

# Analytical Methods for the Rapid Determination of Solid Biofuel Quality

Felix Endriss\*, Daniel Kuptz, Hans Hartmann, Stefan Brauer, Rainer Kirchhof, Andreas Kappler, and Harald Thorwarth

DOI: 10.1002/cite.202200214

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

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

*Received:* December 01, 2022; *revised:* March 15, 2023; *accepted:* May 15, 2023

## 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<sub>x</sub>, 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.

<sup>1</sup>Felix Endriss <https://orcid.org/0000-0002-9768-0449> (endriss@hs-rottenburg.de), <sup>2</sup>Daniel Kuptz, <sup>2</sup>Hans Hartmann, <sup>3</sup>Stefan Brauer, <sup>1</sup>Rainer Kirchhof, <sup>4</sup>Andreas Kappler, <sup>1</sup>Harald Thorwarth

<sup>1</sup>University of Applied Forest Sciences Rottenburg, Schadenweilerohof, 72108 Rottenburg am Neckar, Germany.

<sup>2</sup>Technology and Support Centre in the Centre of Excellence for Renewable Resources, Schulgasse 18, 94315 Straubing, Germany.

<sup>3</sup>APC analytics GmbH, Daimlerstraße 17, 61449 Steinbach, Germany.

<sup>4</sup>University Tübingen, Schnarrenbergstraße 94–96, 72076 Tübingen, Germany.

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 seq. [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

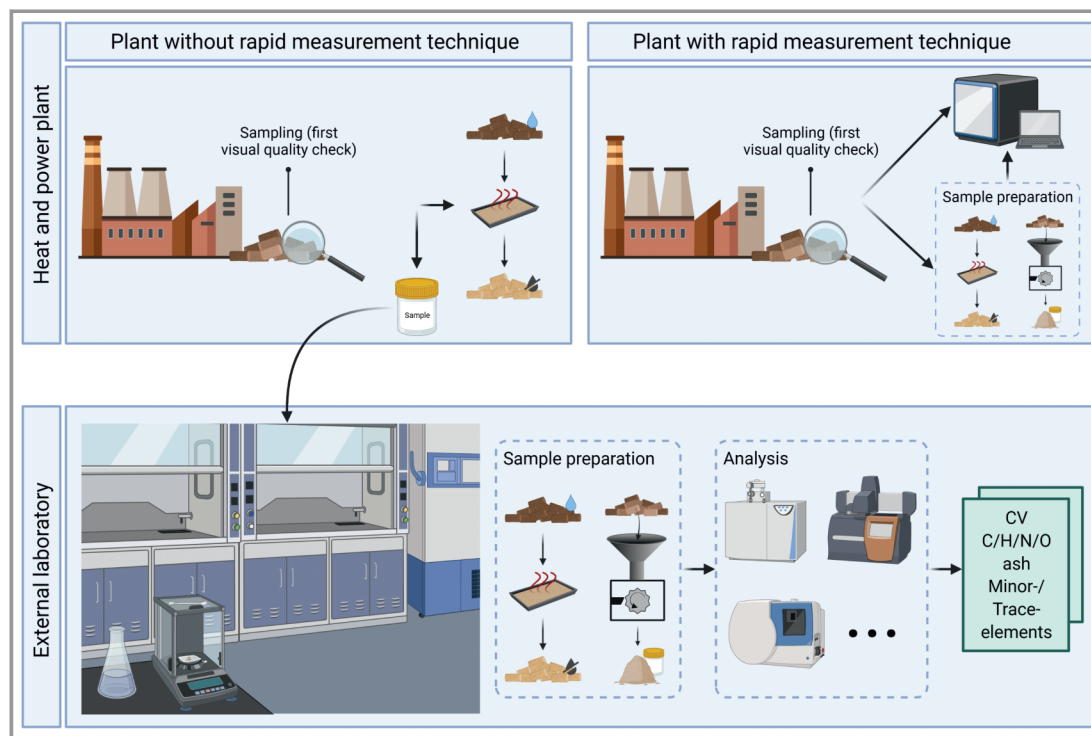
minor sample preparation (e.g., milling) at the plant by the operational staff.

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

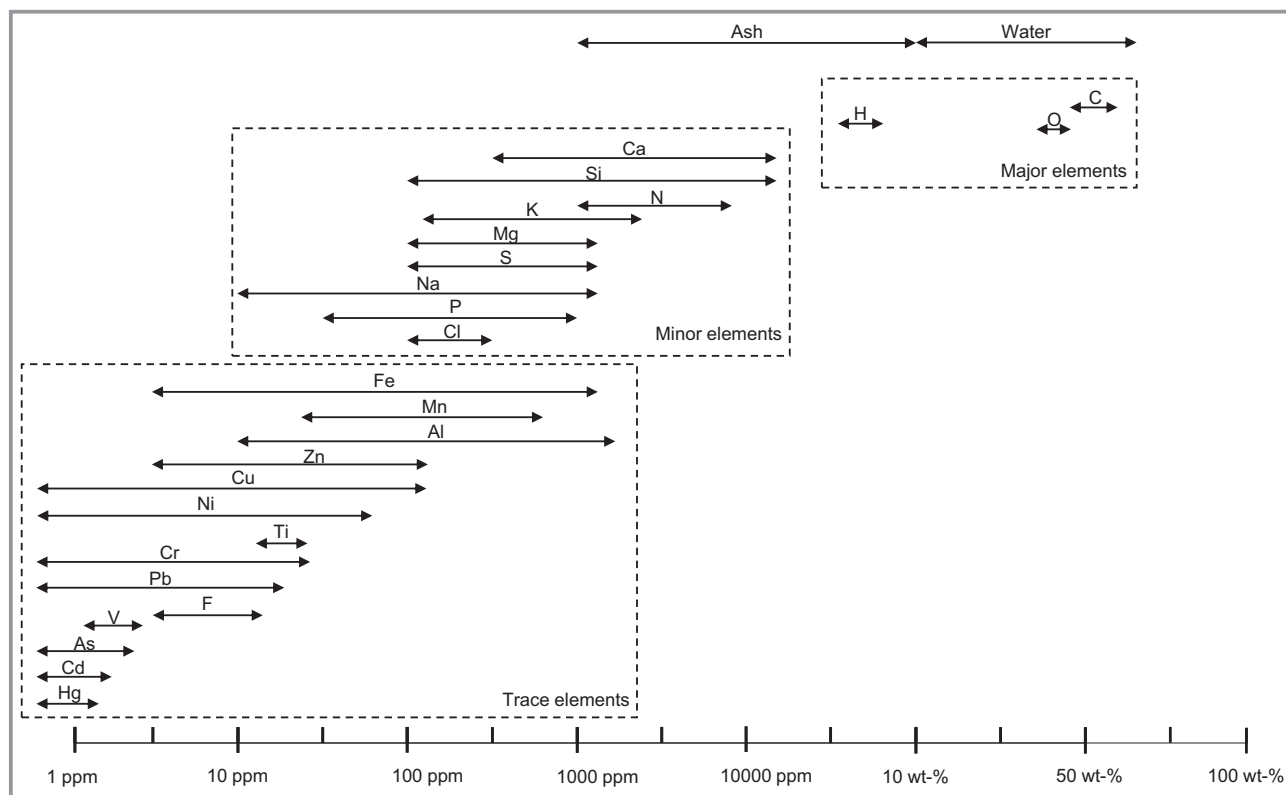


Figure 2. Expected concentrations (wf, excluding water) of different fuel quality parameters in solid biofuels based on ISO 17255-1 [9].

**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 <i>M</i>	Calorific value, storability, fuel mass, combustion temperature, CO emission, TPM emission	ISO 18134-1-3 [13–15]
Ash content <i>A</i>	TPM emissions (dust), residue formation and exploitation, calorific value	ISO 18122 [16]
Calorific value <i>Q</i>	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  $\text{MJ kg}^{-1}$ ). It is specified by wood fuels in gross calorific value with typically  $19.4\text{--}22.7 \text{ MJ kg}^{-1}$  (on dry basis) and net calorific value with  $18.4\text{--}21.3 \text{ MJ kg}^{-1}$  (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 ( $\text{NO}_x$ ) and sulfur dioxide ( $\text{SO}_2$ )

**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, $\text{NO}_x$ - und $\text{N}_2\text{O}$ -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)	$\text{SO}_x$ 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<sub>x</sub> 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

