

PRACTICAL APPLICATION OF EDXRF TECHNOLOGY TO DETERMINE THE CHEMICAL QUALITY OF WOOD CHIPS

D. Zimmermann¹, E. Dietz¹, M. Riebler¹, U. Blum¹, H. Borchert¹, C. Kuchler², D. Kuptz², H. Hartmann²

¹ Bavarian State Institute of Forestry (LWF)
Hans-Carl-von-Carlowitz-Platz 1, D-85354 Freising, Germany
Phone: +49-8161-712628, Fax: +49-8161-715132
david.zimmermann@lwf.bayern.de

² Technology and Support Centre in the Centre of Excellence for Renewable Resources (TFZ)
Schulgasse 18, D-94315 Straubing, Germany

ABSTRACT: Sufficient wood chip fuel quality is important for failure-free combustion and less emissions. Unfortunately, mineral soil-contamination can be a serious issue as it can take place during logging or chipping process. Currently, there is no reliable quality management system for chemical wood chip quality established yet. During a previous study, so called "biomass fuel indexes for the contamination with mineral soil" (BFICS) have been developed, utilizing the ratio of Fe/Mn and Al/200. To get a rather quick impression of chemical element contents, an innovative portable EDXRF analyzer should be applied into wood chip supply chain, when quality issues could be concerned. The EDXRF device was calibrated with pulverized wood chip calibration standards ($n = 30$) of different tree species, in particular spruce and pine, analyzed by ICP-AES. Linear correlations between EDXRF and ICP-AES are quite tight ($R > 0.98$) and all elements show a sufficient limit of detection. Samples with particle sizes > 0.5 mm have a significant influence on EDXRF measurement reliability. Especially Al and Si are overestimated and show high standard deviations. Concentrations of pulverized (particle sizes < 0.5 mm) wood chips and pellets analyzed by EDXRF coincide well with ICP-AES results. Therefore, contaminated wood chips or pellets with 2 or 10 w-% mineral soil can easily be identified by EDXRF as well as clean material.

Keywords: Energy Dispersive X-ray Fluorescence (EDXRF), wood chips, wood pellets, chemical fuel quality, solid biofuels, fuel contamination with mineral soil

1 INTRODUCTION

Wood fuels are an important renewable energy source, especially considering they are available at any time in contrast to solar and wind energy. However, good fuel quality is important for failure-free combustion and less emissions. Unfortunately, wood chips can get contaminated with mineral soil during logging and chipping process, especially when wood chips are supplied from forest residues. Therefore, critical elements in soil such as potassium (K), silicon (Si) and heavy metals such as zinc (Zn), might affect high temperature corrosion, emission behavior and slagging in furnaces using those solid biofuels. In case of mineral soil-contamination, element contents of aluminium (Al) and iron (Fe) are also increased. High content of aluminum (index $Al/200 > 1$) and high ratio of iron to manganese (index $Fe/Mn > 1$) can give a good indication of mineral soil-contamination [1]. Nevertheless, it is difficult to define the source of high concentrations of these critical elements. Concentration of K, Si or Al in wood chips can also be increased, because of a greater amount of biomass crown materials (leaves, needles, fine branches) or bark.

Currently, there is no reliable quality management system for chemical wood chip quality, although regulatory limits must be complied, if ash content of the biofuel exceeds 1.5 % [2].

Conventional analytical methods like ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) need intensive sample preparation like acid-digestion, which makes them expensive, time consuming and require well-educated personnel. In contrast to that, the EDXRF (Energy Dispersive X-ray Fluorescence) technique allows to measure element contents in a range of the periodic table from Na to U, from 1 ppm (mg/kg) to 100 % either of a solid or liquid sample within only a few minutes and rather uncomplicated sample preparation [3]. The range of

industries and science disciplines which already apply EDXRF is wide, including metal, plastic, food and oil industries as well as the sector of mineralogy and geology. Other fields for this technique are environmental analysis of water and waste materials. However, there are only few research papers which used EDXRF for wood analysis [4–6]. Portable EDXRF devices were mostly used to determine CCA (Chromated Copper Arsenate) in wood waste [7–9]. Therefore, integrating an innovative portable EDXRF analyzer in the wood chip supply chain can be a conceivable strategy to determine chemical wood chip quality, which means breaking new ground for chemical characterization of bio fuels.

