

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

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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 $\leq 10\%$ 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

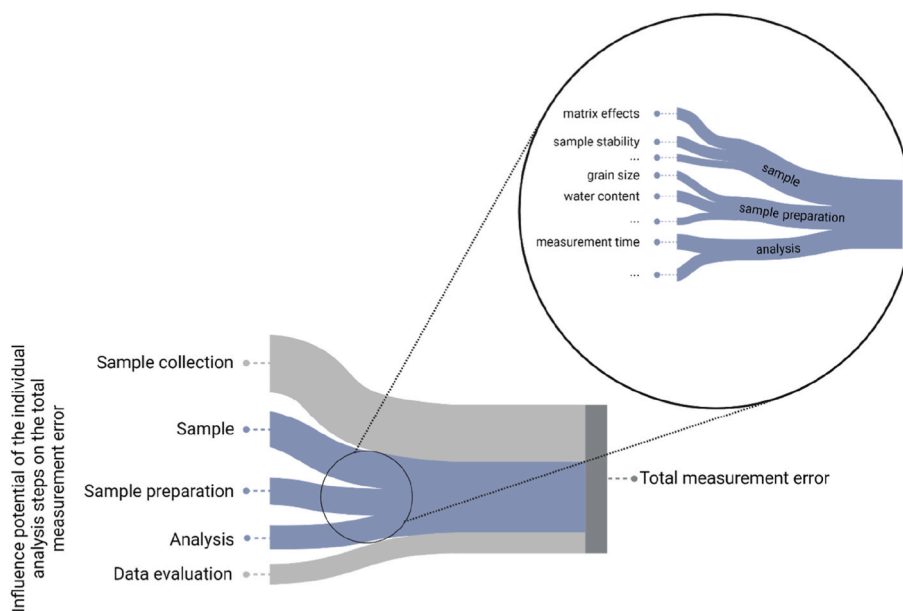


Fig. 1. Schematic drawing of different impacts on the error associated with the measurement of solid biofuels with an X-Ray fluorescence analyser.

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 OPTIMA 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 μ A 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 μ A 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 μ A	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]
Baerenthaler 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 BAERENTHALER 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, SARKOTA 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 $\geq 20\%$ 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 al. (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 SĄPKOTA 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 $105\text{ }^\circ\text{C}$ 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	<ul style="list-style-type: none"> • 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 ($\text{H}_2\text{O} - \text{M } 18.02 \text{ g mol}^{-1} - \text{density } 1.0 \text{ g cm}^{-3}$). 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. $\pm 1 \%$.

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 extent 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 $<130 \text{ eV}$. 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 $4.0 \mu\text{m}$ 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, $400 \pm 1.0 \text{ mg}$ 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 $190 \text{ }^\circ\text{C}$ for 20 min with a heat ramping by $12.6 \text{ }^\circ\text{C min}^{-1}$. 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