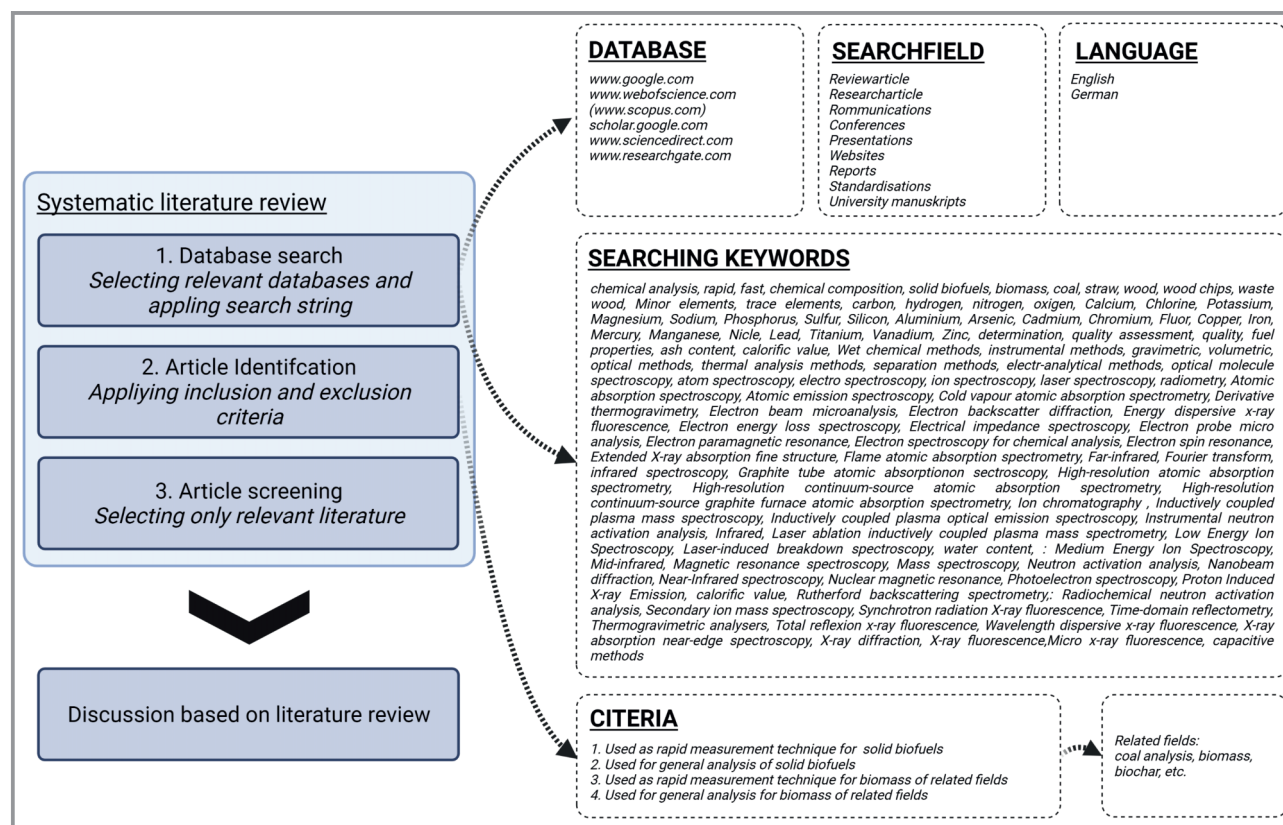


Figure 3. Systematic literature review method.



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<sub>2</sub> 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<sub>2</sub> 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<sup>-1</sup> [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,  $\alpha$ -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 et 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 with 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 back-scattering 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 spectrometry 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 spectrometry.

#### **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 dielectric 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
<i>Gravimetric</i>				
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]		
<i>Volumetric</i>				
Water content		[60]		[41, 60]
Elemental content		[37]		
<i>UV/Vis</i>				
Elemental content	[64]			[67]
Other parameters		[66, 68]		[65, 68, 69]
<i>Infrared spectroscopy</i>				
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]
<i>Raman spectroscopy</i>				
Other parameters		[174]		[79, 104–107]
<i>Microwaves/radio waves</i>				
Water content	[60, 80, 120–125]			[80, 109, 120, 121]
Other parameter		[116, 117, 119]	[118]	[79, 108, 110–115]
<i>Atom absorption spectroscopy</i>				
Elemental content		[140–143]	[150]	[79, 132–134, 136–139]
<i>Atom emission spectroscopy</i>				
Elemental content		[22, 28, 140, 151–153, 162, 177]		[79, 136]
<i>X-Ray spectroscopy</i>				
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]
<i>Electron/ion spectroscopy</i>				
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
<i>Laser spectroscopy</i>				
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]	
<i>Radiometry</i>				
Elemental content			[79, 136]	[198, 216–219]
<i>Mass spectroscopy</i>				
Elemental content	[177]	[140, 151, 180, 253]	[136, 195]	[79, 136, 162]
Other parameters				[72]
<i>Thermal method</i>				
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]		
<i>Electro-analytical measuring methods</i>				
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

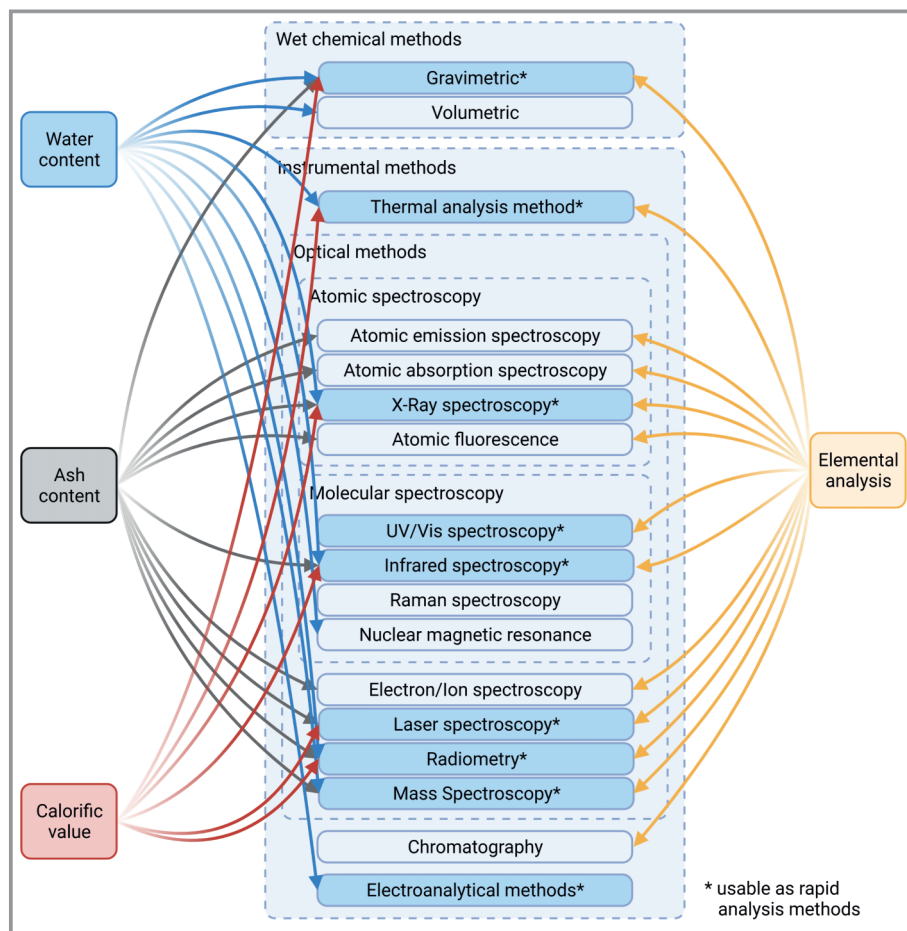
Currently, several well-investigated methods are available for the rapid determination of *M* in solid biofuels, such as capacitive measurement [60, 61, 230], TDR [60, 61, 126–128], electrical resistance [60, 61, 234, 236] infrared drying (gravimetric) [60, 256], NIRS [60, 86–96, 241, 242], microwave-, 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 bio-

mass 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	<i>M</i>	<i>A</i>	<i>Q</i>	<i>C</i>	<i>H</i>	<i>O</i>	<i>N</i>	<i>tec</i>						
Infrared drying	×	–	–	–	–	–	–	–						
Microwave drying	×	–	–	–	–	–	–	–						
TGA	×	×	o	o	o	o	o	–						
DTG	×	×	o	o	o	o	o	–						
NIRS	×	o	×	o	o	o	o	<i>tec</i>						
ED-XRF	–	–	–	–	–	–	–	<i>tec</i>						
WD-XRF	–	–	–	o	–	o	o	<i>tec</i>						
qDXA-XRF	×	×	–	–	–	–	–	–						
LIBS	o	×	×	×	×	×	×	<i>tec</i>						
LA-ICP-MS	–	–	–	×	×	×	×	<i>tec</i>						
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<sub>2</sub>. 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.

## Acknowledgments

The paper is the result of the project “EBA-Holz” funded by the German 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. 1 and Fig. 4 were created with BioRender.com. Open access funding enabled and organized by Projekt DEAL.



technology at the University of Applied Forest Science Rottenburg as researcher.

**Felix Endriss** studied sustainable energy competence (SENCE) at the universities of applied sciences Stuttgart/Ulm/Rottenburg. Currently he works on his PhD in the field of environmental sciences at the University Tübingen and the University of Applied Forest Science Rottenburg. Since 2020, he works at the department of combustion





**Daniel Kuptz** studied forestry science at Technical University of Munich (TUM). He did his PhD at the Chair of ecophysiology of Plants (TUM). Since 2011, he works at the Solid Biofuels Department of the Technology and Support Centre in the Centre of Excellence for Renewable Resources (TFZ), first as a researcher, currently as deputy manager. His research inter-

ests are the production and quality assurance of solid biofuels, i.e. wood pellets, wood chips or log wood but also agricultural biomass such as straw from fen paludic cultures.



**Hans Hartmann** is manager of the department “Solid Biofuels” at the Technology and Support Centre in the Centre of Excellence for Renewable Resources (TFZ). He is active in many national and international standardization committees such as the ISO TC 238 for Solid Biofuels. Additionally, he is a delegate in the IEA Task 32 “Combustion”.



**Stefan Brauer** studied mechanical engineering at the Technical University of Darmstadt. From 1992 to 1998 he worked as project engineer for APC GmbH. During his occupation time he developed “SOLAS”, an automated analyzer for bulk material. From 1998 to 2001 he was working for the Adam Opel AG, first in the department “environment and regulation”, later in the technical development center.



**Rainer Kirchoff** studied Chemistry at the university Berlin. Since 2014 he works at the University of Applied Forest Science Rottenburg as head of laboratory.



