

# Determination of major and minor element contents in solid biofuels

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**ABSTRACT:** The development of reliable and appropriate methods for the accurate determination of major (Al, Si, K, Na, Ca, Mg, Fe, P, Ti) and minor (As, Ba, Cd, Co, Cu, Cr, Hg, Mo, Mn, Ni, Pb, Sb, Tl, V, Zn) ash forming elements in solid biofuels is the major goal of Task III.2 of the EU project BioNorm. For this purpose, wood, straw and olive residues were analysed using several digestion and detection systems. The digestion methods included wet digestion 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. Summarising them different digestion procedures were developed for major and minor elements. Digestion with H<sub>2</sub>O<sub>2</sub>/HNO<sub>3</sub>/HF followed by neutralisation with H<sub>3</sub>BO<sub>3</sub> was validated for major element analyses, while digestion with H<sub>2</sub>O<sub>2</sub>/HNO<sub>3</sub>/HF was validated for minor element analyses. The findings of these investigations will be summarised in “Best practice guidelines for the determination of major and minor elements in solid biofuels”.

## 1 Introduction

The application of fuels of known quality is an essential prerequisite for secure and efficient biomass combustion. One important parameter for assessing the chemical properties of solid biofuels is the content of major (Al, Si, K, Na, Ca, Mg, Fe, P, Ti) and minor (As, Ba, Cd, Co, Cu, Cr, Hg, Mo, Mn, Ni, Pb, Sb, Tl, V, Zn) 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 well as the environmental assessment of the ashes produced and their subsequent utilisation. Specific standard operating procedures for the determination of these elements in biofuels exist (or are under development) only in a few cases. 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 [1, 2]. In cooperation with CEN/ TC 335, Task III.2 of the BioNorm project is therefore concerned with the development of standardised methods for the determination of major and minor element contents in solid biofuels. This includes testing, evaluation and validation of several chemical methods in order to prepare best practice guidelines for the correct determination of these elements. The present paper summarises the main outcome and conclusions of the project work.

## **2 Investigations performed and resulting conclusions**

### **2.1 Sample homogenisation and homogeneity tests**

A sufficient amount of homogeneous material was needed for the tests planned within Task III.2. For this purpose 10 kg wood and straw material were milled to particle sizes <0.25 mm and filled in bottles of 20 g each.

In order to investigate the homogeneities of the prepared materials, XRF and ICP-MS determinations were performed and relative standard deviations (RSD) calculated. Subsequently, F-tests were carried out to check within and between bottle homogeneity. The results for the wood material are depicted in Table 1. Satisfactory RSD values below 10% and 20% were obtained for most of the major and minor elements, respectively. Furthermore, the vast majority of the elements did not show significant F-values, indicating homogeneous distribution of the materials throughout the different bottles, with the exceptions of Zn in wood as well as Fe and Cd in straw. Summarising the outcome of the homogeneity tests, both materials proved to be suitable for the further investigations planned in Task III.2. The experiences gained from sample preparation together with the results of the homogeneity studies and relevant literature sources are summarised in [3] and [4].

### **2.2 Method testing and improvement – part 1**

The prepared materials were used in testing several commonly used analytical methods in order to choose the most suitable for further investigations. For this purpose, sixteen digestion (wet digestion in closed vessels with different mixtures of HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, HF, HCl and HClO<sub>4</sub>, heated conventionally or by microwaves, with or without neutralisation by H<sub>3</sub>BO<sub>3</sub> as well as dry-ashing with subsequent dissolving in acids or dry-ashing with

subsequent fusion in  $\text{LiBO}_2$  or  $\text{Li}_2\text{B}_4\text{O}_7$ ) and eight determination methods (FAAS, GFAAS, CVAAS, hydride generation AAS, ICP-OES, ICP-MS, XRF as well as direct Hg determination) were examined. The main results of the investigation can be summarised as follows (data not shown).

The wet digestion procedures followed by determination using FAAS, GFAAS, CVAAS, ICP-OES or ICP-MS showed good agreement between the different results for many elements investigated.

Substantial fluctuations between the measured concentrations were observed, however, for Si, Ti, Cd and Hg. Lower Si and Ti concentrations were observed in particular for digestions performed without HF. The results for K, Mg, Na and P also revealed that direct XRF measurements (performed on wood and straw pellets) deviated from the results gained with the other measurement systems. Similar observations were also 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. These deviations suggested calibration problems with the XRF systems applied. It was therefore decided to exclude this system from further investigations.

