

Determination of major and minor ash-forming elements in solid biofuels

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Received 17 November 2005; accepted 9 June 2006

Available online 20 September 2006

Abstract

The development of reliable and appropriate methods for the accurate determination of major (Al, Ca, Fe, K, Mg, Na, P, Si, Ti) and minor (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Tl, V, Zn) ash-forming elements in solid biofuels was the major goal of Task III.2 of the EU project BioNorm. For this purpose, wood + bark, straw and olive residues were analysed using several digestion and determination methods. The digestion methods included wet decomposition in closed vessels with different acid mixtures as well as dry-ashing techniques. The determination systems included FAAS, GFAAS, CVAAS, ICP-OES, ICP-MS, XRF as well as direct Hg-determination. Tests were carried out to optimise the methods applied. To summarise the outcomes of these tests, different digestion procedures were developed for major and minor elements. Digestion with $\text{H}_2\text{O}_2/\text{HNO}_3/\text{HF}$ followed by neutralisation with H_3BO_3 was validated for major element analyses, while digestion with $\text{H}_2\text{O}_2/\text{HNO}_3/\text{HF}$ was validated for minor element analyses. The validation results show that the applied digestion methods can be recommended for solid biofuel analyses. For the determination of the elements investigated in solid biofuels, the following detection systems can be recommended: FAAS for Ca, Fe, K, Mg, Na, Si, Mn, Zn; ICP-OES for Al, Ca, Fe, K, Mg, Na, P, Si, Ti, Mn, Zn, Ba, Cr, Cu, Mn, Ni, V, Zn; GFAAS for Cd, Cr, Cu, Ni, Pb; ICP-MS: P, Ti, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, V, Zn and direct determination as well as CVAAS for Hg.

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Keywords: Solid biofuels; Elements; Chemical analyses; Digestion; Determination; Method validation

1. Introduction and objectives

The application of fuels of known quality is an essential prerequisite for secure and efficient biomass combustion. Important parameters for assessing the chemical properties of solid biofuels are the contents of major (Al, Ca, Fe, K, Mg, Na, P, Si, Ti) and minor (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Tl, V, Zn) ash-forming elements. While major elements are of key relevance regarding ash melting, deposit and slag formation as well as corrosion, minor elements are of special importance for particulate emissions as is the environmental assessment of the ashes produced and their subsequent utilisation. Specific stan-

dard operating procedures for the determination of these elements in biofuels exist (or are under development) only in a few cases [1]. Most laboratories thus determine major and minor elements in biofuels using “in house” methods or standards originally developed for solid mineral fuels. This often leads to considerable deviations between the results of different laboratories as shown by several round robins on various solid biofuels [2–4]. In cooperation with CEN/ TC 335, Task III.2 of the EU-funded BioNorm project (ENK6-CT-2001-00556) [5] was therefore concerned with the development of standardised methods for the determination of major and minor element contents in solid biofuels. The specific objectives were to test, evaluate and optimise analytical methods as well as to validate the most suitable analysis procedures in order to prepare best practise guidelines for the correct determination of these elements.

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The following European partner institutions were involved in Task III.2:

- Institute for Resource Efficient and Sustainable Systems, Graz University of Technology, Austria (Coordinator of Task III.2).
- Institute of Process Engineering and Power Plant Technology, University of Stuttgart, Germany.
- Swedish National Testing and Research Institute, Borås, Sweden.
- Department of Energy Process Engineering and Chemical Engineering, Freiberg University of Mining and Technology, Germany.
- University of West-Hungary, Technical Institute of Forestry and Environmental Sciences, Department of Energetics, Sopron, Hungary.
- Elsam A/S (Techwise), Enstedvaerket, Denmark (Partner not funded by the EU).

The project started in January 2002 and was finalised by the end of 2004. The present paper describes the investigations performed and summarises the main outcomes and conclusions of the project work.

2. Sample homogenisation and homogeneity tests

An adequate supply of homogeneous material was needed for the tests planned within Task III.2. A wood + bark mixture and straw were chosen as representative types of solid biofuels to be investigated within Task III.2. Olive residues were also included for some investigations.

Pre-tests were performed in order to determine the particle size to which the final materials should be reduced in order to obtain satisfactory homogeneity. XRF and ICP-MS determinations were performed on three different particle sizes (<1 mm, <0.25 mm, <0.1 mm) and the relative standard deviations (RSD) calculated. The results showed that particle sizes <0.25 mm delivered satisfactory homogeneity ranges with RSD-values below 10% for most of the elements tested (data not shown).

The next step of the practical work dealt with the preparation of sufficient wood + bark and straw materials for the further investigations planned. Ten kg wood + bark and straw material were milled to the agreed particle size (<0.25 mm) and filled in bottles amounting to 20 g each.

In order to investigate the homogeneity of the prepared materials, XRF and ICP-MS determinations were performed once again. Subsequently, *F*-tests were carried out to check the within and between bottle homogeneity (Table 1). Satisfactory RSD-values below 10% and 30%, respectively, were obtained for most of the major and minor elements. Furthermore, the vast majority of the elements did not show significant *F*-values, indicating homogeneous distributions of the materials throughout the different bottles, with the exception of Zn in wood + bark as well as Fe and Cd in straw. To summarise

the outcome of the homogeneity tests, both materials proved to be suitable for the further investigations planned.

3. Method development—part 1

Several commonly used analytical methods were tested with the prepared materials in order to choose the most promising methods for further investigations. For this purpose 16 digestion and eight determination methods were examined (see Table 2). The main results of the investigations can be summarised as follows:

- Wet digestion in closed vessels with a mixture of HNO₃, (H₂O₂) and HF, HCl, HClO₄ or H₂O, heated conventionally or by microwaves, with or without neutralisation (complexation) by H₃BO₃ (digests no. 1–9, see Table 2) followed by determination with FAAS, GFAAS, CVAAS, ICP-OES or ICP-MS showed, for most of the elements, a good conformity between the results gained. However, for Si and Ti, large fluctuations between the measured concentrations were observed. The results of the Na, P, Si, Cr and Zn determinations are shown in Fig. 1 as examples. Lower concentrations of Si and Ti were especially stated when the digestions have been performed without addition of HF. This suggests the requirement of this acid for digestion in the case that Si and Ti are planned for determination.
- Pre ashing at 550 °C, followed by Li-metborate fusion, dissolving in H₂O/HNO₃ (digest no. 10, see Table 2; applied for major element determination according to ASTM D 3682 [6]) or pre ashing (550 °C) and subsequent ash-digestion with HNO₃/HF/H₃BO₃ (digest no. 11, see Table 2; applied for major and (some) minor element determinations according to ASTM D 3683 [7]) resulted in good conformity with the above-mentioned wet digestion procedures. Because of restricted time and budget within the project-working group, however, dry ashing was not included in the following investigations within Task III.2.
- No difference with respect to the applied heating device (conventional (resistance) or microwave heating) was observed.
- Digest no. 3 (see Table 2) which, among others, prescribes filtration through filter paper after decomposition, showed, for several elements, strong deviations from other results (see as examples the results for P and Zn in Fig. 1).
- Results obtained for K, Mg, Na and P further revealed that direct XRF-measurements (performed on wood + bark and straw pellets; digest no. 16, see Table 2) deviated from results gained with the other measurement systems. Similar observations were made for Al, Fe, Na, P, Cd, Cr, Ni, Co, Mn, Sb when XRF-measurements were applied after pre ashing and fusion in Li-tetraborate (digest no. 13–15, see Table 2). As examples of this trend, see the results for Na, P and Cr in Fig. 1. These deviations suggest calibration problems

