and trace elements (Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, and Pb (except for N, F, V, and Hg) that are relevant for the combustion of solid biofuels, following ISO 17225-1 [14].

To assess **sample stability**, four samples of beech stem wood, waste wood (WW), landscape maintenance material (LMM), and forest residue wood (FRW) were measured ten times consecutively with ED-XRF. Variation coefficients for the "sum of concentrations" (all measured elements of this study) were 0.49 % (beech stem wood), 4.08 % (WW), 0.44 % (LMM), and 0.18 % (FRW). WW shows higher variability due to the heterogeneity of waste wood, which contains diverse matrices (e.g., different types of wood, varnishes, glass, metals, sprues, wood preservatives, etc.) [56].

No increasing or decreasing trends were observed in the sum or individual element concentrations throughout the ten measurements (Figure 7). However, higher relative standard deviations (RSD) occurred for elements near the detection limit. It appears that the samples are affected by X-rays in a non-measurable range, and only instrument-specific or heterogeneity-related fluctuations were visible.

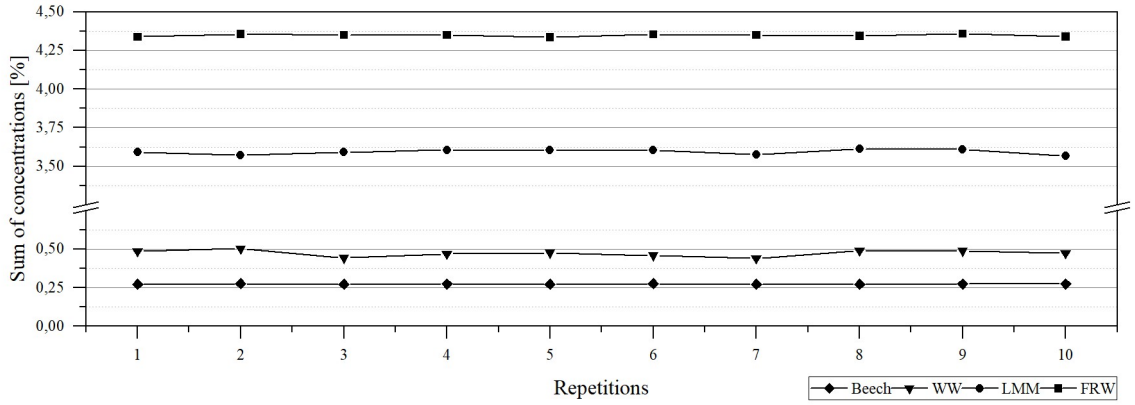

Figure 7: Sum of minor and trace element concentrations of relevant elements of solid biofuels according to ISO 17225-1 ex. N, F, V, and Hg in beech stem wood (Beech), waste wood (WW), landscape management material (LMM), and forest residue wood (FRW); Particle size: 250 µm; n = 10 per material [114].

The sample and its **matrix** may cause further measurement errors. The so-called matrix effect or interferences can lead to element lines influencing each other differently [115].

The study shows the impact of high silicon levels on the measurement of phosphorus concentrations. The composition of the matrix of solid biofuels can vary considerably depending on the type of fuel and its impurities, such as gravel or soil material, which results in high silicon concentrations [116,117].

Samples with a silicon concentration below 5000 mg kg-1 show a significantly higher agreement of phosphorus in the correlation between XRF and ICP-OES. Higher silicon concentrations lead to a decreasing drift in the phosphorus concentrations measured with the ED-XRF (Figure 8), which indicates that the silicon lines partly overlap the phosphorus line.

Additional potential interferences were investigated that are known from the existing literature arising from overlapping, absorption, or pre-concentration effects (Ca-Kα/K-Kβ; Mn-Kα/Cr-Kβ; Fe-Kα/Mn-Kβ; Cu-Kα/Ni-Kβ; As-Kα/Pb-Lα1; Cd-Lβ1/K-Kα) [47].

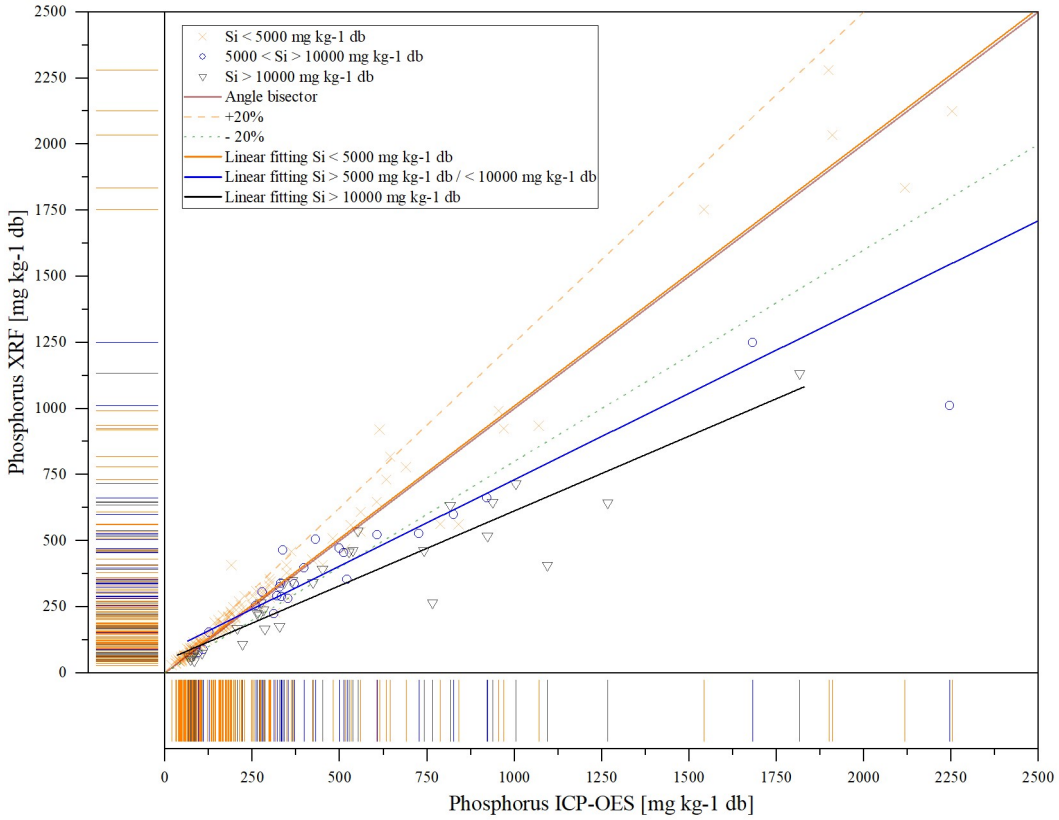

Figure 8: Phosphorus measured by XRF compared to ICP-OES for wood chips with silicon contents below 5000 mg kg-1, between 5000 and 10,000 mg kg-1, and above 10,000 mg kg-1 (n = 207, dry base).

However, no further interferences were detected, suggesting that the device has already chemometrically factored these interferences by the software or that the extent is in a non-measurable range. The deconvolution process employed in the SPECTRO XEPOS software corrects most of these matrix effects, as per ANDERMANN AND KEMP [95].

Another source of error is the sample preparation. **Milling** the sample has positive and possibly negative effects on the measurement results. To examine these, two materials were milled to particle sizes of ≤ 4 mm, ≤ 1 mm, ≤ 250 µm, and ≤ 120 µm. The first sample was a pure beech heartwood sample without contamination (LEC – represents samples with low element concentrations), and the second was a highly mineral-contaminated landscape conservation material sample (HEC – represents samples with high element concentrations).

Comminution is necessary to homogenise a sample [56]. The analyses, which usually require a few grams to µg, must represent the whole sample. Multiple measurements and comminution of the sample achieved this.

The most effective homogenisation in this study was achieved by milling to a particle size of ≤ 120 µm (except Cu and Zn for LEC). According to a study by BAERNTHALER ET AL. (2006), satisfactory homogenisation is achieved with an RSD > 10 % [59].

However, an ultra-centrifugal mill had to be used to achieve this particle size, which is time-consuming and causes contamination with heavy metals. This is mainly due to the abrasive properties (especially of the HEC) material and the steel inlets of the mill. Heavy-metal-free steel inlets would minimise the risk of contamination.

Given that CHP plants primarily combust HEC materials such as LMM, FRW, and WW [33], and considering the importance of efficiency in rapid analysis, a particle size of ≤ 250 µm appears to be adequate for on-site analysis of most elements (only LEC – Cr, Cu; HEC – Cu, As were slightly above the 10 % RSD).

In the case of certain elements, comminution down to a size of ≤ 1 mm or ≤ 4 mm may prove sufficient. This is particularly relevant for elements such as Mg, P, Cl, K, Ca, Ti, Fe, Mn, and Zn, where the relative standard deviation (RSD) does not exceed 10 % at these milling levels.

However, in addition to ensuring homogeneity, it is essential to consider the so-called "grain-size-effect" resulting from variations in particle size. This can result in higher measured concentrations as particle size decreases [60]. According to various studies, particularly from the geology field [60,118], the grain-size-effect significantly influences the measurement. A study by ZIMMERMANN ET AL. (2019) also showed a clear grain-size-effect for wood fuels with mineral impurities [61].

In this study, in the LEC material, the concentration of most elements in the samples increased with decreasing particle size, as reported by MARUYAMA ET AL. (2008) [60]. This phenomenon is probably due to X-ray scattering caused by uneven surfaces and shadowing effects when analysing larger particles [119]. Light elements such as P, K, Ca and Fe are particularly affected due to their low energy and limited penetration depth [119].

Conversely, the HEC material shows significant inter-sample variability due to its inherent heterogeneity, particularly at larger particle sizes of ≤ 4 mm and ≤ 1 mm. This variability may mask the effect of particle size in the HEC material. Nevertheless, the increasing effect of smaller particle sizes on element concentrations was observed for Ca, Fe and certain heavy metals, including Cu, Zn, As and Pb. However, P, S and Si in the HEC material showed a significant decrease in concentration with decreasing particle size – an observation for which there is currently no clear explanation.

The results partially correspond with those of ZIMMERMANN ET AL. (2019), who also did not observe the grain-size effect for all elements, finding it only for Al, Si, Ca and Fe [61].

The absence of an observable grain-size-effect in certain elements (especially for HEC material or mineral-contaminated samples like in [61]) may be because the heterogeneity of the sample

exerts a considerably more substantial influence on the measurement outcomes in some instances.

Overall, a statistically significant difference in the concentrations of minor and trace elements across different particle sizes was observed for most elements (excluding K_{HEC} with $p = 0.235$ and $Pb_{LEC} = 0.348$). While the grain-size-effect – an increase in concentrations with decreasing particle size, as reported in the literature [60,63,119] – was not consistently observed for all elements and materials, the influence of particle size on measurement results was evident.

The study by SAPKOTA (2019) described a compromise between the desired accuracy and the feasibility of the preparation process for forage samples. The study concluded that achieving an optimal effort-to-precision ratio is contingent upon maintaining a particle size of less than 2 mm [63].

Furthermore, it is essential to note that any additional reduction to a finer particle size can lead to contamination of the samples, especially by using hardened steel. DIETZ ET AL. (2016) tested mill-abrasion (cutting-mill Retsch SM2000) by adding 10 g analytic sand and found Ni 12 mg for Cr 28 mg abrasion. Consequently, the sample's elemental composition was augmented by a factor of 4 to 6 for Co and more than 100 times for Cr, Ni and Mo [15]. The employment of heavy metal-free steels could serve as a mitigation strategy; nevertheless, each milling step permits the presence of impurities from alternative sources of contamination and makes the milling process more complex and time-consuming.

WILLIS AND DUNCAN (2008) proposed a methodology for minimising the grain-size-effect by recommending that samples be milled to a particle size smaller than the measuring depth (i.e. the length of X-ray penetration into the sample) of the XRF instrument [120].

Therefore, in addition to the previously mentioned aspects of homogenisation, the grain-size effect, the cost/benefit ratio, and the penetration depth of the X-rays must also be considered when selecting the optimum particle size. The particle size of the analysed elements should remain below this threshold value to ensure optimum measurement accuracy.

The theoretical penetration depth is calculated using the formula:

Formula 1: Calculation of the penetration depth (information depth) with h = penetration depth; ρ = density [g/cm³]; μ = mass attenuation coefficient [cm²/g].

$$h = \frac{\ln(0.01)}{\rho \cdot \mu}$$

For example, using the formula for $(C_6H_{10}O_5)_n$ with an assumed density of 0.5 g/cm³, the calculated penetration depth indicates that optimal analysis of light elements up to Cl would require finer grinding of the sample to ≤ 250 µm (See table 3 in appendix III).

However, empirical data and the required accuracy indicate that homogeneity and measurement precision are sufficient for elements up to Mg. A parallel study by ENDRISS ET AL. (2023) confirms this, showing good correlations for lighter elements such as P and Mg with particle sizes ≤ 250 µm [121]. ZIMMERMANN ET AL. (2019) found the strongest correlations between the ED-XRF and ICP-OES at 500 µm, compared to 1 mm and 2 mm [61].

In this study, identifying an 'optimal' particle size proved challenging, mainly when all factors related to particle size were considered (homogenisation, grain-size-effect, cost/benefit ratio, and penetration depth). Homogeneity analyses suggest that calibration should target a particle size range of ≤ 250 µm to ≤ 1 mm (up to ≤ 4 mm only for certain elements), contingent upon the specific component under investigation. Considering the other factors, a grain size ≤ 250 µm seems recommended. However, a standardised particle size should be maintained across all samples when taking measurements, as this minimises the potential impact of particle size effects. The ≤ 1 mm described in ISO/TS 16996 [44] should, therefore, may be adjusted again.

In sample preparation, the **water content** also has a distinct influence on the XRF measurement. A decrease in element concentrations with increasing water content (all values re-calculated to the water-free reference state) was observed for most elements. As shown in the study by GLANZMANN&CLOSS (2007) on geological samples, this phenomenon may be due to the protective film effect of water, which partially absorbs fluorescence radiation [62].

In this study, a water content ≥ 20 %, as previously noted in [62], often gave significantly different results compared to almost anhydrous samples. Some elements showed a statistically significant difference first at ≥ 30 % wt. (K_{HEC}, Ca_{HEC}, Fe_{HEC}, Mn_{HEC}, and Zn_{HEC}) or ≥ 40 % wt. (Cl_{LEC}). The data of this study also suggests elements that were (almost) unaffected by water content (Si_{LEC}, Cu_{LEC}, Pb_{LEC}; Cu_{HEC}, Pb_{HEC}). Silicon should be excluded from this as the significance analysis was difficult due to high standard deviations.

Considering that the lighter elements had issues with the water content, heavy elements (e.g. Pb) were not affected. This indicates the protective film effect of the water content as described in the study by GLANZMANN&CLOSS (2007) [62].

The results of SOLO-GABRIELE ET AL. (2004) [122], which suggested that arsenic concentrations were unaffected by water content, could not be confirmed in this study. Here, arsenic

concentrations differed significantly at a water content of ≥ 30 % compared to water-free samples.

Wood chip samples have typically a water content of ≤ 10 to ≥ 55 % [14]. To mitigate the impact of water content on XRF measurements, it is recommended that samples be dried to 10 % wt. before analysis.

Following the specifications in ISO 14780, the drying of materials must be conducted at either room temperature or at a maximum of 40 °C. After this, the material has to rest for 24 hours to reach an equilibrium with the temperature and humidity levels of the surrounding environment or laboratory [92]. In contrast, the ISO/TS 16996 described in section 9.2: "Dry a sufficient amount of general analysis sample material according to 14774-3 immediately before pressing pellets for XRF-Analyses" [44].

The sample preparation method described in ISO 14780 is inappropriate for a rapid measurement technique. Consequently, it is necessary to accelerate the drying process (if required). This can be achieved by subjecting the sample (like the oven drying method for water content determination) at temperatures of 105 °C [26] or by subjecting it to drying at temperatures of up to 130 °C [123] for a more expeditious outcome. However, it should be noted that higher temperatures can result in the outgassing of volatile components, such as oils, fats, terpenes, and resins, which can potentially compromise the accuracy of the analysis (Coniferous woods lose volatile components at < 60 °C) [124,125]. Nevertheless, in the context of quality monitoring, where the urgency of measurement takes precedence over exactitude, the impact of outgassing at these temperature levels appears negligible.

In XRF analysis, a longer **measurement time** generates a higher number of counts (more fluorescence radiation strikes the detector), which increases the information provided to the device (Figure 9) [87]. This increase improves the accuracy of the element concentration determination, allowing more precise measurements or reducing the detection limits for individual elements [63–65]. This effect was evident in the analysis of solid biofuels carried out in this thesis.

The results are consistent with other studies using XRF in various fields. Overall, measurement time had a marginal effect on the results [63,65]. Similarly, SAPKOTA (2019) demonstrated that measurement times could be reduced to 60 seconds for the rapid analysis of forage without compromising accuracy, a finding that appears to apply to the rapid analysis of solid biofuels [63]. However, the duration should not be unnecessarily reduced if elements already close to the detection limit should be measured.

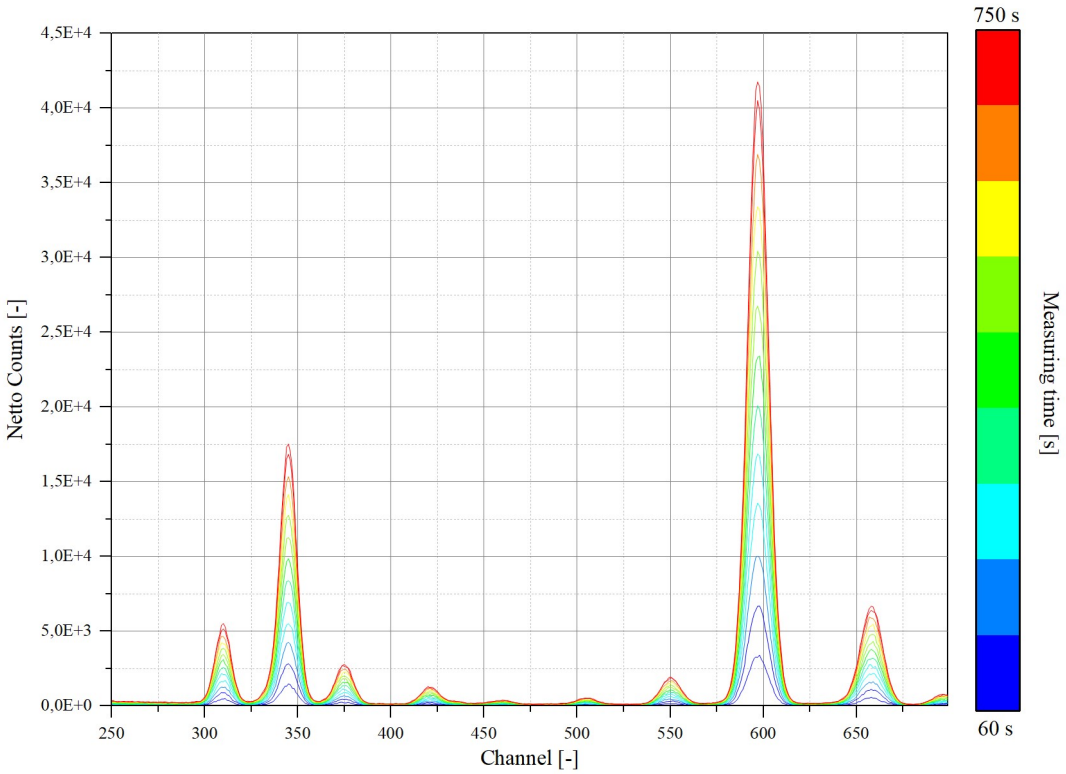

Figure 9: Impact of the measuring time on the LOD of various elements.

4.3 Evaluation and Optimisation of an ED-XRF Analyser for Solid Biofuels

Various impacts on the XRF analysis were identified, and an appropriate sample preparation method was defined. Based on this, the study by ENDRISS ET AL. (2024) [126] investigates the usability of an ED-XRF analyser for the rapid determination of the relevant minor and trace elements (according to ISO 17225-1 ex. N, F, Hg and V [14]) and the possibility of improving the results through calibration.

Therefore, an ED-XRF device from Spectro Analytics GmbH (XEPOS) was evaluated and empirically calibrated with various “real-life” samples.

Besides samples with relatively low element concentrations, such as different types of wood, typical power plant fuels (WC, LMM, FRW, WW) with higher elemental concentrations and impurities were used.

These samples were analysed with the XRF device, immediately digested with aqua regia or hydrofluoric acid digestion and compared with the reference method ICP-OES (n = 264). The XRF analyser was then empirically calibrated with ICP-OES measurement results (n = 64) and subsequently validated (n = 229).

Therefore, all findings and calibrations in this study rely on the precision and accuracy of the ICP-OES method. Various studies have shown that ICP-OES measurements of solid biofuels

or plant materials can fluctuate significantly [7,59,127]. As a standardised and widely employed method for analysing solid biofuels [34–36] – continuously validated through inter-laboratory round-robin tests – ICP-OES emerges as the most suitable choice for empirical calibration.

Figure 10 shows an example of the correlation between the rapid measurement technique and the reference method for lead with factory settings (left) and after the calibration (right).

Before calibration, the values already show a substantial correlation ($r = 0.94$), but not around the angle bisector of the correlation plot, which can be demonstrated using the concordance correlation coefficient ($CCC = 0.65$). The values visualise a correlation of $r = 0.98$ after calibration, representing a slight improvement and a $CCC = 0.95$.

A successful calibration could be demonstrated using lead as an example (Figure 10), but not all calibrations were equally satisfying. The publication by ENDRISS ET AL. (2024) [126] shows a detailed list of various statistical evaluations for the relevant elements to analyse solid biofuels.

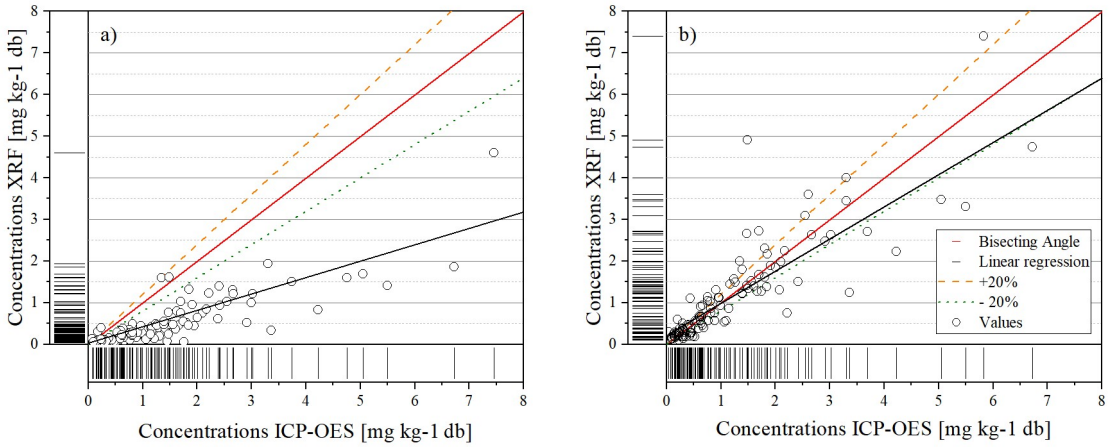

Figure 10: Linear regression of XRF and ICP-OES (Reference method) for the element lead. On the left side (a) before calibration (n = 128); on the right side (b) after empirical calibration (n = 118).

Although the results of the various statistical evaluation methods (values below the LOD, the proportion of extreme values, CCC, mean deviations between ED-XRF and ICP-OES and the percentage of measurements that exceed a deviation of 20 %) do not always fully correspond, their holistic consideration allows conclusions to be made about the measurability of the different elements (all results in Table 5 in the appendix IV).

The measurements conducted in this study show highly comparable results between XRF and the reference method ICP-OES, both before and after calibration, for Mg, P, K, and Ca. Mn, Fe, and Zn show strong correlations, albeit with a slightly higher proportion of values exceeding the 20 % deviation threshold. Supporting evidence from other studies in this field has similarly reported high correlations and reliable measurability for these elements [61,88].

Suitable measurability was achieved for Si, Al, Cr and Pb. Strong correlations were observed, with a mean value within the 20 % deviation corridor. However, a higher degree of scatter was observed, with most values falling outside the optimal deviation range of 20 %.

In addition to elements that demonstrated strong measurability, Ti suggests high correlation and robust linear regression between the rapid measurement device and the reference method using the factory settings ($r = 0.97$, $R^2 = 0.94$). Even if not aligned with the bisector, a strong correlation signifies a high potential for effective calibration. Nevertheless, no satisfactory agreement between XRF and ICP-OES results could be achieved in this calibration. Based on the high correlation coefficients, it is assumed that a specific calibration for the element (in case of particular interest) could achieve a significant improvement. The same applies to this study's elements S, Cl, and Ni.

Similarly, in a study by ZIMMERMANN ET AL. (2019) [61] and a research-report by KUPTZ ET AL. (2020) [7], not all elements were consistently improved by the calibration. While calibration improved the measurability of elements such as P, Ca, Fe, Ni, Cu, Cd and Pb, it slightly reduced the correlation between XRF and ICP-OES for Mg, K and Zn and substantially for S and Cl.

This decrease in measurability and the lack of improvement with calibration for S and Cl can be attributed to using alternative and different standard methods to analyse these elements [116]. Before calibration, Cl ($r = 0.98$; $R^2 = 0.97$; $CCC = 0.97$) were well measurable, and S ($r = 0.89$; $R^2 = 0.78$; $CCC = 0.84$) was partly measurable in comparison to the reference method; this limitation must be accounted due consideration in future calibration efforts.

The slight deterioration of Mg, K and Zn can have various causes. It could be due to the samples used for calibration or potential alterations in the spectrum selection resulting in new interferences [58], but this could not be clarified in this study.

Further investigations should examine whether an element-specific calibration for only one element or a few elements (e.g. elements with legal limit values from the AltholzV [100]) leads to a higher improvement.

Na and Cd showed minimal values above the limit of detection (LOD), with no apparent correlation to the reference method. Consequently, both elements are classified as "not measurable".

For Na, most results were below the LOD or extreme outliers, with no correlation to ICP-OES, confirming its non-measurability at this stage. These findings are consistent with previous studies, which also reported difficulties measuring Na in solid biofuels with ED-XRF [88]. In contrast, a survey by TRIANTAFILLIDIS ET AL. (2023) [89] found good correlations between WD-XRF and ICP-MS.

One potential explanation for the unsatisfactory measurability, particularly to the lightest element Na, may be the membrane foil used for the sample tube. The Prolene Thin-Flim (Chemplex Industries INC.) prevents the transmission of fluorescence radiation to a certain extent from reaching the detector. The absorbing property depends on the radiation intensity of the fluorescence radiation (the lower the intensity, the lower the percentage transmittance) and is, therefore, particularly relevant for light elements. For the thin film used in this study, the percentage transmittance is close to 100 % at an intensity of approx. 5.0 keV, this decreases exponentially with decreasing intensity (Table 1) [128].

Table 1: List of elements analysed with corresponding atomic number, the photon energy Kα [keV], and the X-Ray transmission [%] at the corresponding Kα photon energy [128].

Element	Atomic Number	Photon Energy Kα [keV]	X-Ray Transmission [%] at this Energy Level
Na	11	1.04	32.01
Mg	12	1.25	49,75
Al	13	1.49	64.76
Si	14	1.74	74.94
P	15	2.01	82.38
S	16	2.31	87.59
Cl	17	2.62	91.07
K	19	3.31	95.41
Ca	20	3.69	96.65
Ti	22	4.51	98.01
Cr or higher	24	5.41	~ 100

Although the ED-XRF software chemometrically corrects the transmittance factor of the thin film, it almost no longer exerts a direct radiation-blocking effect on Ti (4.51 keV) or higher atomic number [129]. Conversely, this suggests that elements with an atomic number lower than Ti (thus, for solid biofuels, Na, Mg, Al, Si, P, S, Cl, K, and Ca) would benefit from tablet pressing and measurement without a thin film. A study by ZIMMERMANN ET AL. (2019) [61] also showed that the fluorescence radiation for lighter elements than Al increases for pressed tablets compared to powder filling.

When the results of this study are evaluated in conjunction with the findings from other studies on XRF analysis, a key question emerges: How precise do XRF results need to be for practical applications? This thesis investigates the usability of XRF for quality assessment in waste wood processing, fuel supply, sorting at biomass terminals and optimising combustion processes in CHP plants. In such contexts, laboratory-level precision may not be necessary. For instance,

many trace element values were often below or near the LOD, where a result of "< LOD" might suffice for limit value monitoring.

A comparison of the LOD shows that the ICP-OES detects almost more concentrations of the individual elements than XRF.

In this thesis, the values below the LOD were also declared “not measurable” and not included in the evaluation. Consequently, elements with numerous values below the LOD can only be evaluated to a limited extent. Specifically, Na (74 %), As (81 %), and Cd (100 %) show a high proportion of values below the detection limit.

However, these elements, partly subject to limitations imposed by the Waste Wood Ordinance with specified limit values, should provide reliable measurement results within the specified limit value range to facilitate their use for limit value control.

The detection limit of the ED-XRF for arsenic is 0.1 mg kg-1, while the limit value according to the Waste Wood Ordinance is 2 mg kg-1 [100], i.e. 20 times higher. This suggests that ED-XRF is suitable for limit value monitoring, even if the absolute value for As cannot be determined precisely because it is below the LOD. This is further supported by the high correlation between ED-XRF and ICP-OES values for As ($r = 0.91$).

An accurate determination of whether values close to the LOD should be made in future work using spiked samples that artificially increase the As, Cd and Pb of the samples.

An alternative method would be to use statistical approaches to estimate the values below the LOD. The analysis could be performed using various survival curves (e.g. the Kaplan-Meier method [130]). Using statistical methods, this approach would facilitate the study of values below the detection limit. However, this was not possible in this work, as there is a lack of relevant data. This should be examined in further research.

As the study showed that almost all ash-forming elements of solid biofuels can be reliably measured using ED-XRF, it can be assumed that the ash content can be calculated by summing these concentrations. Rapid ash content determination enhances solid biofuel quality assessment, as TOSCANO ET AL. (2023) found in over 900 samples, identifying it as a representative indicator of fuel quality [1]. Similar results were obtained by MANCINI ET AL. (2020) when they analysed 1700 wood chip samples [131].

The key elements that form ash for biomass are Si, Mg, P, S, Ca, K, Na, Al, Fe, Cl, Mn and Ti [132]. As illustrated in Figure 11, a strong correlation is observed between the summed ash-forming elements measured with ICP-OES (a) and ED-XRF (b) and the ash content measured using the reference method specified in ISO 18122 [29]. Measurements conducted with ICP-OES reveal a correlation ($r = 0.98$; $R^2 = 0.96$), while ED-XRF achieves a slightly lower

correlation (r = 0.92; R^2 = 0.85). Notably, the correlations improve significantly for lower ash contents (< 5 %), where the coefficient of determination for the XRF analysis reaches R^2 = 0.91. Both approaches are suitable for estimating the ash content directly, at least roughly. An alternative method to estimate the ash content involves summing the concentrations of ash-forming oxides. For biomass, these oxides include SiO_2, CaO, K_2O, P_2O_5, Al_2O_3, MgO, Fe_2O_3, SO_3, Na_2O, MnO, and TiO_2 [132]. The evaluation of this approach indicates slightly lower correlations than summing the ash-forming elements directly (r = 0.94; R^2 = 0.84) (Figure 11, c). Furthermore, it is evident that the accuracy of ash content estimation, whether based on oxide sums or ash-forming elements, improves at lower ash contents. For samples with ash contents below 3 %, the coefficient of determination increases to R^2 = 0.93 and the correlation r = 0.96 (Figure 11, d).

