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Digestion Procedures for the Elemental Analysis of Wood by Inductively Coupled Plasma - Optical Emission Spectrometry

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ABSTRACT

For the elemental analysis of woody biomass, different digestion methods exist; among them, microwave digestion is indicated as an European standard method. It provides two dissolution approaches to determine the major and minor element contents in solid biofuels. Because of the small amount of dissolved biomass (≤ 0.5 g), as required in the microwave digestion, analyte concentrations in resulting solutions are low, and inductively coupled plasma - mass spectrometry (ICP-MS) may be necessary for determining some minor element contents. Instead, when inductively coupled plasma - optical emission spectrometry (ICP-OES) is used, the solutions should have higher concentrations than those measured by ICP-MS. Therefore, this work takes into consideration some digestion methods, including wet, dry, and ash fusion digestions, as well as the microwave digestion, to determine the Al, Ca, Fe, Mg, P, K, Si, Na, S, As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn contents in woody biomass. Thereafter, to assess these methods, two certified reference materials (BCR 100 - beech leaves and BCR 62 - olive leaves) were used. The woody biomass analysis after microwave digestion revealed that some elements, namely Cd, Co, Cr, Cu, Ni and Pb, were below the limit of quantification (LOQ). Among the considered digestion methods, wet

digestion was found to be a good method for the elemental analysis of woody biomass, except for Al and Si. In fact, the sample quantities dissolved, that are on the scale of grams, produce solutions that are measurable by ICP-OES. Dry digestion was found to be an accurate method for some elements and ash fusion digestion was confirmed to be the most accurate method for Si determination for these matrices.

INTRODUCTION

Research and development efforts focused on new renewable energy sources are becoming a global phenomenon. Some reasons for using renewable energy are the depletion of fossil fuels, global warming, environmental pollution and deterioration, and possible future gas and oil shortages and their geopolitical distributions (Escobar et al. 2009). Biomass is among the most promising renewable energy sources and, according to recent studies, represents between 10 % and 15 % of global primary energy (Li et al. 2008). Therefore, extensive investigations have been performed worldwide to enhance the use of biomass instead of fossil fuels for energy conversion. The thermo-chemical processes used for biomass conversion are combustion, pyrolysis, and gasification.

Woody biomass is a complex heterogeneous mixture of organic matter and, to a lesser extent, inorganic matter, in which there is a large spectrum of inorganic elements classified into major and minor elements (including alkali metals, transition elements, and halogens). The elemental composition, within certain limits, can be considered characteristic for every woody biomass. Therefore, the elemental composition of biomass is needed to evaluate its suitability for energy conversion processes and to regulate the operating parameters of

plants in accordance with characteristics of the biofuel (Monti et al. 2008). In fact, it is important to know the distribution of the chemical elements between the solid and gaseous phases at the high temperatures achieved during the conversion. A high ash content and, above all, high contents of certain elements (K, Cl, S, etc.) can cause serious problems in plant operation, such as melting ash, slag and deposit formation, and corrosion. Moreover, the solid byproducts generated can have an environmental impact, particularly the fly ash byproducts (Froment et al. 2013; Balat et al. 2009; Simone et al. 2012; Dahl et al. 2010; Tafur-Marinos et al. 2014; Raman et al. 2013).

Although some chemical analyses are performed directly on samples in solid form, the majority of inorganic elemental analytical techniques require the sample to be in solution form. Therefore, solid samples must be efficiently dissolved prior to chemical analysis, e.g., the acid digestion of inorganic solids prior to determination by atomic emission spectrometry. Broadly, different dissolution approaches are available, and in particular, two European standard methods, EN 15290 (European committee for standardization 2011a) and EN 15297 (European committee for standardization 2011b), are related to the determination of the major and minor elements in solid biofuels, respectively. In these methods, 0.5 g of biofuel is dissolved in H_2O_2, HNO_3 and HF using microwave or resistance heating. However, a small sample quantity leads to solutions with concentrations that require the use of inductively coupled plasma - mass spectrometry (ICP-MS) for the determination of trace elements. This can limit the application of these methods because ICP-MS is less widely common than inductively coupled plasma - optical emission spectrometry (ICP-OES).

Therefore, the objective of this study was to compare the effectiveness of three digestion methods (wet, dry, and ash fusion digestions) that can dissolve a sufficient quantity of

woody sample for determining the major and minor elements (Al, Ca, Fe, Mg, P, K, Si, Na, S, As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn) in the same solution by ICP-OES. These methods were applied on pellets and chips. To assess the accuracy of the methods, two certified reference materials (CRMs) were utilized.