Table 1
Homogeneity tests for major and minor elements in wood + bark and straw

	Method precision		Within homogeneity		Between homogeneity		F-Value
	RSD _M	U _{RSDM}	RSD _W	U _{RSDW}	RSD _B	U _{RSDB}	
Wood+bark							
Major elements							
Al	2.4	0.5	9.0	2.1	15.9	3.6	3.18
Ca	2.9	0.6	3.2	0.7	1.8	0.4	3.42
Fe	2.0	0.4	5.7	1.3	4.0	0.9	2.28
K	2.3	0.5	1.0	0.2	0.9	0.2	1.40
Mg	2.6	0.5	2.5	0.5	3.2	0.7	1.67
Mn	1.9	0.4	1.7	0.4	1.0	0.2	3.34
Na	4.2	0.9	4.5	1.0	2.4	0.5	3.43
P	2.9	0.6	4.3	1.0	2.5	0.6	2.68
Si	1.5	0.3	6.9	1.5	13.7	3.1	3.61
Ti	1.4	0.3	1.5	0.3	1.1	0.3	1.67
Minor elements							
Ba	0.4	0.1	1.6	0.3	1.6	0.3	1.05
Cd	2.1	0.5	3.3	0.7	3.7	0.8	1.13
Co	1.8	0.4	3.6	0.7	4.8	1.0	1.79
Cr	6.8	1.5	16.1	3.4	14.1	3.3	1.65
Cu	1.8	0.4	9.3	2.0	14.7	3.3	3.48
Mo	12.4	2.8	38.9	8.0	44.1	9.0	1.00
Ni	1.6	0.3	19.8	4.0	29.0	5.9	2.15
Pb	1.9	0.4	26.9	5.7	50.6	10.3	4.48
Sb	1.6	0.4	18.6	4.0	27.1	5.8	2.53
Tl	2.3	0.5	2.3	0.5	3.7	0.8	2.64
V	2.5	0.6	23.3	4.8	21.3	4.3	1.12
Zn	0.7	0.2	3.1	0.7	8.9	1.9	7.77 *
Straw							
Major elements							
Al	1.4	0.3	5.0	1.1	5.7	1.3	1.09
Ca	1.0	0.2	2.4	0.5	2.0	0.5	1.54
Fe	1.1	0.2	7.0	1.6	2.1	0.5	13.32 *
K	1.5	0.3	2.7	0.6	2.3	0.5	1.55
Mg	1.6	0.3	3.5	0.8	2.6	0.6	2.00
Mn	0.9	0.2	1.1	0.2	1.7	0.4	2.37
Na	3.9	0.8	6.5	1.5	3.3	0.7	3.94
P	1.8	0.4	3.2	0.7	2.2	0.5	1.86
Si	1.1	0.2	3.6	0.8	2.6	0.6	1.84
Ti	1.3	0.3	2.0	0.4	1.7	0.4	1.37
Minor elements							
Ba	0.5	0.1	1.7	0.4	1.0	0.2	3.26
Cd	1.7	0.4	4.0	0.8	1.8	0.4	4.96 *
Co	1.5	0.3	6.4	1.3	4.5	0.9	1.83
Cr	11.1	2.5	15.8	3.2	13.3	2.8	1.88
Cu	2.1	0.5	3.8	0.8	6.6	1.3	2.29
Mo	5.4	1.2	6.7	1.4	7.5	1.5	1.26
Ni	1.9	0.4	45.4	9.3	27.8	5.7	1.54
Pb	1.1	0.3	10.8	2.4	12.1	2.5	1.11
Sb	3.9	0.9	17.8	3.6	8.1	1.6	4.37
Tl	1.5	0.3	2.4	0.5	3.6	0.7	1.48
V	1.8	0.4	5.0	1.0	7.2	1.5	2.10
Zn	0.8	0.2	7.1	1.5	7.0	1.4	1.09

Explanations: major and minor elements were measured by XRF and ICP-MS, respectively; method precision was verified on the basis of 9–12 measurements of one measurement portion; within homogeneity was verified by 9–12 independent determinations of the content of one bottle; between homogeneity was verified on the basis of 9–12 independent determinations from 9 to 12 bottles; RSD_M, RSD_W, RSD_B...relative standard deviations (in %) of method precision, within and between bottles; *U*_{RSD}— respective uncertainties in % (defined as $U \approx \text{RSD}/\sqrt{2n}$, where *n* is the number of replicates; calculation according to [16]); *F*-values—test statistics of the *F*-tests performed to check the within- and between-bottle homogeneity; *—significant *F*-value ($p \leq 0.01$).

Table 2
Detection and digestion methods applied for the investigations within “Method development—part 1”

Code	Laboratory
A	Participating laboratories
D	
E	
L	
I	
N	Detection systems applied
S	
V	
C	
D	CVAAS
E	Direct Hg determination
F	FAES
G	FAAS
M	GFAAS
O	ICP-MS
X	ICP-OES
	XRF
	Digestion methods applied
1	H ₂ O ₂ /HNO ₃ (microwave heating)
2	H ₂ O ₂ /HNO ₃ /HClO ₄ (microwave heating)/HF
3	H ₂ O ₂ /HNO ₃ (conventional heating, 1/2 h cooking, filtration through filter paper)
4	H ₂ O/HNO ₃ /HCl (microwave heating)
5	H ₂ O ₂ /HNO ₃ /HClO ₄ (conventional heating)/HF
6	HNO ₃ /HF (microwave heating)
7	H ₂ O ₂ /HNO ₃ /HF (conventional heating)/H ₃ BO ₃
8	H ₂ O ₂ /HNO ₃ /HF (microwave heating)/H ₃ BO ₃
9	HNO ₃ /HF (microwave heating)/H ₃ BO ₃
10	Pre ashing at 550 °C, Li B O ₂ (1050 °C), HNO ₃ /H ₂ O (ASTM D 3682)
11	Pre ashing at 550 °C, HNO ₃ /HF/H ₃ BO ₃ (ASTM D 3683)
12	Direct Hg determination
13	Pre ashing at 450 °C/Li ₂ B ₄ O ₇ /NH ₄ Br/NH ₄ NO ₃ (only straw was measured)
14	Pre ashing at 525 °C/Li ₂ B ₄ O ₇ /NH ₄ Br/NH ₄ NO ₃ (only straw was measured)
15	Pre ashing at 815 °C/Li ₂ B ₄ O ₇ /NH ₄ Br/NH ₄ NO ₃ (only straw was measured)
16	Pellets (direct measurement of pelletised material)

for the applied XRF-systems. The usage of XRF systems for element determination depends strongly on reliable calibration standards. Currently, such standards are not available for solid biofuels. Therefore, this detection system was not included in the following investigations.

4. Method development—part 2

Based on the results of the first method development examinations, it was decided to focus further work on the optimisation of a wet chemical digestion procedure. The amount of HF required and different digestion temperatures (105, 190 and 220 °C) were investigated within this round of investigations. In order to assure a broader range of application for the analytical methods under investigation, olive residues as well as a certified reference material were included in the examinations in addition to straw. Because of restricted time and budget within the project-working group, wood + bark was excluded from these examinations.

The following investigations were performed for these purposes:

- Digestion tests on straw and olive residues with H₂O₂, HNO₃ and varying amounts of HF at 190 and 220 °C (105 °C by laboratory N).
- Analyses of a certified reference material (GBW 07602 (NCS DC 73348) “Bush Branches and Leaves”, issued 1997 by the China National Analysis Centre for Iron and Steel (Beijing)) digested with varying amounts of HF as well as standard digestion procedures of the participating laboratories.
- Special digestion tests on olive residues by laboratory E (performed with varying amounts of H₂O₂, HNO₃ and HF at 190 and 220 °C, and with or without subsequent heating of the digest solution with H₃BO₃).