The aim of the joint research project "Quality assurance of solid wood fuels in order to decrease mineral soil-contamination and optimize combustion behavior" is to apply the EDXRF technology in a way that wood chips can be rapidly divided in different combustion categories, because of chemical fuel quality. Moreover, it is important to keep wood chip sample preparation for EDXRF analytic relatively simple, whereas there is a trade-off between particle sizes and measurement accuracy. Small particles lead to a more homogenous sample and usually to a better analytical quality with lower standard deviation. In the field, there are often only simple shredders or portable cutting mills. In consequence of this, the influence of different particle sizes on measurement quality is also a relevant issue in this study.

2 MATERIAL AND METHODS

2.1 Calibration of EDXRF device for biomass analysis

In the current study, a portable benchtop EDXRF device (Epsilon 1, Malvern Panalytical) is used to quantify the concentrations of relevant elements like Al,

Fe, Mn, K and Si. The EDXRF was calibrated with pulverized wood chip samples ($n = 30$) from different tree species, in particular spruce ($n = 17$) and pine ($n = 9$). In addition beech, willow, poplar and mixed assortment were used ($n = 1$, each). The raw material of these calibration standards were primarily from forest residues ($n = 15$) and energy roundwood ($n = 12$), but also from SRC (short rotation coppice; $n = 2$) and one sample from a whole tree (with crown but without rootstock). The calibration was set for the elements Al, K, Fe, Mn, Si, Zn, phosphorus (P), sulphur (S), calcium (Ca) and magnesium (Mg). The element values were compared to the analytical results from previous projects, where all samples had been analyzed with ICP-AES using a mixture of nitric acid (HNO_3), hydrochloric acid (HCl) and hydrofluoric acid (HF) and microwaves for digestion.

To calibrate EDXRF, $3.0 \text{ g} \pm 0.1 \text{ g}$ of each calibration standard were filled in a separate sample cup (diameter 27 mm with a $4 \mu\text{m}$ Prolene® thin-film at the bottom). Afterwards, the sample was gently pressed with a punch to remove disruptive air. The measurement time is about 14 min. It splits into five different time intervals in accordance with the elements respective position in the periodic table: Na-Si (420 s), P-Cl (60 s), K-V (120 s), Cr-Co (180 s) and Ni-Mo (60 s). Each calibration standard was measured three times using a new subsample in a new sample cup.

2.2 Wood and soil samples

Four wood (spruce) and three soil samples were collected from different locations in Bavaria:

- Forest residue 1 (FR1)
- Forest residue 2 (FR2)
- Energy roundwood 1 (ER1)
- Energy roundwood 2 (ER2)
- Soil A (SA)
- Soil B (SB)
- Soil C (SC)

The wood samples were technically dried in a container at $50 \text{ }^\circ\text{C}$ until weight balance. The soil samples were dried at room temperature for several days.

FR1 was shredded to different fractions: $< 2 \text{ mm}$, $< 1 \text{ mm}$ and $< 0.5 \text{ mm}$. In addition to that, $5.0 \text{ g} \pm 0.1 \text{ g}$ of each fraction were used to create three pressed tablets, respectively, while using a hydraulic press with 150 kN for 3 min (see Figure 6).

One subsample of FR2 was contaminated with 10 w-% of soil C and shredded to $< 0.5 \text{ mm}$. The other part was left clean and got directly shredded to $< 0.5 \text{ mm}$.

Assortment ER1 was directly shredded to $< 0.5 \text{ mm}$. A subsample was used to create clean wood pellets. With further subsamples wood pellets contaminated with 2 w-% of soil A, B or C, respectively, were produced. The four different pellets were shredded ($< 0.5 \text{ mm}$) and then analyzed by EDXRF and ICP-AES as well.

ER2 was exactly treated like FR2.

2.3 Measurement XRF

Similar to the sample preparation for the calibration (see chapter 2.1), $3.0 \text{ g} \pm 0.1 \text{ g}$ of the shredded wood sample is filled into a sample cup and pressed gently with a punch. The measurement time is also the same. Each sample is measured three times using a new subsample in a new sample cup.

Pressed tablets are measured with same calibration curves and the same measurement time as mentioned before, but without using a sample cup.

3 RESULTS AND DISCUSSION

3.1 Calibration quality

Figure 1 to Figure 5 show the calibration curves of relevant elements. The x-axis displays the respective concentration measured by ICP-AES, the y-axis indicates the measured intensity or count rate in counts per second (cps) for one particular element. Generally, all elements show a decent linear correlation and can be used for upcoming measurements. Though some calibration standards obviously vary from the specifically calculated calibration curve of some elements (e.g. Al and Si), but no trend for particular tree species was identified. As a consequence, this calibration can be used for at least spruce, pine and also for both assortments: forest residues and energy roundwood. The number of beech, poplar, willow and mixed assortment were too small to give a scientific statement, but they usually fit into the calibration curves.