### **2.3 Method testing and improvement - part 2**

In conclusion of the results gained in the course of the first method development examinations it was decided to focus further work on the optimisation of a wet chemical digestion procedure. The needed amount of HF as well as the application of different digestion temperatures ( $190^\circ\text{C}$  and  $220^\circ\text{C}$ ) were investigated within this round of investigations. In order to ensure a broader range of application for the analytical methods under investigation, olive residues and certified reference material (NCS DC 73348 - "bush branches and leaves", China National Analysis Centre for Iron and Steel, Promochem) were included in the examinations.

The main results can be summarised as follows (data not shown).

Most of the elements (Fe, P, As, Cd, Cu, Mo, (Ni), Pb, Sb, Tl, Zn) showed no systematic trends with respect to the HF quantity and digestion temperatures applied.

Digestions without HF showed lower concentrations of Al, Si, Ti, and Cr than digestions with HF. Some laboratories additionally found a tendency towards higher concentrations with increasing amounts of HF for Si in olive residues and the reference material, Ti in straw, and Cr in olive residues. These results suggest the necessity of HF for digestion.

Some laboratories found concentrations of Al, Ca, K and Mg to decrease with increasing amounts of HF, in particular in olive residues. This could indicate the formation of insoluble metal fluorides caused by an excess of HF. The precipitations would have to be brought into solution by heating with  $H_3BO_3$ . These results suggest the necessity of the usage of  $H_3BO_3$  for the determination of major elements.

## **2.4 Method validation**

Based on the results of the method development investigations (see sections 2.2 and 2.3) it was decided to validate different digestion methods for major and minor elements (see Table 2 and Table 3). The validation parameters examined included accuracy (precision and trueness) and application ranges as well as estimations of detection limits. A detailed description of these investigations together with the statistics applied is given in [5]. The present paper summarises the main outcome of these examinations.

### **2.4.1 Definitions, purpose and calculation of validation parameters**

#### **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 [6, 7]. Precision is a measure of how close results are to one another. Three parameters for describing precision are given in the present paper: the mean value (overall robust mean  $X_{rb}$ ), repeatability limit  $r$  and reproducibility limit  $R$  (see Table 4).

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 [6, 7, 8, 9].

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 [6, 7, 8, 9].

The following investigations were performed in order to determine the accuracy measures mentioned above. 3 independent digestions of reference materials (NCS DC 73348 or NIST SRM 1575a) and 6 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 [9]. This method does not require exclusion of outliers and is finding increasing acceptance [10].

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’ [7]. For this purpose critical differences between the found (overall robust means) and certified element concentrations of the investigated reference materials were calculated according to [7, 9].

The calculated precision and trueness parameters are depicted in Table 4.

### **Detection limits and application 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 [6] 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 and depend strongly on the calibration range applied for determination. 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’ [6]. For critical decisions, the relevant values need to be re-determined in line with actual operating performance [6]. In the present study, the 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 [8] 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. 20 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 application range investigations was to clarify the range of the sample element content up to which the applied digestion and determination methods can 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 [11], limit values for some minor elements in wood pellets are given in [12]. As materials other than wood 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 and straw digests. In the case of Hg determinations (performed by direct Hg determination or CVAAS), the spikes were added to the samples prior to digestion.

Depending on the determination system applied, 3 (GFAAS), 5 (FAAS) or 6 (ICP-OES, ICP-MS, CVAAS, direct Hg determination) element additions were performed by the respective laboratories. The linearity between measured and added concentrations was checked by the Mandel test as described in [13]. 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.

Table 5 summarises the results of the detection limit and application range investigations. It should provide an overview of the detection limits to be expected and the concentration ranges to be covered with the digestion methods and detection systems given.

#### **2.4.2 Results and conclusion of method validation**

The results of the trueness examinations proved to be satisfactory. With the exception of Ti, Cd and Mo, the concentrations (overall robust means) found in the reference materials (NCS DC 73348 and NIST SRM 157a) correspond with the certified values (critical differences were not exceeded) (Table 4).