The results obtained can be summarised as follows:

- For most of the elements investigated a good agreement between the results of most laboratories could be stated. Furthermore, most of the elements (Fe, P, As, Cd, Cu,

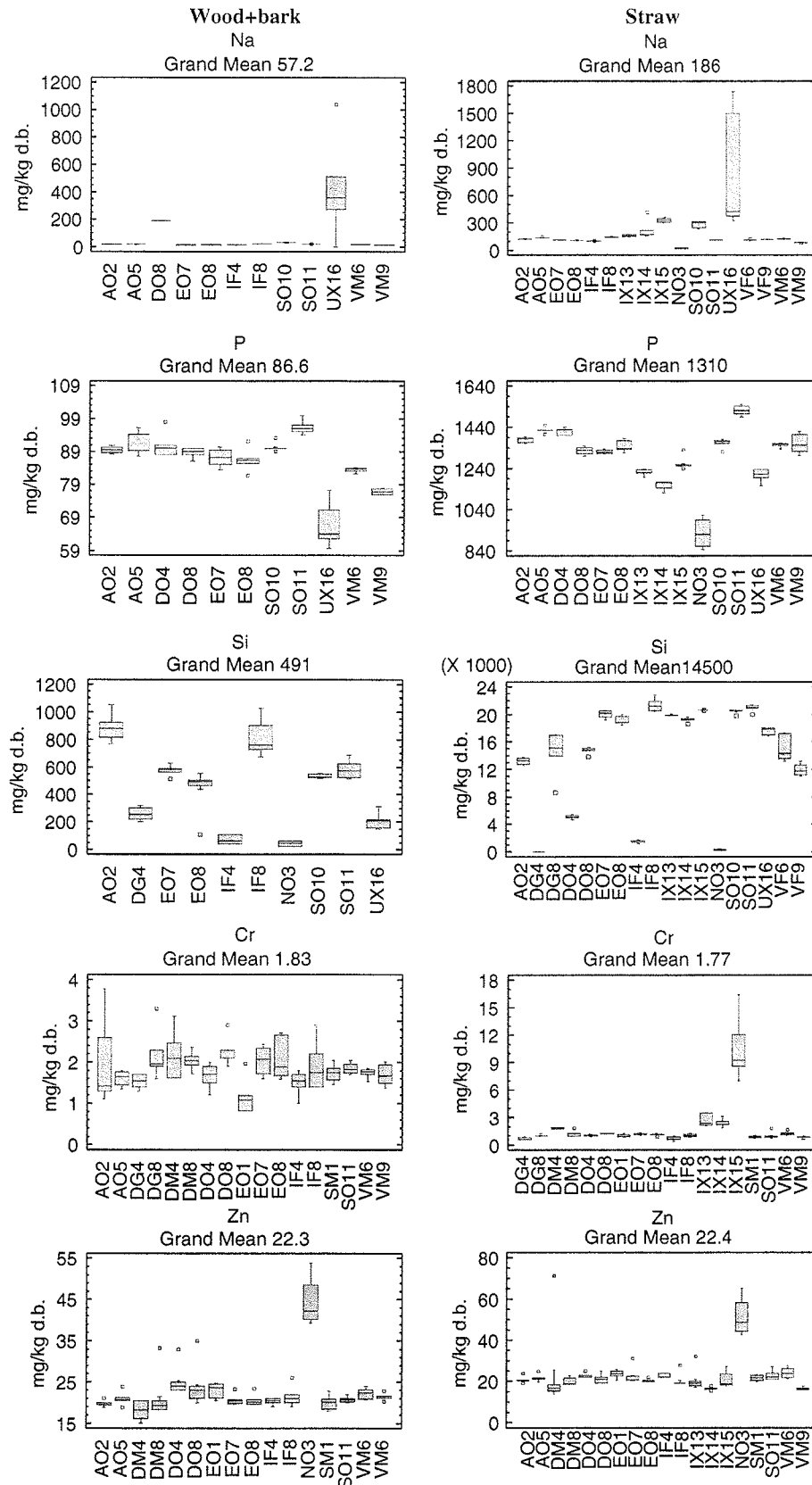


Fig. 1. Results of Na, P, Si, Cr and Zn determinations in the course of "Method development—part 1". Explanations: the boxplots have been calculated from $n = 3-6$ independent determinations; the codes on the x axes refer to the participating laboratories (1st character) as well as the detection systems (2nd character) and digestion methods (digit) applied (see Table 2).