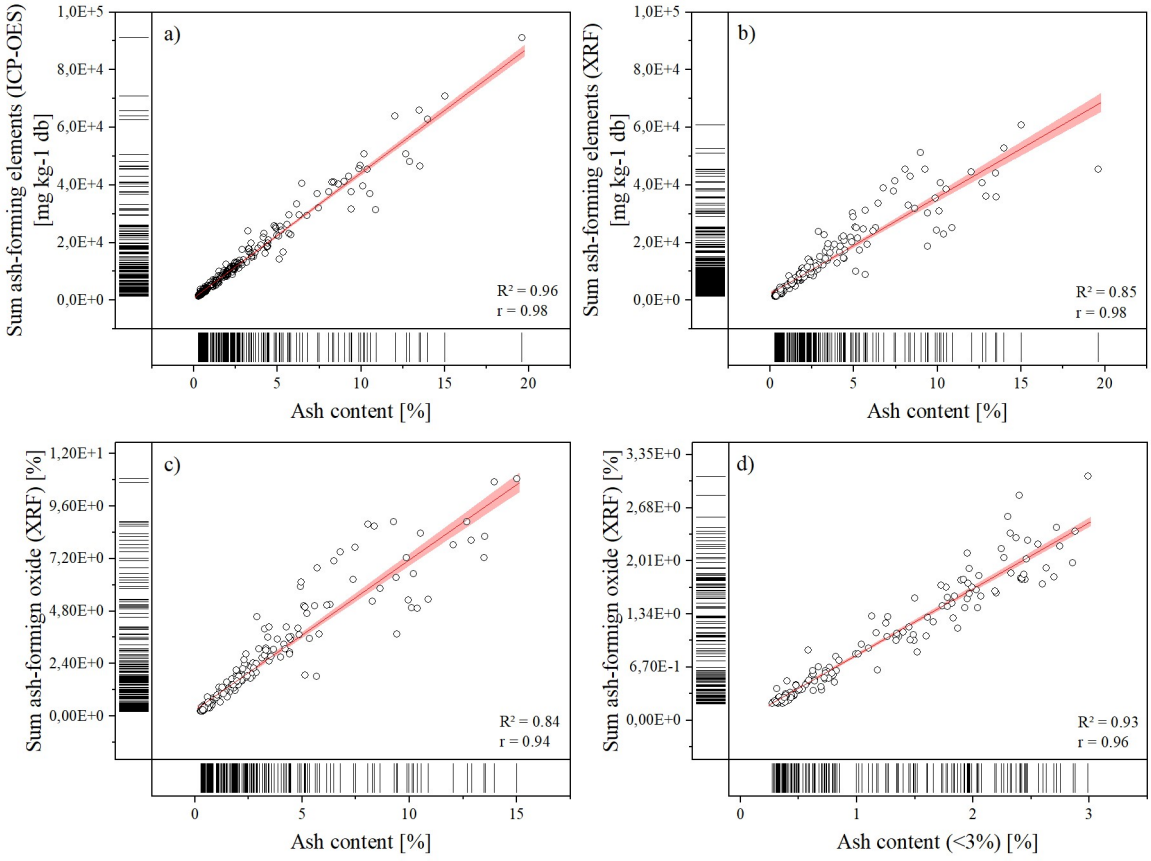

Figure 11: Linear regression and correlation of the ash content and the summed of ash-forming elements (Si, Mg, P, S, Ca, K, Na, Al, Fe, Cl, Mn and Ti) measured with ICP-OES (a) (n = 207), measured with ED-XRF (b) (n=207), the sum of ash-forming oxides (SiO_2, CaO, K_2O, P_2O_5, Al_2O_3, MgO, Fe_2O_3, SO_3, Na_2O, MnO, and TiO_2) measured with ED-XRF (c) (n = 207), and ash content (< 3 %) measured with ED-XRF (d) (n = 143); Endriss et al. (2022) [121].

4.4 Possible Future of Rapid Analysis of Solid Biofuels

As already addressed in Chapter 4.3, a technique for rapid quality assessment always raises the question of the required accuracy of the measurements. For an initial estimation or pre-sorting, approximate orders of quantities are sufficient. In contrast, the values should be significantly more precise for monitoring legal limit values (such as those of the AltholzV).

Moreover, especially with such heterogeneous materials as solid biofuels, various sources of error have a distinctly more substantial impact on the measurement results than the precision of the ED-XRF device.

Other XRF-based devices could also be considered depending on the analytical tasks. For example, WD-XRF is suitable for more precise analysis, with higher detection sensitivity for trace elements. Some studies already investigated the usability of WD-XRF for different elements in solid biofuels and show satisfactory results [89,90,133]. However, wavelength-dispersive devices are generally considerably more expensive than energy-dispersive devices, time-consuming, and less flexible [48]. Nevertheless, due to their higher precision, these devices could be of interest to the waste wood sector, where various legal limit values could be measured quickly and reliably, which could be investigated in further research.

Should economic factors be of higher priority for operators than measurement accuracy, "simpler" and more cost-effective ED-XRF instruments such as handheld or portable ED-XRF analysers could also be considered. The first evaluation of a portable device was published in the report by ENDRISS ET AL. (2024) and showed promising results [134]. Other studies have also demonstrated the possibility of determining various elements of solid biofuels satisfactorily using different XRF analysers, like portable ED-XRF [61,85] and handheld ED-XRF [86–88]. However, these devices should also be evaluated in detail in further work and examined for their specific suitability and precision for analysing different elements of solid biofuels.

The ED-XRF examined in this study could be compared directly with other devices (or device specifications) from the XRF field and with different measurement techniques suitable for rapid analysis of the chemical composition of solid biofuels. The review article by ENDRISS ET AL. (2024) [36] has compiled various methods that could be considered for this (Table 2).

Table 2: Alternatives for the rapid analysis of the chemical composition of solid biofuels from the literature [36]. (ME: Minor elements described in ISO 17225-1; TE: Trace elements described in ISO 17225-1).

Method	Target Elements	Ref
TGA	C, H, O	[135]
UV-VIS	K	[136]
NIR	N, Cl, K, S	[137–140]
XRF	ME & TE	[61,68,71,85,88,122, 133,141–143]
LIBS	ME & TE (ex Cl, S)	[37–41]
LA-ICP-MS	ME & TE	[42,43]

Gravimetric, ultraviolet-visible spectrophotometry (UV-VIS) and near-infrared (NIR) methods are limited in terms of the range of elements that can be measured for the quality assessment of solid biofuels compared to XRF. LA-ICP-MS, on the other hand, can theoretically determine most elements [43] but appears to be very complex and less suitable for use in rapid quality control in CHPs.

In addition to XRF, LIBS technology, in particular, appears to be very promising for the rapid analysis of the chemical composition of solid biofuels [37–41]. According to a study by WESTOVER (2013), Al, Ca, Fe, Mg, Mn, P, K, Na, and Si could be measured satisfactorily compared to the reference method [40]. Additionally, a study by LU ET AL. (2019) demonstrated the feasibility of LIBS in rapidly determining the gross calorific value, carbon content, volatile matter content and ash content in wood pellets [38]. However, as with XRF analysis, the samples for LIBS must also be prepared due to homogenisation, particle size effects and the influence of water content [37].

There is still a lack of LIBS evaluations for the rapid determination of the chemical composition of solid biofuels in typical “real-life” samples. However, LIBS is very promising for solid biofuels and should be investigated further.

In addition to the elemental composition, other important fuel properties are relevant for comprehensive quality control. These include, in addition to the physical parameters (water content, ash content and calorific value), other mechanical properties such as bulk density, particle size distribution, content of fines, etc [17].

A system should use combined analysis principles to determine all or at least several quality parameters. For example, a combination of XRF (elemental composition [126], ash content [121]) and NIR (Water content, N) [140] and a calculated calorific value [17] could cover almost every relevant parameter (excluding mechanical parameters). However, other

combinations, such as microwave sensors (water content, bulk density [36]) and XRF (ash content and elemental composition), are also possible. The review article by ENDRISS ET AL (2024) [36] shows various options for determining different quality parameters. This means a device can be put together depending on the analytical tasks, or a series of measurements with different stations can be implemented.

Figure 12 presents the past and present analysis in biomass-fired CHP plants, together with a possible future for quality control of solid biofuels based on the results of this thesis and the actual literature.

Besides organoleptic quality control, the only standardly measured quality parameter on-site in CHP is usually the water content (using the simplified oven drying method according to ISO 18134-2 [26]). In particular, medium-sized plants (about 200 kW – 50 MW), rarely employ advanced analytics, such as the rapid measurement technology already on the market (e.g. NIR) or external laboratories. In particular, the latter is used either in the waste wood sector or when there is concern about delivering consistently poor materials.

The development of various rapid measurement techniques could soon lead to the standardised integration of further quality parameters such as calorific value, ash content or even elemental composition. A wide range of fuel properties could also be analysed, either specialised by individual devices such as XRF or by combining different measurement techniques (in a single device or, e.g. a measurement container).

New research shows a growing interest in semi-automatic or online measurements of various parameters [23,134,140,144].

Since these technologies are either still in development or not yet cost-effective for medium-sized wood-fired CHPs [23], ED-XRF emerges as a viable solution for rapid quality control of solid biofuels. This enables fair fuel trade and improved fuel quality by sanctioning or rejecting low-grade fuels and pre-sorting different qualities, ultimately reducing maintenance costs, optimising plant operation, and lowering pollutant emissions.

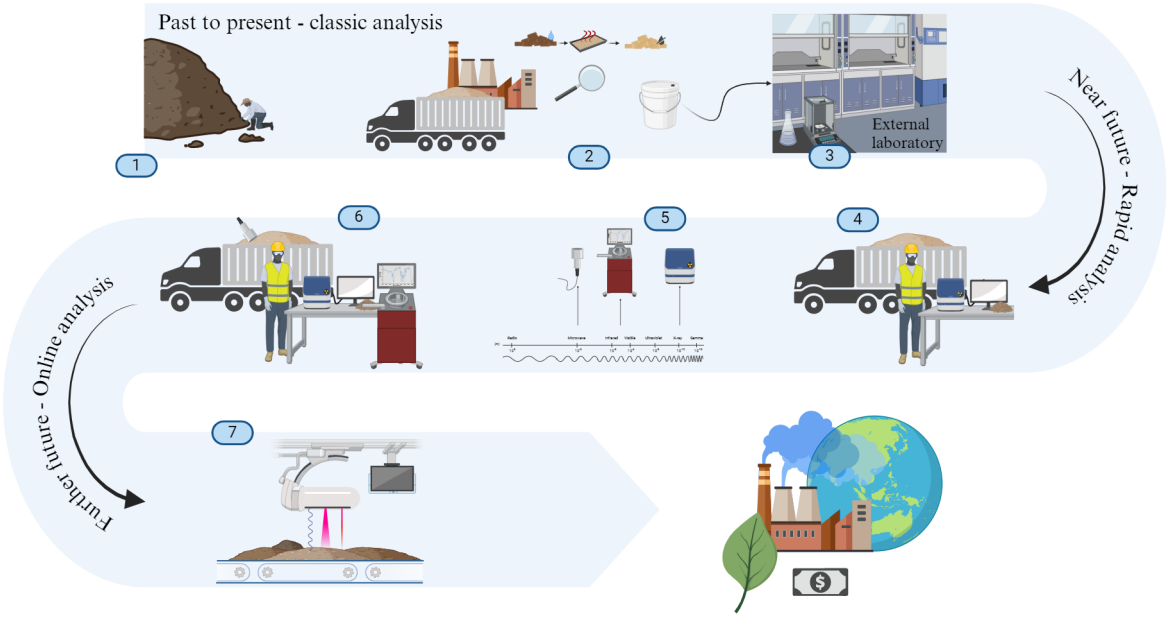

Figure 12: Visualisation of quality monitoring in biomass-fired CHP from the past to a possible future. 1: Organoleptic testing only; 2: On-site testing of the water content with oven drying; 3: Not standard, but samples are taken for special quality controls and sent to external laboratories for analyses such as ash content, calorific value, chemical composition, etc; 4: Rapid analysing methods implemented for special analytical tasks; 5: More rapid analytical devices for different quality parameters are available; 6: Combined rapid analytical methods enable holistic quality control; 7: On-line measurement devices will be implemented.

5 Conclusion and Perspectives

After identifying key quality parameters for solid biofuels, this thesis demonstrates the importance of elemental composition in quality control and the potential of XRF for rapid chemical analysis. It further explores the applications and limitations of ED-XRF for the practical assessment of solid biofuels.

Overall, XRF is suitable for analysing this sector's minor and trace elements. Elements such as Mg, Al, Si, P, K, Ca, Cr, Mn, Fe, Cu, Zn, and Pb can be recommended compared to the standardised method ICP-OES. However, the measurability of elements such as S, Cl, Ti, and Ni suggests the calibration's need for refinement or specialisation. While measuring Na, As, and Cd remains difficult, further investigations with spiked samples or another statistical investigation (like survival curves) could show their potential usability. In addition, the devices are constantly evolving and will probably soon be able to measure Na and even up to C.

Nevertheless, various impacts should be considered when measuring solid biofuels using XRF to ensure optimal measurability. The X-rays do not affect the solid biofuel samples noticeably. Still, special attention should be given to the phosphorus concentrations in samples with high levels of mineral contaminants due to potential interferences.

The samples cannot yet be measured directly but must be partially prepared. Grinding the samples to ≤ 250 µm seemed optimal based on the material's homogenisation, the avoidance of the grain-size-effect, the benefit-to-expense ratio and the penetration depth. It is also recommended to dry the sample to ≤ 10 % wt. to avoid the influence of the water content on the measurement results. This extends the analysis time, but the actual measurement can be reduced to 60 seconds per sample without noticeable loss in accuracy (caution is advised with elements near the detection limit). Despite the required sample preparation time, the analysis with ED-XRF is distinctly faster than in an external laboratory and can be carried out on-site.

It turned out that empirical calibration does not improve the analytical precision of all elements to the same extent as the reference method. While most elements benefited from the calibration (Na, P, Ca, Fe, Ni, Cu, Cd, and Pb), others became less accurately measurable (Mg, S, Cl, K, and Zn) than the reference method. Accordingly, future work should examine the potential for improvement in measurability by calibrating individual elements or element groups (e.g. essential elements of the AltholzV) instead of a holistic calibration. However, a general improvement could be achieved through calibration.

Therefore, ED-XRF is usable for quality assessment during delivery, for various quality parameters, like fuel indices estimations, ash content determination, pre-sorting, fair fuel

trading by taking different elemental concentrations into fuel supply contracts, and probably for limit value monitoring in the waste wood sector for almost all elements (excl. Hg and F).
Future research should combine XRF with other measuring principles, such as NIR, microwave, or others, to include different fuel properties, such as water content and calorific value, for a more comprehensive, rapid assessment of the fuels.
Following the technical demonstration of the technology's suitability, the next crucial step is establishing an incentive for procurement. This can be achieved using a return-on-investment analysis and highlighting the potential for reducing maintenance costs through fuel quality. In further work, the holistic life costs of an XRF analysis for a CHP (including investment costs, variable costs, etc.) should be compared with the potential cost savings through quality control of the supplied fuels.

6 References

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Appendix I

Publication 1

Analytical Methods for the Rapid Determination of Solid Biofuel Quality

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Analytical Methods for the Rapid Determination of Solid Biofuel Quality

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Fuel properties of solid biofuels are essential aspects for the energy-efficient and low-emission operation of biomass heat and power plants. Hence, fuel quality parameters are often defined and used for pricing in supply contracts. To simplify and accelerate analytical approaches, rapid analysis devices are required to determine fuel properties such as water- and ash content, calorific value, and chemical composition on-site. This article gives an overview about available technologies and, if applicable, their current state of use as rapid analysis devices for solid biofuels.

Keywords: Analytical chemistry, Chemical composition, Fuel properties, Rapid measurement, Solid biofuels

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1 Introduction

Fuel quality is an essential aspect for the efficient operation of wood-fired heat and power plants. [1, 2]. In addition to anthropogenic influences (e.g., due to contamination of fuels with impurities such as gravel or mineral soil during harvesting or from storage places), many parameters such as plant species, plant assortment, harvesting date, storage duration or secondary fuel processing steps are decisive for the fuel quality of solid biofuels, often leading to very heterogeneous fuel products [3, 4].

The quality of solid biofuels is mainly defined by physical properties (e.g., water content, ash content, calorific value, particle size distribution, etc.) and by their chemical composition. These parameters strongly affect different aspects of plant operation, such as failure-free and energy-efficient combustion, emission behaviour, and costs. For instance, high ash contents and unsuitable chemical composition of fuels can increase slagging, fouling, and corrosion in furnaces and heat exchangers [5]. The calorific value mainly depends on the combustible components carbon (C) and hydrogen (H) and directly affects the heat output of the plants [6]. The generation of air pollutants such as CO, NO_x, or total particulate matter (TPM) is also directly linked to fuel quality, e.g., to the fuel water content or the concentration of certain chemical elements in fuels such as N or K [7].

Incomplete combustion can also lead to various emissions. For example, this can result in high concentrations of carbon monoxide, hydrocarbons, polycyclic aromatic hydrocarbons, tar, and soot emissions. A reduction of these emissions can be achieved by an optimised combustion process. This ensures that the combustion gases and air are well mixed. In modern heat and power plants with optimised process control, the concentrations of unburned pollutants can be reduced to values close to zero. However, soot and tar, in particular, are primarily influenced by combustion processes and less by the ingredients of the fuels, therefore, they are only mentioned here for the purpose of completeness [6].

To ensure low-emission combustion, low-wear, and energy-efficient operation of wood-fired combustion systems, it is therefore highly recommended to know the exact fuel properties before the material is fed into the boiler, besides optimised process regulation. This knowledge enables the control unit of the plant as well as the operational staff to adjust combustion parameters such as air flow or grate cooling to optimise the system. Consequently, fuel trades often include relevant fuel properties measured before or directly after unloading of the fuels at the plant. Thereby, fuel costs are a significant part of the plant operating costs.

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Disturbances further increase these during plant operation caused by low fuel qualities, resulting in high maintenance costs or standstills. Consequently, defined physical and chemical fuel properties are often part of the pricing in supply contracts between plant operators and fuel suppliers [1, 2].

Suitable and reliable analytical methods have been standardised via various committees for most physical and chemical fuel quality parameters of solid biofuels. In Germany, DIN 51700 [8] provides an overview about different standards for determining multiple fuel parameters for all solid fuels (including peat or coal), in general. Separate standards for solid biofuels have been developed internationally in ISO 17225-1 et sqq. [9].

The conventional analytical procedure at a wood-fired heat and power plant is visualised in Fig. 1 (left). Water content is usually analysed either on-site or in an external analytical laboratory shortly after delivery. This is usually done by drying the fuels until weight constancy in a drying cabinet. If fuel parameters other than water content are to be determined, fuel samples are usually prepared for analysis in an external lab that applies different physical and chemical principles. The results are summed up, validated, and reported back to the client. This time-consuming and cost-intensive process might be simplified using new and rapid analytical pathways on-site, as shown in Fig. 1 (right). Fuels can be analysed directly after delivery or after some minor sample preparation (e.g., milling) at the plant by the operational staff.

In the foreseeable future, standardised analytical methods will remain the reference methods for solid biofuels. However, these methods are usually only suitable for measurements in an accredited laboratory as many of them are very expensive as well as labour and time-consuming and often require highly trained laboratory employees. In contrast, new and easily applicable, rapid fuel determination technologies that might be operated directly at heat and power plants or at biomass terminals to optimise the above-outlined procedure must be affordable, robust and easy to handle by non-laboratory employees.

The following article is primarily concerned with analytical methods for woody fuels. However, the analytical methods described below can also be applied to other solid biofuels. Therefore, in the following this article refers to solid biofuels, even though it mainly focuses on woody fuels.

Measuring the fuel parameters of solid biofuels is a complex process involving a wide range of physical and chemical properties. The selection of suitable analytical methods is crucial for obtaining accurate and reliable results. For some parameters, standardised methods are available, while for others, non-standardised methods are used that vary considerably in terms of accuracy and reliability.

Currently, a wide range of analytical methods are used to measure the physical and chemical fuel parameters of solid biofuels. These methods are available on the market or are

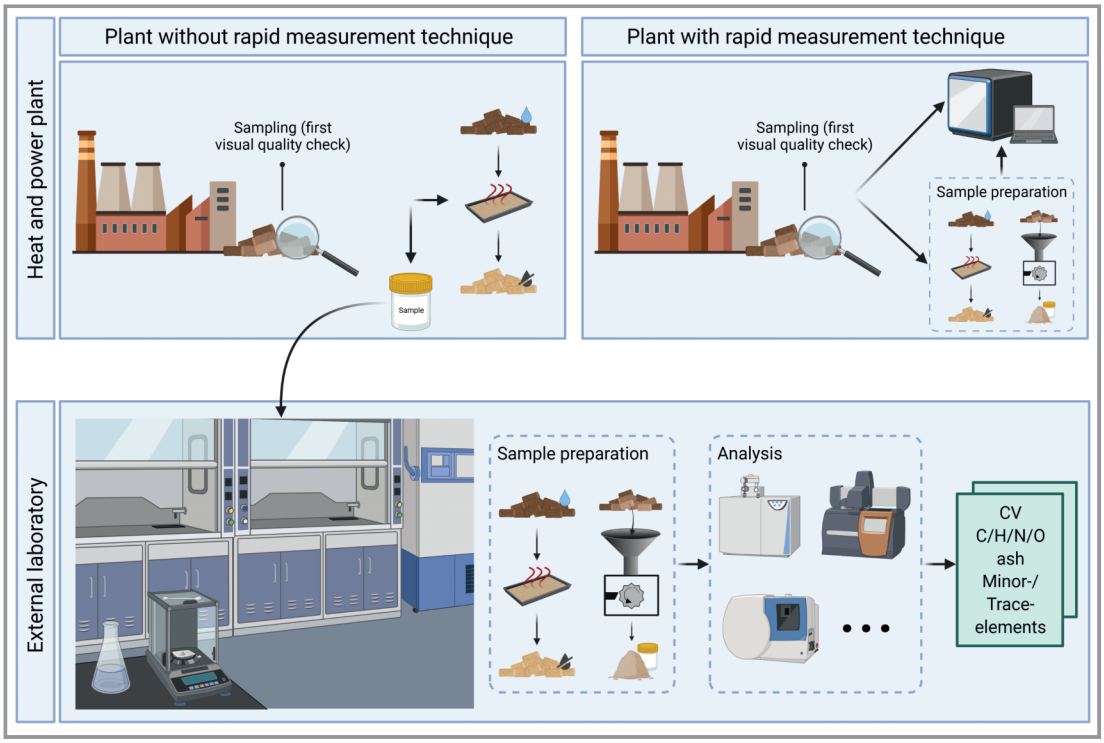

Figure 1. Comparison of the conventional analytical pathway without a rapid measurement technique (left) and a new analytical pathway with a rapid measurement technique (right) (*Q*: calorific value, C/H/N/O: carbon/hydrogen/nitrogen/oxygen).

subject of ongoing research. In this article, the different analytical principles are comprehensively summarised, described and discussed. The assessment of the different analytical principles is required to identify the most suitable methods for specific fuel properties.

The objectives of this work are twofold: firstly, to provide a scientific base for the development of rapid analysis techniques in the future, and secondly, to provide information for operators of medium sized (about 200 kW–50 MW) biomass fired heating and power plants. It is expected that as the development of rapid analysis techniques progresses, these techniques will also become increasingly attractive for smaller plants.

2 Solid Biofuel Properties

A wide variety of relevant solid biofuel properties affect plant operation, including plant efficiency, maintenance, gaseous and particulate emissions, as well as ash composition and its slagging behaviour. The typical concentrations of the relevant parameters in solid biofuels range from ppb to percent as specified in ISO 17255-1 and is shown in Fig. 2 [9].

2.1 Main Fuel Properties

Tab. 1 summarises the effects of the three main physical fuel properties, water content, ash content, and calorific value and gives the respective standard analysis methods. These parameters are deemed highly relevant for combustion and can significantly impact plant lifetime, operation efficiency, and pollutant formation [10]. Other relevant physical fuel properties such as particle size distribution, particle shape or mechanical durability (e.g., for pellets or briquettes) and the respective rapid determination techniques such as image analysis were not considered during this study [11].

The water content (M in %), mainly influences the calorific value and storability [10, 18–20]. Thereby, M is highly relevant for combustion quality as it directly influences the temperatures in the combustion chamber. Cooling may cause incomplete combustion leading to elevated gaseous emissions (especially CO and C_{org}) and increased TPM emissions [10]. Solid biofuels always contain a certain amount of water ranging from <10 to >65 %. M varies significantly depending on the type of feedstock (species, assortment, etc.), time of harvest, storage technique, and storage duration. Thereby, M is the sum of the surface moisture and intrinsic water stored in cell walls, cell cavities, and spaces between cells [21].

The ash content (A in %, dry basis) varies between <0.1 and >10 % [9]. It describes the amount of (mainly) mineral matter remaining after complete combustion at 550 °C in a

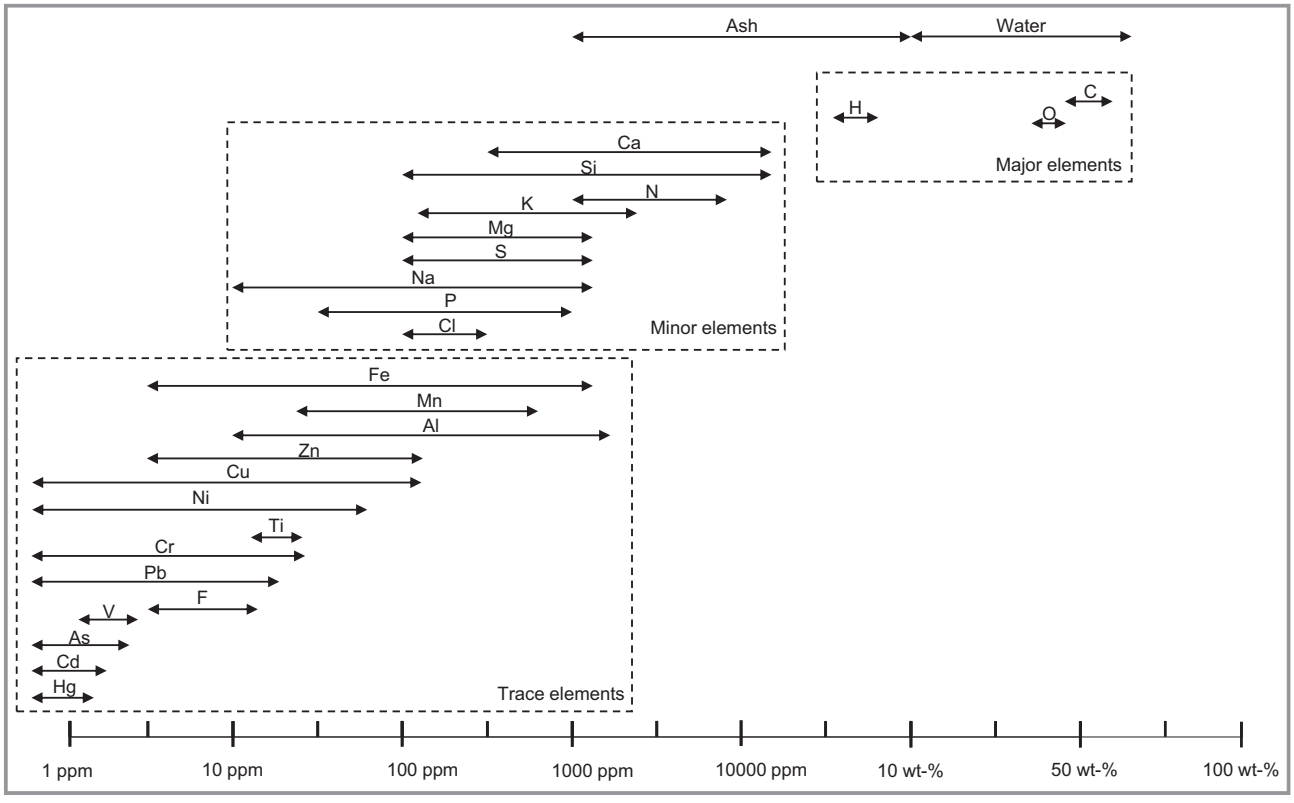

Figure 2. Expected concentrations (wf, excluding water) of different fuel quality parameters in solid biofuels based on ISO 17255-1 [9].

Table 1. Main fuel properties of solid biofuels and their effects on combustion, including the respective standard analysis methods [12] (TPM: total particulate matter).

Parameter	Effects	Standard analysis
Water content *M*	Calorific value, storability, fuel mass, combustion temperature, CO emission, TPM emission	ISO 18134-1-3 [13–15]
Ash content *A*	TPM emissions (dust), residue formation and exploitation, calorific value	ISO 18122 [16]
Calorific value *Q*	The energy content of the fuel, energy density, plant dimensioning	ISO 18125 [17]

muffle furnace according to ISO 18122 [16]. The main ash-forming elements are calcium (Ca), silicon (Si), potassium (K), sodium (Na), chlorine (Cl), and magnesium (Mg). Thereby, high shares of K and Si in fuels lower ash melting temperatures and can lead to sintering or slag formation (see Sect. 2.2). Biomass ashes also contain a large proportion of trace elements (mostly heavy metals [22]) originating from the fuel or external impurities [21]. The contents of individual heavy metals determine their usability, e.g., as fertilizers in agriculture or forestry [23] and have, among other aspects, an impact on corrosion or can impact human health [19, 24–26]. Overall, *A* impacts the technical dimensioning and design of a combustion plant and pollutant emissions during combustion [27]. High *A* can be caused by contamination, mineral residues, high shares of foliage/needles, and a high bark content [24].

The energy released during the combustion is reported as calorific value (Q in $MJ\,kg^{-1}$). It is specified by wood fuels in gross calorific value with typically 19.4–22.7 $MJ\,kg^{-1}$ (on dry basis) and net calorific value with 18.4–21.3 $MJ\,kg^{-1}$ (on dry basis). Other biomass fuels can differ from these values [9]. Combustion plants can be controlled more precisely, and the required fuel amount can be estimated more accurately if Q is known [19].

2.2 Chemical Composition

The major elements of biomass are carbon (C), hydrogen (H), and oxygen (O). Depending on the type of fuel, nitrogen (N), chloride (Cl), and sulfur (S) may also be present in concentrations >1 % (dry basis) and thus belong to the major elements [6].

Minor elements are decisive for ash formation and have various effects on combustion and the formation of air pollutants (Tab. 2). For instance, Na and K contribute to a decrease in the ash melting point and to an increase in mineral aerosol formation during combustion, leading to increased TPM emissions. Due to the formation of alkali chlorides, they can also be significantly involved in corrosion processes [28]. Undesirable compounds such as hydrogen chloride (HCl) can be formed from the bound chlorine. These compounds have a corrosive effect on the plant [29, 30]. N and S in the fuel are also decisive for the formation of nitrogen oxides (NO_X) and sulfur dioxide (SO_2)

Table 2. Selected and minor elements in solid biofuels and their effects on combustion, including the respective standard analysis methods [6, 12, 32, 33].