**Andreas Kappler** is a professor of geomicrobiology at the Univ. of Tübingen. He received his MSc (chemistry) and PhD (environmental microbiology) from the Univ. of Konstanz and held postdoc positions at EAWAG/ETH (Switzerland) in environmental chemistry, and in geobiology at Caltech. The focus of his research is the biogeo-

chemical cycling of Fe and NOM, and the environmental fate of toxic metals. He also investigates microbial Fe oxidation in modern environments and the role it played in the deposition of Precambrian BIFs, biogeochemical processes of biochar, and how iron-carbon interactions control the emission of greenhouse gases in permafrost soils.



After studying mechanical engineering in Stuttgart and Auckland (New Zealand), **Harald Thorwarth** worked as a research assistant at the University of Stuttgart. After completing his doctorate, Prof. Thorwarth moved to EnBW Kraftwerke AG, where he held various positions. In 2013, Prof. Thorwarth accepted a professorship for combustion technology at the University of Applied Forest Sciences in Rottenburg am Neckar. Prof. Thorwarth is associated with the Faculty of Mathematics and Natural Sciences at the Eberhard Karls University of Tübingen.

## Symbols used

A	[%]	Ash content, i.e., the mass fraction of ash in fuels
M	[%]	water content, i.e., the mass fraction of H <sub>2</sub> O in fuels
Q	[MJ kg <sup>-1</sup> ]	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 spectrometry
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 spectrometry
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 spectrometry
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

## References

- [1] A. Neiwert, *Validierung der teilautomatischen Brennstoffanalytik in einem Heizwerk*, Hochschule für Forstwirtschaft, Rottenburg **2016**.
- [2] H. Thorwarth, H. Gerlach, L. Rieger, M. Schroth, R. Kirchoff, J. Tejada, *VGB Powertech* **2018**, *11*, 41–49.
- [3] D. Kuptz, K. Schreiber, F. Schulmeyer, S. Lesche, T. Zeng, F. Ahrens, V. Zelinski, C. Schön, A. Pollex, H. Borchert, V. Lenz, A. Loewen, M. Nelles, H. Hartmann, *Biomass Conv. Bioref.* **2019**, *9* (1), 83–98. DOI: <https://doi.org/10.1007/s13399-019-00389-2>
- [4] E. Lindström, M. Öhman, R. Backman, D. Boström, *Energy Fuels* **2008**, *22* (4), 2216–2220. DOI: <https://doi.org/10.1021/ef700772q>
- [5] S. Kafle, S. H. Euh, L. Cho, Y. S. Nam, K. C. Oh, Y. S. Choi, J.-H. Oh, D. H. Kim, *Energy* **2017**, *129*, 79–85. DOI: <https://doi.org/10.1016/j.energy.2017.04.105>
- [6] I. Obernberger, T. Brunner, G. Baerenthaler, *Biomass Bioenergy* **2006**, *30* (11), 973–982. DOI: <https://doi.org/10.1016/j.biombioe.2006.06.011>
- [7] A. Garcia-Maraver, M. Zamorano, U. Fernandes, M. Rabaçal, M. Costa, *Fuel* **2014**, *119*, 141–152. DOI: <https://doi.org/10.1016/j.fuel.2013.11.037>
- [8] DIN 51700:2015-12, *Testing of solid fuels – Generalities and index of methods of test*, Beuth Verlag, Berlin **2015**.
- [9] ISO 17225-1, *Solid biofuels – Fuel specifications and classes – Part 1: General requirements*, International Organization for Standardization, Geneva **2020**.
- [10] F. Ellner-Schuberth, H. Hartmann, P. Turowski, P. Roßmann, *Partikelemissionen aus Kleinf Feuerungsanlagen für Holz und Ansätze für Minderungsmaßnahmen*, Berichte aus dem TFZ 22, Straubing **2010**.
- [11] D. Kuptz, H. Hartmann, *Biomass Bioenergy* **2021**, *145*, 105948. DOI: <https://doi.org/10.1016/j.biombioe.2020.105948>
- [12] B. Geisen, F. Givers, D. Kuptz, *Handbuch zum Qualitätsmanagement von Holzhackschnitzeln*, 1st ed., Fachagentur Nachwachsende Rohstoffe e.V. (FNR), Gülzow-Prüzen **2017**.
- [13] ISO 18134-2, *Solid biofuels – Determination of moisture content – Oven dry method – Part 2: Total moisture – Simplified method*, International Organization for Standardization, Geneva **2017**.

- [14] ISO 18134-3, *Solid biofuels – Determination of moisture content – Oven dry method – Part 3: Moisture in general analysis sample*, International Organization for Standardization, Geneva **2015**.
- [15] ISO 18134-1, *Solid biofuels – Determination of moisture content – Oven dry method – Part 1: Total moisture – Reference method*, International Organization for Standardization, Geneva **2015**.
- [16] ISO 18122, *Solid biofuels – Determination of ash content*, International Organization for Standardization, Geneva **2016**.
- [17] ISO 18125, *Solid biofuels – Determination of calorific value*, International Organization for Standardization, Geneva **2017**.
- [18] P. Lehtikangas, *Biomass Bioenergy* **2000**, *19* (5), 287–293. DOI: [https://doi.org/10.1016/S0961-9534\(00\)00046-5](https://doi.org/10.1016/S0961-9534(00)00046-5)
- [19] D. Kuptz, F. Schulmeyer, K. Hüttel, E. Dietz, P. Turowski, F. Zormaier, H. Borchert, H. Hartmann, *Optimale Bereitstellungsverfahren für Holzhackschnitzel*, Berichte aus dem TFZ 40, Straubing **2015**.
- [20] T. Seidel, *Schadstoffemissionen bei der Verbrennung von Stroh, Holz und Biogas*, Dissertation, Georg-August-Universität, Göttingen **2013**.
- [21] M. Kaltschmitt, H. Hartmann, H. Hofbauer, *Energie aus Biomasse*, 3rd ed., Springer, Heidelberg **2016**.
- [22] J. Tejada, P. Grammer, A. Kappler, H. Thorwarth, *Energy Fuels* **2019**, *33* (3), 2236–2247. DOI: <https://doi.org/10.1021/acs.energyfuels.8b03732>
- [23] E. Mayer, J. Eichermüller, F. Endriss, B. Baumgarten, R. Kirchhof, J. Tejada, A. Kappler, H. Thorwarth, *Waste Manage.* **2022**, *141*, 92–103. DOI: <https://doi.org/10.1016/j.wasman.2022.01.027>
- [24] U. Stetter, F. Zormaier, *Verwertung und Beseitigung von Holzaschen*, Augsburg **2009**.
- [25] A. Alahabadi, M. H. Ehrampoush, M. Miri, H. Ebrahimi Aval, S. Yousefzadeh, H. R. Ghaffari, E. Ahmadi, P. Talebi, Z. Abas-zadeh Fathabadi, F. Babai, A. Nikoonahad, K. Sharafi, A. Hosseini-Bandegharai, *Chemosphere* **2017**, *172*, 459–467. DOI: <https://doi.org/10.1016/j.chemosphere.2017.01.045>