Table I shows a calibration report for all contemplated elements. According to this report, the correlation for all elements is > 0.978 , except Mg ($R = 0.875$). Furthermore, sensitivity (slope of the calibration curve), RMS (root mean square) value, concentration range and LOD (limit of detection) are listed in this table. The calibration RMS value is a statistical comparison (1 sigma) of the chemical concentration of the calibration standards with the concentration calculated by regression in the calibration procedure. It represents the accuracy of the whole calibration curve for one specific element. Lighter elements like Al, Mg and Si can only be measured less accurate and are consequently harder to detect. They have the highest relative RMS (9 – 16 %) of all calibrated elements. Relative RMS means the deviation of the RMS value from the average of the concentration range in percent. To determine the limit of detection, the “method of blank value” according to DIN 32645 [10] was used. Therefore 11 samples of 100 % pure cellulose were analyzed. Cellulose was selected, because it performs very close to a wooden matrix and is free of elements that can usually be detected by EDXRF. The element specific LOD was calculated afterwards using the 3-sigma standard deviation of the cellulose divided by the sensitivity. As shown in the calibration report, lighter elements with consequently smaller atom weight have a lower sensitivity and a correspondingly higher LOD, which makes them harder to detect in samples with a wooden matrix. Nevertheless, LOD of Al, Fe and Mn can be sufficient to divide into clean and with mineral soil-contaminated wood fuels.

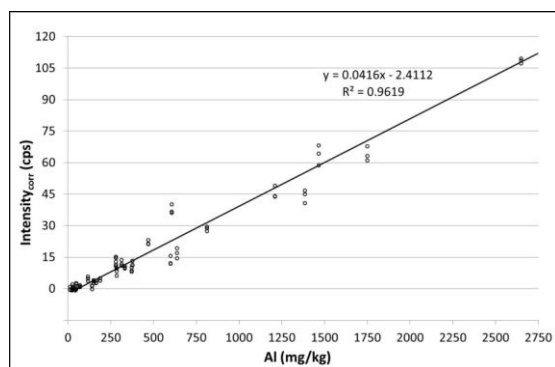


Figure 1: Calibration curve for aluminium (Al)

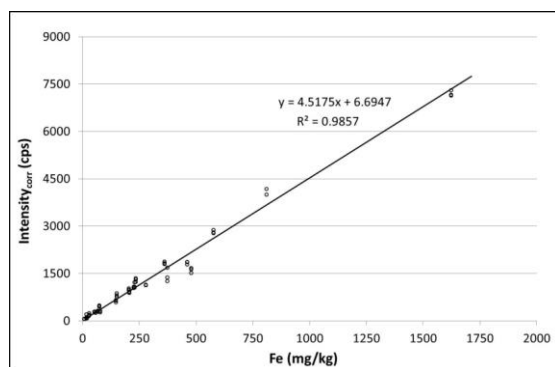


Figure 2: Calibration curve for iron (Fe)

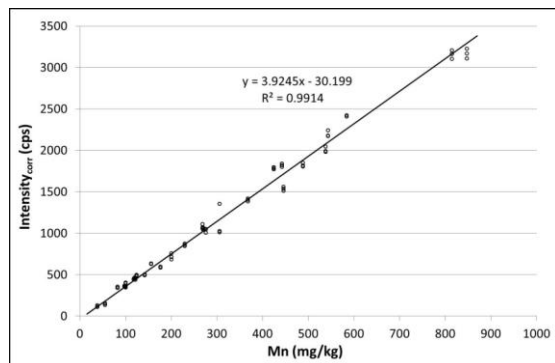


Figure 3: Calibration curve for manganese (Mn)

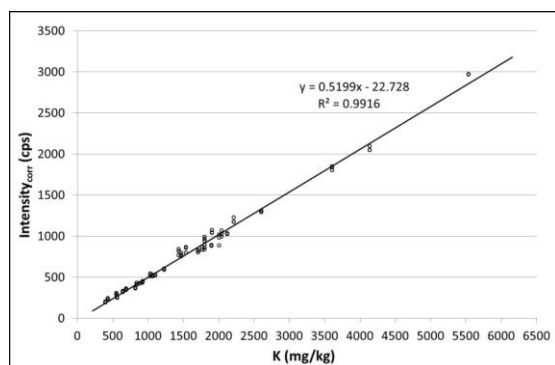


Figure 4: Calibration curve for potassium (K)