Element	Effect	Standard analysis
Calcium (Ca)	Ash melting behaviour, ash retention of pollutants, ash utilisation, Particulate emissions	ISO 16967 [34]
Chlorine (Cl)	Emissions of HCl and organohalogen compounds (e.g., PCDD/F), high-temperature chlorine corrosion, particulate emissions	ISO 16994 [35]
Potassium (K)	Ash melting behaviour, ash utilisation, high-temperature corrosion, particle emissions	ISO 16967 [34]
Magnesium (Mg)	Ash melting behaviour, ash retention of pollutants, ash utilisation, particle emissions	ISO 16967 [34]
Nitrogen (N)	Ash utilisation, NO_x- und N_2O-emissions	ISO 16948 [36]
Sodium (Na)	Ash melting behaviour, ash utilisation, particle emissions	ISO 16967 [34]
Phosphorous (P)	Ash retention of pollutants, ash utilisation, particle emissions	ISO 16967 [34]
Sulfur (S)	SO_x emissions, high-temperature corrosion, particle emissions	ISO 16994 [35]
Silicon (Si)	Ash melting, ash utilisation, particle emissions	ISO 16967 [34]

emissions [31]. Other elements can have positive effects on pollutant formation. For instance, high shares of Ca in fuels are known to bind S in the ash and, thus, reduce SO_x emissions [32].

Most of the trace elements in solid biofuels are heavy metals. Trace elements also have an impact on particulate matter emissions. High concentrations of arsenic (As), cadmium (Cd), zinc (Zn), and lead (Pb) in the fuel considerably increase the toxicity of particulate matter or fly ash separated by cyclones or other filtering units [32]. However, some heavy metals can also positively affect combustion, e.g., by catalytic effects during PCDD/F-formation [21].

3 Research Method

The literature screening approach has three main phases (Fig. 3). In the first step, several databases potentially containing relevant literature, were identified. Subsequently, these were scanned for different keywords and article types. In a second step, criteria were defined for the selection of articles, which were then reviewed in a third step and represent the base for the discussion.

4 Analysis of Solid Biofuels

This section presents various principles and techniques that are typically used or potentially applicable for solid biofuel analysis.

4.1 Wet Chemical Methods

Wet chemical methods are analytical procedures from classical chemistry [37, 38]. Gravimetry and volumetry dominate this field because of their simplicity and reliability [38–40]. In gravimetric methods, samples are analysed based on weighing [38].

Different gravimetric methods can measure M of solid biofuels. These include infrared drying (only small sample quantities, fast measurement: 7–48 min) [41, 42], microwave drying (fast measurement: 2–20 min but often not suitable for determining M because of inhomogeneous microwave fields) [41], and freeze-drying (drying of frozen samples by sublimation in a vacuum, slow measurement) [43].

The most commonly used method is drying a sample in an oven or drying cabinet. This method is standardised by ISO 18134-1 to -3 [13–15] for solid biofuels. A sample is dried at 105 ± 2 °C until its mass remains constant. Due to the standardisation and, thus reproducibility, this method is

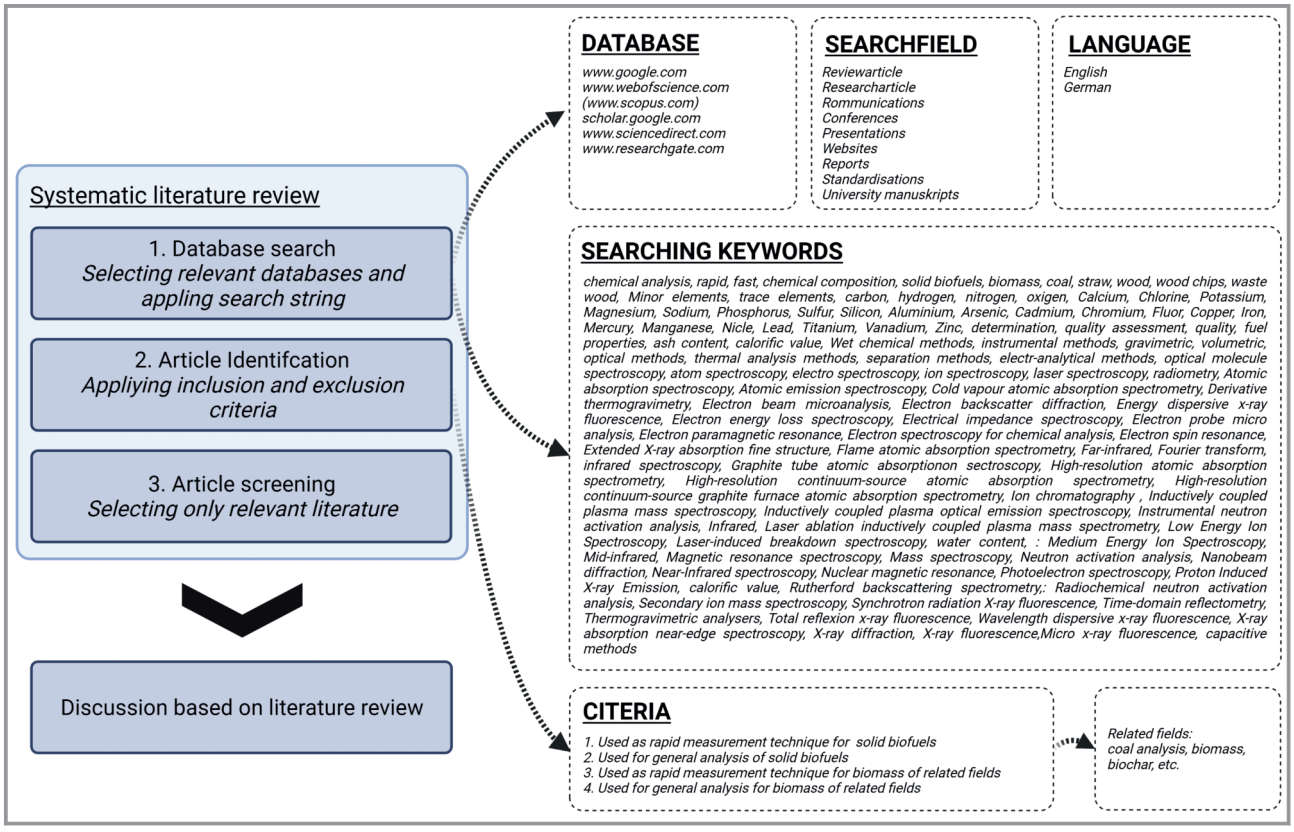

Figure 3. Systematic literature review method.

often used as a reference method for investigations of the accuracy of other or new analysis methods [44–52]. Besides the standardised method at 105 °C, the drying process can also be carried out at lower (e.g., 80 °C) or higher (e.g., 130 °C) temperatures. The drying times are considerably longer at lower temperatures, whereas the outgassing of volatile components (oils, fats, terpenes, and resins) can affect the results at higher temperatures. Softwoods with many essential oils can especially lose volatile components already at 60 °C [53, 54].

Ash content (*A*) of solid biofuels can be determined by a thermogravimetric method, while analysis of *A* is standardised at 550 °C for solid biofuels in a muffle furnace (ISO 18122) [16]. Losses occur at higher temperatures, especially with highly volatile elements (e.g., Na or K). This volatilisation begins at about 500 °C. The outgassing of CO_2 from carbonates starts at 600 °C [55, 56]. A study showed that carbonates are no longer present in the ash at 815 °C [57]. There are losses due to the outgassing of SO_2 from metal sulfides, Cl from chlorides, or water from silicates [58]. Different methods for the thermogravimetric determination of *A* with different temperatures and heating rates depend on the analytical question [16, 55–59].

Several gravimetric methods (e.g., infrared drying) are already well studied today as rapid measurement techniques for determining *M* of solid biofuels. Different studies show good reproducibility of results that are comparable to the standardized method [60, 61]. Saldarriaga et al. investigated the fast determination of various solid biofuel properties (*M, A, Q*, C/H/N/O) using thermogravimetric analysers (TGA) and derivative thermogravimetry (DTG) and calculating tools [62].

The other sub-group in the field of wet chemical methods is volumetry. It is based on the principle of volume measurement. A reaction partner (known concentration) of the analyte is added stepwise to the reagent solution (solution of the analyte) until the reaction is completed. This equilibrium state is determined using a suitable indicator. The concentration of the analyte can be calculated via the consumed amount of the measuring solution [38, 40]. Different volumetric analysis methods determine *M* of a sample, such as the Karl Fischer titration [41, 60]. The Kjeldahl method is a wet analytical process for determining N in solid biofuels [37].

4.2 Instrumental Methods

4.2.1 Optical Methods

Optical methods are based on the interaction of a sample with electromagnetic radiation of different wavelengths. The range is from about 0.005–1.4 Å (gamma rays) to longer than one meter in the nuclear magnetic resonance [38–40, 63]. The optical methods are differentiated into various sub-areas.

Molecular Spectroscopy

Molecular spectroscopy detects interactions between electromagnetic radiation and molecular bonds. The molecules are stimulated by absorption, reflection, and scattering. Molecule rotations and oscillations only occur through absorption [38–40].

UV/Vis spectroscopy is an electron spectroscopy method divided into spectrophotometry and fluorimetry. The physical principle is based on the absorption of specific wavelengths by the sample of visible or ultraviolet light. UV/Vis radiation can also cause oscillations and rotations of molecules. At wavelengths of 100–200 nm, a vacuum is required for the analysis to prevent absorption of radiation by atmospheric oxygen. A study by Mühlenberg et al. investigates the possibility of a rapid potassium determination using a UV/Vis method that shows promising results [64]. UV/Vis methods are used for different biomass properties, like the quantification of lignin [65, 66] or ingredients [67–69].

In infrared (IR) applications, the basic principle is the absorption of polychromatic IR radiation (e.g., by Nernst glower 1600 °C). The absorption of the radiation results in different mechanical oscillations of atoms or rotations of the molecules. These oscillations and rotation can change the dipole moment of the molecules. If the dipole moment does not change, then the oscillations are IR-inactive and cannot be analysed by IR-spectroscopy [38–40]. In far-infrared (FIR), the primary radiation is absorbed by molecular rotations, whereas the absorption occurs by stimulation of the molecular vibrations in mid-infrared (MIR). Molecules with wavelengths of 2500–800 nm are stimulated in near-infrared spectroscopy. CH-, OH-, and NH-bonds can thus be detected and quantified. IR has a large measurement depth (approx. 0.5 mm to several cm) [38–40].

Fourier transform infrared spectroscopy (FTIR) is a special type of infrared spectroscopy. The Fourier transformation's mathematical model allows the recorded interferogram to be evaluated and output as a spectrum. It offers faster measurements and a wider wavelength range of 10–400 cm^{-1} [38, 40]. The Fourier transformation can also be applied to many different basic physical principles like magnetic resonance spectroscopy and mass spectroscopy, and Raman spectroscopy [39].

Near-infrared spectroscopy (NIRS) is able to analyse different parameters like chemical compositions of lignin, α-cellulose, holocellulose, etc., in the analysis of biomass and related fields [70–85]. Due to the wide penetration depth into the sample and the particularly high sensitivity of the moisture measurement, NIRS is useful in the analysis of solid biofuels. Several studies have investigated the ability of NIRS to rapidly measure *M* [60, 61, 86–96], *A* [86–88, 91–97], and *Q* [86, 88, 91–96, 98, 99].

Different studies have investigated the usability of different IR spectroscopy methods and have determined different elemental compositions in solid biofuels. A study by Pitak et al. investigated the possibility of determining C, H, and N via line-scan near-infrared (NIR) hyperspectral image tech-

nology [100]. Mata-Sanchez et al. used NIR to detect Cl, S, and K [101]. FTIR coupled with partial least-squares regression is also used to determine *A* rapidly and different chemical elements like K, Ca, Mg, S, and Si. In this respect, the results of the study by Edmunds at al. show potential for future studies [102]. Various studies investigate the usability of IR methods to measure different parameters of solid biofuels like the carbon content or plastic contaminations [62–64, 72, 92–98]. Kip et al. evaluated the development of spectrometers and showed that they are increasingly robust and less susceptible to vibrations. This makes them especially suitable for heat and power plant analysers [103].

In contrast to IR, Raman spectroscopy uses excitation by monochromatic UV/Vis high-intensity radiation to provide scattering information. This method is a contrary analysis variant to IRS. Raman spectroscopy does not detect absorption spectra. Therefore, it can be used to measure IR-inactive molecules. The examination results in radiation emission because the electrons (without quantum leaps) oscillate at the same frequency as the primary radiation [38–40].

Raman spectroscopy is not directly suitable for determining the different quality parameters of solid biofuels, but it can also provide important information on biomass or related fields. For example, it is possible to classify wood using Raman spectroscopy [104]. Structural investigations are also possible with this method [79, 105–107].

In magnetic resonance spectroscopy (MRS), a sample is excited by long-wave electromagnetic radiation with two subareas: The electron spin resonance (ESR) exciting the electron spins with microwave radiation within a magnetic field. In ESR (or EPR = electron paramagnetic resonance), the radicals of organic and inorganic compounds can be investigated. The condition for this type of analysis is that they are paramagnetic. In nuclear magnetic resonance (NMR), the atomic spin is excited by radio waves to investigate the structure of organic and biomolecules. Inorganic substances can also be analysed structurally and quantitatively [38–40].

NMR can be an analytical method in coal analysis to determine various parameters, including *M* in fuels [79, 108–115]. Biomass analysis by NMR has been a research tool for many years [116–118]. Some studies have carried out biofuel investigations using NMR technology, like structural investigation about the lignin content, etc. [116, 117, 119].

For the rapid measurement of *M* in biomass and solid biofuels, methods based on microwaves are also usable [60, 80, 120–122]. The high measurement depth of radio-frequency technologies is useful for the rapid determination of *M* in large samples [123–125].

Time-domain reflectometry (TDR) is based on the principle of radar technology. In this method, the speed of electromagnetic radiation propagation through a sample is measured. For materials with a high dielectric constant, the deceleration of the radiation is more significant; thus, the speed of propagation is lower. This method is suitable for determining *M* in solid biofuels [60, 126–128].

In atomic spectroscopy, very high energy is required to excite the electrons in the inner atomic shells. Stimulation sources for this method are combustion flames, direct current continuous arcs, high voltage sparks, plasma torches, glow discharge, laser stimulation, hollow cathode lamps, or X-ray tubes [38–40, 129].

Atomic Spectroscopy

In atomic absorption spectroscopy (AAS), the sample is converted into free atoms and then stimulated by light from the UV/Vis spectrum using a hollow cathode lamp (HCL). For the atomisation of a sample, flames (flame AAS, e.g., acetylene/air mixture up to 2500 K) or fast and high electrical heating in a graphite furnace (GF-AAS, 3000 K) are suitable. Some devices use a combination of both methods as a hybrid approach. The detection limit is lower than in flame AAS due to the longer residence time of the sample in the plasma state in the graphite tube. With GF-AAS, solid samples can be measured directly without digestion [38, 40]. The primary sources of measurement errors in AAS are interferences. In classical AAS, each element needs a separate HCL for the excitation. AAS allows many variants for the optimal adaptation of an analytical problem. Most elements of the periodic table can be detected qualitatively and quantitatively. Thus, the detection limits are very low [38–40, 130].

HR-CS-AAS (high-resolution continuum-source atomic absorption spectrometry) methods enable high-resolution multi-element determinations. The excitation of the free atoms uses a continuously radiating xenon short-arc lamp, which covers a large spectral range of 190–900 nm [131–134]. The hybrid generation (HG-AAS) and cold-vapour techniques (CV-AAS) are comparatively simple measuring methods for a few elements (tin (Sn), arsenic (As), antimony (An), bismuth (Bi), selenium (Se), tellurium (Te), and germanium (Ge)) with lower detection limits [135].

In biomass analysis and related fields, AAS is an established method in elemental analysis [79, 132–134, 136–139]. AAS is often used to analyse elemental composition in solid biofuels [140–143]. Different methods of AAS have been standardised for different solid fuels [144–146]. The standardised analysis methods are suitable for coal products, solid biofuels, and solid secondary fuels. Special standards for solid biofuels exist for GF-AAS (ISO 16968), CV-AAS (ISO 12846) and HG-AAS (ISO 17378-2) [147–149]. A review of graphite furnace atomic absorption spectrometry shows the possibility of rapid analysis of various environmental elements and other solid samples by using HR CS GF-AAS [150].

During atomic emission spectroscopy (AES), the atoms are examined by electromagnetic radiation that can change the energy levels of electrons in the atom shells. When the electrons relax to the ground state, they emit characteristic

radiation, which is detected in atomic emission spectroscopy. In AES, different stimulation types exist like flames, electric sparks, arcs, plasma, glow discharge, laser. The temperature of the stimulation source has a significant influence on sensitivity, detection, and determination limits. For AES, the most common type of examination currently used is plasma. There are different types of plasma generation, but the most popular method is the inductively coupled plasma (ICP). With an ICP-OES (inductively coupled plasma optical emission spectroscopy), a maximum of 60 elements can be concurrently determined simultaneously [38–40].

AES is a common method for analysing different solid samples like biomass or materials from related fields [79, 136]. ICP-OES is the most used type in the analysis of trace elements in solid biofuels [22, 140, 151–154]. This procedure has also been standardised for solid biofuels in ISO 16968 and ISO 16967 [34, 147]. Laser excitation can be used for a rapid determination of different solid biofuel properties. These methods overlap with laser spectroscopy (see section laser spectroscopy).

X-Ray Spectroscopy

In X-ray spectroscopy, the sample is excited with high-energy electromagnetic radiation. The interactions between radiation and a sample are divided into primary and secondary processes. Primary processes are represented by the absorption of radiation and, thus, photoionization of the atom. The emission of X-rays and Auger electrons is part of the secondary processes. The resulting spectra show that self-radiation and not the retardation spectra are the primary processes [38–40, 155].

X-ray fluorescence analysis (XRF) is based on the principle of emitting fluorescence radiation when X-rays (high-energy electromagnetic radiation 0.1–100 keV) excite atoms [38–40, 155]. A study by Mosley et al. analysed over 30 elements for the K- and L-series and showed a correlation between the wavenumber (the characteristic X-ray lines) and the proton number [156]. The qualitative analysis of XRF is based on this knowledge.

Studies have shown that a higher atomic number leads to lower detection limits for the elements due to a better fluorescence output [38, 155, 157]. Theoretically, 83 elements can be measured by XRF [40]. There are different types of X-ray spectroscopy. Dispersion is ensured by using crystal grating in wavelength dispersive spectrometers (WD-XRF). The radiation wavelengths are scanned by Bragg reflection on the variable crystal (periodic grating) [158, 159]. Energy dispersive spectrometers (ED-XRF) apply the polychromatic fluorescence radiation directly to a semiconductor detector allowing simultaneous analysis of many elements [38–40, 155]. The ED-XRF has lower resolution and higher detection limits, and significantly less energy consumption than the WD-XRF. Due to this energy efficiency and simpler design, ED-XRF is a cheaper alternative to the classical WD-XRF. However, WD-XRF has considerably better resolution with lower detection limits possible. Another special form of XRF is the total reflection XRF. It achieves lower detection limits than WD-XRF but is more complicated in sample preparation; it has a very low depth of penetration [40].

In the analysis of solid fuels, XRF was standardised to analyse various fuel ashes [160, 161]. X-ray fluorescence analysis is increasingly used for the analysis of the elemental composition of biomass or related fields [162–164] and rapid determination of elements in these sectors [79, 136, 157, 165–176]. X-ray methods are also useful for analysing the elemental composition in solid biofuels [140, 151, 177] and as a rapid measurement technique for such fuels [141, 173, 175, 176, 178–183]. One study reported a method for the analysis of fuel parameters (*M, A* and *Q*) based on qDXA-XRF linking [184].

Other analytical X-ray spectroscopy methods are important for the investigation of biomass and other solid fuels, concerning their composition and structure. X-ray diffraction (XRD) [143, 185, 186] and X-ray absorption analyses like extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge spectroscopy (XANES) are used for structural analysis of biomass, solid fuels, or other solid samples [79, 136, 163, 185, 187–189].

Electron Spectroscopy

Electron spectroscopy is not clearly defined as a principle, and it overlaps several other categories. The method group overlaps from the basic principle with X-ray spectroscopy. Here, the electrons are also removed from the atomic shell with electromagnetic radiation of different wavelengths, and their direct kinetic energy or secondary electron emission is detected. [63]. This allows qualitative and quantitative analyses. Local resolution measurements are also possible with electron spectroscopy [187]. Electron spectroscopy has several subgroups with individual specifications. The most popular methods are photoelectron spectroscopy (PES or ESCA), which excites a sample by UV radiation or X-rays. Auger spectroscopy is based on the Auger effect [190, 191], electron beam microanalysis (EBM), electron energy loss spectroscopy (EELS), and others [38–40]. Another kind of interaction is electron diffraction that offers structural analysis with different methods, e.g., electron backscatter diffraction (EBSD) and nanobeam diffraction (NBD) [187]. Different electron spectroscopy methods are used to analyse biomass or material from related fields for structural investigations, but they are not used to analyse fuel properties [75, 79, 186, 192].

In ion spectroscopy, similar processes occur as in electron microbeam spectroscopy: Ions are taken from their radiation source (gas discharge tube, liquid metal systems) by an extraction electrode and directed onto the sample. This leads to various interactions with the sample. There can be backscattering, striking out of atoms or groups of atoms, or displacement of atoms into the sample. There are different methods based on ion spectroscopy, e.g., low [medium]

energy ion spectroscopy (LEIS, MEIS), Rutherford backscattering spectrometry (RBS), or secondary ion mass spectroscopy (SIMS) [187]. Ion spectroscopy measures important structural information and investigates the surface chemical composition of biomass or related fields [193].

In laser spectroscopy, a sample is stimulated by high-energy, highly focused monochromatic light. The laser beam vaporises the sample, generating free atoms and ions. These can then be measured using analytical methods of atomic spectroscopy (AAS, AES, or MS). The free atoms can also be analysed directly using laser spectrometry. In laser spectrometry, the vaporised sample is irradiated with a laser. The high-energy light beam is defined based on the frequency of the resonance lines of the element to be determined. The light beam is either absorbed, or ionisation products are formed [38, 194].

Laser-based analysers are usable for biomass and related fields as well as for solid biofuels. Laser spectroscopy methods are useable for rapid measurements. An important variant in this field, to determine trace elements in solid biofuels, is laser-induced breakdown spectroscopy (LIBS). This method has already been researched several times for analysing different parameters like *A, Q*, and trace elements of coal, ashes and biomass [79, 136, 175, 176, 195–203]. Various studies show the value of LIBS systems for rapid measurement of defined fuel properties of solid biofuels, excluding *M* [177, 204–210]. Another suitable laser-based method for the rapid analysis of solid biofuels is the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Different studies show the possibility to measure trace elements in solid samples, including solid biofuels near the ppm range [79, 136, 151, 162, 199]. A review shows the market and research of different portable and handheld LIBS systems today [211]. Another review shows different analytical methods for different solid fuels, all laser-based technology [212].

Radiometric Analysis

Radiometric analysis methods are classified into different subgroups. The analysis of the natural radioactivity of elements in a sample is the first subgroup. The second is the analysis by activation of individual components of a sample by irradiation. The activation analysis is usually performed with neutrons (neutron activation analysis NAA). Conclusions can be drawn about the sample elements based on the emitted rays caused by the decay. At the same time, the amount of radiation is directly proportional to the concentration of the elements. A distinction can be made between non-destructive instrumental neutron activation analysis (INAA) and radiochemical neutron activation analysis (RNAA) in which a chemical separation is performed; thus, the sensitivity can be significantly improved [38–40, 213].

Another variant is the prompt gamma radiation activation analysis. In this method, the gamma rays during activation are measured. In principle, this method can be used to determine each element of the periodic table. A further modification of the principle is the prompt fast thermal neutron analysis [38, 40, 214, 215].

The third group is the tracer method. Here, the sample is activated by adding a precisely defined amount of radioactive substance. The radiometric analysis methods are in the ppb/ppt range and applicable for the extreme trace range [38]. In addition to the methods of radiometry mentioned so far, there is also neutron depth profiling. In contrast to the other techniques, this method represents a near-surface analysis technique [79]. In solid fuel analysis, INAA is mostly used in coal elemental analysis [79, 136, 198, 216]. However, other studies have investigated the trace elements of biomass, including wood [217–219].

The other methods in this category use the interaction of the sample with electromagnetic radiation as a physical analysis principle. In contrast, mass spectrometry (MS) uses particle radiation (electron, ion radiation, etc.) for ionisation. For this purpose, the sample is turned into ionised gases. These ionised particles are passed from the ion source through a capacitor with an applied magnetic field. This filter ensures that all particles coming out of the filter have the same speed. Afterwards, the filtered particles enter a further magnetic field in which the Lorentz force deflects them in a semicircle onto a detector. The centripetal force on the particles and separate them by their mass number [38, 39, 220].

Depending on the type of instrument, qualitative and quantitative analyses of inorganic and organic components, even complex matrices, can be determined. Furthermore, organic and inorganic compounds can be structurally investigated, and surface analyses can be carried out to determine isotope ratios of the elements. The exact atomic masses, ionisation, formation, and dissociation energies can also be determined [38, 220]. The individual devices in mass spectroscopy are differentiated primarily according to the type of ionisation and analyser. Gross prepared a selection guide for the suitable ionisation process for different samples [220]. Mass spectrometers are also combined with separation methods. This is described in more detail in Sect. 4.2.3.

Mass spectrometry is usable for many different samples, including biomass and related fields like coal analysis [79, 136]. ICP-MS is also used for trace elemental analysis in solid biofuels [140, 180]. A procedure for determining trace elements using ICP-MS has been standardised by DIN 22022-7 for various fuels, including solid biofuels [221]. There are also many combination opportunities with other analysis methods with mass spectroscopy.

4.2.2 Thermal Analysis Methods

Thermal analysis methods detect the physical and chemical properties of a sample as a function of temperature. In these methods, a sample is heated and cooled down again using a defined temperature program. The result of thermal analysis is a thermogram that provides information about the physical and chemical properties [38, 40, 222]. In the field

of solid biofuels, thermal analysis methods are often used to determine *M* and *A* (see Sect. 4.1). They also determine *Q* [223, 224]. For this purpose, the most widely used method is the bomb calorimeter. This method is defined for solid biofuels as a standard procedure in ISO 18125 [17]. The thermal method for determining the ash melting temperatures has also been standardised in ISO 21404 [225]. Thermogravimetric techniques are also a part of gravimetry principles and cannot be separated from them.

4.2.3 Separation Methods

Separation methods are used to select individual components of a sample to determine several substances in an analytical procedure or to perform more exact quantitative analyses by removing substances from the matrices that interfere with the parameter to be determined. Most separation methods require a supplementary detection method (e.g., spectroscopy) to provide a complete analytical procedure [38, 40]. Chromatography represents the largest subarea of separation methods. In this field, the sample is first dissolved in a mobile phase and passed over a stationary phase. The components of a sample interact with the stationary phase and are separated. Different spectroscopic methods (MS, UV/Vis, IR, AES, AAS, NMR, etc.) can be used for the analysis of the various components [222].

In the analysis of solid biofuels, chromatographic methods are used to analyse organic and inorganic components [22, 152, 153]. Among other things, ion chromatography was standardised in ISO 16994 for the determination of S and Cl of solid biofuels [35].

4.2.4 Electroanalytical Methods

Electroanalytical measuring methods describe interactions of a sample with electrical parameters. These methods range from simple devices, e.g., for the determination of *M*, to complex electrochemical analysers to determine qualitative and quantitative elemental compositions, phase compositions, structure information, etc. [60, 226, 227]. A detailed list of electroanalytical methods has been prepared by IUPAC [226].

Electroanalytical methods are often used as a rapid measurement technique for solid biofuels, especially for *M*. Capacitive analysis compares the dialectic properties of a material and water. Biomass and water have significantly different dielectric constants, and this method can rapidly determine, e.g., *M* in wood fuels [48, 228]. The capacitive analysis method was tested in various studies and confirmed the possibility of using it as a rapid measurement technique [60, 229, 230]. The capacitive methods also have different interferences like the dipole properties and polarisation effects of water [231], bulk density, layer thickness, grain size, ion conductivity, temperature, and the Maxwell-Wagner impact of the material, as well as the measuring frequency of the analysis [41]. Capacitive sensors are designed to be robust and powerful for onsite use at a power plant [232].

Another method for the rapid determination of *M* is electrical capacitance. There, the electrical resistance of the testing material is used as the basic principle [233–236]. This method is suitable for estimating *M* of bulk fuels (e.g., wood chips, logs). Since each type of biomass, such as different wood fuels, has different conductivities, the results must be calculated more precisely, and instruments require a suitable calibration. Many studies have investigated methods for solid biofuels [60, 234, 236]. The various interferences of this method are the temperature and high values for *M* [237, 238]. Another more complex analysis in the field of electrochemical methods is electrical impedance spectroscopy (EIS) [227]. One study determined the heartwood content in wood chips via this method [239].

4.3 Summarising Literature Review

The findings of Sect. 4.1 and 4.2 are summarised in Tab. 3. The results are subdivided into different sectors of applicability (solid biofuels, biomass, related fields). Furthermore, it is differentiated between general analysis (for example, in laboratories) and usability as a rapid measurement technique (on-site).

5 Discussion

Within the literature review presented in Sect. 4, a wide range of various analytical methods for solid biofuels in laboratories could be identified. Fig. 4 summarises methods that were generally considered applicable for the determination of one or more physical or chemical fuel properties. Up to date, only a few of these methods seem suitable for the rapid determination of solid biofuel properties, e.g., at biomass heat and power plants or at biomass terminals. The most promising methods that are already investigated as rapid determination devices are marked with * in Fig. 4.

As Sect. 3 indicated, analytical methods differ largely in terms of their applicability for solid biofuels in general, their current state of research and their usability as a rapid measurement technique (Tab. 3). The identified methods for the rapid determination of solid biofuels are shown in Tab. 4 regarding their ability to measure various fuel properties.

In most cases, a direct comparison of the measurement precision among studies was not possible, as studies varied widely in their methodological approach, e.g. regarding the selection of fuels or reference methods, sample preparation, and their measurement procedure in general. Still, valuable recommendations can be drawn from the literature review giving an outlook on future possibilities for on-site measurement. Thereby, the following section focuses mainly on the physical fuel properties *M, A*, and *Q* that were deemed most relevant for efficient plant operation (see Sect. 2), but

Table 3. Summary of recent studies displaying the state of the art in the science of different physical and chemical analysis methods for the determination of various fuel properties in solid biofuels or in related fields (excluding optical methods).

Fuel property	Rapid measurement technique for solid biofuels	Analysis of solid biofuels	Rapid measurement technique for biomass or related fields	Analysis of biomass or related fields
Gravimetric				
Water content	[60–62]	[22, 52, 60, 142, 174]		[41–43, 47]
Ash content	[62]	[22, 52, 142, 153, 174]		
Calorific value	[62]			
Elemental content	[62]			
Other parameters	[62, 240]	[174]		
Volumetric				
Water content		[60]		[41, 60]
Elemental content		[37]		
UV/Vis				
Elemental content	[64]			[67]
Other parameters		[66, 68]		[65, 68, 69]
Infrared spectroscopy				
Water content	[1, 60, 61, 86–96, 241, 242]		[80]	
Ash content	[1, 86–88, 91–97, 102]		[85]	
Calorific value	[1, 86, 88, 91–96, 98, 99]		[80, 83, 84]	
Elemental content	[100–102]			
Other parameters	[86–88, 96, 243–249]	[174, 250, 251]	[70–82]	[105, 250]
Raman spectroscopy				
Other parameters		[174]		[79, 104–107]
Microwaves/radio waves				
Water content	[60, 80, 120–125]			[80, 109, 120, 121]
Other parameter		[116, 117, 119]	[118]	[79, 108, 110–115]
Atom absorption spectroscopy				
Elemental content		[140–143]	[150]	[79, 132–134, 136–139]
Atom emission spectroscopy				
Elemental content		[22, 28, 140, 151–153, 162, 177]		[79, 136]
X-Ray spectroscopy				
Water content	[184]			
Ash content	[184]			
Calorific value	[184]			
Elemental content	[141, 173, 175, 176, 178–183]	[140, 151, 177]	[79, 136, 157, 165–171, 173–176]	[162–164, 172]
Other parameters		[143, 174, 186, 189]		[75, 79, 136, 163, 185, 188]
Electron/ion spectroscopy				
Other parameters				[75, 79, 186, 192, 193]

Table 3. Continued.