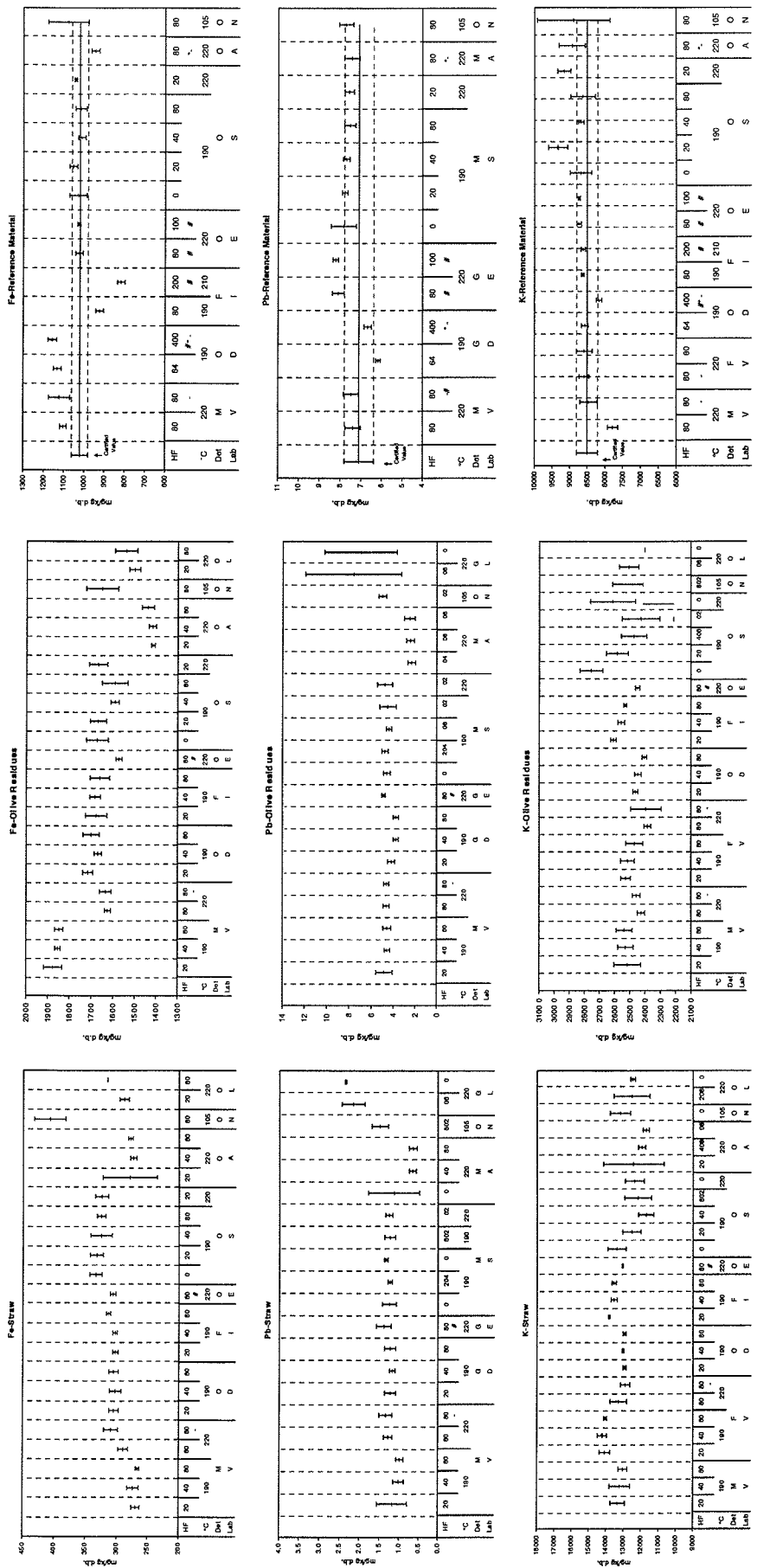


Fig. 2. Results of Fe, Pb and K determinations in the course of "Method development—part 2". Explanations: digestions were performed with 0.5 ml H₂O₂/1 ml HNO₃ (acid quantities are referred to 100 mg sample (d.b.)) and varying amounts of HF (μl) for straw and olive residues and with varying amounts of H₂O₂/HNO₃ and HF (the HF quantities (μl) stated are referred to 100 mg sample (d.b.)) for reference material GBW 07602 (NCS DC 73348) at different temperatures; the solid line refers to the mean value, the dashed line defines the 95% confidence interval; HF...hydrofluoric acid; °C...temperature in degree Celsius; Det...detection system (F...FAAS or FAES, G...GFAAS, M...ICP-MS, O...ICP-OES); Lab...codes of participating laboratories; #...neutralisation (complexation) with H₃BO₃; ----digestion without H₂O₂; *...digestion with addition of HCl; the depicted means plots have been calculated from $n = 2-6$ independent determinations.

Mo, (Ni), Pb, Sb, Tl, Zn) showed no systematic trends with respect to the applied HF quantity at digestion temperatures of 190 and 220 °C. As examples for these observations the results for Fe and Pb are shown in Fig. 2.

- Systematic trends could be observed for Al, Na, Si, Ti, Ba and Cr (as examples for these observations the results for Al, Si and Cr are shown in Fig. 3).
- Digestions without HF showed lower concentrations than digestions with HF for
 - Al in straw and the reference material,
 - Na in straw and olive residues,
 - Si and Ti in straw, olive residues and the reference material,
 - Ba in olive residues and the reference material and
 - Cr in olive residues.
- In addition, the results of some laboratories revealed a tendency towards higher concentration with rising amounts of HF for
 - Si in olive residues and the reference material,
 - Ti in straw and
 - Cr in olive residues,
 with the highest mean values usually shown when 80 µl HF (per 100 mg sample (d.b.)) had been used for digestion. For Si and Ti the same conclusions can be drawn from the findings of laboratory E which performed special investigations on olive residues (Fig. 4). These results suggest the necessity of HF for digestion.
- Concerning olive residues in particular, some laboratories found decreasing concentrations with rising amounts of HF for some major elements like
 - Ca (laboratories D and S),
 - K (laboratories D, I, S and L) and
 - Al (laboratories A, L and S; the latter found decreasing concentrations after an initial concentration increase from the digestions without HF).
 As examples for these observations the results for K are shown in Fig. 2 and for Al in Fig. 3. These results indicate the formation of insoluble fluorides (e.g. CaF_2) caused by an excess of HF. Such precipitations can be brought into solution by heating with H_3BO_3 (formation of stable, soluble complexes). The assumption of fluoride formation is supported by the findings of laboratory E, which found in olive residues decreasing values of Al and Mg with rising amounts of HF in case the HF excess has not been neutralised with H_3BO_3 (see Fig. 4). Important for neutralisation is heating of the solution. Addition of H_3BO_3 without heating was not effective. These results suggest the necessity of the usage of H_3BO_3 for determination of the concerned major elements.
- In addition to the already mentioned results the special digestion tests on olive residues performed by laboratory E (see Fig. 4) revealed no difference with respect to the applied temperatures (190 and 220 °C). No clear difference could also be stated with respect to the different H_2O_2 and HNO_3 quantities applied.

- The investigations also revealed for many elements that the results of the laboratory which performed the digestions at 105 °C deviated from results of the other laboratories where digestions with the same amount of HF but at higher temperatures have been performed. As example of this trend see the results for Al in Fig. 3.

5. Method validation

Based on the results of the method development investigations (see Sections 3 and 4), it was decided to validate different digestion methods for major and minor elements (see Table 3 and 4). The detection systems applied for validation included FAAS, GFAAS, ICP-OES, ICP-MS, CVAAS and direct Hg determination. The validation parameters examined included accuracy (precision and trueness) and upper concentration ranges as well as estimations of detection limits.

5.1. Definitions, purpose and calculation of validation parameters

5.1.1. Accuracy (precision and trueness)

Accuracy expresses the closeness of a result to a true value. It is normally studied as two components: precision and trueness [8,9]. Precision is a measure of how close results are to one another. Important precision parameters are: overall mean \bar{X}_{rb} , repeatability limit r and the reproducibility limit R (see Table 5).

The *repeatability limit* r enables the analyst to decide whether the difference between duplicate analyses of a sample, determined under repeatability conditions (applying the same method on identical test material in the same laboratory by the same operator using the same equipment within short intervals of time), is significant. A further application of r includes the calculation of a critical difference between mean values of two series of investigations performed under repeatability conditions [8–11].

The *reproducibility limit* R enables the analyst to decide whether the difference between duplicate analyses of a sample, determined under reproducibility conditions (applying the same method on identical test material in different laboratories with different operators using different equipment), is significant. Further applications of R and r include the calculation of critical differences for the following cases: comparison of means under reproducibility conditions, comparison of a laboratory mean with a reference value, comparison of several laboratory means with a reference value [8–11].

The following investigations were performed in order to determine the accuracy measures mentioned above. Three independent digestions of reference materials (GBW 07602 (NCS DC 73348) “Bush Branches and Leaves” or NIST SRM 1575a “Trace elements in Pine Needles”) and 6