EXPERIMENTAL

Samples

The samples analyzed were commercial pellets and chips, which are used in an experimental pyro-gasification plant, as reported previously (Tafur-Marinos et al. 2014).

Several kilograms of these biomass were taken from storage, and there was no information on the duration or storage conditions. Once collected, the samples were stored at 4 °C. Large samples were reduced in size by mixing thoroughly and coning and quartering, and then the reduced samples were milled to particle size smaller than 1 mm, with a cutting mill. The ash content of pellets and chips were 1.1 % and 1.2 %, respectively.

Two certified reference materials were used to assess the accuracy of analyses, namely BCR 100 (beech leaves) and BCR 62 (olive leaves). BCR 100 and BCR 62 have been certified by Community bureau of reference (BCR), and BCR 100 has also been revised by Institute for reference materials and measurements. The CRMs were certified for Al, Ca, Cr, K, Mg, P and S in BCR 100, and Al, Cd, Cu, Hg, Mn, Pb and Zn in BCR 62. Indicative values (values not certified) for other elements are also reported for both CRMs. The ash content of BCR 100 and BCR 62 are 6.3 % and 6.1 %, respectively.

Before analysis, the CRMs and the woody samples were dried at 105 °C until constant weight.

Reagents and Instruments

All chemicals used throughout the experiments were puriss. p.a. grade or trace metal basis quality (Sigma Aldrich® Corporation) or suprapur quality® (Merck KGaA), including nitric acid (70 %), hydrogen peroxide solution (30 % w/w), hydrochloric acid (30 %), hydrofluoric acid (40 %), boric acid, lithium metaborate, sodium borohydride, potassium dihydrogen phosphate and potassium sulfate. Additionally, sodium hydroxide and ultrapure water were used.

Multielement standard solution for ICP (Merck KGaA) was used as the stock standard for preparing calibration standard solutions, which were prepared by serial volume/volume dilution in volumetric flask of 100 mL, and using micropipettes with disposable tips for pipetting all solutions. The silicon standard solution was prepared using a standard solution for ICP (Fluka®). The sulfur and phosphorous standard solutions were prepared using potassium dihydrogen phosphate and potassium sulfate. These salts were dried to a constant weight (110 °C).

A Retsch SM 300 cutting mill was used to cut and grind the woody samples. The microwave digestion was performed using a CEM Mars 5, which works with a variable power until to 1200 watts. It's fitted with an automatic pressure and temperature control device. The vessels used were HP-500.

The analyses were performed using Perkin-Elmer optima 7000 ICP-OES instrument equipped with a dual-view (axial-radial) optical system. Mercury and arsenic determinations were performed using a Perkin-Elmer 1100B atomic absorption spectrometer equipped with a MHS-20 unit hydride generation system. The X-ray diffractograms of powdered samples were obtained using a Siemens D 5000 diffractometer.

Digestion procedures

Microwave digestion (mw digestion). The microwave digestion of samples was done in accordance with EN 15290 (European committee for standardization 2011a) with some adjustments as detailed below. Samples of approximately 0.5 g were introduced into the digestion vessel liners, after 8 mL of HNO_3, 3.0 mL of H_2O_2 were added and reacted overnight (this step is useful for safety issues). Lastly, HF (1 mL) was added. One vessel contained only the reagents with no sample to act as analytical reagent blank. The vessels were sealed and placed into the rotor for microwave digestion. The microwave oven program was as follows: heat to 190 °C over 15 min and hold for 20 min at 190 °C. After cooling, boric acid (0.4 g) was added to convert the excess fluorides, and then, the sample was quickly heated to 150 °C and held at 150 °C for 15 min. After digestion, the digestates were diluted to 25 mL with ultrapure water.

Wet digestion. The wet digestion of samples was done in accordance with Method 3050B (United state environmental protection agency 1996).

The samples (5 g) and HNO_3 (15 mL) were placed into 200 mL boiling flasks and held overnight. Then, another 10 mL HNO_3 was added and the samples were refluxed using a heating mantle for 6 h. After cooling, H_2O_2 (20 mL) was added, and the mixtures were refluxed for other 2 h. One boiling flask contained only the reagents with no sample to act as analytical reagent blank. The resulting solutions were filtered and diluted to 50 mL with ultrapure water.