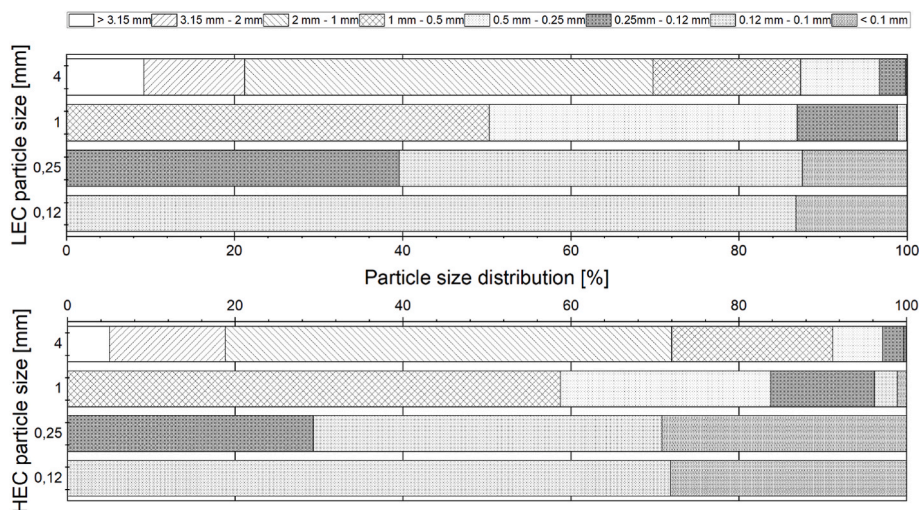


Fig. 2. Particle size distribution (LEC = beech stem wood without bark) and a high element concentrations sample (HEC = landscape maintenance material; $n = 4$).

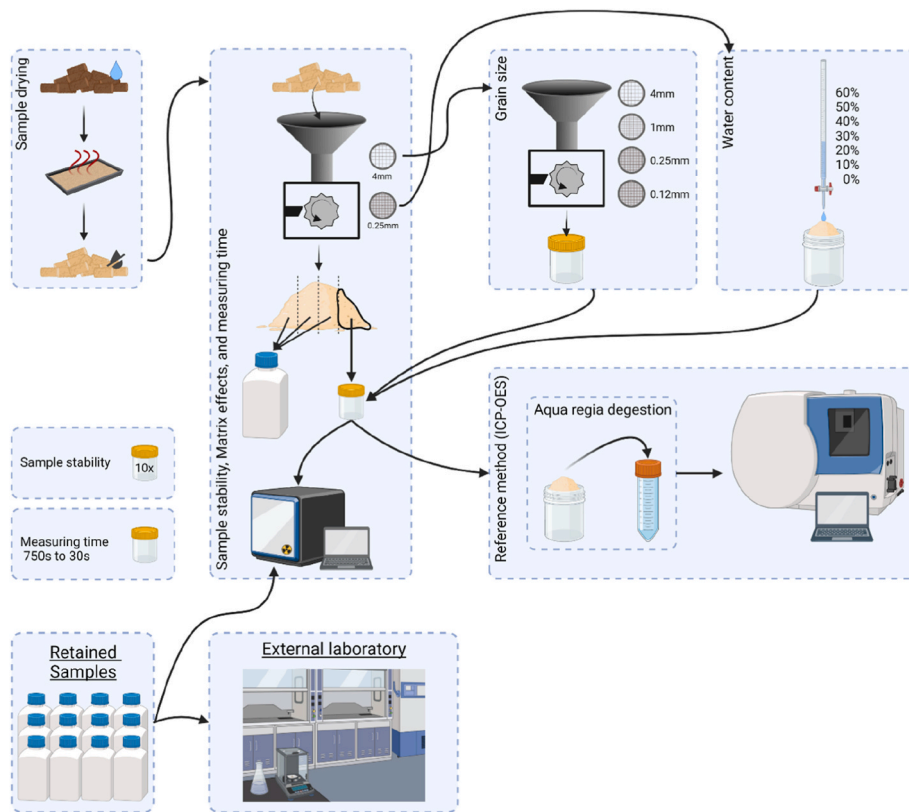


Fig. 3. Overview of sample preparation for the different XRF analysis tests.

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 Wilcoxon 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