Fuel property	Rapid measurement technique for solid biofuels	Analysis of solid biofuels	Rapid measurement technique for biomass or related fields	Analysis of biomass or related fields
Laser spectroscopy				
Ash content	[207, 208, 210]		[79, 197]	
Calorific value	[207, 208, 210]		[79, 197, 202, 203]	
Elemental content	[177, 204–209]	[151]	[79, 136, 175, 176, 195–201]	[162]
Other parameters	[207–210]		[252]	
Radiometry				
Elemental content			[79, 136]	[198, 216–219]
Mass spectroscopy				
Elemental content	[177]	[140, 151, 180, 253]	[136, 195]	[79, 136, 162]
Other parameters				[72]
Thermal method				
Water content	[60–62]			[41, 60]
Ash content	[62]	[22, 52, 153]		
Calorific value	[62]	[52, 174, 224]		[223]
Elemental content	[62]			
Other parameters	[62]	[174]		
Electro-analytical measuring methods				
Water content	[60, 61, 229, 230, 234–236, 241, 254]	[46, 47, 60, 122, 255]	[44, 45, 127]	[51, 126, 128]
Other parameters		[239]		[227]

also on the rapid determination of the chemical composition, as this is an important aspect for the quality assessment of the fuel and the estimation of different plant reactions. However, they are still rather in the development stage compared to *M, A*, and *Q*.

If possible, application of the presented principles at biomass heat and power plants as rapid determination methods or in analytical laboratories as an alternative to international standard methods is discussed in terms of instrument precision, measured sample size, measurement duration, requirements for instrument calibration, required sample preparation, customer support or acquisition costs.

5.1 Water Content Determination

Currently, several well-investigated methods are available for the rapid determination of *M* in solid biofuels, such as capacitive measurement [60, 61, 230], TDR [60, 61, 126–128], electrical resistance [60, 61, 234, 236] infrared drying (gravimetric) [60, 256], NIRS [60, 86–96, 241, 242], microwave-, or radio wave methods [60, 80, 120–125]. Usually, most of these methods do not require any special sample preparation such as milling or grinding of the material and can be applied directly when fuels are delivered to the plant. Only devices based on infrared drying need homogenisation and comminution by milling the collected sample.

In particular, capacitive measurement, infrared drying and NIR spectroscopy have been investigated in detail in various studies in recent years [60, 61, 86–96, 241, 242]. They usually show medium to good results in terms of instrument precision compared to the reference method (ISO 18134-1 to -3) [13–15]. Often, they vary less than 20 % from the reference value [60, 256]. For the use of these devices, e.g., for fuel quality assessment, which is regularly carried out by the German chimney sweep craft as part of the prescribed fireplace inspection, VDI 4206 Sheet 4 gives detailed recommendations on the testing accuracy of the devices required for approval for this purpose [257]. Still, the precision of rapid devices must be considered lower compared to the international standard method in most cases. Thereby, various studies indicate that the best results are provided by NIRS or infrared drying [89, 241, 256].

Due to the wide penetration depth into the sample and the particularly high sensitivity of the moisture measurement, NIRS is especially useful in rapidly analysing *M* in

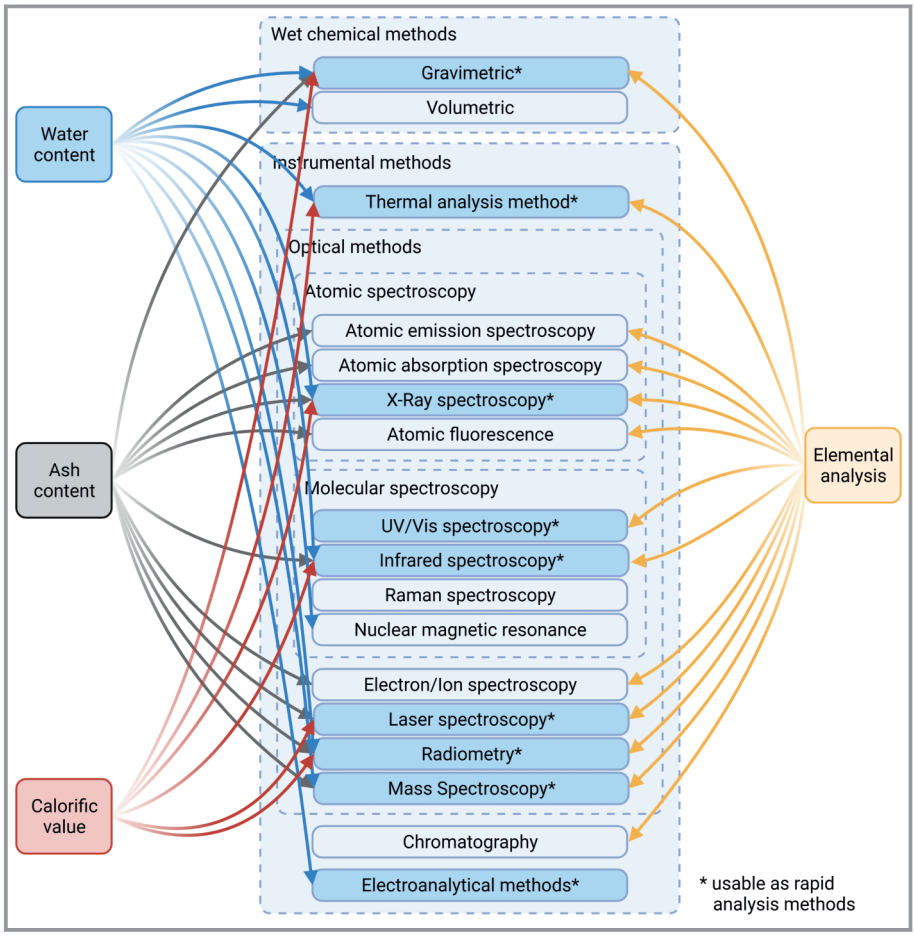

Figure 4. Identified suitable measurement principles to determine fuel quality parameters of solid biofuels (* indicates that the method is, at least in theory, also suitable as a rapid determination technique).

solid biofuels [60, 86–96, 241]. However, instruments require a good calibration to the respective biofuel for precise *M* determination using NIRS methods (likewise capacitive methods). Consequently, precision might differ in practice when e.g., a high share of different and/or heterogeneous biomass feedstocks are used at a combustion plant (e.g., a mixture of wood chips from forest residues, short rotation coppice or stem wood). Some of the market available instruments allow for individual calibration by the operator themselves, while for other devices, customer service is required. In addition, NIRS and capacitive methods are suitable for single measurements and can also be used for continuous material flow [60].

In the case of *M* determination by infrared drying, a precise measurement can be performed directly without the need for further calibration. However, most infrared drying devices are usually only available for the measurement of very small sample sizes (often a few grams), highlighting the necessity for representative sampling of larger fuel deliveries or an increased number of samples [60, 61, 256]. As such high precision in the homogenisation of the sample is hardly achievable in practice, infrared drying seems to be applicable only to a limited extent for the water content determination on-site a plant [61]. For application at biomass heat and power plants, suitable recommendations for representative sampling are given by ISO 18135 [258]. For small-scale applications, ISO 21945 offers recommendations for simplified sampling methods [259].

Overall, a high share of rapid determination devices for measuring *M* at biomass heat and power plants or at biomass terminals are already available on the market differing in portability (piercing lance, tabletop device, sensors installed in the biomass plant, etc.), precision, speed of measurement (few seconds to >45 min) and acquisition costs (ranging from less than 500 € to >10 000 €) [60, 61, 256]. Thereby, selecting a suitable technique depends on specific on-site requirements for *M* determination, usually resulting in a trade-off between low-cost devices with a rather medium to low precision (e.g., many capacitive devices) to high-cost instruments with a very high precision (some NIRS instruments).

In addition to the already existing rapid determination techniques, Torgrid and Fernandez-Cano investigated in a study the possibility of qDXA-XRF coupling to measure *M* of solid biofuels in about one minute. This approach also did not require any special sample preparation. The authors showed good results for this method, but the device needs further evaluation [184].

Table 4. Matrix for the evaluation of various methods for the rapid determination of different fuel properties of solid biofuels (*M*: water content; *A*: ash content; *Q*: calorific value; tec: trace elemental composition; × = full range of expected concentrations (Fig. 2) is measurable; o = the fuel property is fundamentally measurable but not the whole range of concentrations; – = not measurable).

Main fuel properties methods	*M*	*A*	*Q*	C	H	O	N	tec
Infrared drying	×	–	–	–	–	–	–	–
Microwave drying	×	–	–	–	–	–	–	–
TGA	×	×	o	o	o	o	o	–
DTG	×	×	o	o	o	o	o	–
NIRS	×	o	×	o	o	o	o	tec
ED-XRF	–	–	–	–	–	–	–	tec
WD-XRF	–	–	–	o	-	o	o	tec
qDXA-XRF	×	×	–	–	–	–	–	–
LIBS	o	×	×	×	×	×	×	tec
LA-ICP-MS	–	–	–	×	×	×	×	tec
TDR	×	–	–	–	–	–	–	–
Microwave	×	–	–	–	–	–	–	–
Capacitive method	×	–	–	–	–	–	–	–
Electrical resistance	×	–	–	–	–	–	–	–

Minor elements methods	Ca	Cl	K	Mg	Na	P	S	Si
UV-VIS	–	–	×	–	–	–	–	–
NIRS	–	o	o	–	–	–	o	–
ED XRF	×	×	×	×	×	×	×	×
WD XRF	×	×	×	×	×	×	×	×
LIBS	×	–	×	×	×	×	-	×
LA-ICP-MS	×	×	×	×	×	×	×	×

Trace elements methods	Al	As	Cd	Cr	Cu	F	Fe	Hg	Mn	Ni	Pb	Ti	V	Zn
ED XRF	×	×	×	×	×	o	×	×	×	×	×	×	×	×
WD XRF	×	×	×	×	×	×	×	×	×	×	×	×	×	×
LIBS	×	×	×	×	×	×	×	×	×	×	×	×	×	×
LA-ICP-MS	×	×	×	×	×	×	×	×	×	×	×	×	×	×

5.2 Ash Content and Calorific Value

Various approaches for the rapid determination of *A* and *Q* in solid biofuels were investigated in recent studies using, e.g., NIRS [1, 86–88, 91–97, 102], Laser applications [207, 208, 210], or X-ray method [184]. Most of the tested devices are already available on the market but mainly for other sectors and not especially for solid biofuels. Usually, measuring *A* and *Q* with NIRS requires no further sample preparation but similar to *M*, the instruments require a suitable calibration for various solid biofuels. However, in contrast to *M*, studies suggest that determination of *A* with NIRS often does not show satisfying results, indicating rather low instrument precisions [88, 92, 94, 96]. This is due to the fact that with NIRS, the ash content is usually not measured directly but rather by its ability to measure carbon bonds and then ash content can be calculated by chemometric methods.

In this context, the suitability of NIRS for determining ash content can be questioned due to the measurement principle used. However, various studies show good results for the ash content determination of biomass by hyperspectral imaging with PLS regression analysis [84, 85]. Lastander and Rhen achieved good results using this method for wood [91].

In contrast to *A*, studies often suggest that *Q* can be determined quite well using NIRS [86, 88, 91–96, 98, 99]. This approach utilises the high ability of NIRS to rapidly and precisely analyse various calorific value-determining bonds as well as *M* [91, 98].

Q (as received) can also be calculated using *M* applying empirical calibrations to fuel specific values for *Q* (on a dry basis) for preselected biomasses, e.g., for different wood species [1]. Following this approach, *Q* determination should be possible with every rapid determination method for *M* and is not limited to NIRS.

The study by Torgrid and Fernandez-Cano investigated (besides the determination of *M*) the possibility to rapidly determine *A* and *Q* with qDXA-XRF, which offers promising results [184]. Like the determination of water content by qDXA-XRF, further evaluations should be carried out for the determination of *A* and *Q*.

The laser-based method LIBS coupled with the chemometric approaches also showed first good results for determining *Q* and *A* in various studies [207, 208, 210]. However, this method would usually require a certain degree of sample preparation (e.g., drying and milling of the sample for homogenisation) to work. Thus, their application as a rapid determination technique can be questioned, and suitable on-site fuel processing pathways must be considered, as well. Nevertheless, this method seems promising because it is able to determine various fuel properties [207, 208, 210].

Overall, a reliable, precise and cost-efficient solution for rapid determination of *A* in solid biofuels is currently not available on the market and should be a focus of future research.

5.3 Chemical Composition

Many optical methods are theoretically available for the rapid determination of the elemental composition in solid biofuels. However, the different approaches are still in varying states of technology and are mostly the subject of research and not ready for the solid biofuels market. Up to date, most devices would still require a suitable calibration for solid biofuels. Moreover, rather extensive sample preparation is required in most cases. The various types of sample preparation needed for each analytical method (e.g., drying, milling, or pressing) varies between the methods and should be part of future research [140, 151, 178, 182, 210].

Consequently, these techniques can usually not be considered rapid determination methods. However, they are much faster and usually less labour-intensive than the standard methods and can be used on site at the biomass CHP plant. Available instruments include sensors installed in plants, benchtop instruments, portable instruments and in some cases handheld instruments. In most cases, the initial cost of these instruments for biomass CHP plants is quite high. Currently, the most promising methods to determine the chemical composition of solid biofuels are XRF [141, 173, 175, 176, 178–183] and LIBS [177, 204–210]. Various devices have already been evaluated in recent studies. For some elements these techniques have worked well, while for others the precision of the devices is not sufficient, which usually depends on the principle applied (Tab. 4).

These devices are suitable as a rapid determination system, as they can be used directly on site and provide a high proportion of measurements in a short time, but they require not only good homogenisation of the biomass, e.g., in the case of heterogeneous, coarse fuels such as wood chips or waste fuel, but also sufficient measures to ensure occupational safety, e.g., with regard to radiation. Currently, XRF devices are only used very sporadically in Germany in waste wood recycling plants, which integrate them into their processing procedures as a quality assurance system [260].

If a high proportion of ash forming elements such as Ca, Mg, K and Si are correctly measured with an optical device, an empirical estimation of the ash content could theoretically be possible. Thereby, XRF and LIBS might be interesting as these devices are rather suitable instruments to measure the different ash forming elements in solid biofuels. Afterwards, element concentrations need to be converted to oxides such as CaO, MgO or SiO_2. Ash content is then calculated by the sum of oxides. Also, the comparison of the sum of oxides in fuels measured by ICP-OES with the ash content is often used by laboratories as a quality measure to check whether the analysis of chemical elements in fuels has been carried out correctly. While XRF and LIBS methods are suitable for a wide range of the minor and trace elements mentioned in this article, other approaches are appropriate for a narrow range of specific elements.

For example, the element potassium in fuels has been successfully studied by novel precipitation reaction methods in combination with UV/Vis applications, e.g., from soil science, by Mühlenberger et al. [64]. This inexpensive and fast method might be most interesting for application at biomass terminals, e.g., to determine suitable feedstocks that are low in K for the production of high-quality pellets.

Pitak et al. investigated the possibility of determining C, H, and N via line-scan near-infrared (NIR) hyperspectral image technology [100], whereas Mata-Sanchez et al. used NIR to detect Cl, S, and K [101]. Furthermore, FTIR coupled with partial least-squares regression is used to determine the chemical elements like K, Ca, Mg, S, and Si in the study of Edmunds et al. [102]. The various studies show first promising trials, which should be part of future research.

As there are many low-cost NIRS sensors available, e.g., for product testing, these devices might be applied for solid biofuels, as well, e.g., in automatic fuel supply systems of the respective boiler or to select suitable feedstocks that are low in K, e.g., for pelletisation.

All these methods should be further researched and optimised for the analysis of solid biofuels. Especially low-cost

devices are interesting for rapid determination at biomass plants or biomass terminals as most high-end laboratory machines would be too expensive and too demanding regarding labour and training. Depending on the application, accurate measurement results in the low ppm range are less critical. For the acceptance of deliveries in biomass CHP plants, a quick estimation of the fuel quality is more important instead. In contrast, more emphasis is placed on the accuracy of the measurement results when monitoring limit values, e.g., in waste wood recycling plants. More research also needs to be performed for the optical analysis methods regarding influencing parameters originating from sample preparation (e.g. water content, degree of milling, homogenisation, etc.). Knowing the required amount of sample preparation may increase the precision of the measurements and accelerate the analytical process.

6 Conclusion

Currently, various methods are available on the market for the rapid determination of fuel parameters of solid biofuels, while others are part of research and development. These devices are mostly based on only one analytical method. Thus, they cannot simultaneously measure all required physical and chemical fuel parameters satisfactorily. In the case of water content, a high share of suitable devices is already available on the market for rapid determination at biomass plants or biomass terminals. However, most of these devices require sufficient calibration to the different feedstocks.

If the full range of fuel properties (fuel quality parameters) mentioned in this article is to be determined, it is essential to combine different analytical principles in order to develop an analytical tool for biomass CHP plants that covers all these properties. A high proportion of different combinations is possible, depending on whether the focus is on accuracy or cost. For example, the combination of NIRS and XRF might, in theory, be able to determine almost all physical and chemical fuel quality parameters. While NIRS can rather precisely determine *M* (and maybe K and N in fuels), XRF could be used to measure the chemical concentration of ash forming elements and the ash content (calculated). The calorific value can be determined by calculation based on the measuring results of NIRS. Therefore, a combination of different analytical methods should be part of further research.

For some analytical methods, e.g., many optical methods, appropriate sampling and sufficient sample preparation are essential to ensure the required degree of comminution, drying or homogeneity of the relatively small samples. Therefore, the requirements of sample preparation (including the requirements for representative on-site sampling) should be considered in future research and should also focus on the time required to analyse solid biofuels. Suitable sampling options from existing areas of application, e.g., in the combustion of coal in large power plants, could also be adapted for solid biomass.

The costs of different analytical devices for a rapid analysis (for various quality parameters) of solid biofuels can differ significantly and the financial resources that a biomass heat and power plant will spend for an analysis device are limited. As a result, a detailed economic analysis of different methods should be the subject of future research. Furthermore, future devices (single methods or combined) should find a suitable compromise between precision and cost-efficiency.

Overall, rapid determination of solid biofuels at biomass heat and power plants or at biomass terminals might, in theory, be an interesting solution to optimise the energetic use of biomass but needs to be further developed in terms of accurate, low-cost and easy to handle procedures.

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Symbols used

A	[%]	Ash content, i.e., the mass fraction of ash in fuels
M	[%]	water content, i.e., the mass fraction of H_2O in fuels
Q	[MJ kg^{-1}]	calorific value

Abbreviations

AAS	Atomic absorption spectroscopy
AES	Atomic emission spectroscopy
CV-AAS	Cold vapour atomic absorption spectrometry
DTG	Derivative thermogravimetry
EBM	Electron beam microanalysis
EBSD	Electron backscatter diffraction
ED-XRF	Energy dispersive X-ray fluorescence
EELS	Electron energy loss spectroscopy
EIS	Electrical impedance spectroscopy
EPMA	Electron probe micro analysis
EPR	Electron paramagnetic resonance
ESCA	Electron spectroscopy for chemical analysis
ESR	Electron spin resonance
EXAFS	Extended X-ray absorption fine structure
FAAS	Flame atomic absorption spectrometry
FIR	Far-infrared
FTIR	Fourier transform infrared spectroscopy
GT-AAS	Graphite tube atomic absorption spectroscopy
HCL	Hollow cathode lamp
HG-AAS	High-resolution atomic absorption spectrometry
HR-CS-AAS	High-resolution continuum-source atomic absorption spectrometry
HR-CS-GFAAS	High-resolution continuum-source graphite furnace atomic absorption spectrometry
IC	Ion chromatography
ICP-MS	Inductively coupled plasma mass spectroscopy
ICP-OES	Inductively coupled plasma optical emission spectroscopy
INNA	Instrumental neutron activation analysis
IR	Infrared
LA-ICP-MS	Laser ablation inductively coupled plasma mass spectrometry
LEIS	Low energy ion spectroscopy
LIBS	Laser-induced breakdown spectroscopy
MEIS	Medium energy ion spectroscopy
MID	Mid-infrared
MRS	Magnetic resonance spectroscopy
MS	Mass spectroscopy
NAA	Neutron activation analysis
NBD	Nanobeam diffraction
NIRS	Near-Infrared spectroscopy
NMR	Nuclear magnetic resonance
PES	Photoelectron spectroscopy
PIXE	Proton induced X-ray emission
qDXA	Quantitative dual-energy X-ray absorptiometry
RBS	Rutherford backscattering spectrometry
RNAA	Radiochemical neutron activation analysis
SIMS	Secondary ion mass spectroscopy
S-XRF	Synchrotron radiation X-ray fluorescence
TDR	Time-domain reflectometry
TGA	Thermogravimetric analysers
TPM	Total particulate matter
T-XRF	Total reflexion X-ray fluorescence
WD-XRF	Wavelength dispersive x-ray fluorescence
XANES	X-ray absorption near-edge spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
µ-XRF	Micro X-ray fluorescence

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Appendix II

Publication 2

Influence of Milling on Representative Sample Preparation for the Analysis of Trace Elements in Waste Wood

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ABSTRACT

In Germany, waste wood can be used in various ways. The main ones are recycling in particleboards and energy production if the quality is insufficient for material utilisation. For the decision of usage, it is necessary to determine the wood quality by measuring the concentrations of certain pollutants. If given legal limits are exceeded, energetic utilisation in heat and power plants is recommended.

Waste wood is a heterogeneous material. Therefore, special attention has to be given to the sample preparation in order to achieve representative analytical results. This article investigates whether the sample preparation according to ISO 14780 is also useable for a highly heterogeneous material such as waste wood or if a method with better homogenisation is needed. Furthermore, the effect of outliers on the interpretation of measurement results is considered.

For this purpose, two milling methods are compared concerning their homogenisation capability. The samples were milled to 4 mm and homogenised. From this total amount, one half was milled directly to 0.25 mm (full milled), while the other half was separated in a sample divider until 100 g of the sample remained (according to ISO 14780), which was milled to 0.25 mm (partial milled).

The results show that both milling procedures do not achieve a satisfactory homogenisation of the sample. However, with a sufficient number of measurements, limit value monitoring can still be carried out, as individual outliers are not decisive in whether a limit value is exceeded or not.

1. Introduction

In 2016, about 13,3 Mio m^3 of waste wood were produced in Germany considering imports and exports [1]. Currently, there are two main options to use waste wood: recycling in, e.g. chipboards and thermal use [2–4].

For Germany, the Circular Economy Act [5] introduces the European Directive 2008/98/EC [6] into german law and is, therefore, the most important legal framework for the use of waste wood. There, recycling is preferred to energetic use. According to the Waste Wood Ordinance (AltholzV) [7], waste wood is categorised into four categories. In category A1, waste wood that is only mechanically treated is collected. Waste wood classified in A2 can be painted, laminated, or treated in any other similar way. Waste wood in category A3 can contain halogen-containing coatings, and A4 material can also contain wood protection agents. The Waste Wood Ordinance specifies furthermore limits for heavy metals which have to be met for recycling, independent of the categories. In comparison, Table 1 presents also other limits given in standards. The DIN EN ISO 17225-4 addresses limits for wood fuels (wood chips from fresh wood and chemically untreated used wood) to be used in heating appliances and plants with similar attributes as small scale heating facilities. The DIN EN ISO 17225-9 addresses limits for wood fuels to be used in industrial furnaces.

Recycling waste wood reduces the requirement for freshly harvested, high-quality stem wood, which could potentially be used for other, higher-value products of the timber industry. In Germany (2016), approximately 30% of the material for chipboards is from recycled wood [1]. By recycling into chipboards, the bound CO_2 is not released into the atmosphere by degradation or combustion, so recycling increases carbon sequestration [10,11]. However, the main issue with recycling waste wood is its potential contamination with toxic substances, being mainly heavy metals, halogens, and halogenated hydrocarbons [12–14]. If pollutants were not removed from the waste wood stream, this would violate the Circular Economy Act.

Waste wood that cannot be used for recycling due to contamination can be used thermally. Energy production from solid biofuels is an

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Table 1
Comparison of various legal limits and typical element concentrations of waste wood [mg kg-1 d] (d = on dry basis).

Elements	Limit values for industrial use (AltholzV) [7]	*Wood chips classification I4 ISO 17225-9* [8]	Wood chips classification B ISO 17225-4 [9]
Arsenic	2	≤4	≤1
Lead	30	≤30	≤10
Cadmium	2	≤2.0	≤1
Chromium	30	≤30	≤10
Copper	20	≤50	≤10
Mercury	0.4	≤0.1	≤0,1
Chlorine	600	≤1000	≤500

important way to substitute the usage of fossil fuels for heat production in Germany [15]. In 2018, 171 TWh of heat was generated by renewable energy, whereas 66.3% was produced from solid biofuels [16]. Therefore, recycling and burning waste wood help to reduce fossil CO_2 emissions [17]. However, waste wood has to be burned in appropriate facilities, comprising suitable furnaces and air pollution control devices [18–21].

The problem with accurate identification and allocation to the waste wood classes is the material heterogeneity, which is due to the variety of different contaminations [22,23].

Currently, in Germany, the primary sorting of waste wood into batches for recycling or energetic use is based on pre-use of the feedstocks [24], whereby all coated or painted batches are burned and not considered for recycling [25]. A study by Schild and Cool (2021) shows that visual sorting of waste wood is not accurate enough to separate treated from untreated waste wood [22]. Misclassified waste wood can lead to wastage of recyclable resources that could be reused in the circular economy, or it can cause environmental harm by incorrect use of contaminated wood [23,26–28]. Therefore, chemical analysis is relevant for quality assessment and, based on that, reliable decisions concerning the appropriate use of waste wood. Many studies have already examined the concentrations of contaminants in waste wood [29–37]. Furthermore, an increasing amount of studies investigated the potential application of rapid chemical analysis technologies for the quality evaluation of the waste wood, mainly based on X-ray fluorescence and near-infrared analysis to accelerate the sorting process in biomass terminals or heat and power plants [23,29–31,34,35,38–44].

The first main source of error in the chemical analysis of all fuels is the sample collection. In case this is not taken representative, the following analysis results cannot represent the actual composition of the whole delivery [37]. Several studies compared the individual analysis steps (sample collection, sample preparation, instrumental analysis, data evaluation) and revealed the highest analysis error to occur during sample collection. Sample preparation is named as the second-largest source of error, while instrumental analysis accounted for a smaller proportion of the overall analysis error [45–47]. However, it has to be mentioned that the errors cannot be considered individually but propagate during the analysis process [37].

During sample preparation, especially the milling process significantly impacts the homogeneity and quality of the analytical results [48]. Especially for waste wood, as a highly heterogeneous material, representative sampling and sample preparation are crucial for meaningful results.

After a representative sample has been collected, it is essential to prepare it accurately to remain representative. According to the Waste Wood Ordinance, a sample of 500 g has to be produced using a dividing approach from the DIN 51701-3 “Testing of solid fuels - sampling and sample preparation”. Following this standard, a mixed sample of several kilograms has to be divided in different ways (dividing with the ripple divider, cone method, etc.) [49]. Afterwards, this sample is milled to a grain size of <2 mm and has to be taken for continuous elemental analysis [7].

The preparation of solid biofuels is described in ISO 14780 [50], where a sample of several kilograms is collected and milled in various steps (for further details, see section 2.2).

This study aims to investigate the impact of sample milling on the homogeneity of the sample and on the measurement results of the subsequent analysis, with a special focus on heavy metals. For this purpose, it is evaluated if the collection of a partial sample (in accordance with ISO 14780 [50]) generates comparable representativeness or if milling of the entire sample and the associated improvement on homogeneity is appropriate. In addition, the time needed for a complete milling process is to be quantified.

Furthermore, the article clarifies if eliminating outliers in the measurement results enhances the quality of the analytical result. In this case, single local extreme values, which are caused by impurities (e.g. colour particles, metal particles, etc.), are removed from the evaluation.

2. Methods and materials

2.1. Samples

The samples were acquired from several wood-fired heat and power plants throughout Germany. They were sorted according to the german waste wood directive [7]. This is mainly based on a visual assessment of the delivered fuels. After collection, the samples were packed in airtight buckets (20 L) and sent to the University of Applied Sciences Rottenburg for further analysis. The sample preparation procedure (described in Section 2.2) commenced when the samples were received.

This article concentrates on representative sample milling; therefore, the sampling is generally considered representative. However, whether the samples taken at the plants were genuinely representative of the entire delivery cannot be assessed.

Samples of the following classes were obtained: one A1 sample, two samples of an A1 and A2 wood mixture (A2a, A2b), one blended sample with A1, A2, and A3 wood (A3), and two samples of A4 (A4a, A4b).

For illustration, Fig. 1 shows A2a and A4 waste wood with different contaminations. As can be seen, both materials are very inhomogeneous and contain besides wood also plastics, metal, and glass. The A2a wood

Fig. 1. Examples of the used samples for A1-2a (top) and A4 (bottom) with different impurities.

also contains pieces of wood that should be classified as A3 or even A4.

2.2. Sample preparation

All samples were dried in a drying oven (UNP 700 Memmert Ltd.) at 105 °C until water-free condition and milled with a Fritsch Pulverisette 19 with a rotor of hardened steel (typical impurities based on the rotor, are, e.g. Cr, Ni, and Cd) and fixed knives from tungsten carbide. Before milling, the samples were visually checked, and impurities that could damage the mill (e.g. metalware, glass, etc.) were sorted out.

The samples (A1, A2a, A2b, A3) were milled to 4 mm and afterwards homogenised by stirring the sample for several minutes. Furthermore, the sample was divided in a riffle divider (HAVER RT 12,5) and mixed several times again, until the sample was finally divided into two equal parts. Due to the requirement of ISO 16968 for a particle size of <1 mm [51] and common laboratory practice being <0.25 mm, the samples in this study were also milled to an analysis grain size of <0.25 mm [20,48,52,53].

One of the parts was milled directly to 0.25 mm (full milled), while the other part was separated in the sample divider until 100 g of the sample remained (according to ISO 14780), which was then milled to 0.25 mm (partial milled), visualised in Fig. 2.

Two samples of A4 were available. One of the A4 samples (A4a) was prepared according to the full milled method, and the other (A4b) according to the partial milled method. All samples and the preparation methods are displayed in Table 2.

Each sample prepared was separated into four equal parts using the sample divider. Before the aqua regia digestion for the ICP-OES measurement (section 2.3), the water content was checked for each sample, using the rapid water content determination device MA150C from Sartorius Weighing Technology GmbH, Goettingen, Germany. Afterwards, each part was measured four times with the ICP-OES. Therefore, one sample yields 16 measurement results.

2.3. Chemical analysis

The samples were prepared with an aqua regia microwave digestion and measured with an ICP-OES according to the ISO 16968 [51]. For this, 0.4 g of milled wood was treated with 1 ml of 30% H_2O_2 (for Synthesis, Roth), 4 ml of 69% HNO_3 (Rotipuran Supra, Roth), and 9 ml of 35% HCl (Rotipuran Supra, Roth). Then, digestion was completed in a microwave (Multiwave GO, Anton Paar) and diluted to 50 ml with twice distilled water. Analysis was conducted using an ICP-OES (Spectroblue FMX 26, Spectro).