Dry digestion. The ashing temperature was 550 °C as recommended in EN 15290 (European committee for standardization 2011a), so 5 g of samples were placed into a porcelain crucible and held at 550 °C for 4 h in a muffle furnace for the ashing. Afterwards, another incineration was performed for 30 min to ensure complete combustion after a delicate mixing of the previously obtained ashes. The resulting ash was dissolved under hot

conditions with aqua regia (8 mL) and the obtained solution was filtered and brought up to volume (50 mL). The analytical blank was prepared.

Ash fusion digestion. The ashing step was the same as that described above for the dry digestion and the resulting ash was melted with $LiBO_2$ in a graphite crucible at 900 °C for 30 min; the ash/flux ratio was 1:10 (Suhr 1966). Afterwards, the molten drop was quickly transferred to a nitric acid solution (3.5 % v/v), and the resulting solution was brought up to volume 50 mL. The analytical blank was prepared.

All digestion procedures were performed with four independent analyses.

Analyses

The elements considered in the analyses were Al, Ca, Fe, Mg, P, K, Si, Na, S, As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn, and their concentrations were determined by ICP-OES, except for Hg and As, which were measured by cold vapor atomic absorption spectrometry (CVAAS) and hydride generation atomic absorption spectrometry (HGAAS), respectively. **Table 1** shows the wavelengths and axial-radial view mode used in the analyses. For the Ca, K, Mg and Mn determinations, due to their higher concentrations, the solutions were diluted 1:25. The external calibration method was used, and the calibration solutions for analyses of obtained solutions after ash fusion were also prepared with $LiBO_2$.

CVAAS and HGAAS were performed using 3 % $NaBH_4$ in 1 % NaOH as reductant. The radiation sources were electrodeless discharge lamps used at wavelengths of 193.7 nm and 253.6 nm for arsenic and mercury, respectively, with a spectral slit width of 0.7 nm.

The analytical blank is measured ten times and the standard deviation is calculated. The limit of quantification (LOQ) is expressed as the analyte concentration corresponding to the sample blank value plus ten standard deviations (Long and Winefordner 1983; Thomsen et

al. 2003). In **Table 2** are reported the LOQ values of each method, expressed in mg/kg taking into account the dilution factor.

X-ray diffraction analysis

X-ray diffraction (XRD) data were collected using CuKα radiation on the diffractometer at 30 mA and 40 kV. Measurements were made on flat-plate samples in the Bragg-Brentano θ-2θ geometry and all scans were measured over an angular range of 2.5° to 70° 2θ with a 0.02° 2θ step size and an accumulated time per step of 15 s. The scanning and operating conditions were kept constant for all measurements to allow for an immediate comparison between the samples.

Statistical analysis

The accuracy of the analytical methods was assessed on the CRMs. The assessment of the certified element results was made in agreement with the instructions of the BCR (Colinet et al. 1982).

As regards the other elements (not certified), the evaluation of the correctness of the results was carried out in a different way in accordance with certified reference material. In BCR 100 the deviation standards were associated with indicative values, while in BCR 62 only values were given. In order to assess the bias of the results obtained for BCR 100, the difference between the indicative value (μ) and the mean value of replicate measurements ($\bar{x}$) was calculated. The criterion for acceptance is given as follows: the result is considered to be good when $\bar{x} - \mu$ is within the limits of $\pm 2\sigma$ ($-2\sigma \leq \bar{x} - \mu \leq +2\sigma$), while is considered to be satisfactory when it is within the limits of $\pm 3\sigma$ ($-3\sigma \leq \bar{x} - \mu \leq +3\sigma$); beyond these limits the result is unsatisfactory. σ is the standard deviation of the indicative value.

Due to the missing of standard deviations, in BCR 62 Student's t-test was employed to estimate the significance of obtained values with the three dissolution methods. The K and

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Ni results were finally subjected to the non-parametric test of Kruskal-Wallis (Castino and Roletto 1991).

RESULTS AND DISCUSSION

Analysis of the woody samples

The microwave digestion is the one suggested by the European standard for solid biofuels. It provides a rapid and efficient method, and it generally has the advantages of reducing volatilization loss and contamination. However, as reported previously, the microwave procedure often requires the use of ICP-MS to determine trace elements because of the restricted quantity of the digested samples.

The woody samples dissolved according to this method have resulted in solutions in which the concentration of some elements, such as Cd, Co, Cr, Cu, Ni, and Pb are below the LOQ (**Table 2**).

To determine the elemental composition in woody samples, three alternative digestion methods to microwave digestion were considered: wet, dry and ash fusion digestions. These methods use larger amounts of sample compared to the microwave digestion method, and bring to more concentrate solutions.