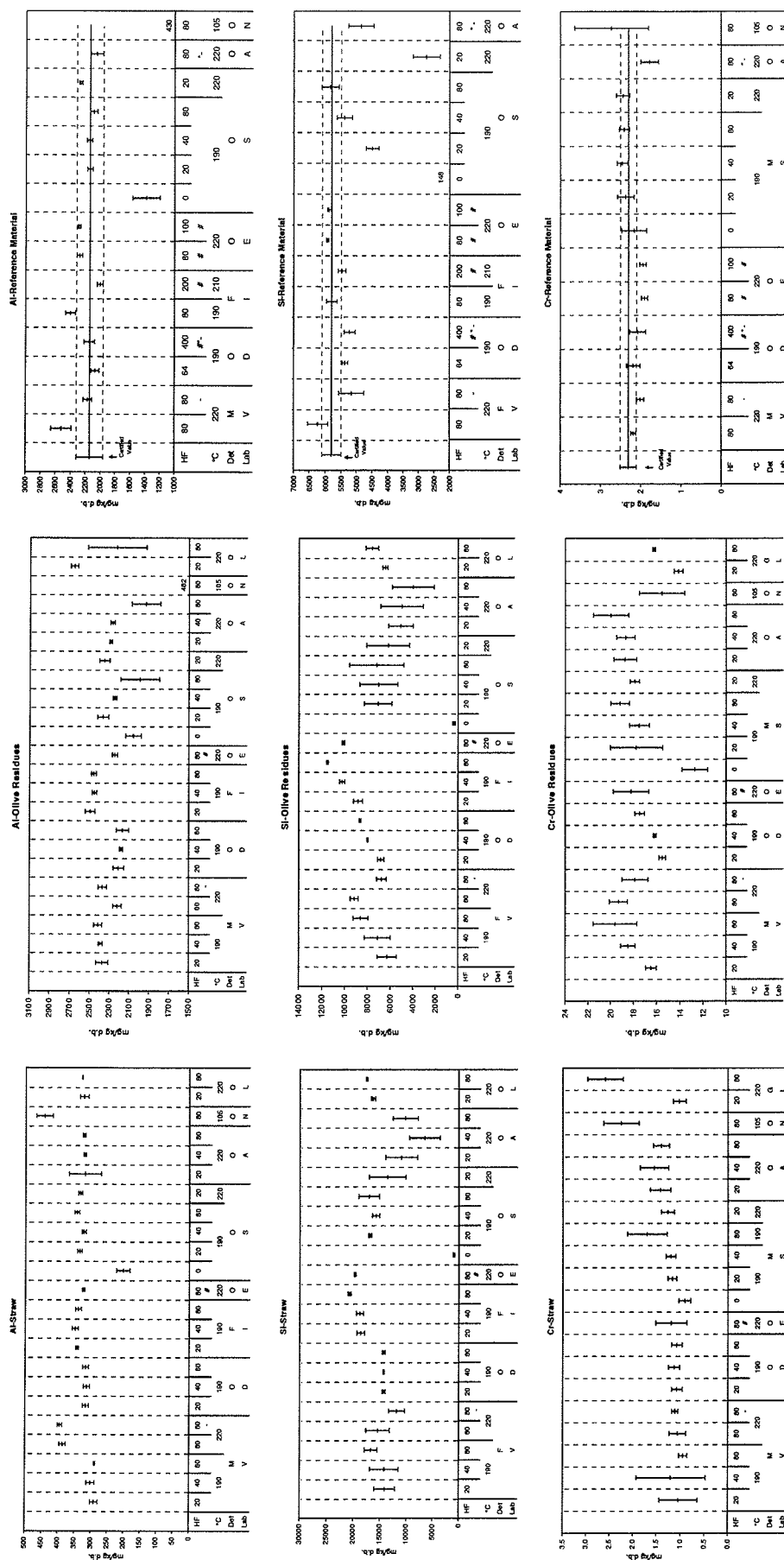


Fig. 3. Results of Al, Si and Cr determinations in the course of "Method development—part 2". Explanations: digestions were performed with 0.5 ml H_2O_2 /1 ml HNO_3 (acid quantities are referred to 100 mg sample (d.b.)) and varying amounts of HF (μl) for straw and olive residues and with varying amounts of H_2O_2 / HNO_3 and HF (the HF quantities (μl) stated are referred to 100 mg sample (d.b.)) for reference material GBW 07602 (NCS DC 73348) at different temperatures; the solid line refers to the mean value, the dashed line defines the 95% confidence interval; HF...hydrofluoric acid; °C...temperature in degree Celsius; Det—detection system (F—FAAS, G—GFAAS, M—ICP-MS, O—ICP-OES); Lab—codes of participating laboratories; #—neutralisation (complexation) with H_3BO_3 , —digestion without H_2O_2 ; *—digestion with addition of HCl; the depicted means plots have been calculated from $n = 2$ –6 independent determinations.

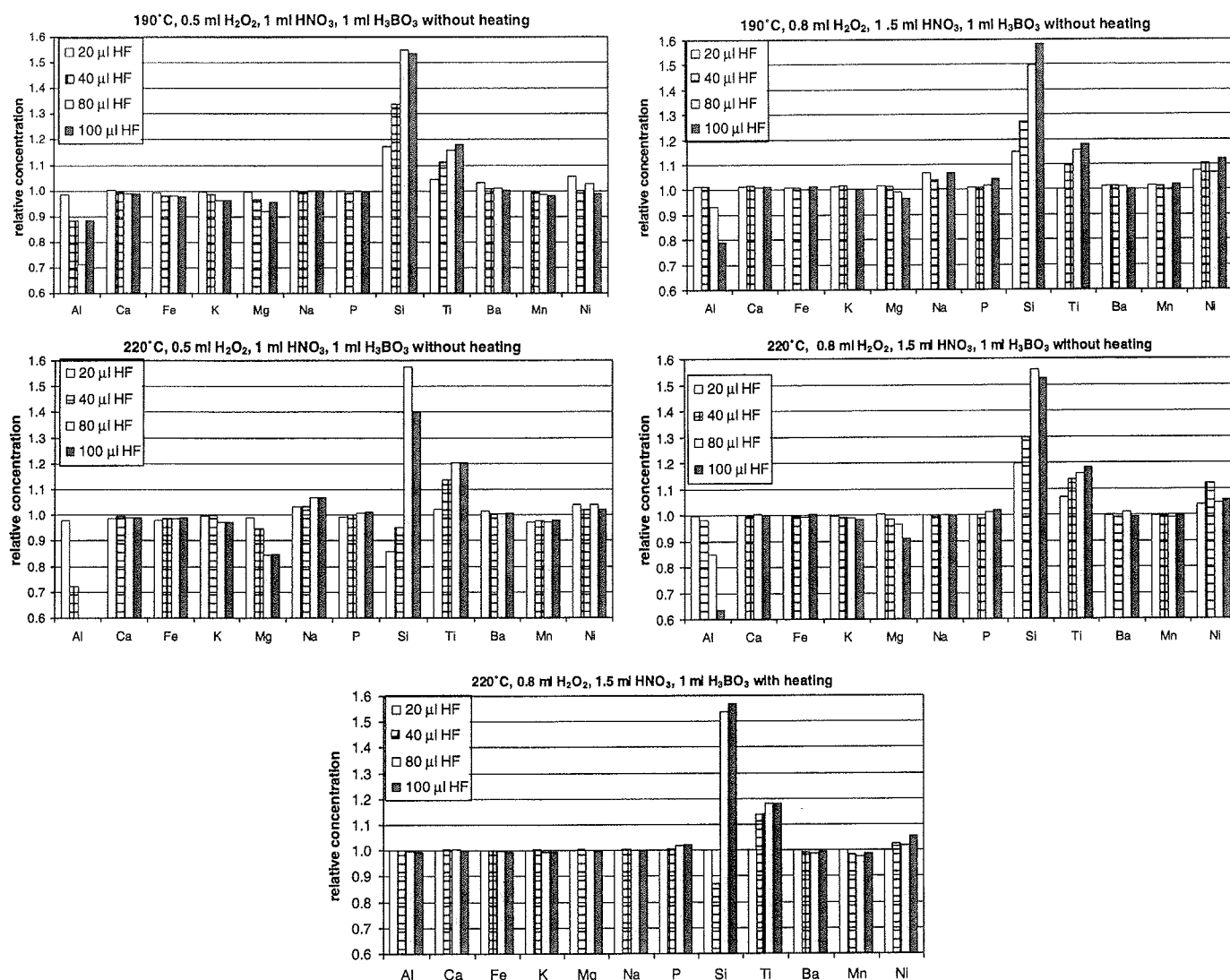


Fig. 4. Digestion tests on olive residues by laboratory E. Explanations: digestions have been performed in a microwave system with varying amounts of H_2O_2 , HNO_3 and HF (acid quantities referred to 100 mg sample (d.b.)) at 190 and 220 °C and with or without heating of digest to 150 °C with H_3BO_3 ; relative concentrations—concentrations normalised to 1 for digestion with 0.8 ml H_2O_2 , 1.5 ml HNO_3 at 220 °C and subsequent heating with 1 ml H_3BO_3 ; the values have been calculated from $n = 2$ independent determinations.

independent digestions of wood+bark and straw (no digestions were carried out for direct Hg determination) were measured by each laboratory (interlaboratory study). Subsequently, X_{rb} (overall robust mean), r and R were calculated using the robust method given in Ref. [11]. This method does not require exclusion of outliers and is finding increasing acceptance [12].