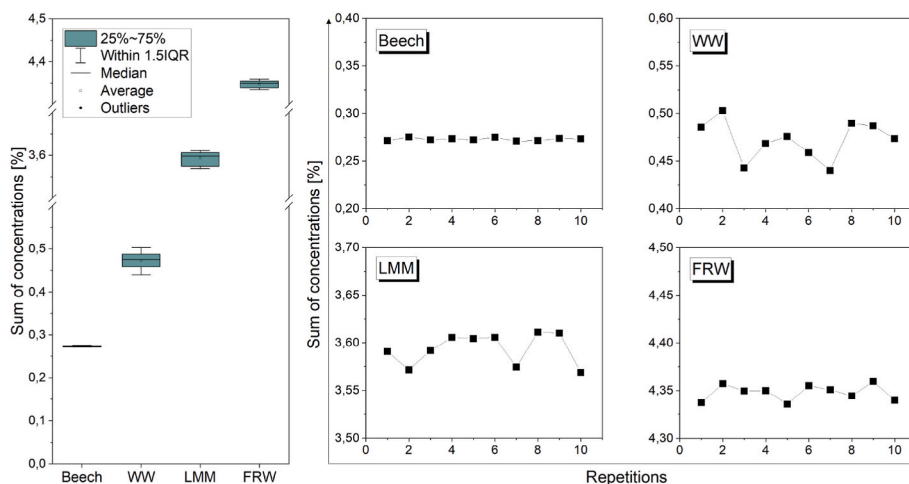


Fig. 4. Sum of concentrations of minor and trace elements according to ISO 17225-1 in beech stem wood (Beech), waste wood (WW), landscape maintenance material (LMM) and forest residue wood (FRW) (Particle size: 0,25 mm; n = 10 per material; left: box plot of all ten measurements, right: individual measurements).

% 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_{α1}; Cd-L_{β1}/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

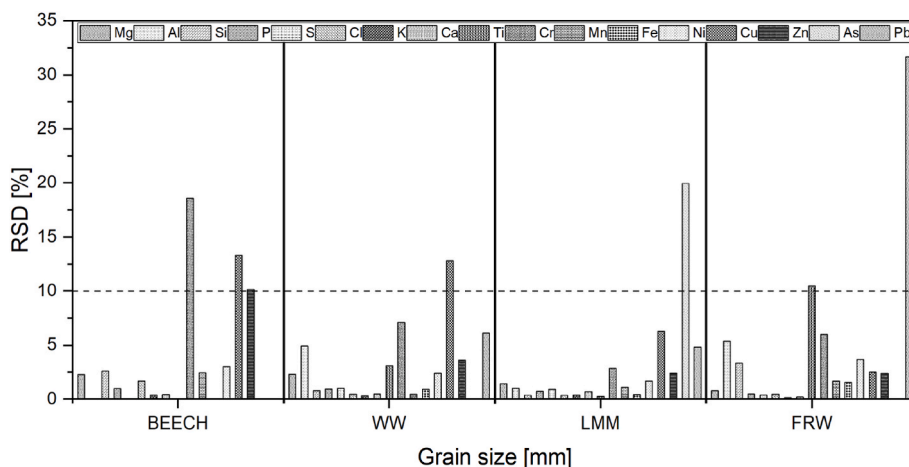


Fig. 5. RSD of element concentrations measured with XRF in four samples (Beech = beech stem wood without bark, WW = waste wood, LMM = landscape maintenance material, FRW = forest residue wood, n = 10 per material).

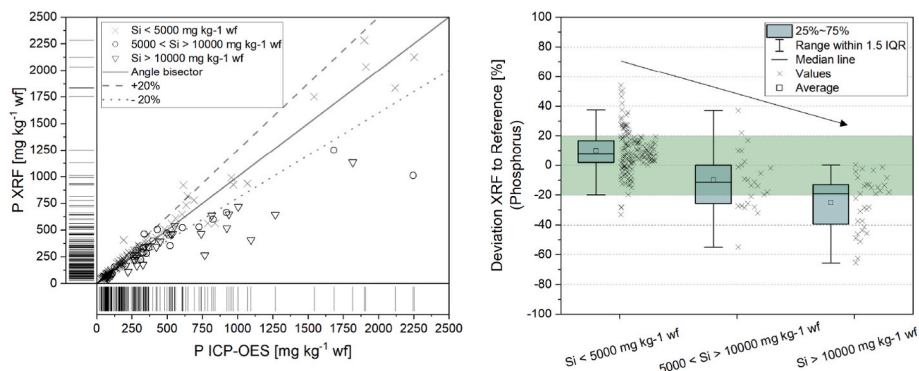


Fig. 6. P measured with XRF in relation to P measured with ICP-OES for wood chips with Si contents below 5000 mg kg⁻¹, 5000 and 10,000 mg kg⁻¹, and above 10,000 mg kg⁻¹ (n = 207, wf = water free; left) and deviation of the XRF values to ICP-OES (right).