The analysis results of the pellets and chips obtained by these digestion procedures, as well as microwave digestion, are presented in **Table 3**.

After dissolution and analysis of the woody samples, the behaviors of some elements were different between the pellets and chips.

The results obtained for K in the pellets showed that the three treatments led to not significantly different results while in the chips, the values after the dry and ash fusion digestions were lower than the wet digestions. These results can be attributed to the

formation of KCl, K_2SO_4, K_2CO_3 (Werkelin et al. 2010; Vassilev et al. 2012) during the pelletizing that limit the volatilization losses. In the chips likely the K associated with organic constituents is transformed into a gaseous form that evaporates (Van Lith et al. 2006; Van Lith et al. 2008).

In the pellets, the volatilization of Cd was low after dry digestion (550 °C) while in the chips no volatilization losses were noted.

Pb may be present in small amounts in the forms of PbS, $PbCO_3$, and $Pb(OH)_2$. During the ashing step (550 °C), $PbCO_3$ may decompose to PbO and begins to volatilize (van Lith et al. 2008). However, in the pellets the Pb result after ash fusion digestion (900 °C) was higher than wet and dry digestions. These results suggests that Pb was present in the form not easily soluble as a result of the pelletization. In the chips, the Pb result after wet digestion, as expected, was higher than dry and ash fusion digestions.

Accuracy of the analytical methods

In order to verified the accuracies and reliabilities of the digestion procedures, two certified reference materials were used: BCR 100 and BCR 62. For wet, dry and ash fusion digestion procedures, 2 g of CRMs were treated according to the corresponding sample processing method as described above.

Table 4 and **Table 5** show the results obtained for BCR 100 and BCR 62 after microwave, wet, dry and ash fusion digestion methods.

The accuracies of the considered methods for Al, Ca, Cr, K, Mg, P and S were verified on BCR 100. After wet digestion, the Ca, Cr, K, Mg, P and S results were in good agreement with the certified values. The Al content was lower than the certified value by approximately 30 %. This result may be due to the presence of insoluble silico-aluminates in the samples. Indeed, to reduce Al toxicity, the plants can concentrate it in the form of Si-Al, for example in

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hydroxyaluminosilicates (Le Blond et al. 2011). Besides, Al (plus Si, Ti, Fe, and Na) may also be introduced into the biomass as sand, clays and other components during harvest, transport, processing or manufacturing operations (Vassilev et al. 2010).

When determining the P and S contents, different values for the emission wavelengths are reported in the literature. In particular, for the determination of P, four emission wavelengths are reported: 177.434, 178.221, 213.617 and 214.914 nm. Of these, only 213.617 and 214.914 nm gave results in the confidence range of the certified value. The other emission wavelengths overestimated the P concentration. Similarly, for S, three emission wavelengths, 180.669, 181.975, and 182.563 nm, are reported. The emissions at 180.669 and 182.563 nm can be affected by interference from Ca and B, respectively (McCurdy and Fry 1986). Thus, 181.975 nm was suitable for the determination of S in this case.

After dry digestion, the BCR 100 ash was not completely soluble in acid. For this reason, the Ca, K, Mg, and P values were approximately 85 % relative to the certified values, and approximately 60 % of the Al, Cr, and S contents were observed. These unsatisfactory results can be attributed to incomplete matrix destruction despite the prolonged incineration phase, which is most likely due to the high Si content (13,000 mg/kg). In fact, Si acted as a delaying agent on the combustion, resulting in incomplete combustion of the organic matter (Phillips et al. 2004). The presence of graphite and char as showed in the BCR 100 ash XRD pattern confirmed this hypotheses (subsection XRD analysis).

S was lost by volatilization during the ashing at 550 °C. In addition to volatilization losses, retention losses generally occur in the presence of silicates or other insoluble compounds due to the sequestration action of the residual matrix (Hoenig 2005). The low Cr value may also be due to these phenomena. Moreover, the Cr transformation in the ashing step from

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chromium bounded to organic matter into chromium oxide (Cr_2O_3) made it resistant to acidic and basic attacks. Therefore, for the reasons reported above, this method is not suitable for the dissolution of this matrix.

After the ash fusion digestion, the results were in good agreement with the certified values for Al, Cr, K, Mg, and P. The Ca and S contents were lower than the certified values. The S value was only 4 % of the certified value due to the heat treatment (900 °C), which suggests the probable decomposition and/or evaporation of alkali metal sulfates (van Lith et al. 2008). Additionally, there is the possibility that B interfere with S during the atomic emission spectroscopy (Rodushkin et al. 1999). Therefore, ash fusion is not suitable for S determination.