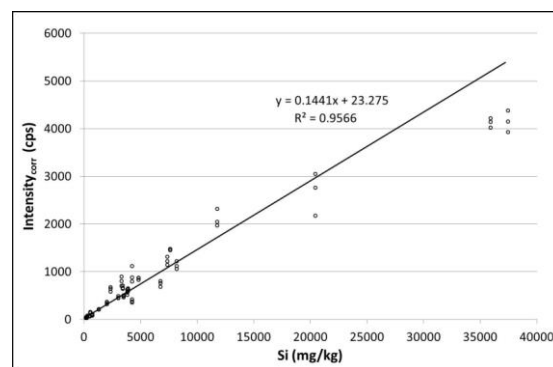


Figure 5: Calibration curve for silicon (Si)

Table I: Calibration report

(R: correlation, RMS: root mean square value of the calibration, LOD: limit of detection)

	R	Sensitivity cps/(mg/kg)	RMS mg/kg	rel. RMS %	Range mg/kg	LOD mg/kg
Mg	0.875	0.0203	131	16	158 - 1453	228
Al	0.981	0.0416	120	9.0	14 - 2650	61
Si	0.978	0.144	2430	13	166 - 37470	68
P	0.993	0.271	27.3	4.5	47 - 1180	13
S	0.978	0.649	38.2	7.8	81 - 894	7
K	0.996	0.520	95.5	3.2	400 - 5536	6
Ca	0.997	0.966	188	2.9	710 - 12080	4
Mn	0.996	3.92	20.2	4.6	38 - 848	3
Fe	0.993	4.52	39.5	4.8	8 - 1624	2
Zn	0.991	4.63	1.69	4.6	11 - 63	1

3.2 Influence of particle size

Figure 6 shows a picture of three pressed tablets with different particle sizes produced from the different fractions of FR1. It cannot be ruled out, that FR1 was slightly contaminated with mineral soil during logging or chipping process, because Al/200-index is higher than 1 (see Al-content by ICP-AES in Table II). The distribution of bark and wood varies among these tablets. The same effect can be observed for sample cups filled with coarse powders in different particle size fractions. The influence of the particle size in coarse powders and pressed tablets on the measurement quality of Al, Fe and Mn is pictured in Figure 7. EDXRF measurement of Al, Fe and Mn in the coarse powder sample with particle size < 0.5 mm gives similar results as ICP-AES. While Al recovery rate is significantly higher in samples with particle size > 0.5 mm in coarse powders as well as in pressed tablets, Fe and Mn do not show the same effect. They are still close to the values measured by ICP-AES.

The influence of the particle size on other elements and their specific standard deviation is listed in Table II (coarse powders) and Table III (pressed tablets). All concentrations measured with EDXRF in coarse powders < 0.5 mm fit with results of ICP-AES. In general, for each element the standard deviation increases with growing particle size in coarse powder samples and pressed tablets, respectively. The particle size effect can be observed for the elements Al, Si, Ca and Fe in coarse powders as well as in pressed tablets. Therefore, the recovery rates for the elements Al and Si are significantly

overestimated in samples with larger particle sizes whereas they are slightly underestimated for the elements Ca and Fe. The effect seems to be smaller on the other elements. The chemical bindings of the elements Al and Si have different specific structures in soil and wood, which would explain an effect on EDXRF measurement quality. Furthermore, wood samples with larger particle size have a rough surface, which could also have an influence. In addition to that, coarse powders with larger particle size have a lower bulk density, which leads to worse measurement quality, because more air can enter the interspaces. It can be possible, that fine material e.g. smaller soil particles could fall down upon the bottom of the sample cup.

Table IV shows the ratio of intensities between pressed tablet and coarse powder samples. Using pressed tablets (<0.5 mm) the signal intensity is higher than in coarse powders (ratio > 1) at any time. The same applies for the <2 mm-fraction, except for Si. Surprisingly, the measured concentrations in pressed tablets (< 1 mm) are lower than in coarse powders, except for Mg, Mn and Zn. An explanation would be that no representative sample of the <1 mm-fraction was taken for the pressed tablet preparation. Therefore, it is very important to mix samples carefully. In a mostly homogenous sample (<0.5 mm), the fluorescent radiation intensity for lighter elements with a smaller atomic weight like Al will be increased, if the sample is pressed to a tablet. But also heavier elements like Zn have a small benefit. However, a separate calibration for pressed tablets would be necessary to get enhanced results.