Table 2
Test matrix of the different waste wood samples.

Sample	Full milled	Partial milled
A1	✓	✓
A2a	✓	✓
A2b	✓	✓
A3	✓	✓
A4a	✓	
A4b		✓

2.4. Data evaluation

The elements As, Cd, Cr, Cu, Pb mentioned in the waste wood directive [7] were examined. Additionally, titanium and barium were considered. These two elements are often contained in wood paint and coatings [54,55]. Therefore, Titanium and Barium are good markers for homogenisation and are thus prone to a high amount of contamination. The two elements are not included in the preparation equipment, so external influences are unlikely.

For the investigation of significant differences between the waste wood classes in general, an ANOVA with a post-hoc test of LSD (least significant difference) and a Scheffe test is performed.

To investigate significant differences in the average element contents in samples after "full milled" and "partial milled" sample preparation by using a *t*-test (alpha = 0,05).

Testing of the fulfilment of the prerequisite for normally distributed populations with Shapiro-Wilk test; in case of significant difference: *U* test by Mann-Whitney as an alternative.

The homogeneity of the samples was investigated by using the relative standard deviation.

For the investigation of the influence of outliers, the samples in the results and discussion section are first considered with all values and then cleaned up from the outliers. The outliers were identified according to John W. Tukey's 1.5 IQR rule. This indicates that a value is considered an outlier when it exceeds the interquartile range by a factor of 1.5 [56,

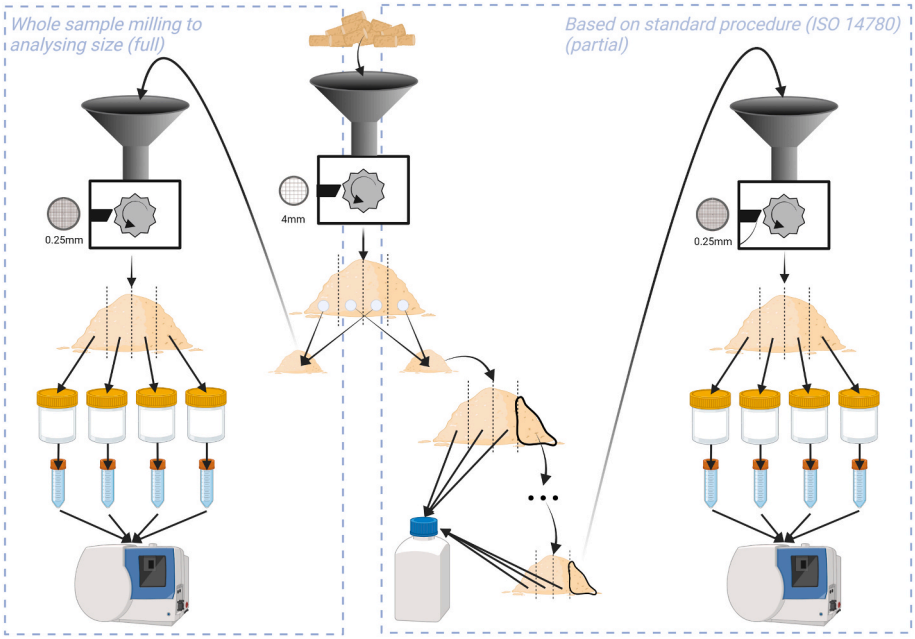

Fig. 2. Sample preparation on the left: full sample milling method; on the right: partial sample milling method.

57].

3. Results and discussion

In the following, the impact of sample milling on measurement results and the homogenisation of the sample are presented and discussed. A clear difference was generally revealed in the amount of time needed for sample milling. While the "full milled" method in this study required more than 5 h, the "partially milled" process was completed after about 30 min. A longer sample preparation time results in higher costs for the client.

3.1. Homogenisation markers – titanium and barium

In Fig. 3, on the left side, the barium content is illustrated. Substantial amounts can be found in all four feedstocks depending on the sorting quality. For A4, it is important to note that different to the other samples, the "full milled" and "partial milled" samples are not from the same origin.

Furthermore, the overall ranges of measurement results for each feedstock and element vary in some cases between the "fully milled" and the "partially milled" samples. This suggests that the first sample division after grinding to <4 mm may increase the heterogeneity between the following treatments. It is expected that the range of the "full milled" samples should encompass the range of the "partially milled" samples.

In Fig. 3, on the right side, the titanium concentration is shown. The A2a and A4 samples have also outliers. The outliers are mainly found in the "full milled" samples. As titanium is the main ingredient of white paint, it should not be found in high concentrations in A1.

Both homogenisation markers show similar results. As expected, the A4 declared wood has the highest concentrations, while the A1 feedstocks have the lowest concentration distinctly ($p < 0.001$). The markers concentrations (Fig. 3) and the visual check (Fig. 1) show paint impurities in the A2 and A3 samples (A2a to A3 $p = 0{,}989$). Additionally, the results do not reveal differences between the Ti and Ba concentrations of the A2 and A3 samples.

The homogeneity markers demonstrate a distinctly higher value scattering with increasing waste wood class. This is mainly due to the considerably increased amount of impurities and the resulting inhomogeneity of the upper waste wood classes. This indicates that the higher the waste wood classes, the more difficult it is creating a representative sample due to the increase in heterogeneity.

3.2. Heavy metals

In Fig. 4, results from all samples are shown for As, Cd, Cr, Cu, and Pb. The dotted horizontal line in the five diagrams gives the respective limit, provided in the German waste wood directive [7]. These elements are typical impurities that should be increasingly present in the higher waste wood classes due to sprayed coatings, paintings and wood preservatives [54,58]. E.g. a study by Huron et al. (2017) showed that Cr and Cu mainly originate from the chemical treatment of the impregnated wood [55]. Since the contaminations can result in selectively high concentrations of the respective elements, these elements can also be considered as "homogenisation markers".

As mentioned for barium and titanium, the overall ranges for each feedstock and element vary in some cases between "fully milled" and "partially milled" samples, also for the heavy metals.

The legal ***arsenic*** limit for recycling waste wood in Germany is 2 (mg kg-1 d).

Since arsenic is rarely used in wood preservatives or paintings anymore, the low concentrations in the A3 and A4 waste wood are expected [54,58]. Different from expectation, the content is highest in the A1 sample ($p < 0.001$) and surpasses the legal limit by a factor of 2.5. The origin of these high concentrations could not be clarified. Potentially this is due to old wood preservatives or paintings [54], which should not be included in A1 declared waste wood. In general, the different samples do not show high scattering values over all classes for arsenic.

The legal ***cadmium*** limit for recycling waste wood in Germany is 2

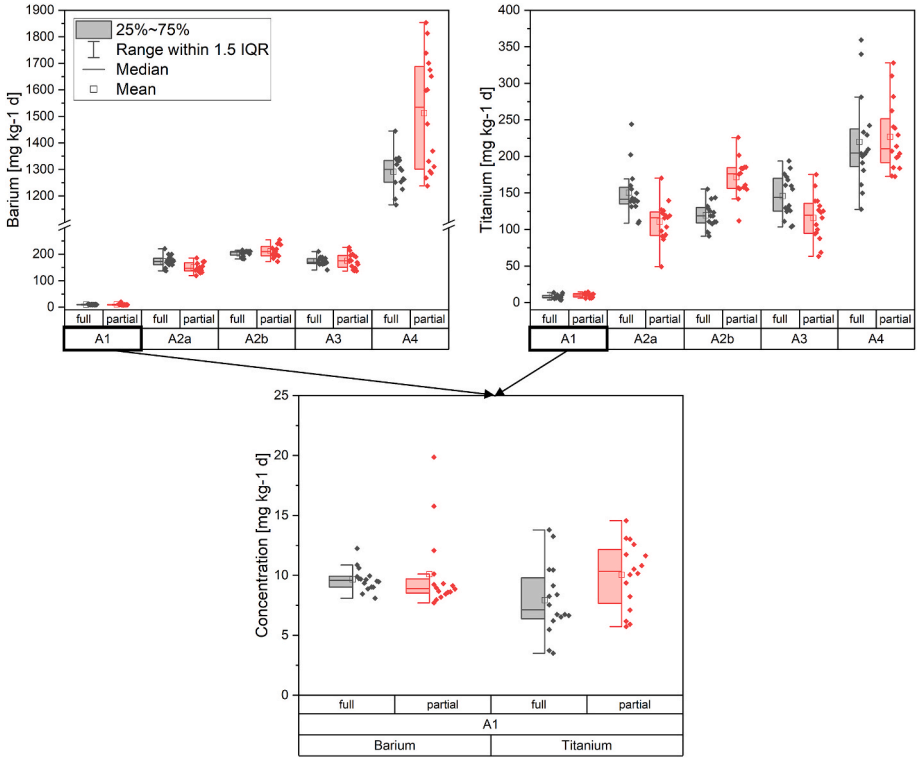

Fig. 3. Barium and titanium content (A1, A1-2a, A1-2b, A1-3, A4) split in "full milled" and "partial milled" (n = 16), (IQR = interquartile range), (d = on dry basis).

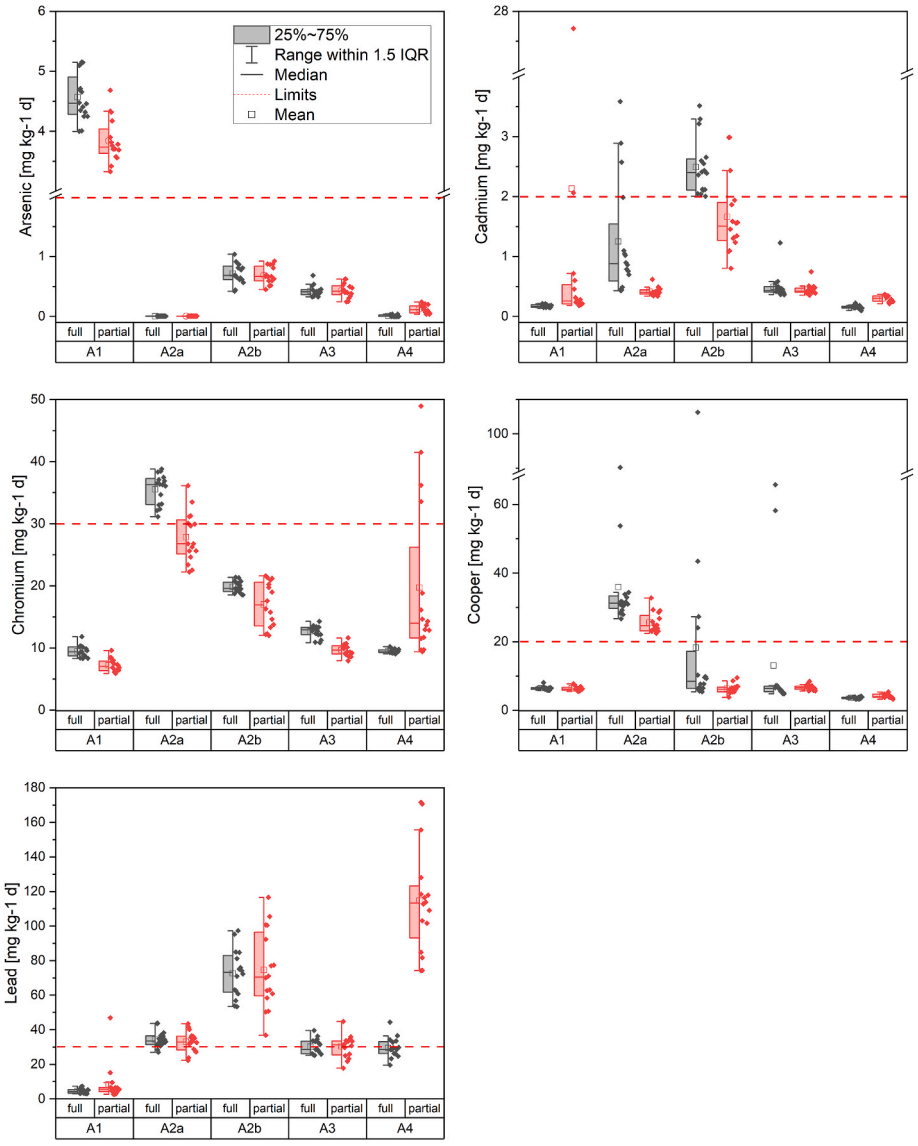

Fig. 4. Elemental concentrations of arsenic, cadmium, chromium, copper, and lead in waste wood classes A1, A1-2a, A1-2b, A1-3, split in "full milled" and "partial milled" (n = 16), (IQR = interquartile range), (d = on dry basis).

(mg kg-1 d). Cadmium is a constituent of the cutting tools used in the mill. Perhaps, this leads to measurement failures and a higher value scattering. Here, outliers are found in A1 waste wood. Both A2 samples have the highest cadmium content compared to the other samples. However, due to the scattering, the ANOVA show no significant differences. The sample "full milled" of A2 has a notably higher cadmium concentration in all four measurements. The scattering of the values of this sample is increased. In A4, there are clear differences between the two different samples used for the "full milled" and "partial milled" sample preparation methods. That is probably due to the different samples in A4. Like arsenic, cadmium is barely allowed anymore in use as wood preservatives or paintings; the low concentrations in the A3 and A4 waste wood are expected [54].

The legal ***chromium*** limit for recycling waste wood in Germany is 30 (mg kg-1 d). Like cadmium, chromium is used in the milling tools. This can result in measurement failures and a higher value scattering. The A1 and A3 samples have the lowest values. Noticeably, the A3 wood has significant lower concentrations than both A2 samples ($p < 0{,}001$). The A4 ("partial milled") has considerably and consistently higher amounts of chromium.

Additionally, a high scattering of the values is shown in this sample. Different from before, it is not a single outlier; instead, all measurements are higher. As the cadmium concentrations in the "partial milled" A4-sample do not vary as much as in the "full milled" sample, the high chromium values are not due to more contamination from milling tools caused by glass or metal impurities.

Presumably, the high Cr concentrations are due to the chemical treatment during the impregnation of wood [55]. Therefore, the two feedstocks can explain the differences in value scattering between the A4 samples, even if they are declared in the same class of waste wood.

The legal ***copper*** limit for recycling waste wood in Germany is 20 (mg kg-1 d). There were three samples with outliers: A2b has one sample where all measurements were considerably higher (between 106 and 24 (mg kg-1 d) instead of around 6 (mg kg-1 d)). A2a has high values in general and two outliers in the "full milled" with 53 (mg kg-1 d) and 90 (mg kg-1 d). Also, A3 had one sample with two deviating measurements of 65.8 and 58.2 (mg kg-1 d) instead of around 6 (mg kg-1 d). The A4 samples have the lowest concentrations in comparison to the other classes. However, the A1, A3, and A4 wood do not differ significantly.

Like Cr, high Cu concentrations are often due to chemical treatment during the impregnation of wood [54,55,58]. Therefore, considerably higher concentrations were expected in the waste wood samples of

classes A3 and A4.

The legal ***lead*** limit for recycling waste wood in Germany is 30 (mg kg-1 d). In the A1 sample, outliers are found. However, the A1 wood is the only one below the legal limit. A2b ("full milled" and "partial milled") have higher scattering compared with A2a. Probably this is due to especially high contamination in this sample, which was distributed during the milling process.

High concentrations are to be expected in classes A3 and A4, as lead was commonly used in paints in the past. Today, paints with lead additives are not allowed anymore, but old stocks still reach the waste wood yards. In addition, lead compounds are sometimes present in wood preservatives [54].

The A4 samples are highly different comparing both milling methods. This can be explained by the circumstance that the A4 samples, in contrast to the other classes, consist of two separate feedstocks.

Considering the measurement results of the "homogenisation markers" and the heavy metals, it should be noted that an analytical error does not only result from the homogeneity of the sample. Many different factors have an impact on the measured values. In addition to milling, the sampling, sample matrix, other sample preparation steps, and the measurement instrument affect the accuracy of the results. The analytical method ICP-OES, like any other analytical method (FAAS, XRF, etc.), has a certain measurement inaccuracy [48,59]. Although, in comparison, most influencing parameters excluding sample milling were neutralised as much as possible in this study, the measurement accuracy of ICP-OES still affects the scattering of the values.

According to the waste wood directive [7] in A1, no paint, coatings or wood preservatives should be included. The visual check and the analytical results for A1 wood suggest that these samples are not naturally based. Arsenic is found in unusually high concentrations.

However, contrary to expectations, the A4 classified wood has the lowest concentrations of heavy metals in most cases. The same applies to A3 waste wood, which is below the legal limits in all heavy metals (excluding lead). Especially the A2 samples often have wide ranges of values and surpass the legal limits several times.

In some cases, the wide scattering of the single values is most likely caused by foreign objects – for example, there was a small circuit board in A3, which probably is the reason for the high copper concentration in one sample. The amount of foreign objects poses challenges for milling. Glass and metal objects can damage the mill and thereby contaminate

Table 3
Investigation for significant differences of the mean element contents (Results incl. outliers and results without outliers) in the samples after "full milled" and "partial milled" sample preparation (grey coloured = outliers were removed).

Elements	***Waste wood classes***			
	A1	***A2a***	***A2b***	***A3***
	Results incl. outliers			
Arsenic	**	-	-	- 1)
Barium	- 2)	**	- 1)	-
Cadmium	** 2)	** 3)	** 3)	- 3)
Chromium	**	**	**	**
Copper	- 3)	** 3)	** 1)	- 1)
Lead	- 3)	-	-	-
Titanium	-	** 1)	**	**
	Results excl. outliers			
Arsenic	**	-	-	- 1)
Barium	* 2)	**	- 1)	-
Cadmium	** 3)	** 2)	** 3)	- 2)
Chromium	**	**	- 2)	**
Copper	- 3)	** 3)	* 1)	-
Lead	- 1)	-	-	-
Titanium	-	** 1)	**	**

- no significant deviation between the methods
* significant deviation (probability of error 5%)
** highly significant deviation (probability of error 1%)
1) "full milled" variant not normally distributed: Mann-Whitney U-test
2) alternative variant not normally distributed: Mann-Whitney U-test
3) "full milled" and alternative variant not normally distributed: Mann-Whitney U-test

the sample. The mill used has blades from chromium steel, which might influence the values for chromium and cadmium.

All of these cases lead to very high concentrations locally, resulting in single outliers, but the bulk of the measurements are relatively consistent (lower RSD after removing outliers). The most apparent result from the individual measurements is that outliers occur for both methods. However, in none of the cases, outliers affect decisions if an element is above or below the given limit.

Furthermore, it has to be mentioned that the majority of laboratories do not measure four subsamples four times each and thus do not have such have a relatively large number of analysis results with n = 16. The ISO 16968 does not define a number of measurements [51], whereas the AltholzV requires a minimum of two determinations [7]. The impact of outliers on the final result is much higher with a reduced number of measurements. Therefore, the optimal approach would be to perform a sufficient amount of measurements so that the outliers are detected and remain in the analysis result but do not affect the representativeness of the total sample.

As a result of this, the following investigations are made twice. One with all values of a sample and the other cleaned up from outliers.

To investigate the significant differences of the mean element contents in samples for the treatments ("full milled" and "partial milled" sample preparation) a *t*-test is used (Table 3). The significances are shown for the samples with and without outliers. The A4 waste wood is not in the statistical investigation because these consist of two different samples.

The grey-coloured fields indicate that outliers have been removed from the evaluation. Even with the elimination of outliers, in most cases, there was no change in the significances between "full milled" and "partial milled". Even Cr (A2b) shows no significant difference between the two sample preparation methods, but Ba (A1) does. This indicates that single outliers have minimal effect on the total measurement results, if a sufficient number of measurements were taken. With a lower number of measurements, not like in this study (n = 16), outliers have a distinctly higher impact on the result.

To summarise, the results show that about half of the samples have a significant difference between the two milling methods. Furthermore, considering that during the first sample division (after milling to 4 mm), perhaps a slight heterogenisation of the sample occurred, it can be seen that the milling method does not show a clear impact on the analytical results.

3.3. Relative standard deviations (RSD)

The relative standard deviation is examined and visualised to clarify the dimension of values scattering in a sample and measure the sample homogenisation (Figs. 5 and 6).

Each sample is divided into four parts, and each part is measured four times with the ICP-OES. Fig. 5 shows the RSDs of the four measurements of the subgroups per sample in the boxplots. Fig. 6 shows the RSD of all 16 measurements of a sample. The occasionally high RSDs demonstrate that homogenisation is challenging for a whole sample and varies considerably even with just four measurements of a very small subsample.

On The left side of Fig. 6, the RSD (overall 16 measurements) is given inclusive outliers, and on the right side, without. For cleaning up

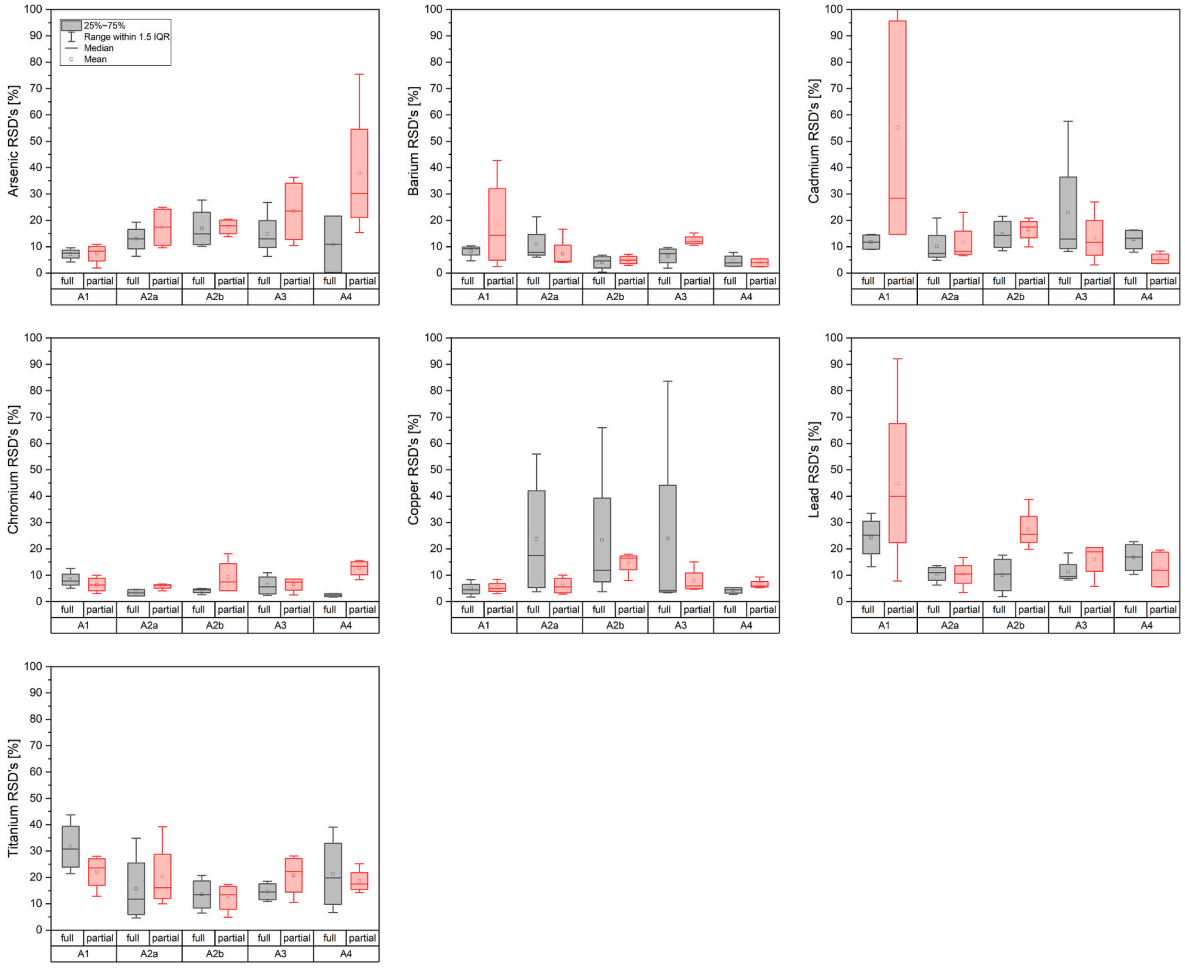

Fig. 5. RSD scattering of the four measured subsamples of each main sample.

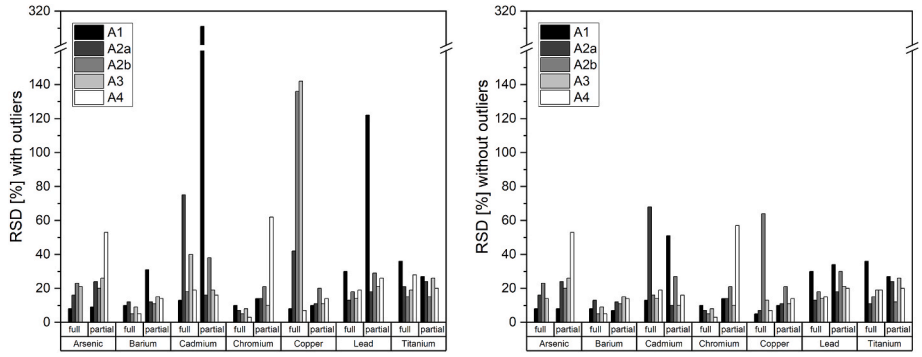

Fig. 6. Relative standard deviation of the samples (Left: Results with outliers; Right: Results without outliers).

Table 4
RSDs of the elements As, Ba, Cd, Cr, Cu, Pb, Ti divided with the number of measurements in a certain percentage range.

		<10%	10–20%	>20%
With outliers	full milled	12	11	11
	partial milled	3	17	15
Without outliers	full milled	13	16	5
	partial milled	6	15	14

samples from outliers, values with 1,5 IQR were removed. For A4 (w/o outliers), no deviation is given for arsenic, as the concentration was extremely low and partly below the detection limit, resulting in high relative standard deviations while the absolute number is very small.

Considering the RSDs, both methods do not provide a satisfactory homogenisation of the samples if the RSD 10% benchmark of Bearnthaler et al. is used [48]. Table 4 presents the number of the individual RSDs of the measurements in a certain percentage range. The range <10% represents a satisfactory homogenisation, while values > 20% constitute a clear analysis error. While the "full milled" method achieved 12 values (out of 68) below an RSD of 10%, the "partial milled" method reached only three values (out of 68). The RSDs improve with the removal of the outliers in general, but only the "full milled" method has an increase in values with an RSD <10% to 13. Furthermore, it is worth noting that high relative standard deviations mainly occur at low concentrations.

This shows the challenge of the representative preparation of highly heterogeneous samples such as waste wood. In this context, it should be mentioned that the milling approach is only a part of the total analytical error. There are various steps in the entire analysis procedure with a high potential for errors. They should also be investigated in more detail in further research [45–47].

4. Conclusion

Waste wood often contains a mixture of wood of different quality and foreign impurities within a feedstock. This makes classification challenging and also the analysis more complex.

In this study, both investigated sample preparation methods do not achieve a satisfactory homogenisation of the samples. Nevertheless, both methods can presumably be used for quality assessment and limit value monitoring of waste wood since the outliers, and the scattering of the values with a number of samples (n = 16) was not decisive in determining whether the mean value was above or below the legal limit. However, it has to be noted that in practice, lower numbers of measurements are generated, which increases the influence of outliers and scatterings considerably.

Based on the data collected, it seems that a partial sample preparation (according to ISO 14780) is comparably effective for waste wood as the milling of the whole sample.

As rapid measurement technology becomes increasingly important, sample preparation should also be reduced in time to a minimum. Not every rapid measurement techniques need sample preparation, but if a device requires sample preparation, time is also an important aspect. In this case, the "partial milled" procedure is clearly more time-effective than milling the complete sample.

Furthermore, the sample preparation, measurement and its optimisation, and representativeness of the sample are only useful as long as the sample collection is done representative. Future studies should investigate the feasibility of using the measurement results scattering to predict the homogeneity of the entire waste wood supply.

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Data availability

Data will be made available on request.

Acknowledgements

The paper is the result of the project "EBA-Holz" funded by the Geman Federal Ministry of Food and Agriculture (BMEL) on decision of the German Bundestag. The grant was administered by Fachagentur Nachwachsende Rohstoffe e.V. (FNR; grant number: 22042618).

Fig. 2 created with Biorender.com.

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Appendix III

Publication 3

Impacts on X-ray Fluorescence Measurements for Rapid Determination of the Chemical Composition of Renewable Solid Biofuels

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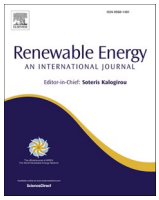

Impacts on X-ray fluorescence measurements for rapid determination of the chemical composition of renewable solid biofuels

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Quality assessment

ABSTRACT

Rapid determination of quality parameters in solid biofuels enables transparent fuel trading and optimised plant operation, e.g. due to lower plant operating costs and lower air pollutant emissions. The present study investigates the impact of interferences caused by the chemical composition, particle size, water content, and measuring time on the rapid measurement technique X-ray fluorescence analysis for solid biofuels. The elements investigated are the minor elements Na, Mg, Si, P, S, Cl, K, Ca and the trace elements Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As Cd, Pb as described in ISO 17225-1. The results provided new insights into the cause of measurement errors and also similarities with findings from other fields. Specifically, we found that grain size <1 mm in sample preparation and water content ≤10 % had a clear benefit on the measurement. In the case of samples with high mineral content, interferences between the elements Si and P occur. Furthermore, the results show that the measurement time for the actual measurement can be significantly reduced to 60 s compared to the factory setting (i.e. from 750 s). The findings of the study contribute to reducing or preventing the indicated measurement errors in future XRF analysis.

1. Introduction

Biomass combustion is an increasingly important renewable energy source [1], especially regarding producing renewable heat. However, due to the potentially harmful gaseous and particular emissions that may occur during solid biomass combustion, such as CO, NO_X, SO_X and total particulate matter, it is essential to optimise the combustion process, e.g. in combined heat and power (CHP) plants [2,3]. Among other factors, fuel quality can significantly influence emissions [4–6]. In addition, using an unsuitable fuel quality can lead to high economic costs for plant operators, e.g. due to increased plant maintenance [4,7].

The most critical fuel parameters affecting combustion are the water content, the ash content, the calorific value and the chemical composition of solid biofuels. Chemical fuel quality, in particular, is becoming increasingly important in fuel quality assessment, as it provides more detailed information about the respective fuel. Newly developed chemical fuel indices [5,6] may be applied to make various statements about the expected combustion behaviour, e.g. regarding gaseous and particular emissions [8], slag formation [9] or corrosion [10,11]. Thus, knowing the chemical fuel composition before combustion may increase plant efficiency and decrease boiler malfunction.