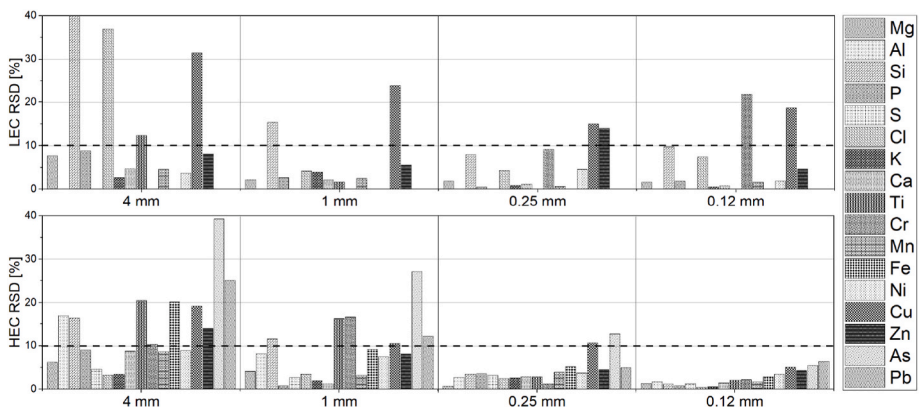


Fig. 7. RSD of element concentrations measured with XRF in a low element concentrations sample (LEC = beech stem wood without bark) and a high element concentrations sample (HEC = landscape maintenance material; n = 4).

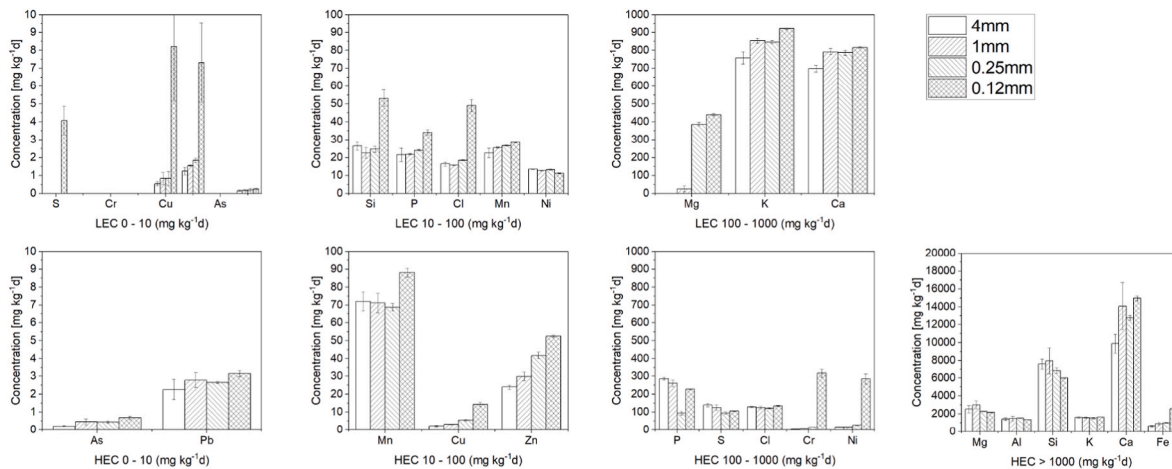


Fig. 8. Concentration of selected elements in two samples (LEC: beech stem wood without bark, HEC = landscape maintenance material; n = 4, each).