The *trueness* (of a method) is defined as “the closeness of agreement between the average value obtained from a large set of test results and an accepted reference value” [9]. For this purpose critical differences between the found (overall robust means) and certified element concentrations of the investigated reference materials were calculated according to [9,11].

The calculated precision and trueness parameters are shown in Table 5.

5.1.2. Detection limits and upper concentration ranges of methods tested

When measurements are made at low analyte levels it is important to know the lowest concentration of the analyte that can be confidently detected by the method (detection limit). According to [8], it is usually sufficient for validation purposes to provide an indication of the level at which detection becomes problematic. Detection limits vary between different brands and instruments. Furthermore, it has to be considered that the detection limits do not represent levels at which quantitation is not possible. “It is simply that the size of the associated uncertainties approach comparability with the actual result in the region of the detection limit” [8]. For critical decisions, the relevant values need to be re-determined in line with actual operating performance [8]. In the present study, the

Table 3
Validated digestion method for major element analyses

Acid quantities (per 100 mg sample (d.b.))	0.6 ml H ₂ O ₂ (30%), 1.6 ml HNO ₃ (65%), 0.2 ml HF (40%)
<i>Temperature programme</i>	
Microwave heating ^a	
Step 1	In 15 min heat to 190 °C, rate 11.3 °C/min
Step 2	Hold for 20 min at 190 °C
Resistance heating ^b	
Step 1	In 1 h heat to 220 °C, rate 3.33 °C/min
Step 2	Hold for 1 h at 220 °C
After cooling to room temperature, addition of 2 ml H ₃ BO ₃ (4%) (= 10 ml H ₃ BO ₃ /ml HF)/100 mg sample (d.b.):	
<i>Temperature programme</i>	
Microwave heating ^a	
Step 1	Heat as fast as possible up to 150 °C
Step 2	Hold for 15 min at 150 °C
Resistance heating ^a	
Step 1	Heat as fast as possible up to 180 °C
Step 2	Hold for 15 min at 180 °C

^aTemperature referred to digestion solution.

^bTemperature referred to heating device (e.g. oven); sample masses applied: 250–500 mg (d.b.).

Table 4
Validated digestion method for minor element analyses

Acid quantities (per 100 mg sample (d.b.))	0.5 ml H ₂ O ₂ (30%), 1 ml HNO ₃ (65%), 0.08 ml HF (40%)
<i>Temperature programme</i>	
Microwave heating ^a	
Step 1	In 15 min heat to 190 °C, rate 11.3 °C/min
Step 2	Hold for 20 min at 190 °C
Resistance heating ^b	
Step 1	In 1 h heat to 220 °C, rate 3.33 °C/min
Step 2	Hold for 1 h at 220 °C

^aTemperature referred to digestion solution.

^bTemperature referred to heating device (e.g. oven); sample masses applied: 250–500 mg (d.b.).

detection limit is defined as three times the standard deviation of the blank (when the analytical work is in support of regulatory or specification compliance, a more exact approach such as that described by [10] is more appropriate). For this purpose, the entire analysis consisting of acid digestion, dilution and instrument run was done in exactly the same way as for the accuracy measurements, with the only exception that no sample material was added to the digestion mixture. Twenty blank determinations were performed using this procedure. The average value of two measurement results was used to state one determination value (which corresponds to ten double determinations). These 10 values were applied for the calculation of the detection limit.

The purpose of the upper concentration range investigations was to clarify the highest possible sample element content up to which the applied digestion and determination methods may be used. This range should cover element concentrations to be expected for different types of solid biofuels as well as limit values specified in

standards relevant for biofuels. Typical concentration ranges for biofuels are given in Ref. [13], limit values for some minor elements in wood pellets are given in Ref. [14]. As materials other than wood + bark and straw were not available, different sample concentrations were simulated by the addition of defined amounts of the elements of interest (spiking). With the exception of Hg, the elements were added to the final solutions of the wood + bark and straw digests. In the case of Hg determinations, the spikes were added to the wood + bark and straw samples, either prior to measurements (in case of direct Hg determination) or prior to digestion (in case CVAAS was used for Hg determination).

Depending on the determination system applied, 3 (GFAAS), 5 (FAAS) or 6 (ICP-OES, ICP-MS, CVAAS, direct Hg determination) element additions were performed and the concentrations of the original and the spiked solutions measured in duplicate (for direct Hg determinations, the original and spiked wood + bark and straw samples were measured). Subsequently, the linearity

Table 5
Precision data for major and minor elements in wood + bark, straw and reference materials

Element	N	Det. system	Wood + bark		Straw		GBW 07602 (NCS DC 73348) ^a							
			X _{rb} [mg/kg d.b.]	r [mg/kg d.b.]	R [mg/kg d.b.]	X _{rb} [mg/kg d.b.]	r [mg/kg d.b.]	R [mg/kg d.b.]	Cert. conc. [mg/kg d.b.]	Crit. diff. [mg/kg d.b.]	Meas. diff. [mg/kg d.b.]			
Major elements														
Al	6	F ^b , O, M	83	6	28	323	18	48	2,220	80	380	2,140	99	80
Ca	7	F, O	1,780	90	190	5,650	270	580	22,400	800	2,000	22,200	494	200
Fe	7	F, O	85	14	14	314	15	32	1,020	30	80	1,020	21	0
K	7	F, O	710	27	178	12,700	500	2300	8,500	180	610	8,500	158	0
Mg	7	F, O	212	13	22	1,370	50	140	2,930	100	250	2,870	62	60
Na	7	F, O	17	7	11	109	12	23	11,000	-	1,200	11,000	315	0
P	6	O, M	87	9	14	1,330	60	170	838	35	58	830	15	8
Si	6	F, O	541	101	192	19,400	1,100	1,500	5,910	230	790	5,800	221	110
Ti	6	O, M	11	1	3	134	9	40	104	4	12	95	3	9
Minor elements														
As	4	G, M	0.07	0.08	0.13	0.22	0.07	0.15	1.02	0.07	0.37	0.95	0.13	0.07
Ba	6	O, M	25	2	3	78	3	13	19.6	0.6	2.6	19.0	0.7	0.6
Cd	5	G, M	0.35	0.03	0.14	0.15	0.02	0.10	0.20	0.04	0.12	0.14	0.04	0.06
Co	4	G, M	0.42	0.16	0.16	0.22	0.05	0.53	0.34	0.05	0.27	0.39	0.10	0.05
Cr	9	O, G, M	2.0	0.8	1.0	1.2	0.3	0.8	2.24	0.42	0.61	2.30	0.12	0.06
Cu	9	O, G, M	2.1	0.9	1.6	4.1	0.8	1.3	5.1	0.6	1.2	5.2	0.3	0.1
Hg	3	C, dHg	0.007	0.003	0.005	0.027	0.006	0.013	0.042	0.005	0.010	0.040	0.004	0.002
Mn	9	F, O, M	298	13	75	43	2	6	58	2	6	58	1	0
Mo	4	G, M	0.09	0.14	0.14	0.37	0.06	0.08	0.304	0.031	0.102	0.260	0.035	0.044
Ni	9	O, G, M	1.7	0.6	0.7	0.7	0.2	0.4	1.7	0.2	0.9	1.7	0.2	0.0
Pb	5	G, M	1.0	0.4	0.6	1.3	0.3	0.5	7.1	0.8	1.5	7.1	0.4	0.0
Sb	4	G, M	0.03	0.12	0.13	0.07	0.03	0.08	0.17	0.02	0.45	0.08	0.16	0.09
Tl	3	G, M	0.01	—	—	0.02	—	—	0.02	—	—	—	—	—
V	7	O, G, M	0.18	0.10	0.32	0.60	0.13	0.38	2.4	0.2	0.5	2.4	0.1	0.0
Zn	9	F, O, M	21	3	6	20	3	3	21.1	0.9	2.9	20.6	0.6	0.5

Explanations: Det. system—determination system; F—FAAS, O—ICP-OES, G—GFAAS, M—ICP-MS, C—CVAAS, dHg—direct Hg determination.