Relevant chemical fuel properties of solid biofuels are presented in ISO 17225-1, with typical concentration ranges of different elements given in the standard's appendix. Furthermore, the various reference methods for fuel analysis are referenced in the ISO standard [12]. Thereby, inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), and atomic absorption spectrometry (AAS) are standardised methods for the chemical analysis of solid biofuels [13,14]. ICP-OES is especially often used because, for most elements, it is suitable [15–17]. However, these methods are time-consuming, expensive and require highly trained employees, especially for acid digestion which is necessary to prepare elements for measuring. Consequently, the analysis is usually

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List of abbreviations

AAS	Atomic Absorption Spectroscopy
ANOVA	ANalysis Of Variance
CHP	Combined Heat and Power
ED-XRF	Energy Dispersive X-Ray Fluorescence
FRW	Forest Residue Wood
HEC	High element concentration
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
LA-ICP-MS	Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry
LEC	Low element concentration
LIBS	Laser-Induced Breakdown Spectroscopy
LMM	Landscape Maintenance Material
LOD	Limit Of Detection
PXRF	Portable X-Ray Fluorescence
RSD	Relative Standard Deviation
SDD	Silicon Drift Detector
WC	Wood Chips
WD-XRF	Wave Dispersive X-Ray Fluorescence
WW	Waste Wood
XRF	X-Ray Fluorescence

performed in external laboratories and not on-site. Using chemical fuel quality as a parameter to optimise plant operation, the measurement procedure needs to be accelerated and performed directly at the plant, e.g. by using rapid determination methods. For this purpose, various analytical methods are theoretically available in practice. In particular, Laser-induced breakdown spectroscopy (LIBS) [18–20], Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) [21] and especially X-ray fluorescence analysis (XRF) [18,19] have provided promising results. In addition, a review article discussed in detail the usability of these analytical principles for solid biofuels [11]. Therefore, the present study focuses on XRF to rapidly determine the chemical composition of renewable solid biofuels.

2. State of the art

XRF analysis is based on the emission of fluorescent radiation by irradiating a sample with high-energy electromagnetic radiation (0.1–100 keV) [22]. This approach is useful for qualitative and quantitative analysis of chemical elements in various types of solid samples [23]. For instance, XRF is an often-used method for multi-elemental determinations of biomass in general (plant [24,25], wood [26,27], bio-based waste [28,29], algae/seaweeds [30,31], seeds [32], fossil fuels (coal [33], sewage sludge [34], others [35–38]), or related fields (Biomass char [39–41], environmental samples [42], ash analysis [43]).

Similar to ICP-OES, the analytical procedure of XRF consists of several steps. These range from sample collection to data evaluation. Every step has the potential for analytical errors. They may occur throughout the procedure and result in an individual level of analytical reliability per measurement.

Various waste processing studies showed that sampling is usually the primary source of error (heterogeneity of the materials), while sample preparation is the second-highest source [44,45]. Data analysis also has some potential for error, which appears negligible compared to the others [44,45].

In the case of XRF analysis, the sample matrix, the sample preparation, and the instrumental setup of the analyser impact the analysis (Fig. 1) [46,47]. In this study, only these sources of error were considered (e.g. by analysing interferences, sample stability during repeated measurements, water content, particle size and measurement time). In contrast, sampling is a challenge that should be investigated independently, and data analysis offers only a low potential for error. Thus, these steps were excluded from this work.

Various studies have already investigated elemental compositions and different sources of error during XRF analysis of solid biofuels to some extent (Table 1).

In general, XRF is a non-destructive method of analysis. However, radiation exposure can cause damage to sensitive samples, which can distort the analysis results [60]. Therefore, the **sample stability**, respectively, changes due to the X-rays, should be investigated.

XRF measurements can be subject to various 'interferences' caused by the chemical composition of the sample (matrix) which can distort the results of the analysis. Spectral interferences can be significant sources of error in XRF analysis, e.g. when the measurement signal of

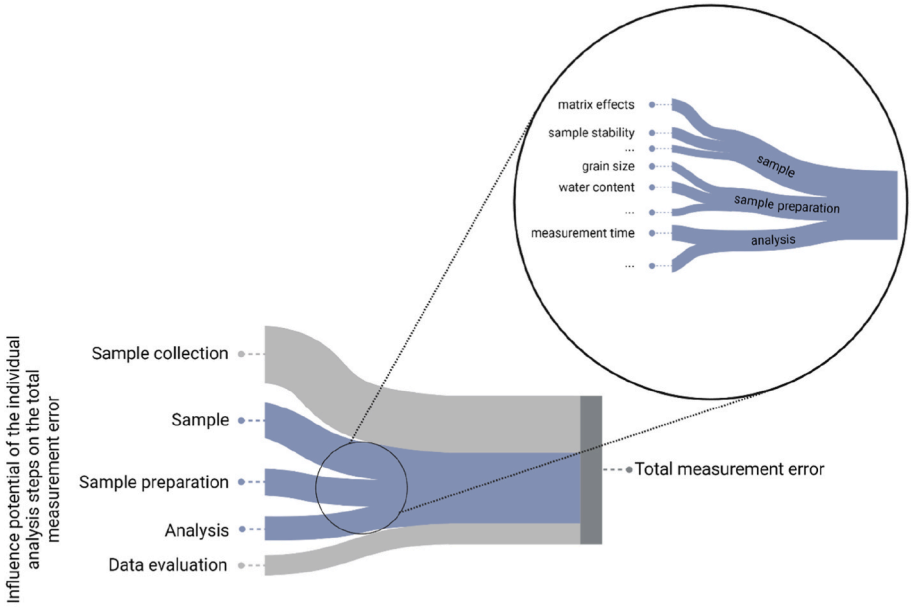

Fig. 1. Schematic drawing of different impacts on the error associated with the measurement of solid biofuels with an X-Ray fluorescence analyser.

Table 1
Recent studies on XRF analysis of solid biofuels.

Article authors	Manufacturer of the XRF device	Device	Type of instrument	Datasheet	Samples investigated	Targeted elements	Investigations & interferences	Ref.
Zimmermann et al. (2019)	**Malvern Panalytical**	Epsilon 1	Portable benchtop	ED-XRF 7–50 kV SDD	wood chips, spruce, pine, beech, willow, mixed	Mg, Al, Si, P, S, K, Ca, Mn, Fe, Zn	Calibration, mineral contamination	[48]
Sajdak et al. (2019)	**Thermo Fisher Scientific Inc**	ARL OPTIM'X	Stationary	WD-XRF 1.7 kVA 200W Rh-anode	agrarian biomass, forest biomass, and furniture waste		Model development and validation	[49]
Reinhardt et al. (2018)	**APC Analytics**	SOLAS	Online analyser	N/A	wood chips, landscape management material	Na, Mg, Al, Si, P, S, K, Ca, Ti, Fe	Usability for solid biofuels	[50]
Torgrip, & Fernández–Cano (2017)	**Mantex**	Biofuel Analyser	Prototype roll container	qDXA-XRF 40–90 kV 1.4 and 0.3 mA	wood chips	Moisture and ash content, calorific value	Usability for the determination of moisture content, ash content, and calorific value	[51]
Golubev (2015)	**Thermo Fisher Scientific Inc**	Niton XL3t 980 GOLDD+	Handheld	ED-XRF 50 kV/ 200 μA 185 eV SDD	wood chips	N, Na, S, Cl, K, V, Cr, Mn, Co, Ni, Cu, Zn, As, Br, Cd, Sb, Hg, Tl, Pb	Chemical composition, particle size, measurement time, measurement distance, Wood moisture	[52]
Fellin et al. (2014)	**Oxford Instruments**	X-MET 5100	Handheld	ED-XRF 45 kV/40 μA Rh-anode	wood waste	As, Ba, Br, Cd, Cl, Cr, Cu, Hg, Pb, Sb, Sn, Ta, Ti	Usability of XRF for multi-elemental analysis of wood waste, LOD	[53]
Riedel et al. (2014)	**Spectro Thermo Fisher Scientific Inc**	XEPOS plus Niton XL3t 700	Stationary portable	ED-XRF 50 W/60 kV <130 eV SDD ED-XRF 50 kV/20 μA	waste wood	As, Ca, Cl, Cr, Cu, Hg, Pb	Usability for different elements of waste wood	[54]
Andersen et al. (2013)	**Bruker AXS**	S8 Tiger	Stationary	WD-XRF 60 kV Rh-anode	biomass, reference materials	Na, Mg, Al, P, S, Cl, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Mo, Ba, Pb.	LOD, correlation with reference, Ash yield, Matrix corrections, sample moisture, grain-size	[55]
Rasem-Hasan et al. (2011)	**Austin AI, Inc, Austin TX**	Model QXR-W	Online sorting analyser	N/A	wood waste	As, Cu, Cr	Online sorting of wood waste	[56]
Block et al. (2007)	**Innov-X Systems, Inc.**	Alpha Analyser (α-2000s) Inspector (I-3000c)	Handheld	N/A	treated wood	As	Precision and detection limit tests, identification of arsenic in treated wood	[57]
Baernthaler et al. (2006)	**N/A**	N/A	XRF device	N/A	wood + bark, straw pellets	K, Mg, Na, P, Cd, Cr, Ni, Co, Mn, Sb	Usability of XRF for chemical analysis of solid biofuels, particle size	[58]
Solo-Gabriele et al. (2004)	**Marble Falls, TX**	Spectro-ASOMA Model 400	Online sorting analyser	N/A	wood waste	As, Cr, Cu	Online sorting of wood waste	[59]

one element is falsely assigned to another element. Interferences can differ in overlapping, enhancement and absorption of individual signals. Thereby, the matrix of solid biofuels is complex. The main components of biomass are cellulose, hemicellulose, and lignin [61], while the major chemical elements are carbon, hydrogen, and oxygen. In the case of solid biofuels, these elements are combustible components and significantly influence the calorific value of wood fuels and the combustion air demand [62]. The remaining elemental composition of solid biofuels, the so-called "minor" and "trace" elements such as N, Cl, S, K or heavy metals, vary due to different parameters such as plant species, plant parts, harvesting date or external impurities such as soil material. For instance, solid biofuels are often contaminated with gravel or soil material during harvest, storage or transport [63–68]. The mixture combines two or more matrices in one sample, making correct measurements with XRF difficult.

The **particle size** of a sample affects the XRF measurements in different ways. One positive effect of extensive sample milling is the increasing homogeneity with decreasing particle size. A study by BAERNTHALER et al. (2006) shows, among other aspects, the impact of milling on the homogeneity of solid biofuel samples. For this purpose, a sample was measured several times and the homogeneity was evaluated by means of relative standard deviations (RSD). An RSD >10 % was defined as sufficiently satisfactory homogenisation of a sample. This value was achieved with a particle size of <0.25 mm [58]. Another positive effect, as several studies suggest, is that the measurement error during XRF analysis decreases with decreasing particle size. So far, no optimal particle size for analysing solid biofuels with XRF has been defined. However, MARUYAMA et al. (2008) found that the intensity of the emitted rays increases with decreasing particle sizes leading to a better measurement signal [69]. According to YAMADA (2014), particle size influences depend on X-ray scattering from non-planar surfaces and shadowing effects. This affects lighter elements, particularly as they have lower radiation energy and, thus, a significantly lower depth [70]. Using a PXRF, i.e. a portable XRF analyser, SAPKOTA et al. (2019) concluded that ground feed samples reduced to a particle size of 2 mm had the best effort: benefit ratio while the overall measurement results showed increasing values with decreasing particle size. This effect was detected for P, K, Ca, and Fe [71]. ZIMMERMANN et al. (2019) also used a

portable EDXRF device, but in this case, for the chemical analysis of wood chips. They also investigated the influence of particle size on the measurement results. In a first approach, it was found that for Al, Fe, and Mn, the best results were generated with particle sizes <0.5 mm compared to ICP-OES. The grain size effect with increasing concentrations at decreasing particle sizes was found in this study for Al, Si, Ca, and Fe [48].

During sample preparation, the **water content** might also affect the XRF measurement. A study by GLANZMANN & CLOSS (2007) from the field of geochemical analysis with XRF shows that water contents of ≥20 % can have a negative impact on the XRF measurement. This is because water on the surface of a sample forms a barrier to the fluorescence ray [72]. In another study by SOLO-GABRIEL et al. (2004), the influence of water content in waste wood was investigated. They measured no significant difference while detecting arsenic in a wet (soaking water for 30 min) and a dried sample [59]. Thus, up to date, the effect of water content on XRF analysis of solid biofuels remains uncertain.

During the analysis with an XRF analyser, the **measuring time** is one of the most relevant parameters that the users can influence themselves. The results of an XRF analysis are usually more accurate the longer the measurement takes place [52], i.e. when more counts per second can be detected, and the LOD increases. For instance, in a study by FELLIN et a. (2014), a quadrupled measurement time reduced the LOD by half [53]. While various studies showed no significant impact of the measuring time on the accuracy of the quantified analysing results or the correlation with the reference method (ICP-OES), the increasing net counts usually decreased the LOD [71,73,74]. A study by SAPKOTA et al. (2019) with forage samples concluded that their samples are measurable with 60 s detecting time without a loss of accuracy (compared to 120 and 180 s) [71]. Additionally, the LOD depends on the atomic number of an element. The higher the atomic number, the lower the LOD because of the higher fluorescence radiation output [23,33,75].

In this study, various effects like sample stability, interferences, particle size, water content, and the measuring time on X-ray fluorescence measurements known from other fields are investigated and transferred to the rapid analysis of solid biofuels. In contrast to previous work in this field, this study considers many impacts on all relevant minor (Na, Mg, Si, P, S, Cl, K, Ca) and trace elements (Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As Cd, Pb) for solid biofuel combustion (excluding N, F, V, and Hg) according to ISO 17225-1. The knowledge of this study should make renewable energy production by biomass-fired CHPs more efficient, cleaner, and fair for all involved.

3. Material and methods

For the different investigations of the influences on the XRF analysis, several samples of various origins and compositions (bark-free stems, wood chips from forestry, landscape management material and waste wood, etc.) were used (section 3.1). These were processed in a variety of approaches for the individual tests. This ranged from drying, milling and rehydration (section 3.2).

The different samples were then measured with the XRF instrument and partly compared with the reference method for solid biofuels, ICP-OES (section 3.3).

The description of the different experiments to investigate the influence of XRF is given in section 3.4.

After the experiments had been carried out, the data generated were statistically evaluated (section 3.5).

3.1. Samples

The samples (n = 223) for the different investigations came from various sources. Stem wood of beech without bark was collected from a forest in Rottenburg am Neckar, 72108, Germany. The material was chipped and prepared for analysis (n = 4). Other samples originated from wood-fired heat and power plants in South Germany. They were collected directly from the premise of the plants during fuel delivery or from storage sites (n = 12) according to ISO 21945 [76]. These materials comprised wood chips from natural wood (forest residues, landscape maintenance material) but also waste wood (classification AIII according to the German Waste Wood Ordinance). They are used for the investigations of sample stability. With the exception of the waste wood, all samples had a high water content of >30 %, indicating no substantial drying occurred before sampling. After sample collection, the materials were packed airtight in buckets and delivered to the University of Applied Forest Sciences at Rottenburg (HFR). After a maximum of one day, the samples were processed further.

Two of the samples (Beech stem wood and landscape management material) were deployed to investigate the impact of the water content, the particle size and the measuring time. In order to observe the difference between contaminated and non-contaminated or “high” and “low” elemental concentrations, the two samples are selected accordingly.

- The low elemental concentration sample (LEC) was made from pure beech stem wood without bark, leaves, soil or other impurities. Thus, a homogeneous matrix with low elemental concentrations was expected.
- The high elemental concentration samples (HEC) were made from landscape management material with high mineral and other (metal, etc.) impurities. Thus, a very heterogeneous matrix with comparably high elemental concentrations was expected.

Four samples were used for the investigation of sample stability. In addition to the 16 samples collected in this project, various retained samples derived from previous projects from the Technology and Support Center in the Center of Excellence for Renewable Resources in Straubing (TFZ) were used (n = 207) to investigate the interferences. Some of these samples originated from joined projects of TFZ together with the Bavarian Forestry Research Institute (LWF). They derived from a wide range of different sources (e.g. chipping operations in the forest, biomass terminals, biomass heating plants, etc.) comprising, e.g. wood chips from stem wood, forest residues, roadside maintenance, urban forestry but also from pellets (both from the German pellet market and pellets produced at TFZ). They were contaminated with mineral impurities to varying degrees, both by chance and on purpose. An overview of all samples used is summarised in Table 2.

3.2. Sample preparation

All samples processed at HFR were dried at 105 °C in a drying oven (UNP 700 Memmert Ltd.) to constant mass to obtain a stable sample without the influence of water content (below 2 % water content). Afterwards, the thick wood pieces were coarsely broken to fit into a cutting

Table 2
Overview of the different samples used.

Samples	Origin	Used for investigations
LEC	from pure beech stem wood without bark, leaves, soil or other impurities	Particle size, water content, and measurement time
HEC	landscape management material with high mineral and other (metal, etc.) impurities	Particle size, water content, and measurement time
Different wood samples	• Beech stem wood without bark •Waste wood •Landscape management material •Forest residue wood	Sample stability
Retained samples	Retained samples derived from previous projects from chipping operations in the forest, biomass terminals, biomass heating plants, etc.	Interferences

mill (Pulverisette19 Fritsch Ltd.) with heavy metal-free inlet milling cassettes. With this device, the samples were milled in the first step to a particle size of approx. 4 mm, in a second step to 1 mm and finally to 0.25 mm. After each comminution step, a part of the sample was divided representatively in a riffle divider with 18 culverts. One part was stored for different analyses (approx. 0,5 l) while the rest was milled up to the following particle size. The standard particle size for the investigations (excluding the particle size examinations) was 0.25 mm. For the HEC and LEC samples, the remainder of the 0.25 mm samples were additionally milled in an ultra-centrifugal mill (ZM200 Retsch GmbH) to a particle size of 0.12 mm. The inlets of the ultra-centrifugal mill are made of stainless steel.

The particle size distribution of the individual comminution steps for LEC and HEC was investigated according to the sieving method of ISO 17827-2 (Fig. 2).

For the investigation of the water content impact on XRF measurements, the dried samples were rehydrated with twice distilled water (H_2O – M 18.02 g mol^{-1} – density 1.0 g cm^{-3}). The initial water content of the sample was determined with a rapid water content analyser (MA150 Satorius), and the required amount of water was calculated based on that. The rehydrated samples were placed in airtight buckets for several days to let the moisture equilibrate. The rehydrated samples were finally tested with the rapid analyser to ensure that the calculated water content was achieved. The water content levels were achieved with a deviation of max. +- 1 %.

Depending on the original research project, retained samples from TFZ that were used for the analysis of interferences might deviate from this procedure to some extend i.e. by applying different temperatures for pre-drying and different digestion procedures for ICP-OES [77].

3.3. Analytical devices

The samples were analysed with an energy-dispersive X-ray fluorescence analyser XEPOS (SPECTRO Analytical Instruments GmbH). The excitation was done by a 50 W X-ray tube with a binary-alloy cobalt-palladium anode with a high-resolution silicon drift detector with <130 eV. As the tube uses a binary alloy PdCo anode, the device use Pd Compton scattering for higher energy X-rays and Co Compton scattering for correction when analysing lower energy X-rays. The method used can analyse samples from the range close to the detection limits (down to 0.1 mg kg^{-1}) up to the measurable mass percentage range. The device-specific method used is described in more detail in the study Endriss et al. (2022) [78].

The used sample tubes have a 4.0 µm membrane (SpectroMembrane Prolene Thin-Film, chemplex Industries INC.). The typical impurities of the membrane can be Ca, P, Sb, Fe, Zn, Cu, Zr, Ti, and Al in a ppm range. The sample was filled up in the tubes as a bulk powder to a 10 mm filling level. The measuring atmosphere was helium flushed. The standard measuring time was 750 s per analysis (excluding the investigations of the effect of different measuring times). The samples rotate entirely once every 30 s and are excited in a 10 mm radius.

The reference method for the HFR samples is based on inductively coupled plasma optical emission spectroscopy (ICP-OES) and is used to comprehend the XRF analyser. The material was microwave digested according to ISO 16968 [14] with Multiwave GO 3000 (Anton Paar Ltd.). Therefore, 400 ± 1.0 mg 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) were 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. Depending on the original research project, retained samples from TFZ might deviate from this procedure to some extent.

3.4. Experimental procedures

Several experiments were conducted to investigate the diverse factors that influence the XRF measurement of solid biofuels (Fig. 3). A standard particle size of 0.25 mm was utilised in all experiments, except in particle size testing, achieved through stepwise comminution of the sample (Section 3.2).

To assess sample stability, the same sample was measured ten times in succession (four different materials) (Section 3.1). To observe the interferences, distinct retained samples from past TFZ projects were employed and compared with reference methods (Section 3.3).

LEC and HEC samples were used for the other analyses, including particle size, water content, and measuring time. Four samples per stage were assessed for each investigation. For particle size analysis, the samples were prepared following the procedure described in Section 3.2. During water content experimentation, the samples were rehydrated (Section 3.2) and measured using the XRF instrument. The measurement duration was gradually reduced in increments of 60 s, starting from the factory setting of 750 s, with the final step at 60 s to investigate the influence of measuring time.

3.5. Statistical data evaluation

The data evaluation was carried out with regard to the individual element concentrations or the “sum of concentrations”, i.e. the

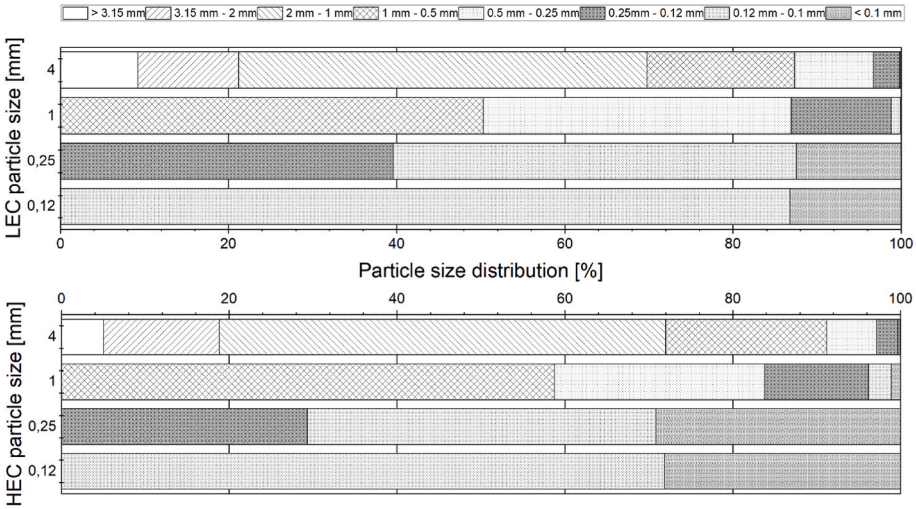

Fig. 2. Particle size distribution (LEC = beech stem wood without bark) and a high element concentrations sample (HEC = landscape maintenance material; n = 4).

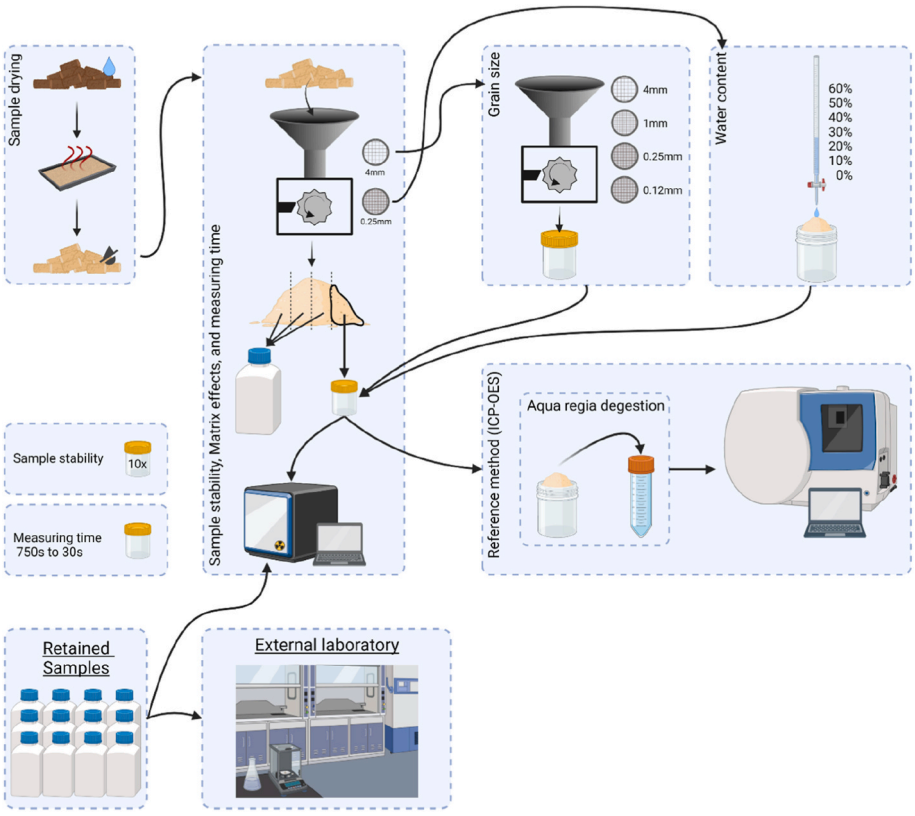

Fig. 3. Overview of sample preparation for the different XRF analysis tests.

cumulative concentrations of all measured minor and trace elements according to ISO 17225-1: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn As, Cd, and Pb (excluding N, F, V, and Hg). Various methods were used for the statistical evaluation of the data. The data were tested for homogeneity with the Shapiro-Wilk test and for heteroscedasticity with the Levene test. The coefficient of variation (VarC [%] = standard deviation/mean × 100) shows the relative variation of the values. To examine the statistical difference between the values, an ANOVA with paired *t*-test was performed as a post-hoc test (without p-adjustment). The non-parametric alternative was the Kruskal-Wallis test, with the Wilcox test as post-hoc (no p-adjustment).

4. Results and discussion

4.1. Sample stability

For the investigations of the sample stability, i.e. whether the radiation or the analyser affects the sample, four different samples were measured ten times directly in succession (Fig. 4). The samples included materials with low element concentrations of minor and trace elements, i.e. with a comparatively homogeneous matrix (beech stem wood without bark) to high element concentrations with mineral and other impurities (waste wood (WW), landscape maintenance material (LMM), forest residue wood (FRW)).

The variation coefficients for the "sum of concentrations" were 0.49

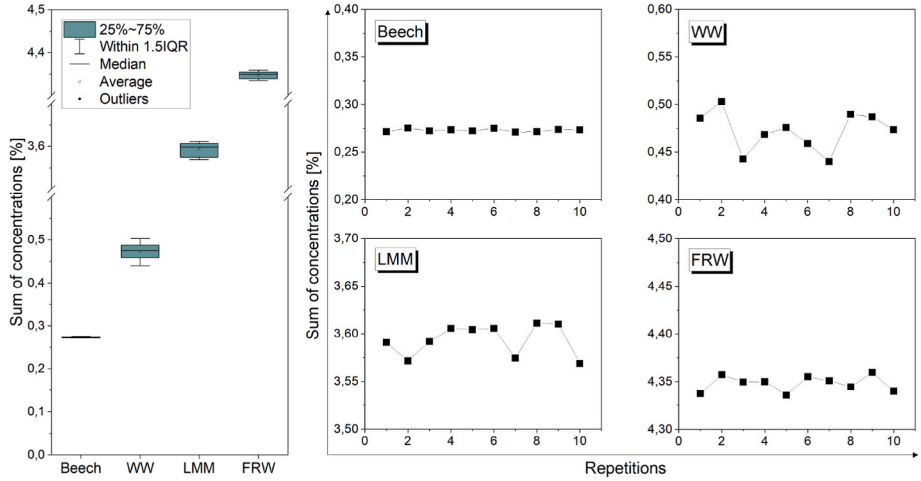

Fig. 4. Sum of concentrations of minor and trace elements according to ISO 17225-1 in beech stem wood (Beech), waste wood (WW), landscape maintenance material (LMM) and forest residue wood (FRW) (Particle size: 0,25 mm; n = 10 per material; left: box plot of all ten measurements, right: individual measurements).

% for beech stem wood, 4.08 % for WW, 0.44 % for LMM and 0.18 % for FRW. The coefficient of variation of WW is significantly higher in comparison to the other materials. This is due to the heterogeneity of waste wood. A study on the subject of homogeneity of waste wood samples showed the wide fluctuations of measurements within a batch [47]. Thus, variation among measurements per material was rather low. Fig. 4 shows the sum of concentrations and the stability of the samples over the ten measurements. Thereby, no clear trend was visible in any of the four samples (Fig. 4, right). Similarly, no trend was detected when individual elements were considered. However, individual elements showed different amounts of variation (Fig. 5). The homogeneity was regarded to be satisfying with an RSD< 10 % [58]. High relative standard deviations (RSD) often occurred at elements with low concentrations, especially when the values were close to the limit of detection (LOD). Thus, since even the high RSD values were considered low and no general trends were observed, the samples were regarded as unaffected by the X-rays or the analyser and could be assumed to be stable.

4.2. Interferences

A strong interference (caused by the other elements) of silicon on phosphorus was observed in the XRF measurements of solid biofuel (Fig. 6). Solid biofuel matrices can vary significantly depending on the fuel type and their impurities, such as gravel or soil material [79]. These impurities, especially when mineral soil is present in materials like FRW or LMM [74–79], can lead to high silicon concentrations within the sample.

Although the XRF readings correlated linearly with the measurements of the reference method ICP-OES, it can be seen that for samples with a high silicon content, the phosphorus concentration was systematically underestimated in the analysis compared to the reference method. Samples with a silicon concentration below 5000 mg kg^{-1} showed significantly better accordance from P with the reference method (Fig. 6, right). The measuring device was not specifically calibrated for Si or wood samples. A factory calibration for plant materials was used for the investigations. Thus, results might be improved by applying a better calibration, including Si.

Other interferences, which can occur due to overlap or absorption and enhancement effects, were not evident for this device and these samples. For this purpose, interferences known from the literature were examined (Ca-K_α/K-K_β; Mn-K_α/Cr-K_β; Fe-K_α/Mn-K_β; Cu-K_α/Ni-K_β; As-K_α/Pb-$L_{\alpha1}$; Cd-$L_{\beta1}$/K-K_α) [75], but no further irregularities were found. This is probably explained by the fact that the device already calculates several interferences in the software. The deconvolution used in the software of the SPECTRO XEPOS takes care of the major part of these effects.

4.3. Impact of the particle size

The particle size of a sample may have different impacts on the measurement, e.g. due to increased homogenisation of the sample due to extensive milling or due to an improved measurement when particle size is low. Moreover, the absolute concentration measured in a sample might vary depending on the particle size, i.e. the so-called “grain size effect” (see below) [52,69–71]. During this study, the samples were milled in different intensities and in two mills, i.e. one cutting mill and one ultra-centrifugal mill, resulting in particle sizes of ≤4 mm, ≤1 mm, ≤0.25 mm, and ≤0.12 mm (Fig. 7).

The relative standard deviation (RSD) per element was calculated as an indicator for the homogeneity of the materials (n = 4 per sample and milling step, each). The homogeneity was regarded to be satisfying with an RSD< 10 % [58]. This was the case for most elements of the LEC material (excluding Si and Cu) at a particle size ≤1 mm and the HEC material at a particle size ≤0.25 mm (excluding Cu and As). The best homogenisation was generated by milling the samples to a particle size of ≤0.12 mm. However, an ultra-centrifugal mill had to be used to achieve the finest particle size. This might lead to contamination of the sample to a substantial amount with heavy metals due to abrasion of the hardened steel. This was especially relevant for Cr in the LEC sample (Fig. 7). In contrast, the cutting mill uses heavy metal-free steel and should not lead to sample contamination. Although it was not the case for the here investigated samples, mill contamination might usually be considerably more prevalent in HEC material due to the abrasive properties of mineral impurities (e.g. sand) in the sample matrix. Furthermore, each additional milling step requires a considerable amount of additional time and effort for sample preparation. Based on the assumption that in CHP plants, mostly HEC material (LMM, FRW, WW) is combusted [17], and considering time as an essential aspect during rapid analysis, the particle size of ≤0.25 mm seems suitable for the analysis of most elements on-site. For some elements, even a comminution to ≤1 mm or ≤4 mm might be considered sufficient. This applies to the elements Mg, P, Cl, K, Ca, Ti, Fe, Mn and Zn, as RSD was already close to 10 % at these milling intensities.