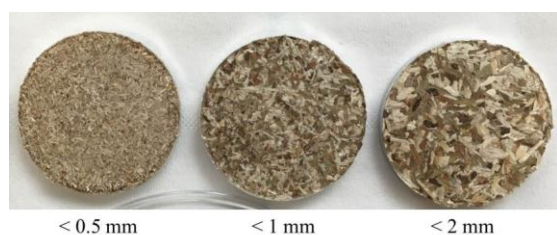


Figure 6: Pressed tablets from different shredding fractions (FR1)

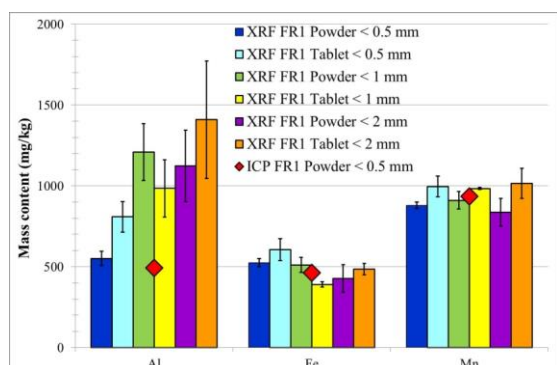


Figure 7: Influence of particle size on the elements Al, Fe and Mn fractions in coarse powders and pressed tablets from different shredding (FR1)

Table II: Particle size effect in coarse powders of FR1

	EDXRF coarse powder (n = 10)			ICP-AES (n = 2)
	0.5 mm mg/kg	1 mm mg/kg	2 mm mg/kg	0.5 mm mg/kg
Al	551 (± 44)	1209 (± 176)	1124 (± 222)	492 (± 1)
Ca	4924 (± 122)	4127 (± 220)	3674 (± 436)	4960 (± 57)
Fe	525 (± 25)	511 (± 47)	427 (± 86)	462 (± 19)
K	2155 (± 116)	2280 (± 121)	2093 (± 254)	2155 (± 50)
Mg	656 (± 43)	752 (± 42)	675 (± 64)	643 (± 16)
Mn	880 (± 21)	911 (± 54)	837 (± 86)	936 (± 17)
P	455 (± 31)	525 (± 31)	441 (± 35)	468 (± 1)
S	457 (± 20)	552 (± 37)	466 (± 38)	431 (± 6)
Si	7642 (± 608)	13099 (± 1747)	9032 (± 1373)	6762 (± 212)
Zn	38 (± 0.9)	37 (± 1.9)	35 (± 4.5)	35 (± 1)

Table III: Particle size effect in pressed tablets of FR1

	EDXRF pressed tablet (n = 3)			ICP-AES (n = 2)
	0.5 mm mg/kg	1 mm mg/kg	2 mm mg/kg	0.5 mm mg/kg
Al	808 (± 94)	985 (± 177)	1409 (± 363)	492 (± 1)
Ca	5360 (± 473)	3555 (± 273)	3904 (± 744)	4960 (± 57)
Fe	605 (± 68)	391 (± 16)	485 (± 35)	462 (± 19)
K	2336 (± 175)	2120 (± 35)	2350 (± 610)	2155 (± 50)
Mg	908 (± 85)	833 (± 4)	909 (± 108)	643 (± 16)
Mn	996 (± 65)	984 (± 6)	1015 (± 94)	936 (± 17)
P	566 (± 65)	465 (± 15)	585 (± 171)	468 (± 1)
S	566 (± 62)	464 (± 13)	530 (± 138)	431 (± 6)
Si	8578 (± 1288)	6287 (± 944)	6620 (± 947)	6762 (± 212)
Zn	52 (± 3.1)	51 (± 0.3)	52 (± 4.8)	35 (± 1)

Table IV: Ratio of intensities between pressed tablet and coarse powder (I: Intensity in counts per second)

	Ratio I(Tablet)/I(Powder)		
	0.5 mm	1 mm	2 mm
Al	1.52	0.81	1.27
Ca	1.07	0.90	1.07
Fe	1.13	0.81	1.13
K	1.07	0.97	1.13
Mg	1.38	1.11	1.35
Mn	1.11	1.14	1.21
P	1.24	0.91	1.35
S	1.24	0.87	1.15
Si	1.12	0.49	0.74
Zn	1.43	1.51	1.55

3.3 Measurement of wood chips and wood pellets with and without soil contamination

Shredded wood pellets (< 0.5 mm) of assortment ER1 were analyzed as coarse powders by the EDXRF calibration and by ICP-AES. Element values in wood pellets without soil-contamination (ER1) coincide well (deviation XRF/ICP < 20 %) with ICP-AES-results (left part of Table V). Wood pellets contaminated with 2 w-% of soil A show higher element values for Al, Mg and Si, when using EDXRF (right part of Table V). Contamination with soil B provides similar results, except Al-content fits perfect and Si-content is underestimated (left part of Table VI). EDXRF and ICP-AES measurement of wood pellets contaminated with soil C give similar results for all elements (right part of Table VI).