- [26] B. Jagustyn, M. Kmiec, L. Smedowski, M. Sajdak, *J. Energy Inst.* **2017**, *90* (5), 704–714. DOI: <https://doi.org/10.1016/j.joei.2016.07.007>
- [27] S. Döring, *Pellets als Energieträger: Technologie und Anwendung*, Springer-Verlag, Heidelberg **2011**.
- [28] A. Mlonka-Mędrala, A. Magdziarz, M. Gajek, K. Nowińska, W. Nowak, *Fuel* **2020**, *261*, 116421. DOI: <https://doi.org/10.1016/j.fuel.2019.116421>
- [29] H. Kassman, J. Pettersson, B.-M. Steenari, L.-E. Åmand, *Fuel Process. Technol.* **2013**, *105*, 170–180. DOI: <https://doi.org/10.1016/j.fuproc.2011.06.025>
- [30] H. P. Nielsen, F. J. Frandsen, K. Dam-Johansen, L. L. Baxter, *Prog. Energy Combust. Sci.* **2000**, *26* (3), 283–298. DOI: [https://doi.org/10.1016/S0360-1285\(00\)00003-4](https://doi.org/10.1016/S0360-1285(00)00003-4)
- [31] S. Sonwani, P. Saxena, *Int. J. Eng. Tech. Res.* **2016**, *6* (2), 111–130.
- [32] P. Sommersacher, T. Brunner, I. Obernberger, *Energy Fuels* **2012**, *26* (1), 380–390. DOI: <https://doi.org/10.1021/ef201282y>
- [33] M. Öhman, C. Boman, H. Hedman, A. Nordin, D. Boström, *Biomass Bioenergy* **2004**, *27* (6), 585–596. DOI: <https://doi.org/10.1016/j.biombioe.2003.08.016>
- [34] ISO 16967, *Solid biofuels – Determination of major elements – Al, Ca, Fe, Mg, P, K, Si, Na and Ti*, Beuth Verlag, Berlin **2015**.
- [35] ISO 16994, *Solid biofuels – Determination of total content of sulfur and chlorine*, International Organization for Standardization, Geneva **2016**.
- [36] ISO 16948, *Solid biofuels – Determination of total content of carbon, hydrogen and nitrogen*, International Organization for Standardization, Geneva, **2015**.
- [37] T. von Puttkamer, *Charakterisierung biogener Festbrennstoffe*, Dissertation, Universität Stuttgart **2005**.
- [38] G. Schwedt, T. C. Schmidt, O. J. Schmitz, *Analytische Chemie: Grundlagen, Methoden und Praxis*, Wiley-VCH, Weinheim **2016**.
- [39] H. Hug, *Instrumentelle Analytik: Theorie und Praxis*, 4th ed., Europa-Lehrmittel, Haan **2020**.
- [40] M. Otto, *Analytische Chemie*, 5th ed., Wiley-VCH, Weinheim **2019**.
- [41] K. Kupfer, *Materialfeuchtemessung: Grundlagen – Meßverfahren – Applikationen – Normen*, Expert-Verlag, Tübingen **1997**.
- [42] K. Kupfer, *Tech. Mess.* **1999**, *66* (6). DOI: <https://doi.org/10.1524/teme.1999.66.6.227>
- [43] G.-W. Oetjen, *Gefriertrocknen*, VCH Verlag, Weinheim **1997**.
- [44] G. Böhner, L. Wagner, M. Säcker, *Holz Roh- Werkst.* **1993**, *51*, 163–166.
- [45] T. Boltze, Parameterschätzung für die Feuchtemessung mit Mikrowellen, *Fortschr.-Ber. VDI, Reihe 8* **1996**, 568.
- [46] Q. P. Du, A. Geissen, D. Noack, *Holz Roh- Werkst.* **1991**, *49* (1), 1–6. DOI: <https://doi.org/10.1007/BF02627523>
- [47] D. D. Johnston, R. H. Wynands, *Wood November* **1958**, 458–463.
- [48] A. Kail, A. Gratzl, *Holzforsch. Holzverwert.* **1962**, (14), 82–85.
- [49] F. Kollmann, G. Höckele, *Holz Roh- Werkst.* **1962**, *20* (12), 461–473. DOI: <https://doi.org/10.1007/BF02619168>
- [50] J. F. Rijdsdijk, *Holz Roh- Werkst.* **1969**, *27* (1), 17–23. DOI: <https://doi.org/10.1007/BF02619411>
- [51] M. Stacheder, *Die Time Domain Reflectometry in der Geotechnik – Messungen von Wassergehalt, elektrischer Leitfähigkeit und Stofftransport*, Dissertation, Universität Karlsruhe **1995**.
- [52] F. Endriss, P. Grammer, M. Russ, H. Thorwarth, *Chem. Ing. Tech.* **2020**, *93* (3), 412–420. DOI: <https://doi.org/10.1002/cite.202000098>
- [53] D. Fengel, G. Wegener, *Wood: Chemistry, ultrastructure, reactions*, Walter de Gruyter, Berlin **1989**.
- [54] R. Trendelenburg, *Das Holz als Rohstoff – Seine Entstehung, stoffliche Beschaffenheit und chemische Verwertung*, J. F. Lehmanns Verlag, München **1939**.
- [55] C. Nielsen, S. Westborg, *IEA round robin analysis of straw and straw ashes*, report NEI-DK-979, DK-Teknik, Soeborg **1992**.
- [56] I. Obernberger, J. Dahl, A. Aric, *Round Robin on biomass fuel and ash analysis*, Office for Official Publications of the European Communities, Luxembourg **1998**.
- [57] S. Westborg, C. Nielsen, *Analysis of straw and straw ashes. Part 1. Recommended methods for basic parameters*, DK-Teknik, Soeborg, Denmark **1994**.
- [58] G. C. A. M. Heemskerk, *Best practice list for biomass fuel and ash analysis*, Novem-EWAB report no. 9820, Utrecht, **1998**.
- [59] P. P. Parikh, K. B. S. Reddy, P. K. Banerjee, *On Proximate Analysis Procedures for Biomass Characterization*, ASAE Meeting, Phoenix, July **1996**.
- [60] T. Böhm, *Verfahren zur Bestimmung physikalischer Qualitätsmerkmale und des Wassergehaltes biogener Festbrennstoffe*, Dissertation, Technischen Universität München **2006**.
- [61] T. Mendel, D. Kuptz, A. Überreiter, H. Hartmann, *Schnellbestimmung des Wassergehalts von Holzhackschnitzeln*, Berichte aus dem TFZ 52, Straubing **2017**.
- [62] J. F. Saldarriaga, R. Aguado, A. Pablos, M. Amutio, M. Olazar, J. Bilbao, *Fuel* **2015**, *140*, 744–751. DOI: <https://doi.org/10.1016/j.fuel.2014.10.024>
- [63] K. Siegbahn, *Phys. Bl.* **1986**, (42), 2–8.
- [64] J. Mühlberg, A. Pollex, T. Zeng, *Biomass Bioenergy* **2021**, *152*, 106172. DOI: <https://doi.org/10.1016/j.biombioe.2021.106172>
- [65] K. Kohli, S. Katuwal, A. Biswas, B. K. Sharma, *Bioresour. Technol.* **2020**, *303*, 122897. DOI: <https://doi.org/10.1016/j.biortech.2020.122897>
- [66] R. A. Lee, C. Bédard, V. Berberri, R. Beauchet, J.-M. Lavoie, *Bioresour. Technol.* **2013**, *144*, 658–663. DOI: <https://doi.org/10.1016/j.biortech.2013.06.045>
- [67] A. P. Mörschbacher, A. Dullius, C. H. Dullius, C. R. Bandt, D. Kuhn, D. T. Brietzke, F. J. Malmann Kuffel, H. P. Etgeton, T. Altmayer, T. E. Gonçalves, E. Q. Oreste, A. S. Ribeiro, C. F. V.