In addition to homogeneity, the so-called grain size effect of different particle sizes has to be considered. For instance, in the LEC material, the concentration of most elements in the samples increased with decreasing particle size, as described by MARUYAMA et al. (2008) [69] (Fig. 8). This is likely caused by the scattering of the X-rays by uneven surfaces and shadowing effects when larger particles are measured [70]. Light elements such as P, K, Ca and Fe are especially susceptible to this effect due

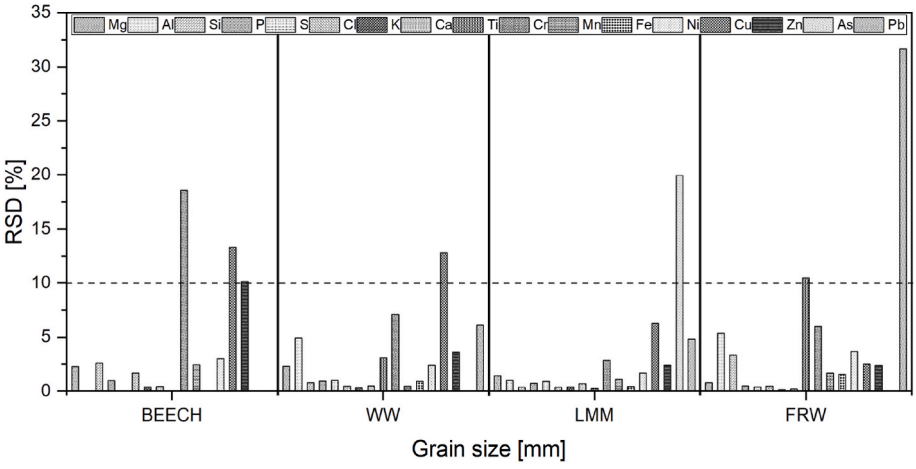

Fig. 5. RSD of element concentrations measured with XRF in four samples (Beech = beech stem wood without bark, WW = waste wood, LMM = landscape maintenance material, FRW = forest residue wood, n = 10 per material).

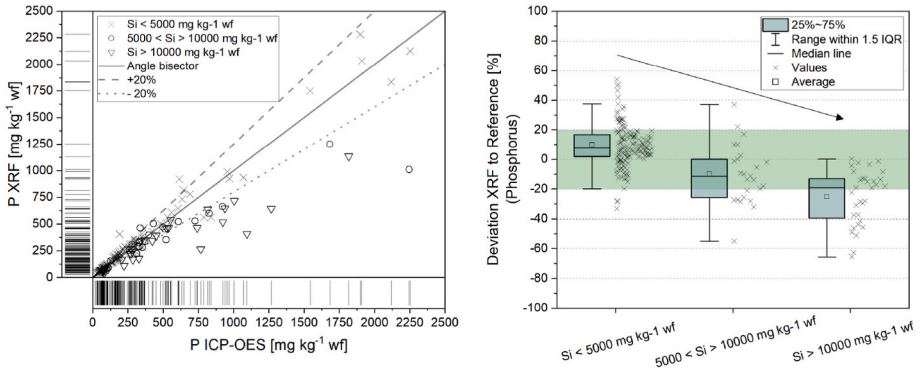

Fig. 6. P measured with XRF in relation to P measured with ICP-OES for wood chips with Si contents below 5000 mg kg^{-1}, 5000 and 10,000 mg kg^{-1}, and above 10,000 mg kg^{-1} (n = 207, wf = water free; left) and deviation of the XRF values to ICP-OES (right).

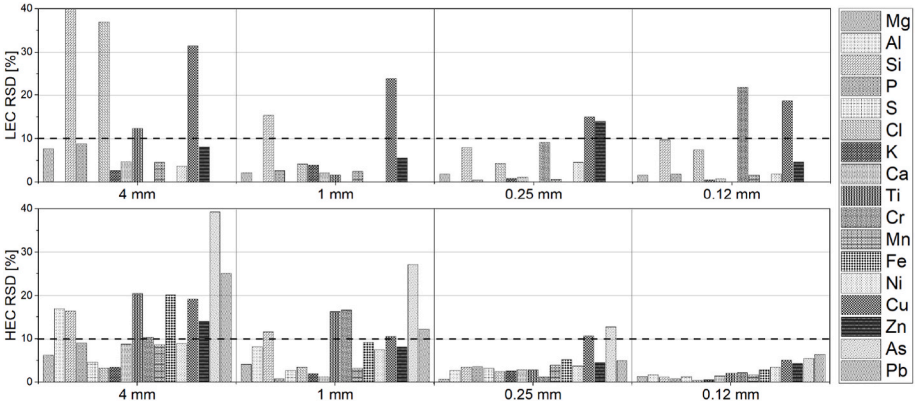

Fig. 7. RSD of element concentrations measured with XRF in a low element concentrations sample (LEC = beech stem wood without bark) and a high element concentrations sample (HEC = landscape maintenance material; n = 4).

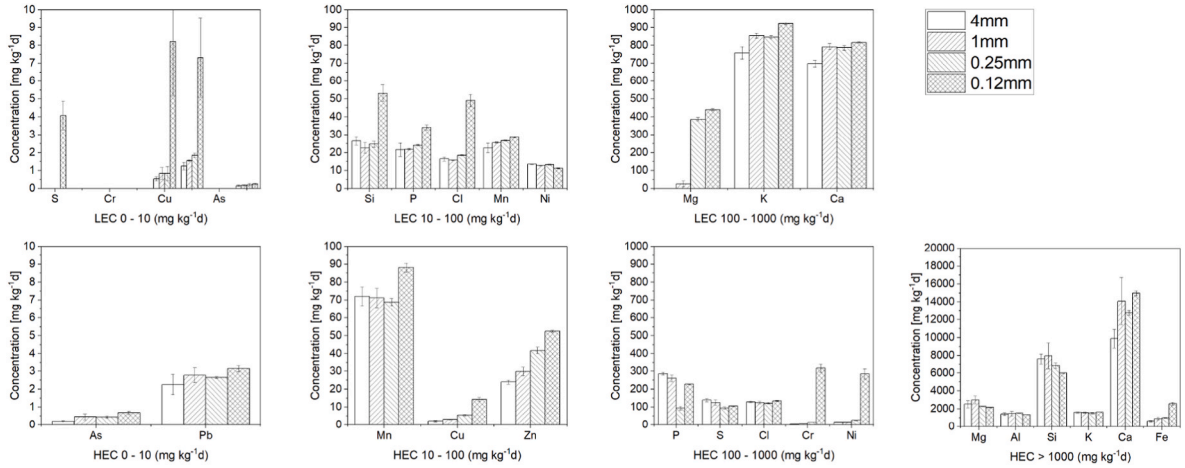

Fig. 8. Concentration of selected elements in two samples (LEC: beech stem wood without bark, HEC = landscape maintenance material; n = 4, each).

to their low energy and shallow penetration [70]. Consequently, these elements showed increasing concentrations in the LEC material at small particle sizes in this study. In contrast, the HEC material already resulted in high scattering among samples due to sample heterogeneity (i.e. a high RSD as seen in Fig. 7), especially at larger particle sizes of ≤4 mm and ≤1 mm, which might conceal the grain size effect for the HEC material. Here, the increasing effect on element concentration at small particle sizes is recognisable only for Ca, Fe and selected heavy metals such as Cu, Zn, As and Pb.

Significant differences in element concentration could be seen for most minor and trace elements across the different particle sizes and materials. In the HEC material, only K showed no significant differences in concentration regarding milling intensities ($p = 0.235$). Similarly, no significant differences could be detected for Pb in the LEC material ($p = 0.348$). The often observed trend of increasing concentrations at small particle sizes was more evident for trace elements than for minor elements. Interestingly, for P, S and Si, a significant decrease in concentration with decreasing particle size was observed in the HEC material

that cannot be explained at the moment.

Overall, a statistically significant difference between the concentrations of minor and trace elements at different particle sizes was observed for most elements. Although the "grain size effect", i.e. the increase of concentrations with decreasing particle size as described in the literature [69–71], could not be observed consistently for all elements and materials, an evident influence of the particle size on the measurement results can be seen.

SAPKOTA (2019) described a compromise between desired accuracy and feasibility of preparation in forage samples. They found that less than 2 mm particle size is the optimal effort-to-precision ratio [71]. WILLIS & DUNCAN (2008) described the best solution to minimise the particle size effect is to mill the samples to a size below the measurement depth (i.e. the length of x-ray penetration into the sample) of the XRF device [80]. However, any further size reduction to a finer particle size offers potential contamination of the samples with heavy metals from steel abrasion, e.g. Ni and Cr. Due to the hardened chrome/nickel steel components especially in the ultra-centrifugal mill, these two elements are excluded from the analysis. Heavy metal-free steels could prevent this, but nevertheless, each milling step allows for impurities from other sources of contamination. Dietz et al. (2016) tested mill-abrasion (cutting-mill Retsch SM2000) by adding 10 g analytic sand and found Ni 12 mg for Cr 28 mg abrasion. The element content of the sample this way was raised at 4 to 6 times for Co and more than 100 times for Cr, Ni and Mo [63].

In this study, a definite "optimal" particle size could not be objectively determined when the grain size effect is also considered. In practice, one particle size should be selected, and the XRF instrument should be calibrated to this particle size. Results from homogeneity indicate that this should be done for a particle size class between 0.25 and 4 mm, depending on the element investigated. During on-site measurement, the particle size should not vary among samples but should be fixed in order to minimise the particle size effect as much as possible. In addition, the penetration depth should be considered, and the particle size (if at all feasible) for the elements should be below this.

The theoretically penetration depth (or information depth) is determinded according to the formula: $h = \frac{\ln(0.01)}{\rho \bullet \mu}$ (h = penetration depth; ρ = density [g/cm^3]; μ = mass attenuation coefficient [cm^2/g]). Exemplary for $(C_6H_{10}O_5)n$ with an assumed density of 0.5 g/cm^3 the calculated penetration depth shows that for an optimal analysis of the light elements up to Cl a finer milling of the sample to < 250 μm would be required (Table 3). However, the empirical values and required accuracies show that the homogeneity and measurement are also sufficient for elements up to Mg. This was shown in a parallel study by Endriss et al. (2023) where good correlations were found for lighter elements such as P and Mg with a particle size <250 μm [78].

4.4. Impact of the water content of a sample

Results on chemical elements typically are presented on a dry basis to exclude any influence of changing water contents in between the results. This is usually done by determining the water content of a sample parallel to the chemical analysis. Still, a direct influence of the water content in a sample on the XRF measurement might affect the instrument's precision. Fig. 9 shows the deviation of the element concentration measured with XRF in the rehydrated samples compared to the (almost) water-free sample (all values re-calculated to the water-free reference state). A decrease in concentration with increasing water content was observed for almost all elements. As shown in the study by GLANZMANN et al. (2007) with geological samples, this could be due to the protective film function of water, which blocks a part of the fluorescence radiation.

In the results of this study, different trends are obtained for the LEC and HEC samples. In general, a water content of ≥20 %, as previously reported in Ref. [72], often led to significantly different results compared to the (almost) water-free sample. This was also the case for some elements at 10 % water content (Fig. 9). Thus, samples should be dried to values ≤ 10 % to exclude any effect of the water content on the XRF measurement.

Due to the varying reactions of each element to the water content, it is difficult to generalise the impact. Nevertheless, measurements with the XRF analyser used in this study indicate that increasing water contents in a sample might decrease measured element concentration for almost all elements (Fig. 10). The filled values in Fig. 10 represent the lowest water content with a statistically significant difference to the water-free sample. Elements not listed in the Figure are below the detection limit and could not be assessed.

The results of SOLO-GABRIELE et al. (2004) [59], which showed that arsenic is not affected by the water content, could not be confirmed in our study, as arsenic was significantly different at a water content of ≥30 % compared to the water-free sample. Nevertheless, the overall change in arsenic concentration was low. This is presumably due to the high fluorescence radiation emitted by arsenic as a relatively heavy element [81,82].

Overall, results indicate that the water content affects the measurement results, so samples with high water content ≥10 % should be considered with caution or should be dried before the measurement. In this way, the possible influence of the water content factor can be avoided.

4.5. Impact of measuring time

The longer the measurement time in X-ray fluorescence analysis, the more counts are generated [53]. This means that more fluorescence radiation strikes the detector, and thus more information about the specific element is gathered (Fig. 11, left).

Consequently, better information on element concentration should be obtainable with longer measurement times, resulting, e.g. in a more precise measurement or in a lower detection limit for each element [71,73,74]. This effect was noticeable in the measurements of solid biofuels performed here. Overall, a decrease in the LOD was typically observed with increasing measurement time. This function is exponential (see example in Fig. 11, right).

When the individual element concentrations measured are

Table 3
X-ray attenuation length determination for the matrix of cellulose $C_6H_{10}O_5$ with an assumed density of 0.5 g/cm^3 and an angle of 45° with 1 % returning photons (Attenuation Length ($I/I_0 = 1/e$): The depth into the material measured along the surface normal where the intensity of x-rays falls to 1/e of its value at the surface; Information depth ($I/I_0 = 1/100$): The depth into the material measured along the surface normal where the intensity of x-rays falls to 1/100 of its value at the surface).

Element	Atomic number	Photon Energy Kα [keV]	Attenuation length [μm]	Information depth [μm]
Na	11	1.04	5	23
Mg	12	1.25	8	37
Al	13	1.49	13	60
Si	14	1.74	20	92
P	15	2.01	30	138
S	16	2.31	44	202
Cl	17	2.62	64	294
K	19	3.31	126	580
Ca	20	3.69	176	810
Ti	22	4.51	320	1472
Cr	24	5.41	561	2581
Mn	25	5.90	730	3358
Fe	26	6.40	940	4324
Co	27	6.93	1203	5534
Ni	28	7.48	1494	6872
Cu	29	8.05	1912	8795
Zn	30	8.64	3274	15,060
As	33	10.54	4415	20,309
Cd	48	23.17	35,000	161,000
Pb (Lα)	82	10.55	4500	20700

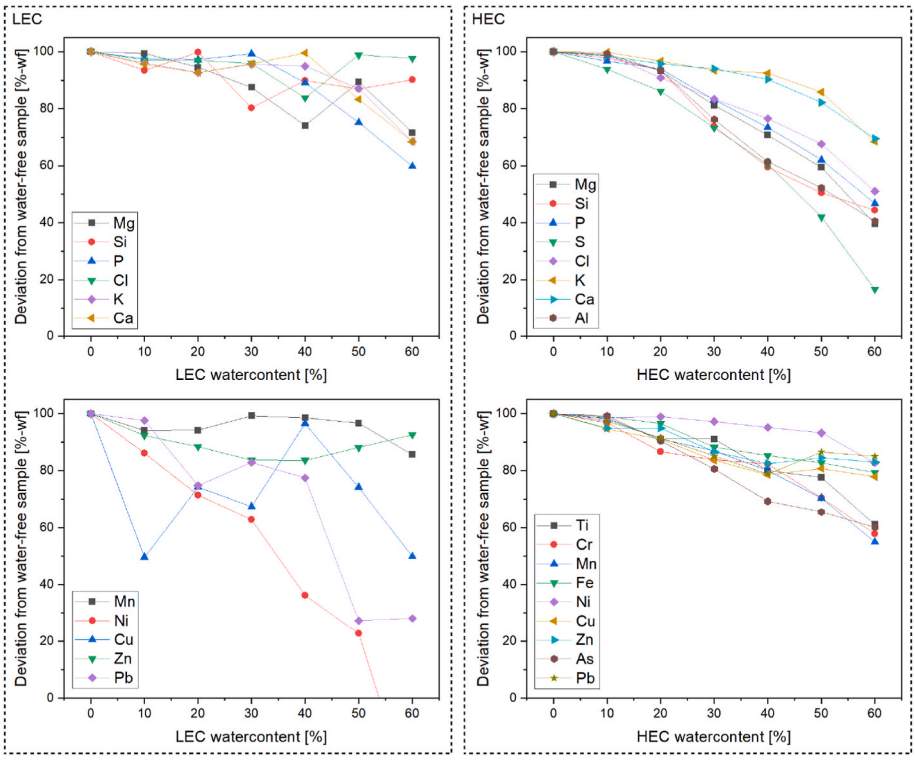

Fig. 9. Deviation in element concentration from the concentration in a water-free sample in % in relation to the sample water content (re-calculated to water-free) [%] (LEC = beech stem wood without bark, HEC = landscape maintenance material, n = 4 per water content level).

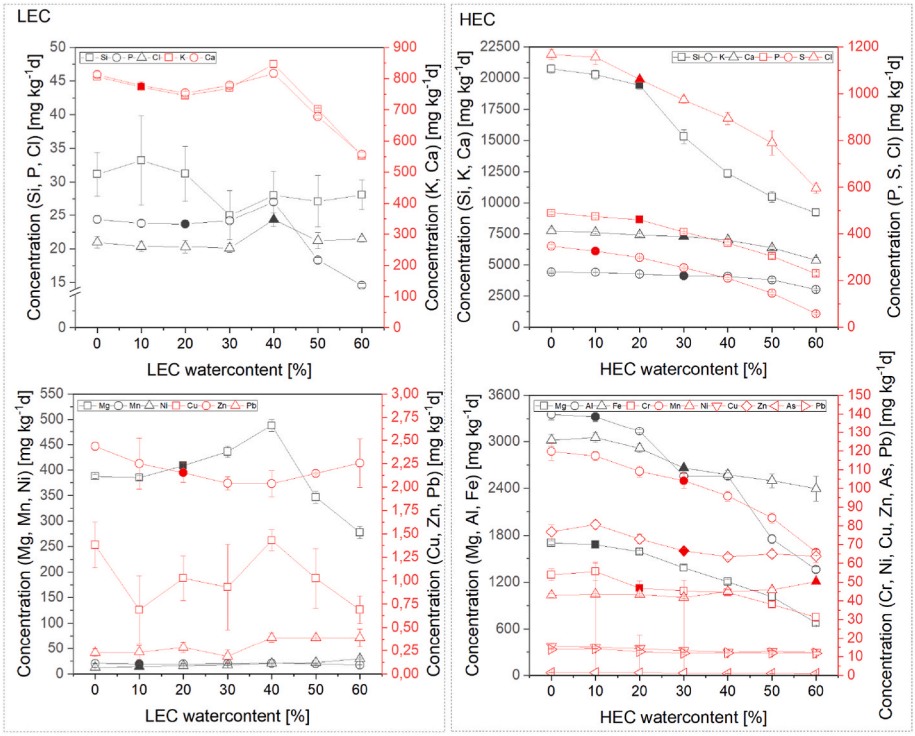

Fig. 10. Concentration of elements measured with XRF in relation to the water content of the sample (LEC = beech stem wood without bark, HEC = landscape maintenance material; n = 4 (wf) per water content level; filled values represent the earliest water content with a statistically significant difference to the water-free sample).

considered in relation to the measurement times, almost no element shows statistically significant deviations (Fig. 12). Only Mn in the HEC sample showed a significant deviation from all other measuring times from the 750 s sample ($p = 0.0317$). In this case, an increasing trend of the concentrations with decreasing measurement duration can be seen.

The findings presented here are consistent with other studies using

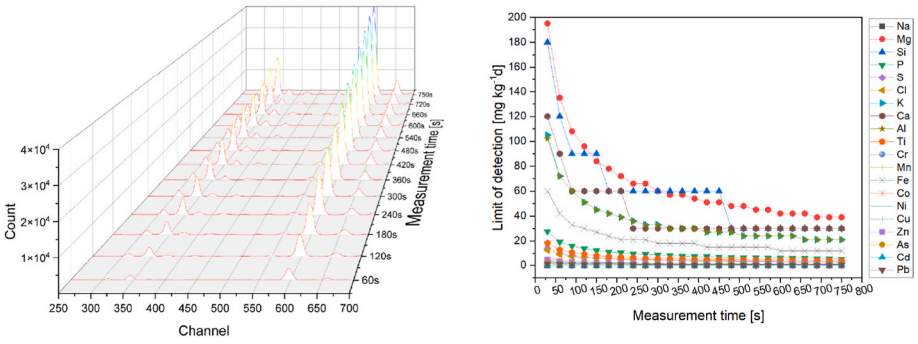

Fig. 11. Count during a measurement using XRF in relation to the channel and the measurement time (left) and the limit of detection (LOD) during an XRF analysis in relation to measurement time (right).

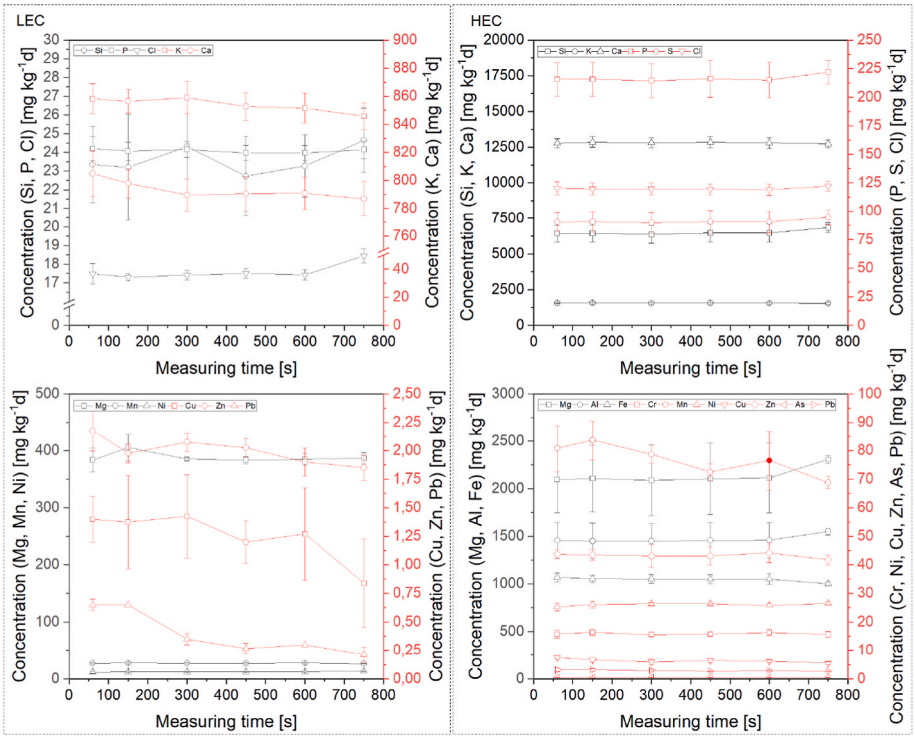

Fig. 12. Concentration of chemical elements measured with XRF in relation to the measuring time from 60 s to 750 s (LEC = beech stem wood without bark, HEC = landscape maintenance material; n = 4 per sample point, wf = water free).

XRF in different sectors. Overall, the measurement time had only a minor influence on the measurement results [71,74]. Similarly, in a study by SAPKOTA (2019) on the rapid analysis of forage, the measurement time for the rapid analysis of solid biofuels could be reduced to 60s without a loss of accuracy [71].

5. Conclusions

The study investigated various effects on XRF analysis for solid biofuels. The following conclusions can be drawn from the results:

The sample stability was not affected by the analyser. Thus, the same sample can be measured several times without altering the results allowing it to use, e.g. as a retained sample that can be stored even after the whole batch is combusted.

Interferences occurred between Si and P in samples that were contaminated with mineral impurities. Thus, results on P from samples with high ash contents should be considered critically. Alternatively, the XRF device might be calibrated especially to samples that are high in Si.

Extensive milling leads to highly homogenised samples. However, when XRF should be used as a rapid measurement device, e.g. for limit value control, the absolute precision may be less important and easy, and fast handling in the field might be of higher relevance.

The water content had a considerable influence on the measurement results. Water contents should not exceed 20 %, while even smaller values $\leq$ 10 % are recommended.

The factory setting using a measuring duration of 750s could be distinctly reduced to 60s without losing precision. Attention has to be paid to the LOD as it exponentially increases at lower measuring times.

Results from this study should be validated with other XRF devices using solid biofuels to reveal which of the effects are device-specific and which are typical sources of errors in XRF measurement.

CRediT authorship contribution statement

Felix Endriss: Conceptualization, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft. **Daniel Kuptz:** Investigation, Methodology, Writing – review & editing. **Dirk Wissmann:** Formal analysis, Resources, Writing – review & editing. **Hans**

Hartmann: Writing – review & editing. **Elke Dietz:** Resources, Writing – review & editing. **Andreas Kappler:** Writing – review & editing. **Harald Thorwarth:** Conceptualization, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Dirk Wissmann reports a relationship with Spectro Analytical Instruments GmbH that includes: employment.

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Appendix

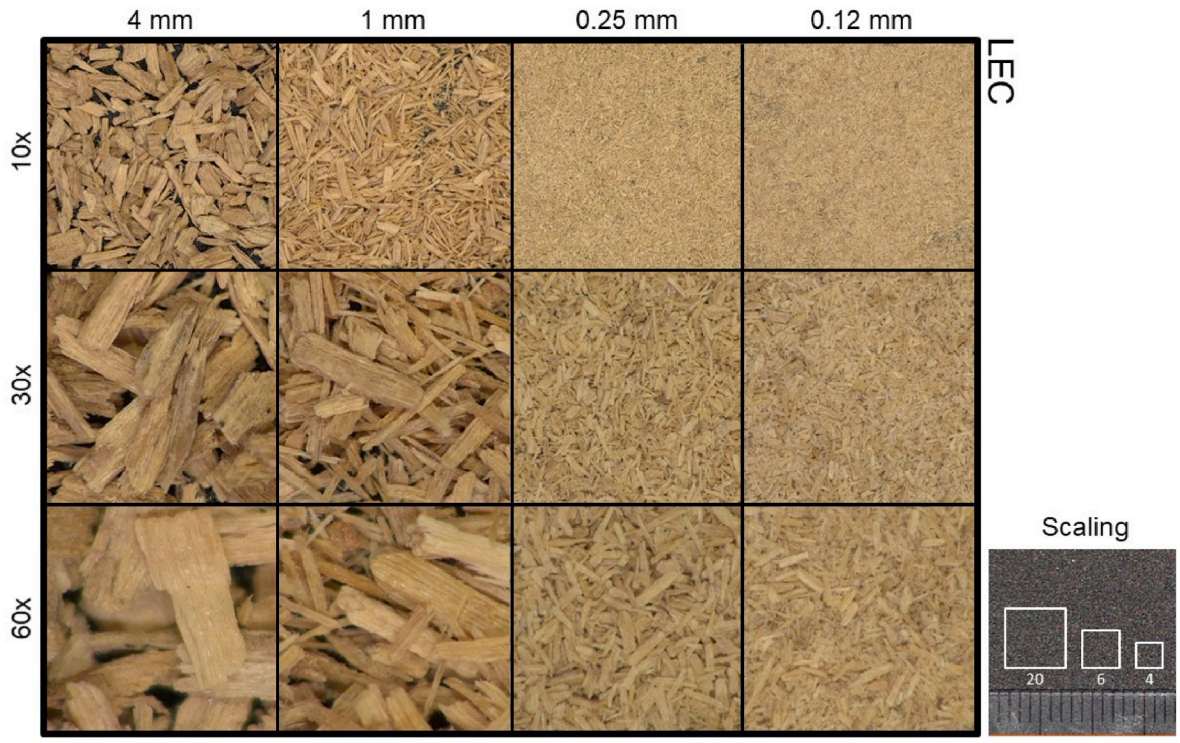

Fig. 13. Different microscope images magnified 10×, 30×, and 60× of various sample preparations. Sample Material: Stemwood of beech without bark (LEC = low element concentration sample)

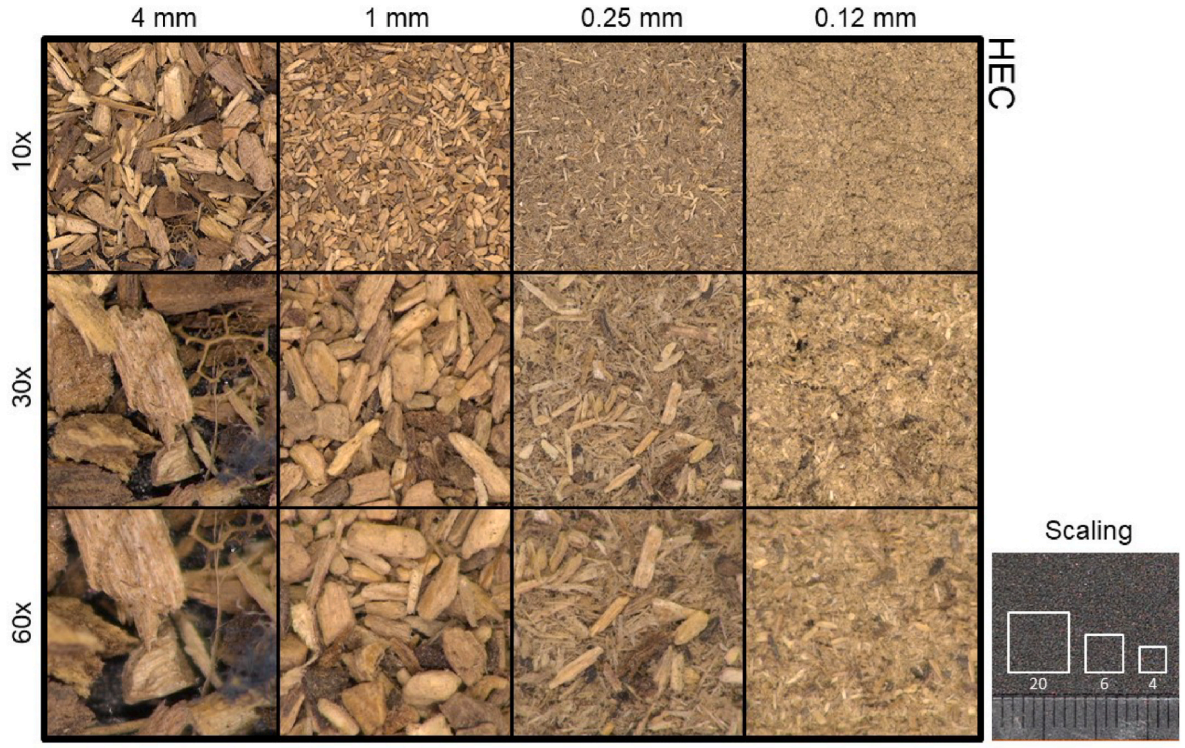

Fig. 14. Different microscope images magnified 10×, 30×, and 60× of various sample preparations. Sample material: landscape maintenance material (HEC = high element concentration sample)

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Appendix IV

Publication 4

Evaluation and Optimisation of an X-Ray Fluorescence Analyser for Rapid Analysis of Chemical Elements in Solid Biofuels

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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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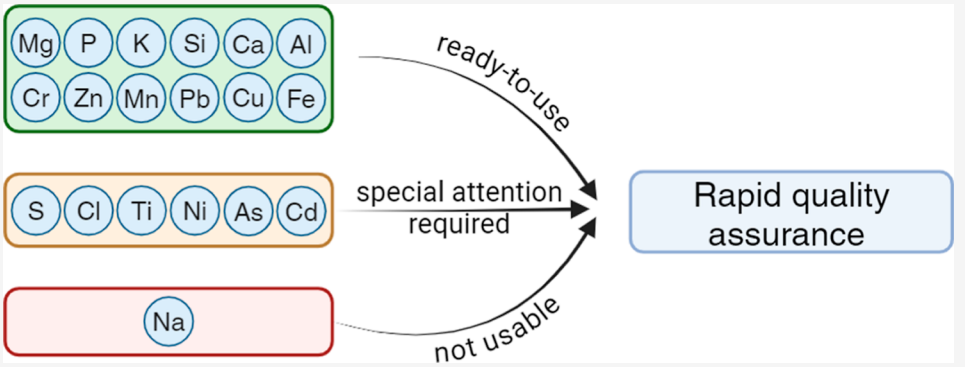

ABSTRACT: To optimize wood-fired heat (and power) plants, it is essential to rapidly determine the chemical composition of solid biofuels on-site shortly before combustion. However, the standard procedures for chemical analysis [inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively 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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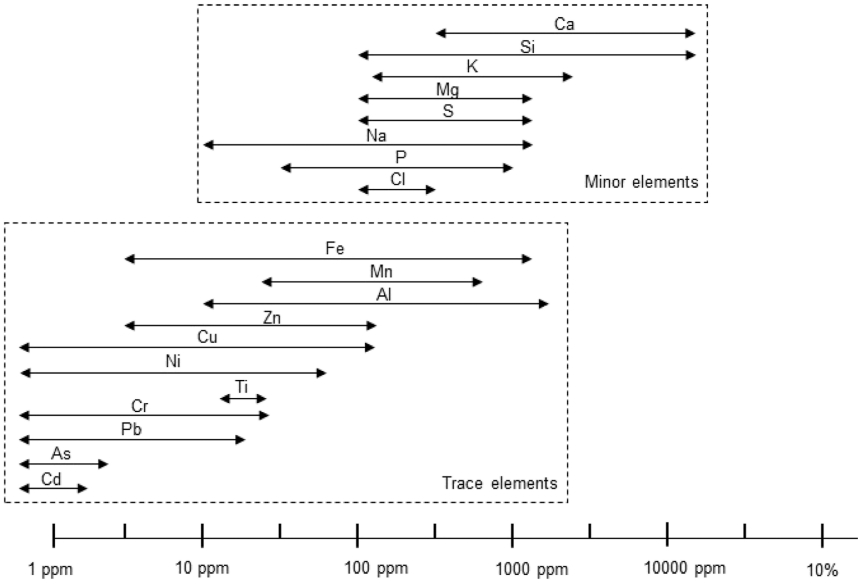

Figure 1. Range of minor and trace element concentrations (db = on dry basis) in solid biofuels which are investigated in this study (selected elements excluding N, F, Hg and V; data: ISO 17225-1[12]).