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 determined according to the formula: $h = \frac{\ln(0.01)}{\rho \cdot \mu}$ (h = penetration depth; ρ = density [g/cm^3]; μ = mass attenuation coefficient [cm^2/g]). Exemplary for $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ with an assumed density of $0.5 \text{ g}/\text{cm}^3$ the calculated penetration depth shows that for an optimal analysis of the light elements up to Cl a finer milling of the sample to $< 250 \mu\text{m}$ 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 $< 250 \mu\text{m}$ [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 $\geq 20 \%$, 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

Table 3

X-ray attenuation length determination for the matrix of cellulose $\text{C}_6\text{H}_{10}\text{O}_5$ with an assumed density of $0.5 \text{ g}/\text{cm}^3$ 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 $K\alpha$ [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 ($L\alpha$)	82	10.55	4500	20700

some elements at 10 % water content (Fig. 9). Thus, samples should be dried to values $\leq 10 \%$ 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 $\geq 30 \%$ 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 $\geq 10 \%$ 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

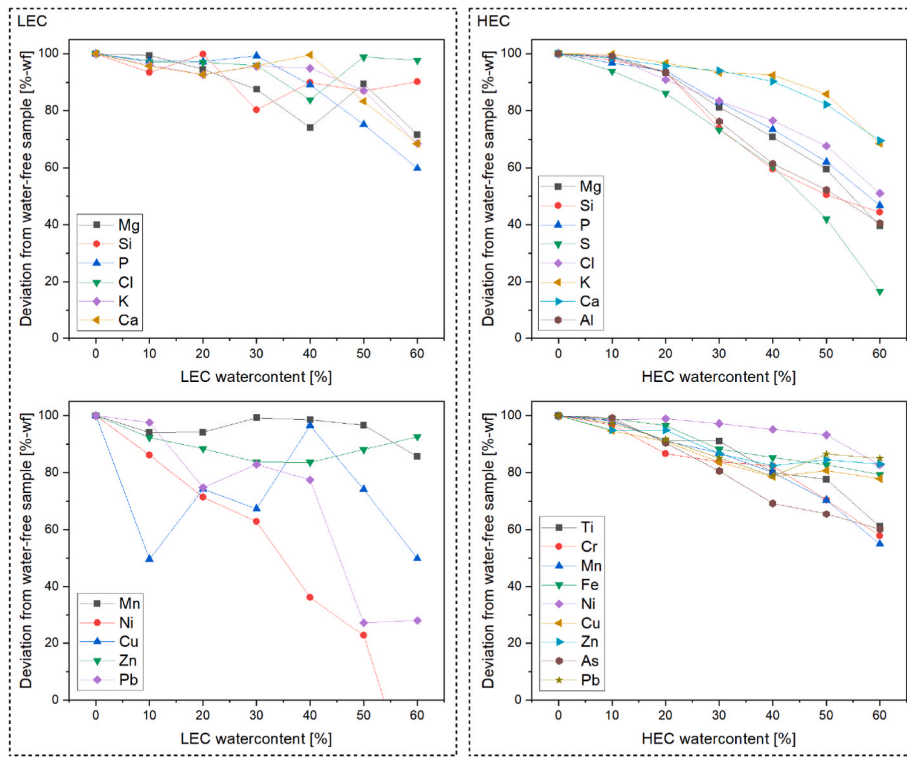


Fig. 9. Deviation in element concentration from the concentration in a water-free sample in % in relation to the sample water content (re-calculated to water-free) [%] (LEC = beech stem wood without bark, HEC = landscape maintenance material, n = 4 per water content level).