- de Souza, L. Hoehne, *Food Chem.* **2018**, *255*, 182–186. DOI: <https://doi.org/10.1016/j.foodchem.2018.02.057>
- [68] A. Alzagameem, B. E. Khaldi-Hansen, D. Büchner, M. Larkins, B. Kamm, S. Witzleben, M. Schulze, *Molecules* **2018**, *23* (10), 2664. DOI: <https://doi.org/10.3390/molecules23102664>
- [69] H. Zhang, X. Wang, J. Wang, Q. Chen, H. Huang, L. Huang, S. Cao, X. Ma, *Wood Sci. Technol.* **2020**, *54* (4), 837–846. DOI: <https://doi.org/10.1007/s00226-020-01199-w>
- [70] S. Hou, L. Li, *J. Integr. Plant Biol.* **2011**, *53* (2), 166–175. DOI: <https://doi.org/10.1111/j.1744-7909.2010.01003.x>
- [71] S. Jin, H. Chen, *Ind. Crops Prod.* **2007**, *26* (2), 207–211. DOI: <https://doi.org/10.1016/j.indcrop.2007.03.004>
- [72] S. Kelley, R. Rowell, M. Davis, C. Jurich, R. Ibach, *Biomass Bioenergy* **2004**, *27* (1), 77–88. DOI: <https://doi.org/10.1016/j.biombioe.2003.11.005>
- [73] L. Liu, X. P. Ye, A. R. Womac, S. Sokhansanj, *Carbohydr. Polym.* **2010**, *81* (4), 820–829. DOI: <https://doi.org/10.1016/j.carbpol.2010.03.058>
- [74] K. Nkansah, B. Dawson-Andoh, J. Slahor, *Bioresour. Technol.* **2010**, *101* (12), 4570–4576. DOI: <https://doi.org/10.1016/j.biortech.2009.12.046>
- [75] R. C. Oliveira, P. Hammer, E. Guibal, J.-M. Taulemesse, O. Garcia, *Chem. Eng. J.* **2014**, *239*, 381–391. DOI: <https://doi.org/10.1016/j.cej.2013.11.042>
- [76] C. S. Raju, A. J. Ward, L. Nielsen, H. B. Møller, *Bioresour. Technol.* **2011**, *102* (17), 7835–7839. DOI: <https://doi.org/10.1016/j.biortech.2011.05.049>
- [77] Y. Wang, M. Yang, G. Wei, R. Hu, Z. Luo, G. Li, *Sens. Actuators, B* **2014**, *193*, 723–729. DOI: <https://doi.org/10.1016/j.snb.2013.12.028>
- [78] F. Xu, J. Yu, T. Tesso, F. Dowell, D. Wang, *Appl. Energy* **2013**, *104*, 801–809. DOI: <https://doi.org/10.1016/j.apenergy.2012.12.019>
- [79] Q. Zhu, *Coal sampling and analysis standards*, IEA Clean Coal Centre, London **2014**.
- [80] S. T. Wagland, R. Dudley, M. Naftaly, P. J. Longhurst, *Waste Manage.* **2013**, *33* (11), 2449–2456. DOI: <https://doi.org/10.1016/j.wasman.2013.06.021>
- [81] D. Mauruschat, B. Plinke, J. Aderhold, J. Gunschera, P. Meinschmidt, T. Salthammer, *Wood Sci. Technol.* **2015**, *50* (2), 313–331. DOI: <https://doi.org/10.1007/s00226-015-0785-x>
- [82] E. Smidt, K. Meissl, M. Schwanninger, P. Lechner, *Waste Manage.* **2008**, *28* (10), 1699–1710. DOI: <https://doi.org/10.1016/j.wasman.2007.08.003>
- [83] C. J. Huang, L. J. Han, L. Liu, Z. L. Yang, *J. Energy Inst.* **2016**, *81*, 153–157.
- [84] C. Huang, L. Han, Z. Yang, X. Liu, *Energy Convers. Manage.* **2008**, *49* (12), 3433–3438. DOI: <https://doi.org/10.1016/j.enconman.2008.08.020>
- [85] N. Labbé, S.-H. Lee, H.-W. Cho, M. K. Jeong, N. André, *Bioresour. Technol.* **2008**, *99* (17), 8445–8452. DOI: <https://doi.org/10.1016/j.biortech.2008.02.052>
- [86] D. T. Chadwick, K. P. McDonnell, L. P. Brennan, C. C. Fagan, C. D. Everard, *Renewable Sustainable Energy Rev.* **2014**, *30*, 672–681. DOI: <https://doi.org/10.1016/j.rser.2013.11.006>
- [87] C. D. Everard, C. C. Fagan, K. P. McDonnell, *J. Near Infrared Spectrosc.* **2012**, *20* (3), 361–369. DOI: <https://doi.org/10.1255/jnirs.997>
- [88] C. C. Fagan, C. D. Everard, K. McDonnell, *Bioresour. Technol.* **2011**, *102* (8), 5200–5206. DOI: <https://doi.org/10.1016/j.biortech.2011.01.087>
- [89] L. Fridh, S. Volpé, L. Eliasson, *Int. J. For. Eng.* **2017**, *28* (1), 42–46. DOI: <https://doi.org/10.1080/14942119.2017.1297521>
- [90] T. A. Lestander, B. Johnsson, M. Grothage, *Bioresour. Technol.* **2009**, *100* (4), 1589–1594. DOI: <https://doi.org/10.1016/j.biortech.2008.08.001>
- [91] T. A. Lestander, C. Rhén, *Analyst* **2005**, *130* (8), 1182–1189. DOI: <https://doi.org/10.1039/b500103j>
- [92] J. Skvaril, K. Kyprianidis, A. Avelin, M. Odlare, E. Dahlquist, *Energy Procedia* **2017**, *105*, 1309–1317. DOI: <https://doi.org/10.1016/j.egypro.2017.03.476>
- [93] M. Mancini, D. Duca, G. Toscano, *J. Near Infrared Spectrosc.* **2019**, (27), 15–25. DOI: <https://doi.org/10.1177/0967033518825341>
- [94] E. Leoni, M. Mancini, D. Duca, G. Toscano, *Processes* **2020**, *8* (11), 1413. DOI: <https://doi.org/10.3390/pr8111413>
- [95] X. Feng, C. Yu, Z. Shu, X. Liu, W. Yan, Q. Zheng, K. Sheng, Y. He, *Fuel* **2018**, *228*, 197–205. DOI: <https://doi.org/10.1016/j.fuel.2018.04.149>
- [96] G. D. Gillespie, C. D. Everard, K. P. McDonnell, *Energy* **2015**, *80*, 582–588. DOI: <https://doi.org/10.1016/j.energy.2014.12.014>
- [97] G. G. Allison, C. Morris, E. Hodgson, J. Jones, M. Kubacki, T. Barraclough, N. Yates, I. Shield, A. V. Bridgwater, I. S. Donnison, *Bioresour. Technol.* **2009**, *100* (24), 6428–6433. DOI: <https://doi.org/10.1016/j.biortech.2009.07.015>
- [98] C. D. Everard, K. P. McDonnell, C. C. Fagan, *Biomass Bioenergy* **2012**, *45*, 203–211. DOI: <https://doi.org/10.1016/j.biombioe.2012.06.007>
- [99] D. Gillon, C. Hernando, J. Valette, R. Joffre, *Can. J. For. Res.* **1997**, *27*, 760–765. DOI: <https://doi.org/10.1139/x97-021>
- [100] L. Pitak, P. Sirisomboon, K. Saengprachatanarug, S. Wongpichet, J. Posom, *Energy* **2021**, *220*, 119698. DOI: <https://doi.org/10.1016/j.energy.2020.119698>
- [101] J. Mata-Sánchez, J. A. Pérez-Jiménez, M. J. Díaz-Villanueva, A. Serrano, N. Núñez-Sánchez, F. J. López-Giménez, *Energy Fuels* **2014**, *28* (8), 5136–5143. DOI: <https://doi.org/10.1021/ef500854z>
- [102] C. W. Edmunds, C. Hamilton, K. Kim, N. André, N. Labbé, *Energy Fuels* **2017**, *31* (6), 6080–6088. DOI: <https://doi.org/10.1021/acs.energyfuels.7b00249>
- [103] B. J. Kip, T. Berghmans, P. Palmen, A. van der Pol, M. Huys, H. Hartwig, M. Scheepers, D. Wienke, *Vib. Spectrosc.* **2000**, *24* (1), 75–92. DOI: [https://doi.org/10.1016/S0924-2031\(00\)00081-3](https://doi.org/10.1016/S0924-2031(00)00081-3)
- [104] B. K. Lavine, C. E. Davidson, A. J. Moores, P. R. Griffiths, *Appl. Spectrosc.* **2001**, *55* (8), 960–966. DOI: <https://doi.org/10.1366/0003702011953108>
- [105] Y. Cao, Y. Lu, Y. Huang, *J. Mol. Struct.* **2004**, *693* (1–3), 87–93. DOI: <https://doi.org/10.1016/j.molstruc.2004.02.017>
- [106] U. P. Agarwal, S. A. Ralph, *Appl. Spectrosc.* **1997**, *51* (11), 1648–1655. DOI: <https://doi.org/10.1366/0003702971939316>
- [107] G. Yang, Q. Wang, C. Liu, X. Wang, S. Fan, W. Huang, *Spectrochim. Acta, Part A* **2018**, *200*, 186–194. DOI: <https://doi.org/10.1016/j.saa.2018.04.026>
- [108] A. Georgakopoulos, *J. Serb. Chem. Soc.* **2003**, *68* (8–9), 599–606. DOI: <https://doi.org/10.2298/JSC0309599G>
- [109] R. Guo, K. Mannhardt, A. Kantzas, *J. Can. Pet. Technol.* **2007**, *46* (10). DOI: <https://doi.org/10.2118/07-10-05>
- [110] S. Kalaitzidis, A. Georgakopoulos, K. Christanis, A. Iordanidis, *Geochim. Cosmochim. Acta* **2006**, *70* (4), 947–959. DOI: <https://doi.org/10.1016/j.gca.2005.10.014>
- [111] J. G. Liu, D. M. Liu, Y. B. Yao, J. G. Wu, J. Q. Li, *Adv. Mater. Res.* **2013**, *718–720*, 1012–1017. DOI: <https://doi.org/10.4028/www.scientific.net/AMR.718-720.1012>
- [112] K. Mao, G. J. Kennedy, S. M. Althaus, M. Pruski, *Energy Fuels* **2013**, *27* (2), 760–763. DOI: <https://doi.org/10.1021/ef301804p>
- [113] P. Straka, J. Brus, J. Endrysova, *Coals. Chem. Pap.* **2002**, *56* (3), 182–187.
- [114] Y. Yao, D. Liu, *Fuel* **2012**, *95*, 152–158. DOI: <https://doi.org/10.1016/j.fuel.2011.12.039>
- [115] Y. Yao, D. Liu, Y. Che, D. Tang, S. Tang, W. Huang, *Fuel* **2010**, *89* (7), 1371–1380. DOI: <https://doi.org/10.1016/j.fuel.2009.11.005>
- [116] M. Foston, *Curr. Opin. Biotechnol.* **2014**, *27*, 176–184. DOI: <https://doi.org/10.1016/j.copbio.2014.02.002>