X_{rb}—overall robust mean; r—repeatability limit; R—reproducibility limit; N—number of participating laboratories; Cert. Conc.—certified concentration; Crit. Diff.—critical difference between certified concentration and X_{rb}; Meas. Diff.—measured difference between certified concentration and X_{rb}; measurement values from n = 6 independent digestions of wood + bark and straw or n = 3 independent digestions of reference materials per laboratory (no digestions were carried out for direct Hg determination) were used to calculate r and R according to the robust method given in Ref. [11].

^aExcept for Hg where NIST SRM 1575a was analysed.

^bExcept for wood + bark where FAAS was not applied.

between added and measured concentrations was examined. A deviation from linearity in the upper concentration ranges would indicate non-suitability of the applied analytical methods for these ranges. The linearity between measured and added concentrations was checked by the Mandel test as described in Ref. [15]. For this purpose, linear and quadratic regression lines were calculated. In case of significant deviations from linearity (significantly better fitting of quadratic regression), the concentration range was constricted and the evaluation repeated until linearity was confirmed by a non-significant test value.

Tables 6 and 7 summarise the results of the detection limit and upper concentration range investigations. They should provide an overview of the detection limits to be expected and the maximum concentrations which can be covered by the digestion methods and detection systems given. The detection limits given were compiled as follows: 2–4 labs performed element determinations with one detection system. The resulting measurement values were used to calculate detection limits for each laboratory. These figures were compared; the highest of these figures (rounded up to the next highest significant digit) is stated in the tables as “<value”. For instance, four laboratories performed ICP-OES measurements for Al. The calculated detection limits were 4.9, 1.7, 26 and 3.1 mg/kg (d.b.). The highest figure is 26. Therefore, the ICP-OES detection limit given for Al is <26 mg/kg (d.b.). A similar approach was used in stating the upper application ranges. The results of the different labs were compared and the figures rounded to the next reasonable digit. For instance, the ICP-OES results for Al were 3080, 3090, 3090 and 3300 mg/kg (d.b.) for the wood + bark and 3270, 3330, 3290 and 3190 mg/kg

Table 6
Detection limits and upper concentration ranges for major elements

Major elements	Determination system	Detection limits [mg/kg]	Upper concentrations tested [mg/kg]
Al	FAAS	<23	2000
	ICP-OES	<26	3000
Ca	FAAS	<20	40,000
	ICP-OES	<4	20,000
Fe	FAAS	<3	4000
	ICP-OES	<16	2000
K	FAAS	<10	50,000
	ICP-OES	<75	30,000
Mg	FAAS	<6	10,000
	ICP-OES	<20	4000
Na	FAAS	<1	1000
	ICP-OES	<30	3000
P	ICP-OES	<10	7000
	ICP-MS	<1	4000
Si	FAAS	<60	150,000
	ICP-OES	<240	40,000
Ti	ICP-OES	<1	500

Explanations: detection limits and upper concentration ranges for the different measurement systems were compiled from the results of 2–4 laboratories (see Section 5.1.2).

Table 7
Detection limits and upper concentration ranges for minor elements

Minor elements	Determination system	Detection limits [mg/kg]	Upper concentrations tested [mg/kg]
As	GFAAS	<0.2	5
	ICP-MS	<0.02	5
Ba	ICP-OES	<0.3	100
	ICP-MS	<0.2	100
Cd	GFAAS	<0.08	2
	ICP-MS	<0.02	5
Co	GFAAS	<0.4	20
	ICP-MS	<0.02	20
Cr	ICP-OES	<1	50
	GFAAS	<0.4	50
Cu	ICP-MS	<0.03	50
	ICP-OES	<0.8	40
	GFAAS	<0.3	40
	ICP-MS	<0.1	40
Hg	Direct Hg determin.	<0.0006	0.3
	CVAAS	<0.002	0.5
Mn	FAAS	<3	2500
	ICP-OES	<0.2	800
	ICP-MS	<0.02	500
Mo	GFAAS	<0.4	20
	ICP-MS	<0.015	20
Ni	ICP-OES	<0.8	20
	GFAAS	<0.65	10
	ICP-MS	<0.4	20
Pb	GFAAS	<0.2	25
	ICP-MS	<0.04	25
Sb	GFAAS	<0.35	20
	ICP-MS	<0.02	20
Ti	GFAAS	<0.08	n.d.
	ICP-MS	<0.003	20
V	ICP-OES	<0.35	20
	GFAAS	<0.40	10
	ICP-MS	<0.02	20
Zn	FAAS	<2	500
	ICP-OES	<0.4	500
	ICP-MS	<0.09	200

Explanations: Detection limits and upper concentration ranges for the different measurement systems were compiled from the results of 2–4 laboratories (see Section 5.1.2).

(d.b.) for the straw digests. The upper concentration range given for ICP-OES detection of Al in Table 6 therefore is 3000 mg/kg (d.b.).

5.2. Results and conclusions from method validation

The results of the trueness examinations proved to be satisfactory (Table 5). With the exception of Ti, Cd and Mo, the concentrations (overall robust means) found in the reference materials (GBW 07602 (NCS DC 73348) “Bush Branches and Leaves” and NIST SRM 157a “Trace elements in Pine Needles”) correspond with the certified values (critical differences were not exceeded).

For the majority of the elements investigated (Al, Ca, Fe, K, Mg, Na, P, Si, Ti, Ba, Cr, Cu, Mn, Ni, Zn), the

precision data obtained present a realistic picture of measurement results which may be expected when different laboratories apply the tested methods for analyses of the respective elements in solid biofuels such as wood + bark, straw, bush branches and leaves (see Table 5). The detection limits given represent estimations to be expected when the biofuels under consideration are analysed by means of the methods tested. The defined upper concentration ranges indicate the suitability of the tested methods for a wide range of concentrations (see Tables 6 and 7). To summarise these findings, the applied digestion methods ($\text{H}_2\text{O}_2/\text{HNO}_3/\text{HF}$ / neutralisation with H_3BO_3 for major elements (Table 3), $\text{H}_2\text{O}_2/\text{HNO}_3/\text{HF}$ for minor elements (Table 4)) as well as the applied determination systems (see Table 5) proved to be suitable for analyses of the above-mentioned elements.