For the majority of the elements investigated (Al, Si, K, Na, Ca, Mg, Fe, P, Ti, Ba, Cr, Cu, Mn, (Ni), Zn), the precision data obtained present a realistic picture of measurement results to be expected when different laboratories apply the methods tested to the analysis of the respective elements in solid biofuels such as bush branches and leaves, wood or straw (Table 4). The detection limits given represent estimations to be expected when the biofuels under consideration are analysed by means of the methods tested. The application ranges indicate suitability of the tested methods for a wide range

of concentrations, including potential concentrations in both natural and contaminated solid biofuels (Table 5).

The precision data obtained for Cd, Pb and Hg must be considered under the aspect that only 5 (Cd, Pb) or 3 (Hg) laboratories participated in the investigations. This is below the minimal number of 7 that is required for statistical evaluation [9]. 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 for the materials investigated. The applied determinations 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 estimated values to be expected when the biofuels under consideration are analysed with the methods tested. The application ranges indicate suitability of the tested methods for a wide range of concentrations, including potential concentrations in both natural and contaminated solid biofuels (Table 5).

The precision data for As, Co, Mo and Sb show 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 NCS DC 733481) exceeded the calculated mean concentrations of these elements in the respective materials (Table 4). 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 dispersion of the GFAAS measurement results and relatively poor GFAAS detection limits (see Table 5). GFAAS determination is therefore not well suited 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.

The precision data for V show that the R value of wood+bark exceeded the calculated mean concentration (Table 4). V was analysed by ICP-OES, ICP-MS and GFAAS. In comparison to ICP-OES and ICP-MS, GFAAS analysis showed higher V concentrations, higher dispersion of measurement results, and smaller linear ranges, and, in comparison to ICP-MS, poor detection limits (Table 5). GFAAS is therefore not well suited for determinations in concentration ranges to be expected for typical non-contaminated solid biofuels.

No precision will be given for Tl. This is due to the fact that only 3 laboratories delivered measurement values for the wood and straw materials

investigated. This low number combined with deviating results produced unrealistic calculation data. In addition, the GFAAS detection limits are clearly above the TI concentrations found in wood and straw. Therefore, GFAAS is not suited to determine TI in these solid biofuels. ICP-MS showed better performance, providing smaller spreads of measurement results and lower detection limits.

### 3 Summary and conclusion

The following major goals were achieved within Task III.2 of the BioNorm project:

- Methodological investigations were performed to optimise analytical techniques for the determination of major and minor elements in solid biofuels. For this purpose, wood, straw, olive residues and reference materials 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 dry-ashing techniques. The determination systems examined included FAAS, GFAAS, CVAAS, ICP-OES, ICP-MS, XRF as well as direct Hg determination.
- As conclusion 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 methods validation took place. For this purpose wood, straw and reference materials were analysed and the following statistical and technical parameters calculated: overall mean, repeatability limit  $r$ , reproducibility limit  $R$ , critical difference to certified reference values, detection limit as well as application ranges of methods for the different elements.
- Summarising the validation results, the applied digestion methods can be recommended for solid biofuel analyses. Detection by FAAS and ICP-OES can be recommended for the determination of Al, Ca, Fe, K, Mg, Na, P, Si and Ti. Detection by FAAS, ICP-OES and ICP-MS can be recommended for Mn and Zn, detection by ICP-OES and ICP-MS for Ba, Ni and V, detection by ICP-OES, GFAAS and ICP-MS for Cr and Cu, detection by GFAAS and ICP-MS for Cd and Pb and detection by ICP-MS for As, Co,

Mo and Sb determination. Direct determination or CVAAS can be recommended for Hg determination.

The outcome of the work performed within Task III.2 will form the basis for “Best practice guidelines for the determination of major and minor elements in solid biofuels”, which will support the compilation of the relevant European Standards.

**Table 1:** Homogeneity tests for major and minor elements in wood+bark (particle size <0.25 mm)

Explanations: method precision was verified on the basis of 9 to 12 repeated measurements of 1 test portion; the within-bottle homogeneity was verified by 9 to 12 independent determinations of the content of one bottle while the between-bottle homogeneity was verified on the basis of 9 to 12 independent determinations from 9 to 12 bottles; RSD<sub>M</sub>, RSD<sub>W</sub>, RSD<sub>B</sub>... relative standard deviations (in %) of method precision, within and between bottles; U<sub>RSD</sub>... respective uncertainties in % (defined as  $U_{RSD} \approx RSD/\sqrt{2n}$ , where n is the number of replicates; calculation according to [14]; F-values...test statistics of the F-tests, performed in order to check the equality of within- and between-bottle variances; \*)...significant F-Value (p ≤ 0.01)