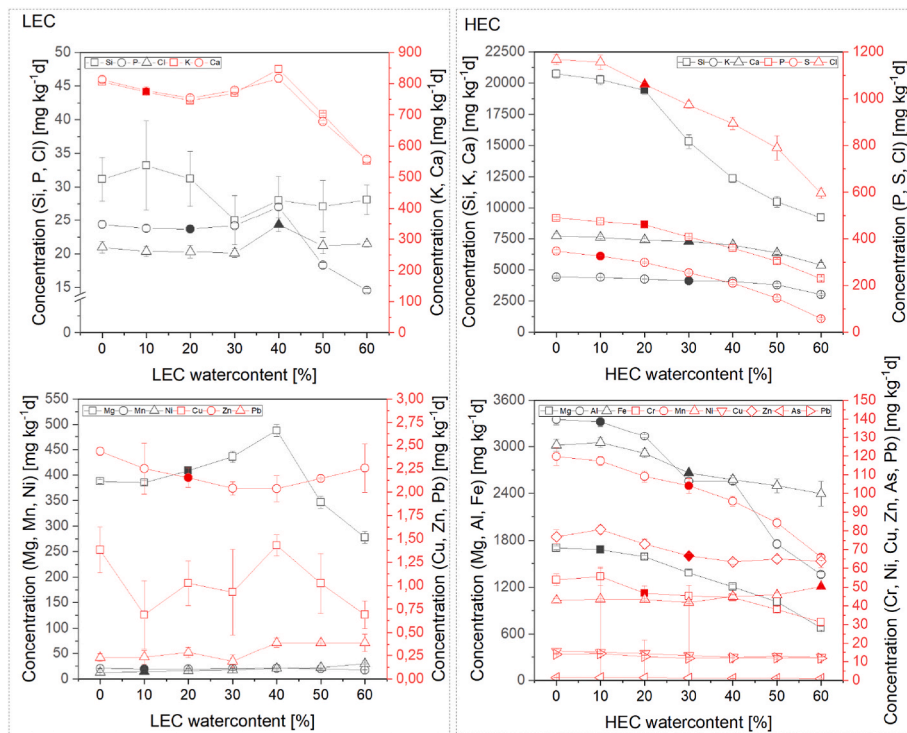


Fig. 10. Concentration of elements measured with XRF in relation to the water content of the sample (LEC = beech stem wood without bark, HEC = landscape maintenance material; n = 4 (wf) per water content level; filled values represent the earliest water content with a statistically significant difference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

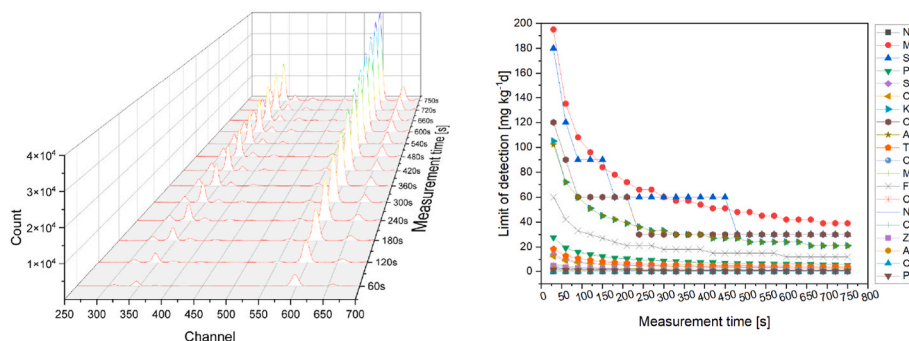


Fig. 11. Count during a measurement using XRF in relation to the channel and the measurement time (left) and the limit of detection (LOD) during an XRF analysis in relation to measurement time (right).