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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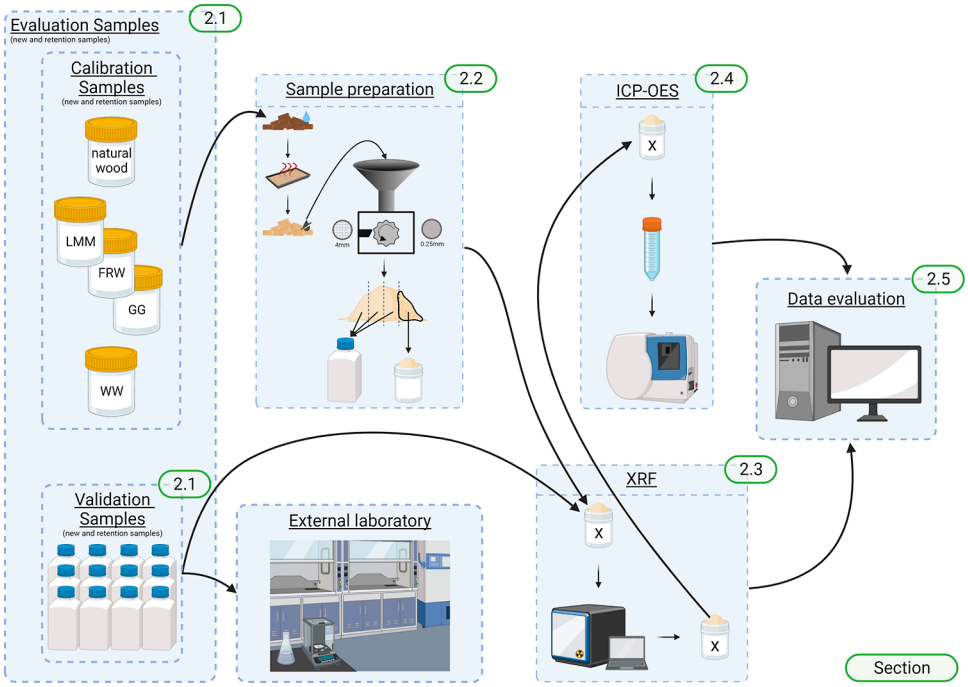

Figure 2. Sequence of sample preparation, analysis and statistical evaluation during this study.

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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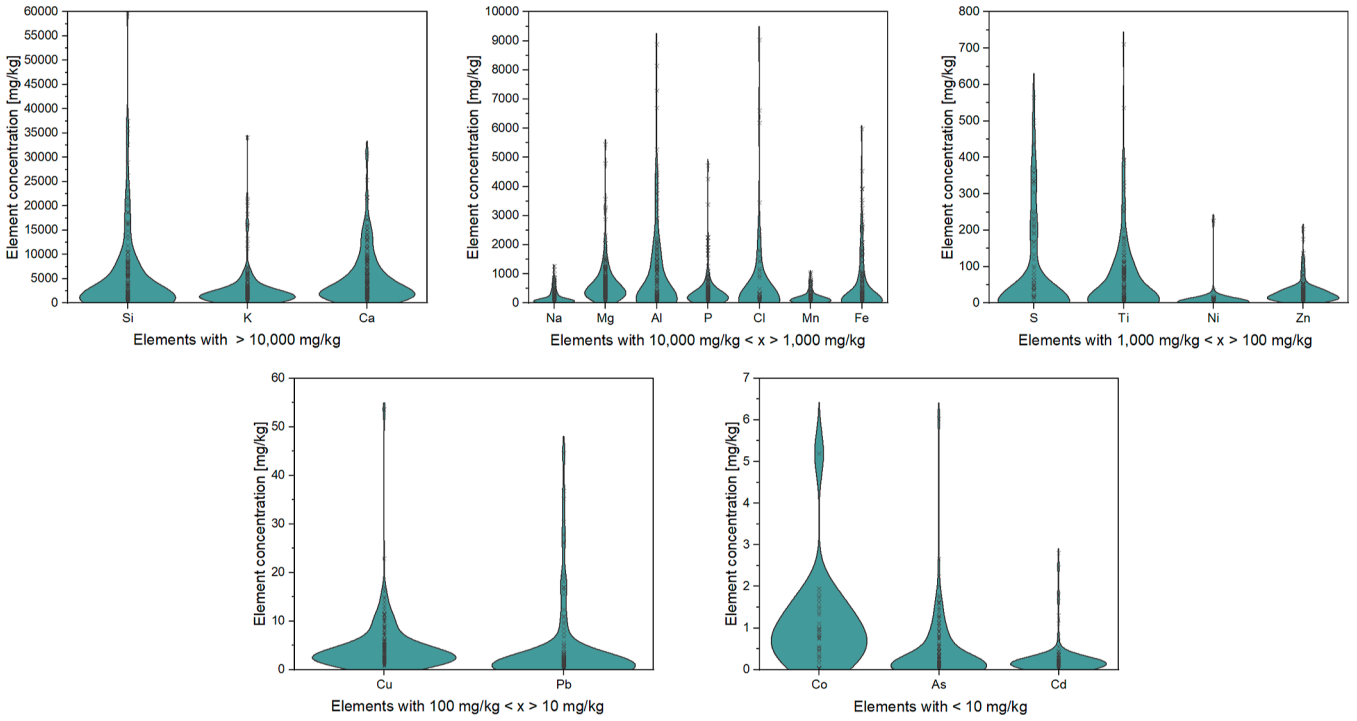

Figure 3. Concentrations of selected chemical elements (ICP-OES) in the different calibration samples (n = 64) and validation samples (n = 229). Combined presentation of all samples as violin plot with Kernel-smoothing.

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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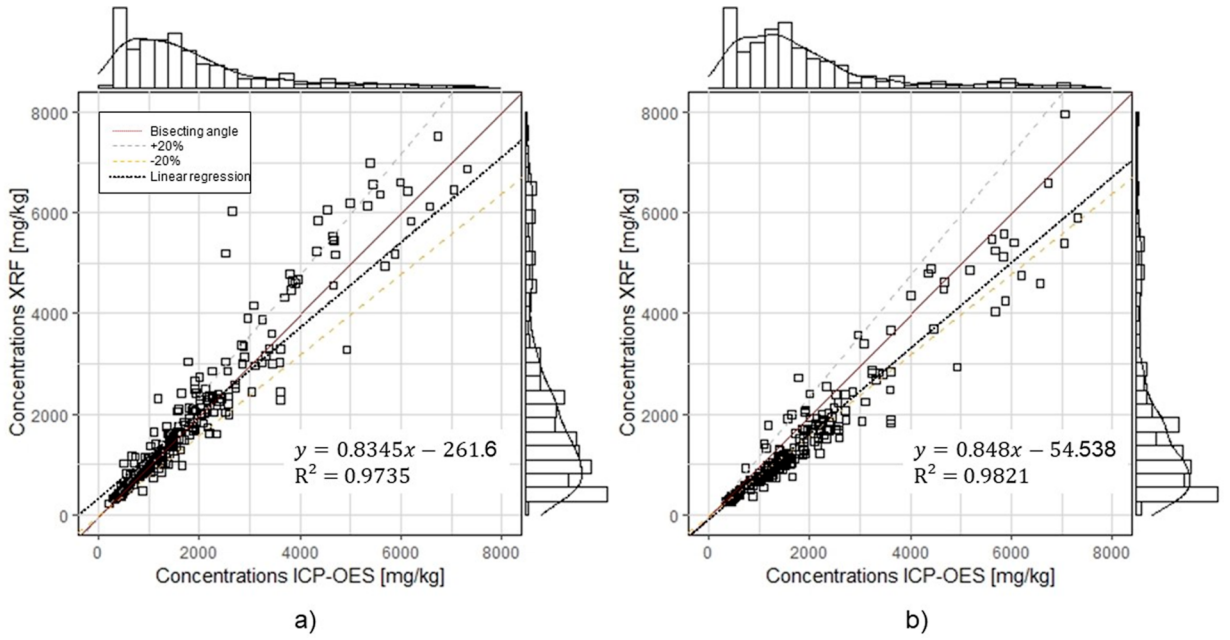

Figure 4. Linear regressions between XRF measurements and reference method ICP-OES for potassium before calibration (a) n = 262 and after calibration (b) n = 229 (all values on dry basis including outliers and values < LOD).

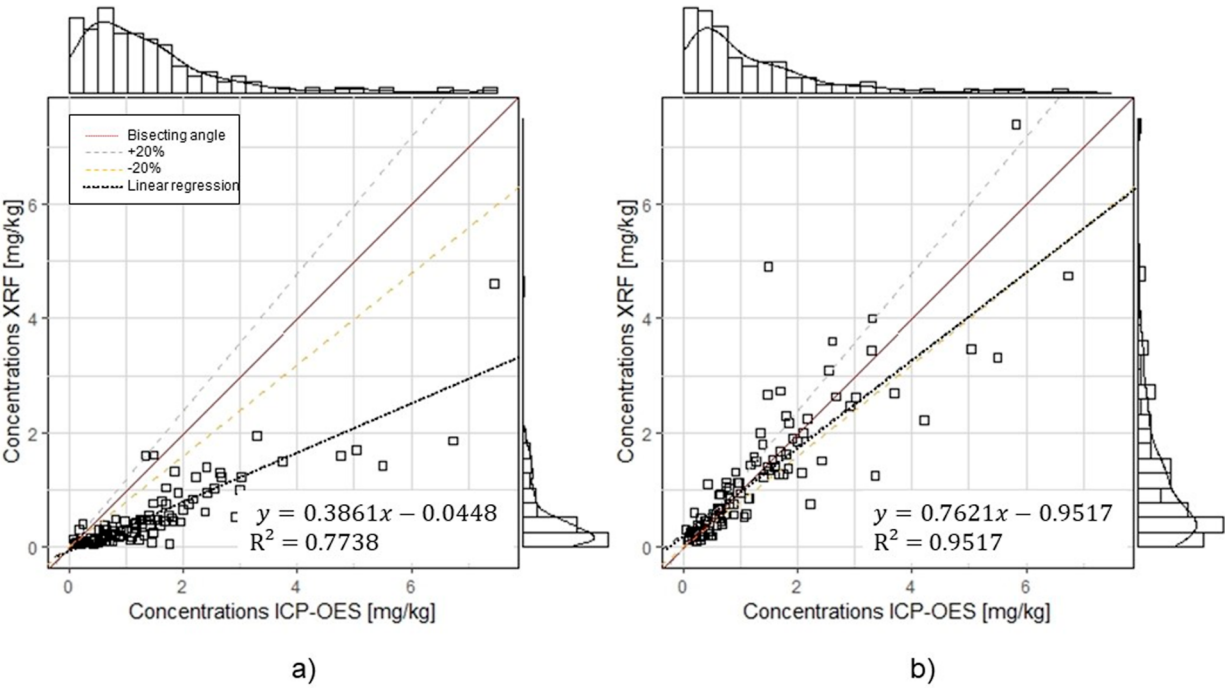

Figure 5. Linear regressions between XRF measurements and reference method ICP-OES for lead before calibration (a) n = 128 and after calibration (b) n = 118 (all values on dry basis including outliers and values < LOD).

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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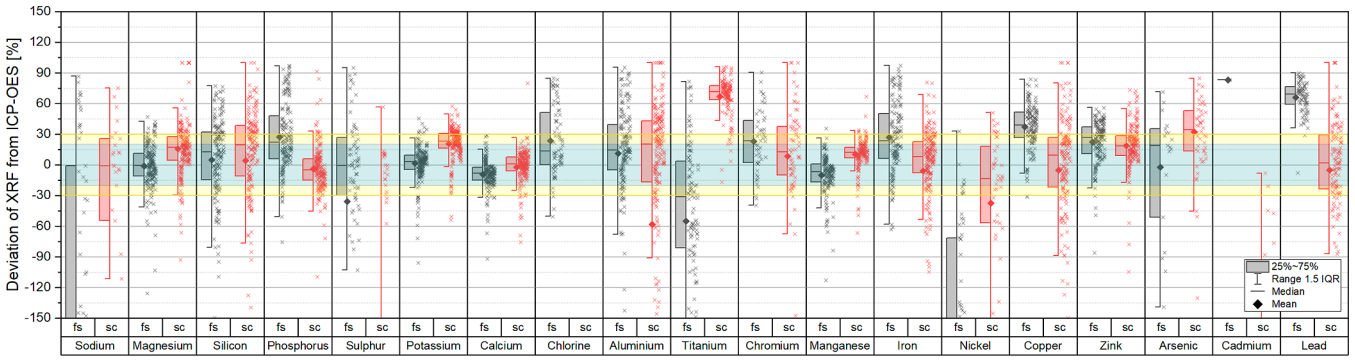

Figure 6. Deviation of the XRF measurements from the reference method ICP-OES in [%] with outliers for solid biofuels (n = Table 4; fs: factory settings used during the initial evaluation, sc: specific calibration used during final validation).

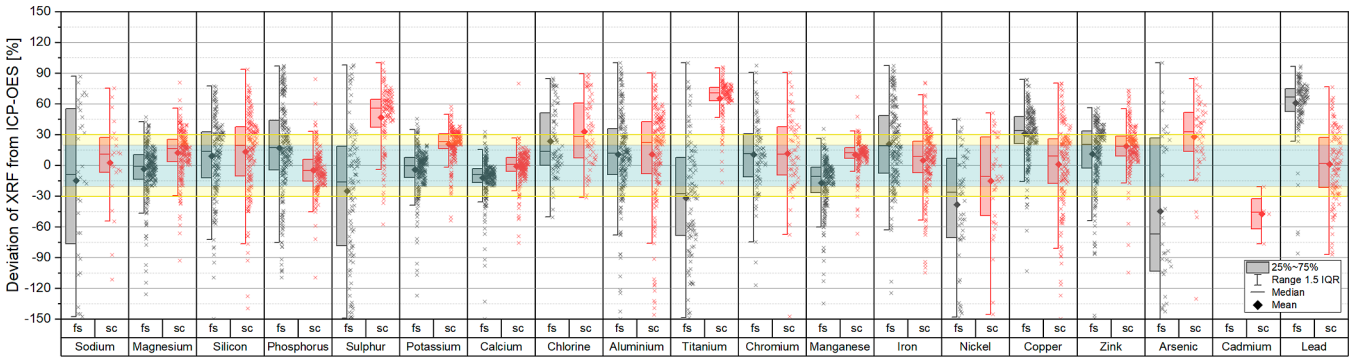

Figure 7. Deviation of the XRF measurements from the reference method ICP-OES in [%] without outliers for solid biofuels ($n \leq 229$; fs: factory settings used during the initial evaluation, sc: specific calibration used during final validation).

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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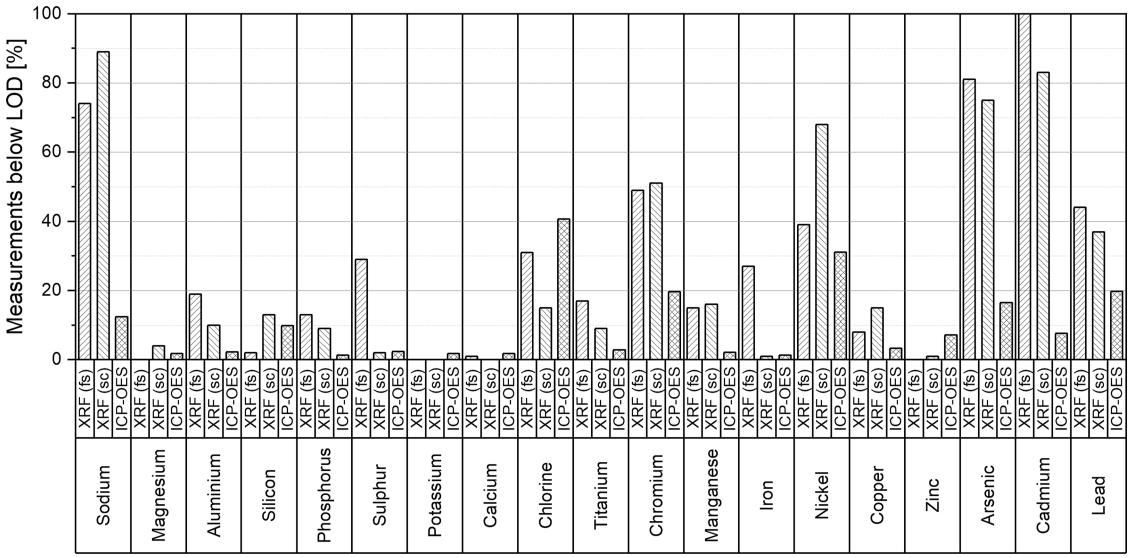

Figure 8. Measurements below the LOD in [%] (n = 229; values of XRF relate to "after calibration").

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

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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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Supporting Information

Evaluation and optimisation of an X-Ray fluorescence analyser for rapid analysis of chemical elements in solid biofuels

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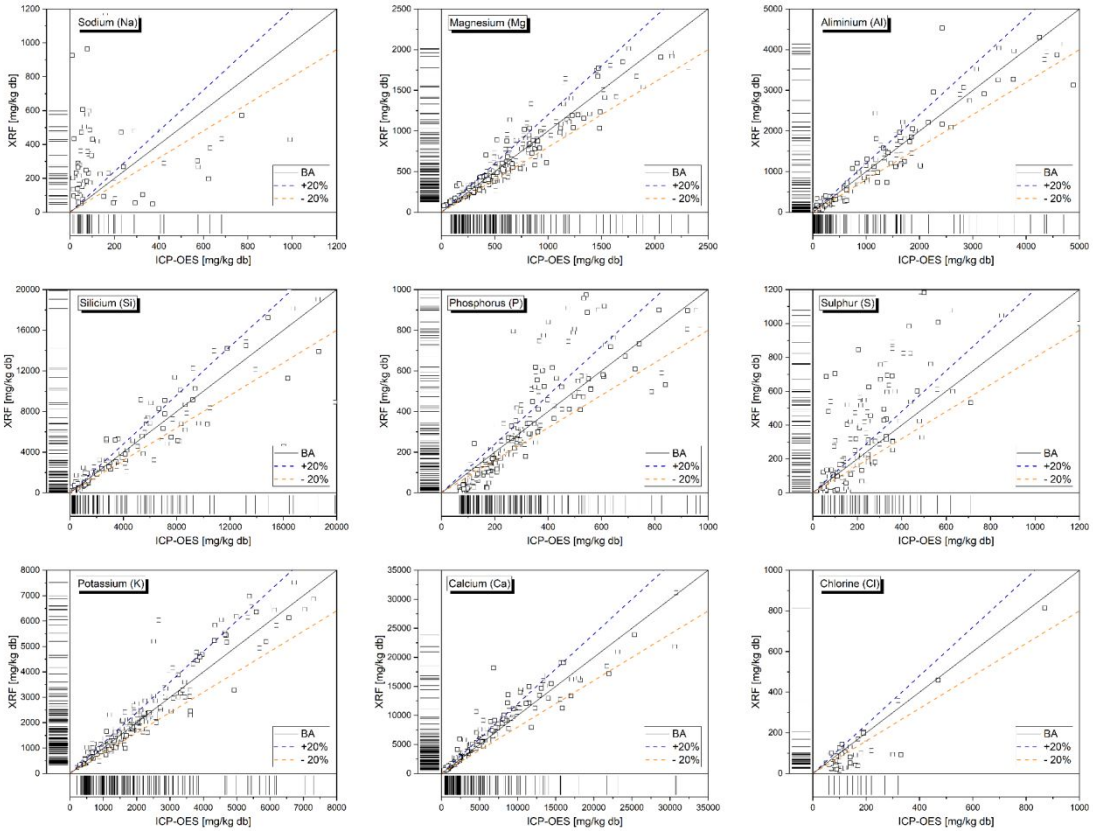

Figure S1: Linear regression between XRF (rapid analysis) and ICP-OES (reference method) by measurement of minor elements (including Al) of solid biofuels using the factory setting (BA = Bisecting angle)

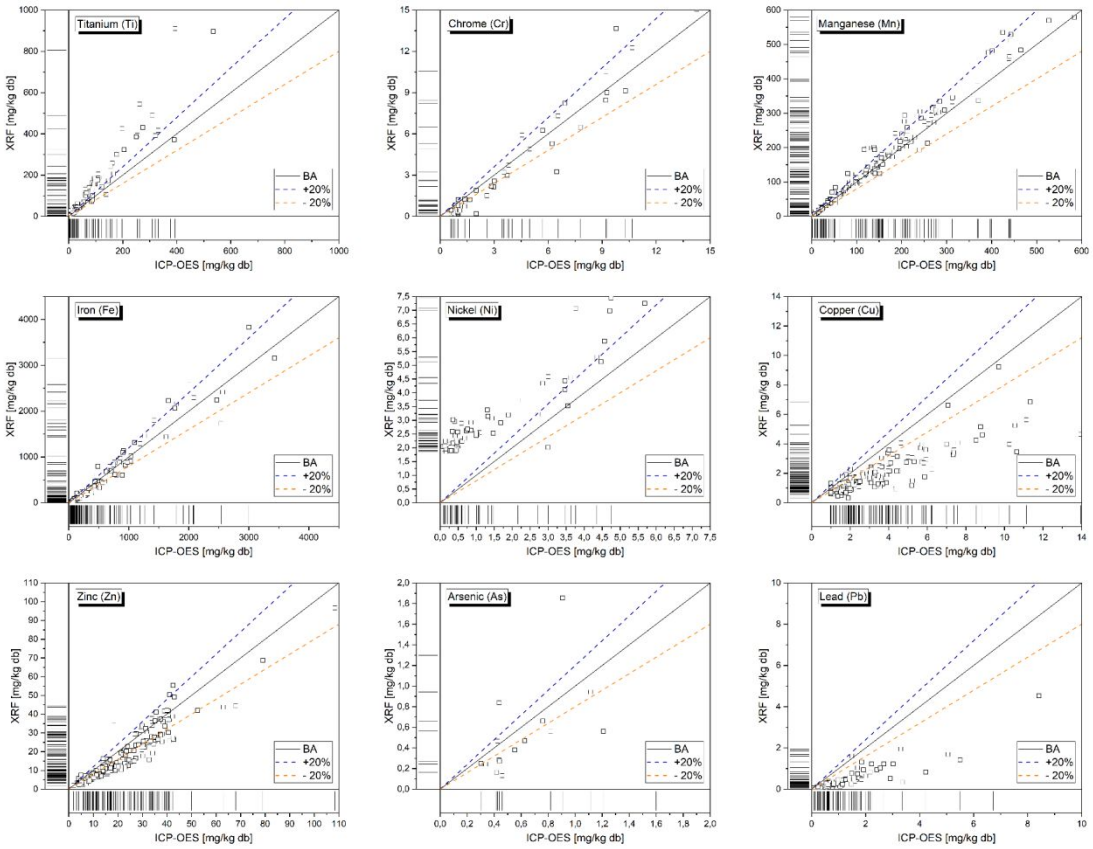

Figure S2: Linear regression between XRF (rapid analysis) and ICP-OES (reference method) by measurement of trace elements of solid biofuels using the factory method, excluding Al (included in minor elements), and Co & Cd (almost under LOD) (BA = Bisecting angle)

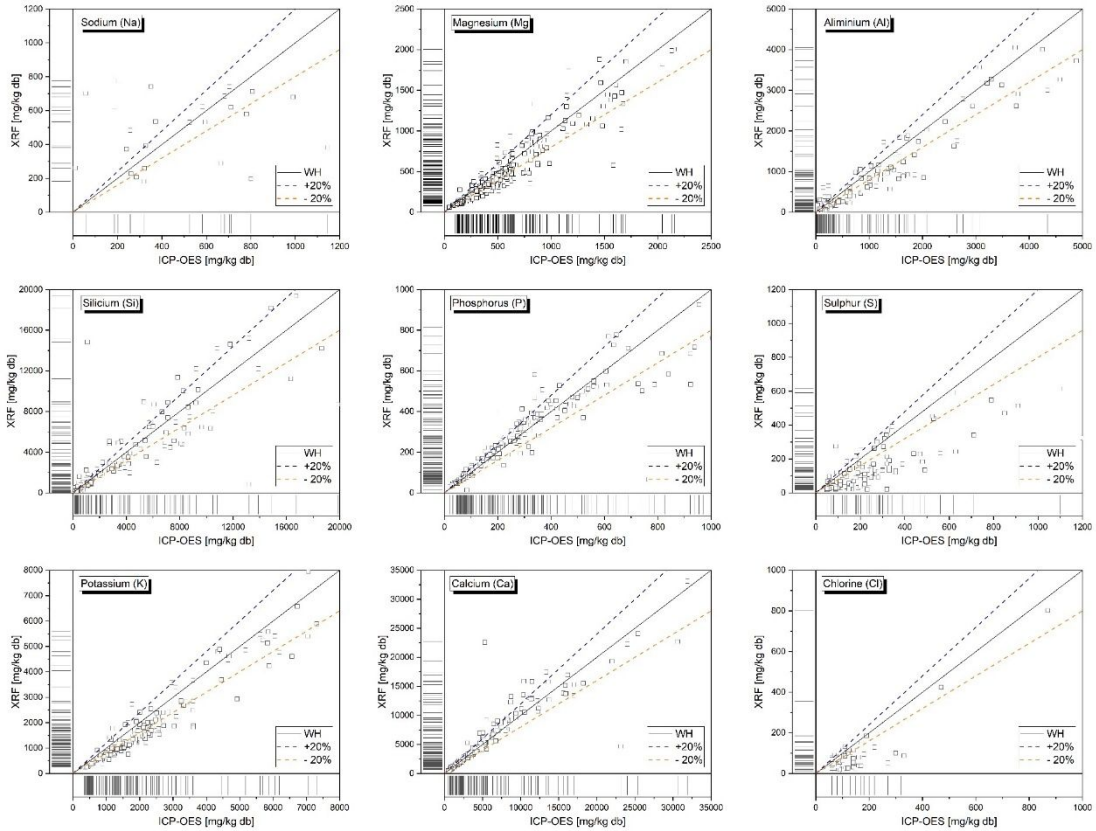

Figure S3: Correlation of the minor elements of the XRF measurement and the reference method ICP OES (including Al) based on a specific calibration (BA = Bisecting angle)

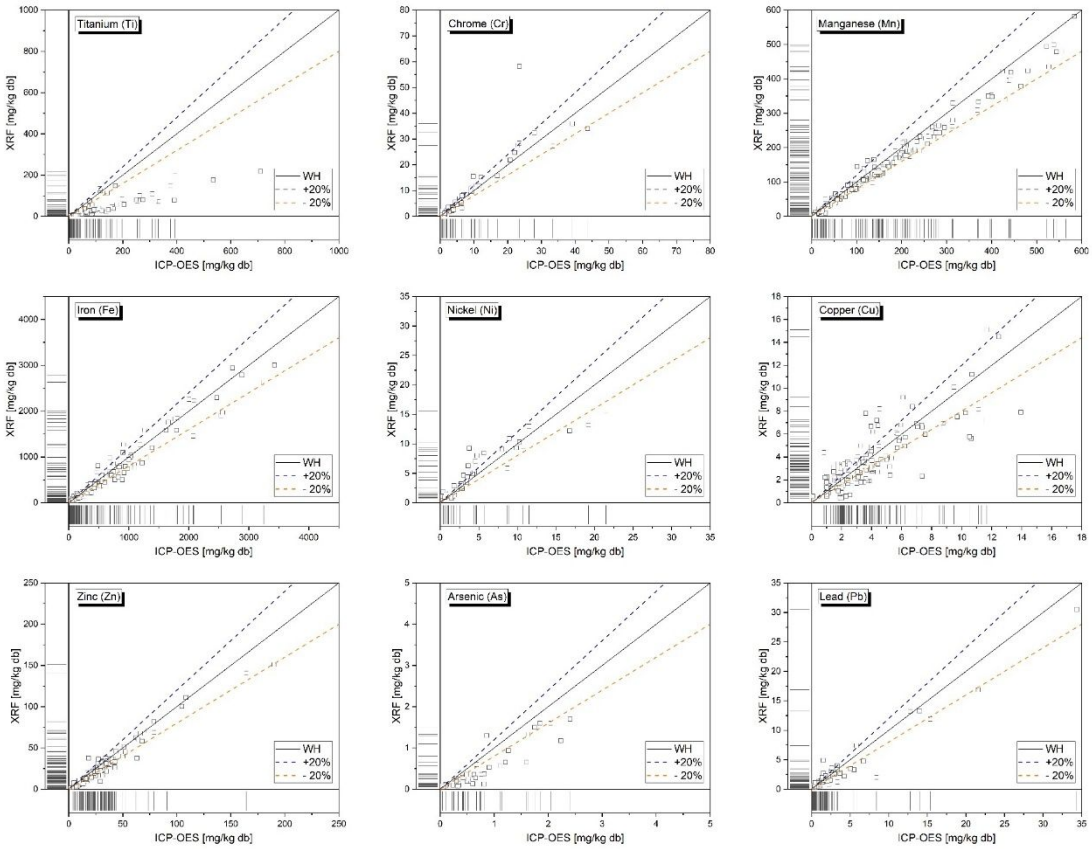

Figure S4: Correlation of the trace elements of the XRF measurement and the Reference method ICP OES based on a specific calibration, excluding Al (included in minor elements), and Cd (almost under LOD) (BA = Bisecting angle)