Wood	MP		WH		BH		F-Value
	R <sub>M</sub>	U <sub>M</sub>	R <sub>W</sub>	U <sub>W</sub>	R <sub>B</sub>	U <sub>B</sub>	
<b>Major elements</b>							
Al	2.43	0.52	9.03	2.13	15.94	3.56	3.18
Ca	2.86	0.61	3.18	0.71	1.75	0.39	3.42
Fe	1.97	0.42	5.66	1.33	4.00	0.89	2.28
K	2.30	0.49	1.04	0.24	0.90	0.20	1.40
Mg	2.58	0.55	2.46	0.55	3.17	0.71	1.67
Mn	1.91	0.41	1.73	0.39	0.95	0.21	3.34
Na	4.21	0.90	4.46	1.00	2.42	0.54	3.43
P	2.87	0.61	4.31	0.96	2.53	0.56	2.68
Si	1.49	0.32	6.91	1.54	13.70	3.06	3.61
Ti	1.43	0.30	1.48	0.33	1.15	0.26	1.67
<b>Minor elements</b>							
Ba	0.40	0.09	1.63	0.33	1.58	0.32	1.05
Cd	2.10	0.47	3.33	0.74	3.69	0.75	1.13
Co	1.84	0.41	3.65	0.74	4.79	0.98	1.79
Cr	6.84	1.53	16.07	3.43	14.07	3.32	1.65
Cu	1.81	0.40	9.34	1.99	14.68	3.28	3.48
Mo	12.41	2.77	38.95	7.95	44.14	9.01	1.00
Ni	1.56	0.35	19.77	4.04	29.01	5.92	2.15
Pb	1.87	0.42	26.88	5.73	50.56	10.32	4.48
Sb	1.58	0.35	18.63	3.97	27.10	5.78	2.53
Tl	2.31	0.52	2.34	0.48	3.73	0.76	2.64
V	2.48	0.55	23.31	4.76	21.27	4.34	1.12
Zn	0.74	0.17	3.13	0.67	8.88	1.89	7.77 *)

**Table 2:** Validated digest for major elements

Explanations: <sup>1)</sup>...temperature referred to digest solution;  
<sup>2)</sup>...temperature referred to heating device (e.g. oven)

Acid quantities (per 100 mg sample intake (d.b.)):	0.6 ml H <sub>2</sub> O <sub>2</sub> (30%), 1.6 ml HNO <sub>3</sub> (65%), 0.2 ml HF (40%)
<i>Temperature programme:</i>	
Microwave heating	
Step 1:	in 15 min to 190°C <sup>1)</sup> , (11.3°C/min)
Step 2:	for 20 min keep at 190°C <sup>1)</sup>
Conventional heating	
Step 1:	in 1 h to 220°C <sup>2)</sup> , (3.33°C/min)
Step 2:	for 1 h hold at 220°C <sup>2)</sup>
After cooling to room temperature, adding of 2 ml H <sub>3</sub> BO <sub>3</sub> (4%) (= 10 ml H <sub>3</sub> BO <sub>3</sub> / ml HF) per 100 mg sample intake (d.b.):	
Microwave heating	
Step 1:	as fast as possible up to 150°C <sup>1)</sup>
Step 2:	for 15 min. keep at 150°C <sup>1)</sup>
Conventional heating	
Step 1:	as fast as possible up to 180°C <sup>2)</sup>
Step 2:	for 15 min. keep at 180°C <sup>2)</sup>

**Table 3:** Validated digest for minor elements

Explanations: see Table 2

Acid quantities (per 100 mg sample intake (d.b.)):	0.5 ml H <sub>2</sub> O <sub>2</sub> (30%), 1 ml HNO <sub>3</sub> (65%), 0.08 ml HF (40%)
<i>Temperature programme:</i>	
Microwave heating	
Step 1:	in 15 min to 190°C <sup>1)</sup> , (11.3°C/min)
Step 2:	for 20 min keep at 190°C <sup>1)</sup>
Conventional heating	
Step 1:	in 1 h to 220°C <sup>2)</sup> , (3.33°C/min)
Step 2:	for 1 h hold at 220°C <sup>2)</sup>