Table V: Element contents of shredded wood pellets (< 0.5 mm) ER1 and ER1 contaminated with soil A 2 w-%

	ER1			ER1 with SA 2 w-%		
	XRF (n = 3)	ICP (n = 2)	Deviation XRF/ICP	XRF (n = 3)	ICP (n = 2)	Deviation XRF/ICP
	mg/kg	mg/kg	%	mg/kg	mg/kg	%
Al	104 (± 14)	99 (± 5)	4.9	1667 (± 64)	1348 (± 18)	24
Ca	2411 (± 42)	2429 (± 30)	-0.7	2333 (± 84)	2404 (± 1)	-3.0
Fe	53 (± 2)	53 (± 1)	0.2	786 (± 20)	684 (± 10)	15
K	736 (± 11)	698 (± 4)	5.4	1003 (± 41)	990 (± 1)	1.4
Mg	234 (± 47)	221 (± 2)	5.9	500 (± 22)	328 (± 1)	53
Mn	150 (± 5)	151 (± 1)	-0.6	159 (± 3)	157 (± 1)	0.8
P	118 (± 5)	100 (± 2)	18	123 (± 3)	109 (± 1)	12
S	109 (± 6)	132 (± 1)	-18	117 (± 6)	141 (± 2)	-17
Si	453 (± 86)	529 (± 14)	-14	7034 (± 220)	5597 (± 21)	26
Zn	28 (± 0.5)	33 (± 2)	-13	37 (± 0.2)	42 (± 2)	-13

Table VI: Element contents of shredded wood pellets (< 0.5 mm) ER1 contaminated with soil 2 w-% B or C (N/D: No Data)

	ER1 with SB 2 w-%			ER1 with SC 2 w-%		
	XRF (n = 3)	ICP (n = 2)	Deviation XRF/ICP	XRF (n = 3)	ICP (n = 2)	Deviation XRF/ICP
	mg/kg	mg/kg	%	mg/kg	mg/kg	%
Al	1042 (± 98)	1019 (± 30)	2.3	1584 (± 82)	1716 (± 10)	7.7
Ca	2187 (± 74)	2296 (± 16)	-4.7	2208 (± 30)	2437 (± 18)	9.4
Fe	371 (± 13)	362 (± 6)	2.6	1116 (± 29)	1026 (± 23)	-8.8
K	996 (± 81)	1196 (± 36)	-17	853 (± 10)	967 (± 30)	12
Mg	406 (± 94)	265 (± 2)	53	464 (± 29)	484 (± 5)	4.0
Mn	135 (± 2)	138 (± 1)	-1.6	146 (± 2)	158 (± 2)	7.6
P	93 (± 9)	92 (± 1)	1.1	87 (± 3)	88 (± 1)	1.3
S	100 (± 2)	127 (± 1)	-21	112 (± 22)	130 (± 1)	14
Si	5461 (± 568)	6877 (± 418)	-21	5047 (± 244)	N/D	N/D
Zn	28 (± 0.5)	34 (± 2)	-18	31 (± 0.2)	30 (± 1)	-4.7

The indexes for the contamination of wood fuels with mineral soil (Fe/Mn and Al/200) can be determined in wood pellets very well by EDXRF. The difference between wood pellets with 2 w-% mineral soil and without soil is obvious. While in the clean wood pellets the ratio of Fe/Mn is 0.35 and of Al/200 is 0.52, the ratio of Fe/Mn varies between 2.8 and 7.6 and of Al/200 between 5.2 and 8.3 in soil-contaminated wood pellets.