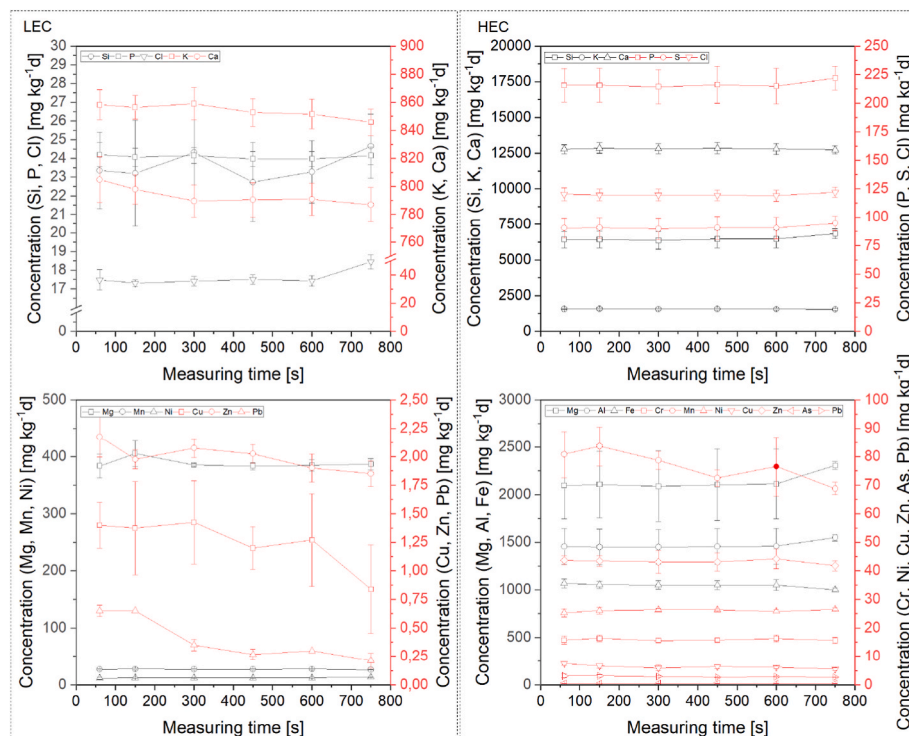


Fig. 12. Concentration of chemical elements measured with XRF in relation to the measuring time from 60 s to 750 s (LEC = beech stem wood without bark, HEC = landscape maintenance material; n = 4 per sample point, wf = water free).

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 ≤ 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