**Table 4:** Precision data for major and minor elements in wood+bark, straw and reference materials

Explanations: Det. System...determination system; F...FAAS, O...ICP-OES, G...GFAAS, M...ICP-MS, C...CVAAS, dHg...direct Hg determination; <sup>1)</sup>...except for Hg where NIST SRM 1575a was analysed ; <sup>2)</sup>...except for wood material where FAAS was not applied; X<sub>rb</sub>...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<sub>rb</sub>; Meas. diff...measured difference between certified concentration and X<sub>rb</sub>

Element	N	Det. System	Wood+bark			Straw			NCS DC 73348 <sup>1)</sup>					
			X <sub>rb</sub> [mg/kg d.b.]	r mg/kg d.b.]	R [mg/kg d.b.]	X <sub>rb</sub> [mg/kg d.b.]	r [mg/kg d.b.]	R [mg/kg d.b.]	X <sub>rb</sub> [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 <sup>2)</sup> , 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

**Table 5:** Summary of detection limits and application range determinations for major and minor elements

Explanations: the figures given were compiled as follows: 2 to 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 table as <value; for example: four laboratories performed ICP-OES measurements for Al; the calculated detection limits are 4.9, 1.7, 26 and 3.1 mg/kg (d.b.); the highest figure is 26; therefore, the detection limit given for Al is <26; a similar approach was used in stating the application ranges; the results of the different labs were compared and the figures rounded to the next reasonable digit

Major elements	Determination system	Detection limits [mg/kg]	Application ranges studied [mg/kg]
Al	FAAS	<23	250 - 3,000
	ICP-OES	<26	100 - 3,000
Ca	FAAS	<20	2,000 - 50,000
	ICP-OES	<4	2,000 - 25,000
Fe	FAAS	<20	100 - 5,000
	ICP-OES	<4	100 - 5,000
K	FAAS	<10	1,000 - 50,000
	ICP-OES	<75	1,000 - 20,000
Mg	FAAS	<6	200 - 10,000
	ICP-OES	<20	200 - 5,000
Na	FAAS	<1	20 - 1,000
	ICP-OES	<15(30)	20 - 3,000
P	ICP-OES	<10	100 - 5,000
	ICP-MS	<1	100 - 5,000
Si	FAAS	<60	500 - 150,000
	ICP-OES	<40	500 - 50,000
Ti	ICP-OES	<1	10 - 1,000

Minor elements	Determination system	Detection limits [mg/kg]	Application ranges studied [mg/kg]
As	GFAAS	<0.2	0.2 - 5
	ICP-MS	<0.02	0.1 - 5
Ba	ICP-OES	<0.3	25 - 250
	ICP-MS	<0.2	25 - 100
Cd	GFAAS	<0.08	0.1 - 2
	ICP-MS	<0.016	0.1 - 5
Co	GFAAS	<0.4	n.d. - n.d.
	ICP-MS	<0.02	0.2 - 20
Cr	ICP-OES	<1	2 - 100
	GFAAS	<0.4	2 - 100
	ICP-MS	<0.03	2 - 50
Cu	ICP-OES	<0.8	2 - 50
	GFAAS	<0.3	2 - 50
	ICP-MS	<0.1	2 - 50
Hg	Direct Hg	<0.0006	0.01 - 0.5
	CVAAS	<0.002	0.01 - 0.5
Mn	FAAS	<3	50 - 2,500
	ICP-OES	<0.2	50 - 1,000
	ICP-MS	<0.02	50 - 500
Mo	GFAAS	<0.4	0.1 - 20
	ICP-MS	<0.015	0.1 - 20
Ni	ICP-OES	<0.8	1 - 20
	GFAAS	<0.65	1 - 20
Pb	ICP-MS	<0.4	1 - 20
	GFAAS	<0.2	1 - 25
Sb	ICP-MS	<0.04	1 - 25
	GFAAS	<0.35	0.5 - 20
Tl	ICP-MS	<0.02	0.1 - 20
	GFAAS	<0.08	n.d. - n.d.
V	ICP-MS	<0.003	0.01 - 20
	ICP-OES	<0.4	0.2 - 20
Zn	GFAAS	<0.4	1 - 10
	ICP-MS	<0.02	0.1 - 20
	FAAS	<2	25 - 500
Ti	ICP-OES	<0.4	20 - 500
	ICP-MS	<0.09	20 - 200

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