- [117] Y. Pu, S. Cao, A. J. Ragauskas, *Energy Environ. Sci.* **2011**, *4* (9), 3154. DOI: <https://doi.org/10.1039/c1ee01201k>
- [118] E. Gjersing, R. M. Happs, R. W. Sykes, C. Doeppeke, M. F. Davis, *Biotechnol. Bioeng.* **2013**, *110* (3), 721–728. DOI: <https://doi.org/10.1002/bit.24741>
- [119] L. A. Colnago, Z. Wiesman, G. Pages, M. Musse, T. Monaretto, C. W. Windt, C. Rondeau-Mouro, *J. Magn. Reson.* **2021**, *323*, 106899. DOI: <https://doi.org/10.1016/j.jmr.2020.106899>
- [120] S. Trabelsi, A. M. Paz, S. O. Nelson, *Biosyst. Eng.* **2013**, *115* (3), 332–338. DOI: <https://doi.org/10.1016/j.biosystemseng.2013.04.003>
- [121] Y. Zhang, Y. Ogura, *J. Microwave Power Electromagn. Energy* **2010**, *44* (3), 163–167. DOI: <https://doi.org/10.1080/08327823.2010.11689785>
- [122] J. Landgraf, A. Göller, *Mikrowellen-Feuchtemessung in Biomaterialien*, hf-sensor, Leipzig, <http://www.hf-sensor.de/deutsch/umwelt.html>
- [123] J. Nyström, E. Dahlquist, *Fuel* **2004**, *83* (7–8), 773–779. DOI: <https://doi.org/10.1016/j.fuel.2003.11.002>
- [124] P. Ottosson, D. Andersson, D. Ronnow, *IEEE Sensors J.* **2018**, *18* (22), 9112–9119. DOI: <https://doi.org/10.1109/JSEN.2018.2870760>
- [125] M. Merlan, T. Ditchi, Y. Oussar, S. Holé, E. Géron, J. Lucas, *Meas. Sci. Technol.* **2019**, *30* (12), 125108. DOI: <https://doi.org/10.1088/1361-6501/ab26a1>
- [126] S. Leitschuh, E. Bolcu, K. Fischer, *WLB, Wasser, Luft Boden* **1996**, 71–74.
- [127] O. Hensel, *Schnellfeuchtebestimmung bei nachwachsenden Rohstoffen mit hohem Feuchtegehalt durch das Time Domain Reflectometry-Verfahren*, VDI Verlag **1997**.
- [128] M. Khoshbakht, M. W. Lin, *Meas. Sci. Technol.* **2006**, *17* (11), 2989–2996. DOI: <https://doi.org/10.1088/0957-0233/17/11/019>
- [129] S. L. C. Ferreira, M. A. Bezerra, A. S. Santos, W. N. L. dos Santos, C. G. Novaes, O. M. C. de Oliveira, M. L. Oliveira, R. L. Garcia, *TrAC, Trends Anal. Chem.* **2018**, *100*, 1–6. DOI: <https://doi.org/10.1016/j.trac.2017.12.012>
- [130] B. Welz, M. Sperling, M. Resano, *Atomic Absorption Spectrometry*, Wiley-VCH, Weinheim **2008**.
- [131] B. Welz, *Anal. Bioanal. Chem.* **2005**, *381* (1), 69–71. DOI: <https://doi.org/10.1007/s00216-004-2891-8>
- [132] N. Ozbek, M. Ozcan, *Talanta* **2016**, *148*, 17–21. DOI: <https://doi.org/10.1016/j.talanta.2015.10.041>
- [133] W. Boschetti, A. R. Borges, A. T. Duarte, M. B. Dessuy, M. G. R. Vale, J. B. de Andrade, B. Welz, *Anal. Methods* **2014**, *6* (12), 4247–4256. DOI: <https://doi.org/10.1039/C4AY00241E>
- [134] Á. T. Duarte, A. R. Borges, A. V. Zmozinski, M. B. Dessuy, B. Welz, J. B. de Andrade, M. G. R. Vale, *Talanta* **2016**, *146*, 166–174. DOI: <https://doi.org/10.1016/j.talanta.2015.08.041>
- [135] A. D'Ulivo, *Spectrochim. Acta, Part B* **2016**, *119*, 91–107. DOI: <https://doi.org/10.1016/j.sab.2016.03.003>
- [136] N. Mketto, P. N. Nomngongo, J. C. Ngila, *TrAC, Trends Anal. Chem.* **2016**, *85*, 107–116. DOI: <https://doi.org/10.1016/j.trac.2016.09.002>
- [137] F. V. Nakadi, C. Prodanov, W. Boschetti, M. G. R. Vale, B. Welz, J. B. de Andrade, *Talanta* **2018**, *179*, 828–835. DOI: <https://doi.org/10.1016/j.talanta.2017.12.022>
- [138] A. Cárdenas Valdivia, E. Vereda Alonso, M. M. López Guerrero, J. Gonzalez-Rodriguez, J. M. Cano Pavón, A. García de Torres, *Talanta* **2018**, *179*, 1–8. DOI: <https://doi.org/10.1016/j.talanta.2017.10.033>
- [139] N. Ozbek, A. Baysal, *TrAC, Trends Anal. Chem.* **2017**, *88*, 62–76. DOI: <https://doi.org/10.1016/j.trac.2016.09.014>
- [140] G. Baerthaler, M. Zischka, C. Haraldsson, I. Obernberger, *Biomass Bioenergy* **2006**, *30* (11), 983–997. DOI: <https://doi.org/10.1016/j.biombioe.2006.06.007>
- [141] S. M. Pereira Junior, V. A. Maihara, E. G. Moreira, V. L. R. Salvador, I. M. Sato, *J. Radioanal. Nucl. Chem.* **2016**, *308* (1), 7–12. DOI: <https://doi.org/10.1007/s10967-015-4669-1>
- [142] M. Walkowiak, M. Witczak, *DREWNO* **2018**, *61* (202), 99–118. DOI: <https://doi.org/10.12841/wood.1644-3985.312.10>
- [143] I. Höfer, M. Kaltschmitt, *Biomass Conv. Bioref.* **2016**, *7* (1), 101–116. DOI: <https://doi.org/10.1007/s13399-016-0217-7>
- [144] DIN 22022-3, *Solid fuels – Determination of trace elements – Part 3: AAS-flame method*, Beuth Verlag, Berlin **2001**.
- [145] DIN 22022-4, *Solid fuels – Determination of contents of trace elements – Part 4: Atomic absorption spectrometry applying the flameless hydride system or the cold-vapour-method*, Beuth Verlag, Berlin **2001**.
- [146] DIN 22022-5, *Solid fuels – Determination of trace elements – Part 5: Atomic absorption spectrometry applying the electrothermal atomization*, Beuth Verlag, Berlin **2001**.
- [147] ISO 16968, *Solid biofuels – Determination of minor elements*, International Organization for Standardization, Geneva **2015**.
- [148] ISO 17378-2, *Water quality – Determination of arsenic and antimony – Part 2: Method using hydride generation atomic absorption spectrometry (HG-AAS)*, International Organization for Standardization, Geneva **2014**.
- [149] ISO 12846, *Water quality – Determination of mercury – Method using atomic absorption spectrometry (AAS) with and without enrichment*, International Organization for Standardization, Geneva **2012**.
- [150] D. J. Butcher, *Appl. Spectrosc. Rev.* **2017**, *52* (9), 755–773. DOI: <https://doi.org/10.1080/05704928.2017.1303504>
- [151] M. H. Piispanen, M. E. Niemelä, M. S. Tiainen, R. S. Laitinen, *Energy Fuels* **2012**, *26* (4), 2427–2433. DOI: <https://doi.org/10.1021/ef300173w>
- [152] V. Knappe, S. Paczkowski, J. Tejada, L. A. Diaz Robles, A. Gonzales, S. Pelz, *J. Anal. Appl. Pyrolysis* **2018**, *134*, 162–166. DOI: <https://doi.org/10.1016/j.jaap.2018.06.004>
- [153] J. Tejada, J. Wiedenmann, B. Gall, B. Kaiser, O. Greißl, S. Unterberger, A. Kappler, H. Thorwarth, *Fuel* **2020**, *267*, 116887. DOI: <https://doi.org/10.1016/j.fuel.2019.116887>
- [154] F. Endriss, P. Grammer, M. Russ, H. Thorwarth, *Chem. Ing. Tech.* **2021**, *93* (10), 1598–1609. DOI: <https://doi.org/10.1002/cite.202100096>
- [155] M. Haschke, J. Flock, *Röntgenfluoreszenzanalyse in der Laborpraxis*, 1st ed., Wiley-VCH, Weinheim **2017**.
- [156] H. G. J. Moseley, *London, Edinburgh Dublin Philos. Mag. J. Sci.* **1913**, *26* (156), 1024–1034. DOI: <https://doi.org/10.1080/14786441308635052>
- [157] *Analysis of inorganic major and minor compounds in unashed coals samples prepared as pressed pellet*, Malvern Panalytical, Malvern, UK, March **2018**.
- [158] W. Friedrich, P. Knipping, M. Laue, *Ann. Phys.* **1913**, *346* (10), 971–988. DOI: <https://doi.org/10.1002/andp.19133461004>
- [159] W. H. Bragg, W. L. Bragg, *Proc. R. Soc. Lond. A* **1913**, *88* (605), 428–438. DOI: <https://doi.org/10.1098/rspa.1913.0040>
- [160] DIN 51729-10, *Testing of solid fuels – Determination of chemical composition of fuel ash – Part 10: X-Ray Fluorescence Analysis*, Beuth Verlag, Berlin **2011**.
- [161] ISO 13605, *Solid mineral fuels – Major and minor elements in coal ash and coke ash – Wavelength dispersive X-ray fluorescence spectrometric method*, International Organization for Standardization, Geneva **2018**.
- [162] M. H. Piispanen, S. A. Arvilommi, B. van den Broeck, L. H. Nuutinen, M. S. Tiainen, P. J. Perämäki, R. S. Laitinen, *Energy Fuels* **2009**, *23* (7), 3451–3456. DOI: <https://doi.org/10.1021/ef801037a>
- [163] J. Gonzalez, G. Simões, R. Bernini, L. Coutinho, F. Stedile, C. Nunes, F. Vicentin, G. de Souza, *J. Braz. Chem. Soc.* **2019**. DOI: <https://doi.org/10.21577/0103-5053.20190098>