The precision data obtained for Cd, Pb and Hg must be considered in the light of the fact that only 5 (Cd, Pb) or 3 (Hg) laboratories participated in the investigations (see Table 5). This is below the minimal number of 7 that is required for statistical evaluation [11]. Therefore, the data may not be used to calculate critical differences in order to compare analytical measurements. Nevertheless, the data well indicate the performance of the tested methods. The applied determination systems (GFAAS, ICP-MS for Cd and Pb determination; CVAAS and direct measurements for Hg determination) provided comparable element concentrations for the materials investigated. The detection limits given are typical values to be expected when the biofuels under consideration are analysed with the methods tested. The upper concentration ranges stated indicate the element contents up to which the tested analytical methods may be applied (Table 7). To summarise these results, digestion by $\text{H}_2\text{O}_2/\text{HNO}_3/\text{HF}$ (see Table 4) as well as determination by GFAAS and ICP-MS may be recommended for Cd and Pb analyses. CVAAS and direct measurement of Hg may be recommended for Hg determinations.

The precision data for As, Co, Mo and Sb revealed that the R (sometimes also the r) values of As (in wood + bark), Co (in straw), Mo (in wood + bark) and Sb (in wood + bark, straw and GBW 07602 (NCS DC 73348)) exceeded the calculated mean concentrations of these elements in the respective materials (see Table 5). This and the fact that only 4 laboratories participated in the investigations make the data unsuitable for calculating critical differences in order to compare analytical measurements. One reason for the high repeatability (r) and reproducibility limits (R) is the low As, Co, Sb and Mo concentrations in wood + bark and straw, which make determinations by GFAAS difficult. This is indicated by high dispersions of the GFAAS measurement results as well as relatively poor GFAAS detection limits (Table 7). GFAAS determination is therefore not well suitable for materials containing low concentrations of the above-mentioned elements. ICP-MS showed better performance providing smaller spreads of measurement results and

lower detection limits. To summarise these results, the applied digestion method ($\text{H}_2\text{O}_2/\text{HNO}_3/\text{HF}$; Table 4) and determination by ICP-MS may be recommended for As, Co, Mo and Sb analyses. GFAAS determination is only suitable for materials with high concentrations of these elements. For As determinations, hydride generation AAS, offering better performance with respect to dispersion of measurement results and detection limits could be used alternatively.

The precision data for V show that the R -value of wood + bark exceeded the calculated mean concentration (Table 5). V was analysed by ICP-OES, ICP-MS and GFAAS. In comparison to ICP-OES and ICP-MS, GFAAS analysis resulted in higher V concentrations, higher dispersion of the measurement results, a lower value for the upper concentration range, and, especially in comparison to ICP-MS a poor detection limit (Table 7). This might have caused the high R -value found in wood + bark. GFAAS is therefore not well suitable for V determinations in low concentration ranges. To summarise the results, the applied digestion method ($\text{H}_2\text{O}_2/\text{HNO}_3/\text{HF}$, see Table 4) as well as determination by ICP-OES and ICP-MS can be recommended for V analyses. Due to the high dispersion of measurement results and poor detection limits, GFAAS determination is not well suitable for V determinations in lower concentration ranges.

No precision data are given for Tl. This is due to the fact that only 3 laboratories delivered measurement values for the wood + bark and straw materials investigated. This low number combined with strong differences between the results of the applied measurement systems, ICP-MS and GFAAS, produced unrealistic calculation data. The detection limits and upper concentration ranges found may be used as an indicator for the applicability of the methods tested. With respect to ICP-MS determination the upper concentration range assessed and the low detection limit obtained indicate the potential suitability of this detection system for Tl analyses in solid biofuels (Table 7). GFAAS determination led to non-linear relations between added and found Tl quantities and a poor detection limit. This indicates that GFAAS is not suitable to determine Tl in solid biofuels with low concentrations of this element.

In conclusion of the validation results, the applied digestion methods ($\text{H}_2\text{O}_2/\text{HNO}_3/\text{HF}$ / neutralisation with H_3BO_3 for major elements, see Table 3, and $\text{H}_2\text{O}_2/\text{HNO}_3/\text{HF}$ for minor elements, see Table 4) may be recommended for solid biofuel analyses.

For determination of the different elements in solid biofuels, the following detection systems may be recommended:

- FAAS: Ca, Fe, K, Mg, Na, Si, Mn, Zn;
 - because of relatively poor detection limits, Al determination by FAAS is not recommended for solid biofuels containing low concentrations of this element.

- ICP-OES: Al, Ca, Fe, K, Mg, Na, P, Si, Ti, Mn, Zn, Ba, Cr, Cu, Mn, Ni, V, Zn;
 - The ICP-OES detection limit given for Al in Table 6 is in the same magnitude as the FAAS detection limit for Al. This figure resulted from one laboratory which found a relatively high detection limit (26 mg/kg (d.b.)), compared to the values found by the other laboratories (4.9, 1.7, 3.1 mg/kg (d.b.)).
- GFAAS: Cd, Cr, Cu, Ni, Pb;
 - because of relatively poor detection limits, As, Co, Mo, Sb and V determination by GFAAS is not recommended for solid biofuels containing low concentrations of these elements.
- ICP-MS: P, Ti, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, V, Zn;
- Direct Hg determination, CVAAS: Hg.

6. Summary and conclusions

Methodological investigations were performed to optimise analytical techniques for the determination of major and minor elements in solid biofuels. For this purpose, wood + bark, straw, olive residues and a biomass reference material (GBW 07602 (NCS DC 73348) “Bush Branches and Leaves”) were analysed using several digestion and determination methods. The digestion methods investigated included wet digestion in closed vessels with different acid mixtures as well as pre ashing prior to digestion. The determination systems examined included FAAS, GFAAS, CVAAS, ICP-OES, ICP-MS, XRF as well as direct Hg determination.

As conclusions of these examinations the following methods proved to be the most suitable for digestion:

- Covering major elements: wet digestion with $\text{H}_2\text{O}_2/\text{HNO}_3/\text{HF}/\text{H}_3\text{BO}_3$.
- Covering minor elements: wet digestion with $\text{H}_2\text{O}_2/\text{HNO}_3/\text{HF}$.

The most suitable determination methods included FAAS, GFAAS, ICP-OES, ICP-MS, CVAAS and direct Hg determination.

In order to evaluate the performance of these recommended methods validations were carried out. For this purpose several independent analyses of wood + bark, straw and biomass reference materials (GBW 07602 (NCS DC 73348) “Bush Branches and Leaves” or NIST SRM 1575a “Trace elements in Pine Needles”) were performed by different laboratories and the following precision and trueness parameters calculated: overall mean, repeatability limit r , reproducibility limit R , critical difference to certified reference values. Furthermore, blank determinations and spiking experiments were carried out in order to determine detection limits and upper concentration ranges of the methods for the different elements.

In conclusion of the validation results, the recommended digestion methods proved to be suitable for solid biofuel analyses.

For determination of the different elements in solid biofuels, the following detection systems may be recommended: FAAS for Ca, Fe, K, Mg, Na, Si, Mn, Zn; ICP-OES for Al, Ca, Fe, K, Mg, Na, P, Si, Ti, Mn, Zn, Ba, Cr, Cu, Mn, Ni, V, Zn; GFAAS for Cd, Cr, Cu, Ni, Pb; ICP-MS for P, Ti, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, V, Zn and direct Hg determination as well as CVAAS for Hg.

Acknowledgements

This work was performed within the BioNorm project (no. ENK6-CT-2001-00556), a research project supported by the European Commission under the Fifth Framework Programme and contributing to the implementation of key action 6 “Economic and Efficient Energy for Competitive Europe” within the “Energy”-sub-programme of “Energy, Environment and Sustainable Development”.

We also acknowledge the co-operation with E. Thomsen, ELSAM A/S, Denmark; T. Arnold, Freiberg University of Mining and Technology, Germany; T. Puttkamer, University of Stuttgart, Germany; and Prof Marosvölgyi and A. Vityi, University of West-Hungary, Department of Energetics, Sopron, Hungary.

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