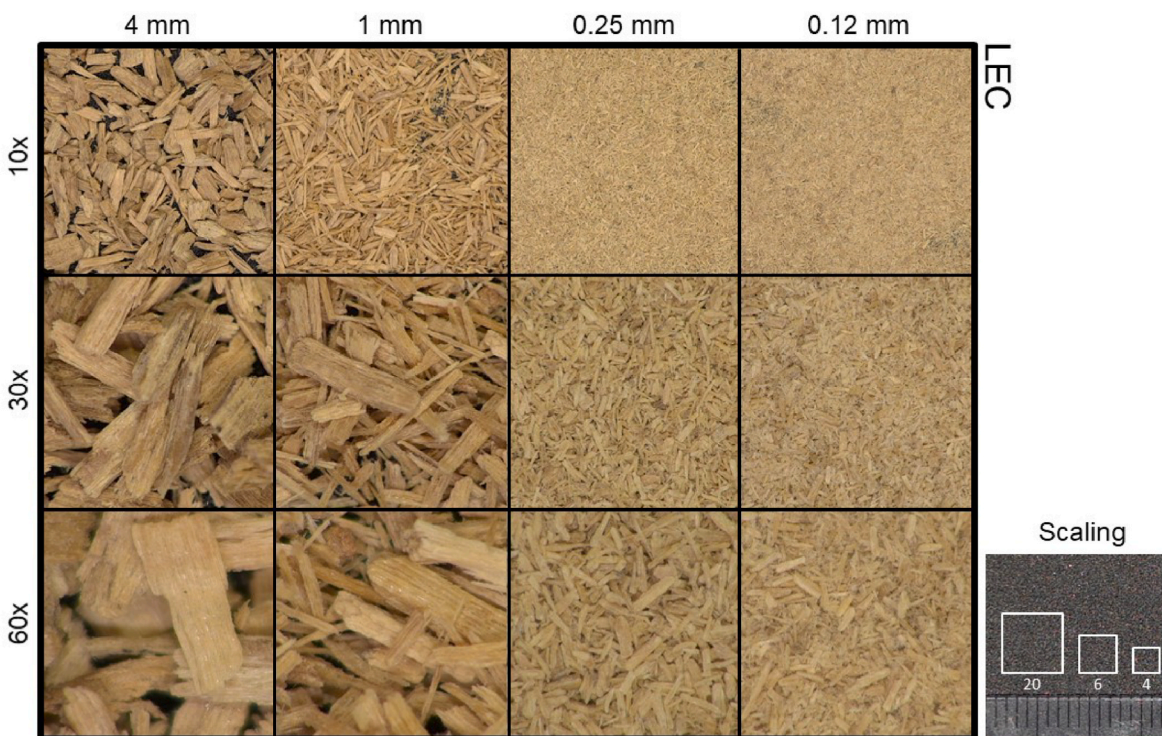


Fig. 13. Different microscope images magnified 10×, 30×, and 60× of various sample preparations. Sample Material: Stemwood of beech without bark (LEC = low element concentration sample)

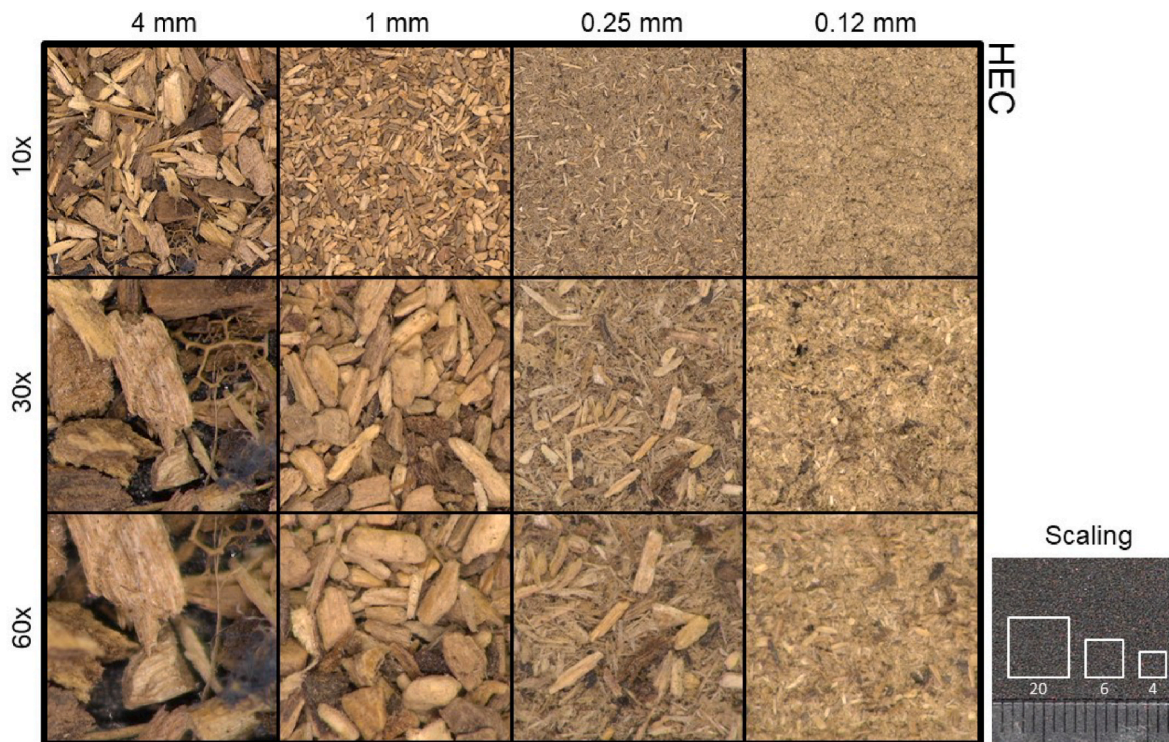


Fig. 14. Different microscope images magnified 10 \times , 30 \times , and 60 \times of various sample preparations. Sample material: landscape maintenance material (HEC = high element concentration sample)

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