In clean wood chip samples (FR2 and ER2) without soil-contamination, element values generally fit with ICP-AES (left parts of Table VII and Table VIII). The contents of Fe, P and S of FR2 deviate more than 20 % from ICP-AES results. The same applies for ER2, except Mg differ very high (68 %), whereas the determination of S works well. However, the contents of Fe, Mg, P and S are relatively small. Furthermore, the samples seem to be rather inhomogeneous, because of the high standard deviation of Fe determined by ICP-AES. Taking this in account, EDXRF and ICP-AES give same results for Fe. EDXRF results of FR2 contaminated with 10 w-% soil C are close to results of ICP-AES, except the values of Al and P are higher (right part of Table VII). In assortment ER2 contaminated with 10 w-% soil C the element value of P is strong overestimated, while the one of Mg is strong and of Ca and K are moderate underestimated (right part of Table VIII). Element values of the two mineral soil-contaminated assortments differ from each other, even though the same amount of soil C was used. The ash content of FR2 with 10 w-% soil C is 2.38 % ± 0.21 % and of ER2 contaminated with 10 w-% soil C is 9.71 % ± 0.13 %. The ash content of clean wood chips is 0.72 % ± 0.10 % (FR2) and 0.51 % ± 0.04 % (ER2). According to the ash contents, FR2 show just about 2 w-% soil, while ER2 have the full 10 w-% of soil on it. It cannot be ruled out, that soil fell off the wood chips (FR2) while sampling. The exact circumstances are still under investigation.

Nevertheless, the indices Fe/Mn and Al/200 can be

determined with a mediocre statistical uncertainty. The difference between wood chips with 10 w-% mineral soil and without soil is clearly evident. So the ratio of Fe/Mn is 0.30 (FR2) and 0.26 (ER2) for clean wood chips and rises to 5.1 (FR2) and 22 (ER2) when the samples are contaminated with 10 w-% soil C. The index Al/200 is increased from 0.69 (FR2) and 0.42 (ER2) to 11 (FR2) and 30 (ER2) after soil-contamination.

Table VII: Element contents of shredded wood chips (< 0.5 mm) FR2 and FR2 contaminated with soil C 10 w-% (N/D: No Data)

	FR 2			FR2 with SC 10 w-%		
	XRF (n = 3)	ICP (n = 3)	Deviation XRF/ICP	XRF (n = 3)	ICP (n = 3)	Deviation XRF/ICP
	mg/kg	mg/kg	%	mg/kg	mg/kg	%
Al	137 (± 20)	169 (± 42)	-19	2253 (± 198)	1640 (± 153)	37
Ca	1545 (± 50)	1427 (± 81)	8.3	1366 (± 57)	1317 (± 35)	3.7
Fe	65 (± 9)	82 (± 23)	-21	1050 (± 35)	940 (± 72)	12
K	1261 (± 14)	1214 (± 59)	3.9	1228 (± 54)	1288 (± 84)	-4.7
Mg	406 (± 24)	415 (± 14)	-2.2	555 (± 7)	638 (± 41)	-13
Mn	217 (± 7)	218 (± 11)	-0.40	206 (± 10)	205 (± 2)	0.68
P	227 (± 8)	168 (± 12)	35	178 (± 8)	126 (± 4)	41
S	228 (± 4)	189 (± 14)	21	174 (± 3)	169 (± 5)	3.3
Si	1144 (± 64)	N/D	N/D	6068 (± 947)	N/D	N/D
Zn	38 (± 1)	36 (± 2)	6.9	37 (± 1)	35 (± 1)	6.4

Table VIII: Element contents of shredded wood chips (< 0.5 mm) ER2 and ER2 contaminated with soil C 10 w-% (N/D: No Data)

	ER 2			ER2 with SC 10 w-%		
	XRF (n = 3)	ICP (n = 3)	Deviation XRF/ICP	XRF (n = 3)	ICP (n = 3)	Deviation XRF/ICP
	mg/kg	mg/kg	%	mg/kg	mg/kg	%
Al	84 (± 16)	71 (± 7)	19	5947 (± 178)	7043 (± 484)	-16
Ca	946 (± 41)	927 (± 14)	2.1	1102 (± 49)	1424 (± 113)	-23
Fe	38 (± 8)	48 (± 12)	-21	4051 (± 304)	3907 (± 273)	3.7
K	967 (± 15)	967 (± 19)	0.07	1649 (± 62)	2161 (± 81)	-24
Mg	434 (± 38)	258 (± 6)	68	525 (± 5)	1531 (± 60)	-66
Mn	148 (± 5)	150 (± 1)	-1.3	184 (± 10)	203 (± 5)	-9.1
P	68 (± 5)	56 (± 1)	23	98 (± 12)	68 (± 4)	44
S	102 (± 4)	96 (± 2)	6.2	114 (± 5)	105 (± 2)	9.2
Si	231 (± 41)	N/D	N/D	16753 (± 712)	N/D	N/D
Zn	28 (± 1)	27 (± 1)	3.3	34 (± 2)	34 (± 1)	1.1

4 CONCLUSION

Chemical fuel quality of wood chips and wood pellets can be identified by a portable EDXRF device. Measured element values coincide well with element values detected by ICP-AES. According to this, determination of biomass fuel indexes for the contamination with mineral soil (Fe/Mn and Al/200) and also determination of K are sufficiently accurate. The determination of K is in this sense relevant, because it is the most important indicator for the formation of fine particulates during the combustion process. The difference between clean and soil-contaminated wood chips or wood pellets (2 or 10 w-% soil) is obvious, when using EDXRF. However, low concentrations of light elements (Mg, Al and Si) in a wooden matrix are hard to quantify. While measured values of Mg are quite uncertain, those of Al coincide better with determination by ICP-AES.