- [164] B. Lapo, J. J. Bou, J. Hoyo, M. Carrillo, K. Peña, T. Tzanov, A. M. Sastre, *Environ. Pollut.* **2020**, *264*, 114409. DOI: <https://doi.org/10.1016/j.envpol.2020.114409>
- [165] M. Bettinelli, P. Taina, *X-Ray Spectrom.* **1990**, 19 pages.
- [166] M. Fellin, M. Negri, R. Zanuttini, *Eur. J. Wood Prod.* **2014**, *72* (2), 199–211. DOI: <https://doi.org/10.1007/s00107-013-0766-4>
- [167] J. Q. McComb, C. Rogers, F. X. Han, P. B. Tchounwou, *Water Air Soil Pollut.* **2014**, *225* (12). DOI: <https://doi.org/10.1007/s11270-014-2169-5>
- [168] D. Neubert, *Röntgenfluoreszenzanalyse zur prozessnahen Analytik von Reduktionsmitteln für den Hochofenprozess*, Dissertation, Universität Duisburg-Essen, Duisburg **2013**.
- [169] S. Reidinger, M. H. Ramsey, S. E. Hartley, *New Phytol.* **2012**, *195* (3), 699–706. DOI: <https://doi.org/10.1111/j.1469-8137.2012.04179.x>
- [170] R. Terzano, M. A. Denecke, G. Falkenberg, B. Miller, D. Paterson, K. Janssens, *Pure Appl. Chem.* **2019**, *91* (6), 1029–1063. DOI: <https://doi.org/10.1515/pac-2018-0605>
- [171] C. Williams, *J. Sci. Food Agric.* **1976**, (27), 561–570.
- [172] P. Lienemann, W. Vock, *Elementgehalt in Holzaschen und Validierung der Holzaschenkontrolle*, Zürcher Hochschule für Angewandte Wissenschaften, Wädenswil **2013**.
- [173] A. Rasem Hasan, J. Schindler, H. M. Solo-Gabriele, T. G. Townsend, *Waste Manage.* **2011**, *31* (4), 688–694. DOI: <https://doi.org/10.1016/j.wasman.2010.11.010>
- [174] S. Sasmal, V. V. Goud, K. Mohanty, *Biomass Bioenergy* **2012**, *45*, 212–220. DOI: <https://doi.org/10.1016/j.biombioe.2012.06.008>
- [175] H. M. Solo-Gabriele, T. G. Townsend, D. W. Hahn, T. M. Moskal, N. Hosein, J. Jambeck, G. Jacobi, *Waste Manage.* **2004**, *24* (4), 413–424. DOI: <https://doi.org/10.1016/j.wasman.2003.09.006>
- [176] C. Vrancken, P. J. Longhurst, S. T. Wagland, *Waste Manage.* **2017**, *61*, 40–57. DOI: <https://doi.org/10.1016/j.wasman.2017.01.019>
- [177] M. Piispanen, *Direct analysis of solid biofuels for the prediction of ash-related problems in fluidized bed boilers*, Dissertation, Oulu University, Oulu **2013**.
- [178] V. Golubev, *Biofuel quality control by portable XRF analyser*, Bachelor Thesis, MAMK University of Applied Sciences, Mikkeli **2015**.
- [179] J. Reinhardt, *Evaluierung von Schnellmesstechnik zur Brennstoffanalytik*, Studienarbeit, Hochschule für Forstwirtschaft, Rottenburg **2018**.
- [180] H. Riedel, G. Schmoedel, C. Marb, *Holztechnologie* **2014**, *55*, 31–38.
- [181] E. Selin Lindgren, D. Henriksson, M. Lundin, P. Therning, J. Laursen, N. Pind, *X-Ray Spectrom.* **2006**, *35* (1), 19–26. DOI: <https://doi.org/10.1002/xrs.883>
- [182] D. Zimmermann, E. Dietz, M. Riebler, U. Blum, H. Borchert, C. Kuchler, D. Kuptz, H. Hartmann, *European Biomass Conference and Exhibition*, Lisbon, May **2019**.
- [183] M. Sajdak, B. Micek, J. Hrabak, *J. Energy Inst.* **2019**, *92* (6), 1619–1629. DOI: <https://doi.org/10.1016/j.joei.2019.01.012>
- [184] R. J. O. Torgrip, V. Fernández-Cano, *Biomass Bioenergy* **2017**, *98*, 161–171. DOI: <https://doi.org/10.1016/j.biombioe.2017.01.005>
- [185] G. P. Awasthi, D. P. Bhattarai, B. Maharjan, K.-S. Kim, C. H. Park, C. S. Kim, *J. Ind. Eng. Chem.* **2019**, *72*, 265–272. DOI: <https://doi.org/10.1016/j.jiec.2018.12.027>
- [186] S. Yoo, S. S. Kelley, D. C. Tilotta, S. Park, *ACS Sustainable Chem. Eng.* **2018**, *6* (2), 2621–2629. DOI: <https://doi.org/10.1021/acssuschemeng.7b04119>
- [187] J. Bauch, R. Rosenkranz, *Physikalische Werkstoffdiagnostik: Ein Kompendium wichtiger Analytikmethoden für Ingenieure und Physiker*, Springer Vieweg, Berlin **2017**.
- [188] F. E. Huggins, G. P. Huffman, *Int. J. Coal Geol.* **1996**, *32* (1), 31–53. DOI: [https://doi.org/10.1016/S0166-5162\(96\)00029-8](https://doi.org/10.1016/S0166-5162(96)00029-8)
- [189] C. Shen, H. Wang, H. Shen, J. Wu, Y. Zhu, W. Shi, X. Zhang, Z. Ying, *Energy Fuels* **2020**, *34* (8), 9872–9884. DOI: <https://doi.org/10.1021/acs.energyfuels.0c01642>
- [190] P. Auger, *J. Phys. Radium* **1925**, *6* (6), 205–208. DOI: <https://doi.org/10.1051/jphysrad:0192500606020500>
- [191] M. P. Seah, *Surf. Sci.* **1972**, *32* (3), 703–728. DOI: [https://doi.org/10.1016/0039-6028\(72\)90196-3](https://doi.org/10.1016/0039-6028(72)90196-3)
- [192] R. Kumar, G. Mago, V. Balan, C. E. Wyman, *Bioresour. Technol.* **2009**, *100* (17), 3948–3962. DOI: <https://doi.org/10.1016/j.biortech.2009.01.075>
- [193] H. Y. Mou, S. Wu, P. Fardim, *Bioresources* **2016**, *11*, 5581–5599.
- [194] W. Demtröder, *Laserspektroskopie*, 4th ed., Springer, Heidelberg **2000**.
- [195] C. A. Booth, D. A. Spears, P. Krause, A. G. Cox, *Fuel* **1999**, *78* (14), 1665–1670. DOI: [https://doi.org/10.1016/S0016-2361\(99\)00113-1](https://doi.org/10.1016/S0016-2361(99)00113-1)
- [196] J. Kaiser, K. Novotný, M. Z. Martin, A. Hrdlička, R. Malina, M. Hartl, V. Adam, R. Kizek, *Surf. Sci. Rep.* **2012**, *67* (11–12), 233–243. DOI: <https://doi.org/10.1016/j.surfrep.2012.09.001>
- [197] S. Sheta, M. S. Afgan, Z. Hou, S.-C. Yao, L. Zhang, Z. Li, Z. Wang, *J. Anal. At. Spectrom.* **2019**, *34* (6), 1047–1082. DOI: <https://doi.org/10.1039/C9JA00016j>
- [198] R. Hemalaxmi, N. Aparna, N. J. Vasa, S. Seshadri, Nanosecond and Femtosecond Laser Induced Breakdown Spectroscopic Studies of Coal and Ash, in *Proc. 2018 Conference on Lasers and Electro-Optics Pacific Rim (CLEO-PR)*, IEEE, Piscataway, NJ **2018**.
- [199] D. A. Spears, *Fuel* **2004**, *83* (13), 1765–1770. DOI: <https://doi.org/10.1016/j.fuel.2004.02.018>
- [200] M. Z. Martin, N. Labbé, T. G. Rials, S. D. Wullschleger, *Spectrochim. Acta, Part B* **2005**, *60* (7–8), 1179–1185. DOI: <https://doi.org/10.1016/j.sab.2005.05.022>
- [201] T. M. Moskal, D. W. Hahn, *Appl. Spectrosc.* **2002**, *56* (10), 1337–1344. DOI: <https://doi.org/10.1366/000370202760355316>
- [202] W. Li, J. Lu, M. Dong, S. Lu, J. Yu, S. Li, J. Huang, J. Liu, *Energy Fuels* **2018**, *32* (1), 24–32. DOI: <https://doi.org/10.1021/acs.energyfuels.7b01718>
- [203] C. Yan, T. Zhang, Y. Sun, H. Tang, H. Li, *Spectrochim. Acta, Part B* **2019**, *154*, 75–81. DOI: <https://doi.org/10.1016/j.sab.2019.02.007>
- [204] J. W. B. Braga, L. C. Trevizan, L. C. Nunes, I. A. Rufini, D. Santos, F. J. Krug, *Spectrochim. Acta, Part B* **2010**, *65* (1), 66–74. DOI: <https://doi.org/10.1016/j.sab.2009.11.007>
- [205] T. Westover, *Rapid Analysis of Ash Composition Using Laser-Induced Breakdown Spectroscopy (LIBS)*, Idaho National Laboratory, Idaho Falls, ID **2013**.
- [206] A. Wakil, *Elemental Detection at Ambient Condition by LIBS and Microwave-assisted LIBS*, PhD Thesis, University of Adelaide **2020**.
- [207] Z. Lu, X. Chen, S. Yao, H. Qin, L. Zhang, X. Yao, Z. Yu, J. Lu, *Fuel* **2019**, *258*, 116150. DOI: <https://doi.org/10.1016/j.fuel.2019.116150>
- [208] Z. Lu, X. Chen, Y. Jiang, X. Li, J. Chen, Y. Li, W. Lu, J. Lu, S. Yao, *Renewable Energy* **2021**, *164*, 1204–1214. DOI: <https://doi.org/10.1016/j.renene.2020.10.112>
- [209] X. Liu, X. Feng, Y. He, *Renewable Energy* **2019**, *143*, 176–182. DOI: <https://doi.org/10.1016/j.renene.2019.04.137>
- [210] X. Liu, X. Feng, L. Huang, Y. He, *Energies* **2020**, *13* (14), 3741. DOI: <https://doi.org/10.3390/en13143741>
- [211] G. S. Senesi, R. S. Harmon, R. R. Hark, *Spectrochim. Acta, Part B* **2021**, *175*, 106013. DOI: <https://doi.org/10.1016/j.sab.2020.106013>
- [212] D. J. Ryan, K. Qian, *Energy Fuels* **2020**, *34* (10), 11887–11896. DOI: <https://doi.org/10.1021/acs.energyfuels.0c02374>