The quality of EDXRF measurement depends strongly on the homogeneity and the particle size of the sample, because elements can be detected just in a minor depth of the sample (micrometer range; depends on element and sample matrix). If a sample is not well mixed or has larger particle sizes, fine material can fall down to the bottom of the sample cup and dominate the results of the measurement. Also samples with larger particle sizes have more air-filled interspaces. The air absorbs the fluorescent radiation of the elements and therefore has a negative influence on the measurement quality. While a strong effect of the particle size on the measurement of Al and Si is observed, the effect seems to be smaller on the measurement of Fe, Mn and K. For all elements, pressed tablets increase the intensity of the fluorescent radiation. However, a separate calibration would be necessary, if wood chip samples should be quantified as pressed tablets by EDXRF. Unfortunately, pressing tablets is impossible, if wood chips have to be analyzed in the field.

5 ACKNOWLEDGEMENTS

- This study was funded by the Bavarian State Ministry of Food, Agriculture and Forestry (BayStMELF) under the reference number "KS/17/03"
- We thank our colleagues Cristian Babut, Albert Maierhofer, Irmgard Kern, Stephan Winter, Sophie Ederer, Sandra Egger, Mandy Kaps, Elisabeth Solic and Katharina Gruber for their support during this study
- The study was conducted in close cooperation with the Bavarian State Forest Enterprise (BaySF)

6 REFERENCES

- [1] Dietz, E.; Kuptz, D.; Blum, U.; Schulmeyer, F.; Borchert, H.; Hartmann, H. (2016): New Indexes for the contamination of wood chips with mineral soil. 24th European Biomass Conference and Exhibition: 630–633.
- [2] Deutsches Institut für Normung e.V. (DIN) (2014): DIN EN ISO 17225-4. Solid Biofuels – Fuel specifications and classes – Part 4: Graded wood chips. Berlin: Beuth

- [3] Haschke, M.; Flock, J. (2017): Röntgenfluoreszenz-analyse in der Laborpraxis. 1. Aufl. Weinheim: WILEY-VCH, 495 pages, ISBN 978-3-527-34292-1.
- [4] Zielenkiewicz, T.; Radomski, A.; Zawadzki, J. (2012): XRF examination of matrix uniqueness in chosen deciduous wood species. *European Journal of Wood and Wood Products* 70(6): 845–849.
- [5] Fellin, M.; Negri, M.; Mazzei, F.; Zanuttini, R. (2014). Characterization of ED-XRF technology applied to wooden matrix. *Wood Research* 59(4): 533–546.
- [6] Zielenkiewicz, T.; Zawadzki, J.; Radomski, A. (2012): XRF spectrometer calibration for copper determination in wood. *X-Ray Spectrometry* 41(6): 371–373.
- [7] Fellin, M.; Negri, M.; Zanuttini, R. (2014): Multi-elemental analysis of wood waste using energy dispersive X-ray fluorescence (ED-XRF) analyzer. *European Journal of Wood and Wood Products* 72(2): 199–211.
- [8] Block, C. N.; Shibata, T.; Solo-Gabriele, H. M.; Townsend, T. G. (2007): Use of handheld X-ray fluorescence spectrometry units for identification of arsenic in treated wood. *Environmental Pollution* 148(2): 627–633.
- [9] Jacobi, G.; Solo-Gabriele, H.; Townsend, T.; Dubey, B. (2007): Evaluation of methods for sorting CCA-treated wood. *Waste Management* 27(11): 1617–1625.
- [10] Deutsches Institut für Normung e.V. (DIN) (2008): DIN 32645. Chemical analysis - Decision limit, detection limit and determination limit under repeatability conditions - Terms, methods, evaluation. Berlin: Beuth

7 LOGOS

LWF Bayerische Landesanstalt
für Wald und Forstwirtschaft

<http://www.lwf.bayern.de>

Technologie- und Förderzentrum
im Kompetenzzentrum
für Nachwachsende Rohstoffe



<http://www.tfz.bayern.de>