- [213] R. R. Greenberg, P. Bode, E. A. de Nadai Fernandes, *Spectrochim. Acta, Part B* **2011**, *66* (3–4), 193–241. DOI: <https://doi.org/10.1016/j.sab.2010.12.011>
- [214] *Handbook of Prompt Gamma Activation Analysis: With Neutron Beams* (Eds: G. L. Molnár), Springer US, Boston, MA **2004**.
- [215] Z. Révay, T. Belgya, Principles of the PGAA method, in *Handbook of Prompt Gamma Activation Analysis* (Ed: G. L. Molnár), Springer, Boston, MA **2004**. DOI: [https://doi.org/10.1007/978-0-387-23359-8\\_1](https://doi.org/10.1007/978-0-387-23359-8_1)
- [216] C. A. Palmer, P. C. Lyons, *Int. J. Coal Geol.* **1996**, *32* (1–4), 151–166. DOI: [https://doi.org/10.1016/S0166-5162\(96\)00035-3](https://doi.org/10.1016/S0166-5162(96)00035-3)
- [217] M. I. V. Martínez, R. Zeisler, E. A. de Nadai Fernandes, M. A. Bacchi, D. J. Turkoglu, *J. Radioanal. Nucl. Chem.* **2018**, *318* (1), 739–744. DOI: <https://doi.org/10.1007/s10967-018-6162-0>
- [218] M. H. N. Tahir, M. D. Casler, K. J. Moore, E. C. Brummer, *Bioenerg. Res.* **2011**, *4* (2), 111–119. DOI: <https://doi.org/10.1007/s12155-010-9105-3>
- [219] R. A. Lagad, D. Alamelu, R. Acharya, S. K. Aggarwal, *J. Radioanal. Nucl. Chem.* **2011**, *288* (2), 613–620. DOI: <https://doi.org/10.1007/s10967-010-0978-6>
- [220] J. H. Gross, *Massenspektrometrie*, Springer, Heidelberg **2013**.
- [221] DIN 20202-07, *Solid fuels – Determination of contents of trace elements – Part 7: ICP-MS*, Beuth Verlag, Berlin **2014**.
- [222] DIN 51005, *Thermische Analyse (TA) – Begriffe*, Beuth Verlag, Berlin **2019**.
- [223] I. Boumanchar, Y. Chhiti, F. E. M'hamedi Alaoui, A. El Ouinani, A. Sahibed-Dine, F. Bentiss, C. Jama, M. Bensitel, *Waste Manage.* **2017**, *61*, 78–86. DOI: <https://doi.org/10.1016/j.wasman.2016.11.012>
- [224] M. Wöhler, D. Jaeger, S. K. Pelz, H. Thorwarth, *Energy Fuels* **2017**, *31* (7), 7562–7571. DOI: <https://doi.org/10.1021/acs.energyfuels.7b00803>
- [225] ISO 21404, *Solid biofuels – Determination of ash melting behaviour*, International Organization for Standardization, Geneva **2020**.
- [226] A. Doménech-Carbó, J. Labuda, F. Scholz, *Pure Appl. Chem.* **2012**, *85* (3), 609–631. DOI: <https://doi.org/10.1351/PAC-REP-11-11-13>
- [227] E. P. Randviir, C. E. Banks, *Anal. Methods* **2013**, *5* (5), 1098. DOI: <https://doi.org/10.1039/c3ay26476a>
- [228] G. I. Torgovnikov, *Dielectric properties of wood and wood-based materials*, Springer, Heidelberg **2012**.
- [229] J. Yan, W. Zhang, Y. Yan, 1–5. DOI: <https://doi.org/10.1109/I2MTC43012.2020.9129280>
- [230] A. Fuchs, M. J. Moser, H. Zangl, T. Bretterkieber, *Int. J. Smart Sens. Intell. Syst.* **2009**, *2* (2), 293–308. DOI: <https://doi.org/10.21307/ijssis-2017-352>
- [231] J. B. Hasted, *Aqueous dielectrics, Studies in chemical physics*, Chapman and Hall, London **1973**.
- [232] G. Brasseur, *IEEE Trans. Instrum. Meas.* **2003**, *52* (4), 1261–1265. DOI: <https://doi.org/10.1109/TIM.2003.816812>
- [233] A. J. Stamm, *Ind. Eng. Chem.* **1927**, *19* (9), 1021–1025. DOI: <https://doi.org/10.1021/ie50213a022>
- [234] Y. Tan, Z. Miao, M. M. Abdul, T. E. Grift, K. C. Ting, *Comput. Electron. Agric.* **2017**, *134*, 102–108. DOI: <https://doi.org/10.1016/j.compag.2017.01.013>
- [235] C. V. Kandala, R. Holser, V. Settaluri, S. Mani, N. Puppala, *IEEE Sensors J.* **2016**, *16* (11), 4509–4514. DOI: <https://doi.org/10.1109/JSEN.2016.2541081>
- [236] L. Fridh, L. Eliasson, D. Bergström, *Silva Fenn.* **2018**, *52* (5), 6993. DOI: <https://doi.org/10.14214/sf.6993>
- [237] C. Skaar, *Water in wood, Syracuse wood science series*, Vol. 4, Syracuse University Press **1972**.
- [238] A. J. Stamm, *Ind. Eng. Chem. Anal. Ed.* **1929**, *1* (2), 94–97. DOI: <https://doi.org/10.1021/ac50066a021>
- [239] M. Tiitta, V. Tiitta, J. Heikkinen, R. Lappalainen, L. Tomppo, *Sensors (Basel, Switzerland)* **2020**, *20* (4). DOI: <https://doi.org/10.3390/s20041076>
- [240] V. Cozzani, A. Lucchesi, G. Stoppato, G. Maschio, *Can. J. Chem. Eng.* **1997**, *75* (1), 127–133. DOI: <https://doi.org/10.1002/cjce.5450750120>
- [241] P. Jensen, H. Hartmann, T. Böhm, M. Temmerman, F. Rabier, M. Morsing, *Biomass Bioenergy* **2006**, *30* (11), 935–943. DOI: <https://doi.org/10.1016/j.biombioe.2006.06.005>
- [242] L. Liang, G. Fang, Y. Deng, Z. Xiong, T. Wu, *For. Sci.* **2019**, *65* (5), 548–555. DOI: <https://doi.org/10.1093/forsci/fxz007>
- [243] M. A. Acuna, G. E. Murphy, *For. Prod. J.* **2006**, 67–72.
- [244] J. Mata Sánchez, J. A. Pérez Jiménez, M. J. Diaz Villanueva, A. Serrano, N. Núñez, J. López Giménez, *Renewable Energy* **2015**, *78*, 566–572. DOI: <https://doi.org/10.1016/j.renene.2015.01.049>
- [245] C. E. Payne, E. J. Wolfrum, *Biotechnol. Biofuels* **2015**, *8*, 43. DOI: <https://doi.org/10.1186/s13068-015-0222-2>
- [246] X. Feng, C. Yu, X. Liu, Y. Chen, H. Zhen, K. Sheng, Y. He, *Biotechnol. Biofuels* **2018**, *11*, 88. DOI: <https://doi.org/10.1186/s13068-018-1090-3>
- [247] M. Mancini, Á. Rinnan, A. Pizzi, C. Mengarelli, G. Rossini, D. Duca, G. Toscano, *Fuel* **2018**, *217*, 650–655. DOI: <https://doi.org/10.1016/j.fuel.2018.01.008>
- [248] M. Sajdak, M. Kotyczka-Morańska, *Biomass Bioenergy* **2018**, *112*, 99–109. DOI: <https://doi.org/10.1016/j.biombioe.2018.02.019>
- [249] G. Toscano, Á. Rinnan, A. Pizzi, M. Mancini, *Energy Fuels* **2017**, *31* (3), 2814–2821. DOI: <https://doi.org/10.1021/acs.energyfuels.6b02421>
- [250] J. B. Reeves, *Commun. Soil Sci. Plant Anal.* **2012**, *43* (1–2), 478–495. DOI: <https://doi.org/10.1080/00103624.2012.641844>
- [251] M. A. Sanderson, F. Agblevor, M. Collins, D. K. Johnson, *Biomass Bioenergy* **1996**, *11* (5), 365–370. DOI: [https://doi.org/10.1016/S0961-9534\(96\)00039-6](https://doi.org/10.1016/S0961-9534(96)00039-6)
- [252] P. A. Akin, B. Sezer, S. R. Bean, K. Peiris, M. Tilley, H. Apaydin, I. H. Boyacı, *J. Sci. Food Agric.* **2021**, *101* (3), 1076–1084. DOI: <https://doi.org/10.1002/jsfa.10717>
- [253] E. Dietz, D. Kuptz, U. Blum, Hackschnitzel – die Chemie muss stimmen!, *LWF aktuell* **2014**, *103*, 12–14.
- [254] A. Fuchs, H. Zangl, G. Holler, in *Smart Sensors and Sensing Technology, Vol. 20, Lecture Notes Electrical Engineering* (Eds: S. C. Mukhopadhyay, G. S. Gupta), Springer, Heidelberg **2008**.
- [255] E. Musser, *Holz Roh- Werkst.* **1938**, *1* (11), 417–420. DOI: <https://doi.org/10.1007/BF02605258>
- [256] T. Mendel, A. Überreiter, D. Kuptz, H. Hartmann, *Comparison of rapid moisture content determination methods for wood chips*, 24th European Biomass Conference and Exhibition, Amsterdam, June **2016**.
- [257] VDI 4206 Blatt 4, *Performance criteria and test procedures for measuring devices for monitoring emissions at small firing installations – Measuring devices for the determination of moisture of wood fuels*, Beuth Verlag, Berlin **2021**.
- [258] ISO 18135, *Solid Biofuels – Sampling*, Beuth Verlag, Berlin **2017**.
- [259] ISO 21945, *Solid biofuels – Simplified sampling method for small scale applications*, International Organization for Standardization, Geneva **2020**.
- [260] S. Flamme, S. Hams, J. Bischoff, *Evaluierung der Altholzverordnung im Hinblick auf eine notwendige Novellierung*, Umweltbundesamt, Dessau-Roßlau **2020**.