The accuracy of the considered method for Al, Cd, Cu, Hg, Mn, Pb and Zn were verified on BCR 62. The BCR 62 results are reported in **Table 5**, as previously mentioned. The results of the Cd, Cu, Mn, Pb, and Zn contents were in good agreement with the certified values after wet and dry digestions. The Hg content was in good agreement with the certified values after wet digestion.

Although the ashing procedures may result in the loss by volatilization of certain elements, the Zn, Cd and Pb results did not confirm this fact likely due to the formation of their oxides, which are stable at the ashing temperature (Van Lith et al. 2006). After the ash fusion at 900 °C, Cd were completely lost by volatilization while Pb volatilized less. The concentration of Cd was lower than the LOQ (0.02 mg/kg), so no data were given for it. For Zn, no losses by volatilization were found in this method because it is still stable at high temperatures in the ZnO form (Lamoreaux et al. 1987).

In addition to the certified values, indicative values were also reported for other elements in the certified reference material report. In BCR 100, the indicative values of Cd, Cu, Fe, Hg,

Mn, Pb, Si and Zn were reported. As shown in **Table 4**, similar to the results for certified elements, dry digestion led to unsatisfactory results. Excluding the dry digestion, the results obtained using the other two dissolution methods showed that the resulting values were generally close to the indicative values. In BCR 62 (**Table 5**), the indicative values of Ca, Co, Cr, Fe, K, Mg, Ni, P, S and Si Zn were reported. They were generally close to the indicative values. Concerning K results, the concentrations generally were higher than indicative value. The non-parametric test of Kruskal-Wallis showed that the wet digestion result does not belong to distribution to which dry and ash fusion digestions belong. The latter are lower than wet digestion, because these methods imply an ashing step. The Ni results were lower than indicative value. The statistical analysis showed that the dry and ash fusion digestion results originated from the same distribution. Moreover, ash fusion was not reliable for Co determination, in fact, its concentration was lower than the LOQ (< 0.09 mg/kg). Finally, the Si content was only correctly quantified by the ash fusion.

Therefore, considering the results of the certified elements in BCR 100 and BCR 62 it is highlighted that the wet digestion method is found to be suitable for this type of matrix (woody biomass) for the elemental analysis, apart from aluminum and silicon. But, while Si is not almost totally brought into solution, Al is partially dissolved, therefore, it is possible to quantify it even if not accurately. In addition, the conventional wet digestion method allows for the analysis of large sample quantity. The dry digestion was not found to be an accurate method for some elements, in fact losses by volatilization was shown. It is important to highlight that the temperature of 550 °C is a good compromise between the almost total destruction of the matrix and the limitation of losses due to volatilization (Tafur-Marinos et al. 2014; Baernthaler et al. 2006). Finally, the ash fusion method determined the Si content correctly, however, the resulting solution is more complex due to the presence of the flux.

X-ray diffraction analysis

The XRD of the CRMs and their ashes (550 °C) were performed to identify the crystalline phases. The XRD of the two CRMs showed a typical non-crystalline character with a double or triple hump distribution. The only crystalline phase undoubtedly identifiable in both samples was calcium oxalate (whewellite). The Ca oxalates are typical plant minerals. These biominerals are an end product of plant metabolism and are commonly present in the cytoplasm (Suárez-García et al. 2002). In addition, the certified reference material XRD patterns are in agreement with the studies of Vassilev et al. (Vassilev et al. 2012) who reported that wood char, coal, coal char, petroleum coke and woody biomass have similar XRD patterns, and some positions and shapes (maxima) of the amorphous halo can be related to organic matter.

The diffractograms of the BCR 100 and BCR 62 ashes are shown in **Figure 1** and **Figure 2**, respectively. BCR 100 ash (**Figure 1**) showed an amorphous residual signal centered at 28.9° 2θ. Among the crystalline phases, the graphite was due to the reducing conditions during the sample ashing. The other phases were calcite ($CaCO_3$), sylvite (KCl), gypsum ($CaSO_4 \cdot 2H_2O$), bassanite ($CaSO_4 \cdot 0.5H_2O$), quartz (SiO_2), ankerite ($Ca(Fe(II), Mg)(CO_3)_2$) and hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$). The BCR 62 ash (**Figure 2**) showed a very high degree of crystallinity. The most intense signal was from calcite ($CaCO_3$) due to calcium oxalate decomposition. The other phases present were fairchildite ($K_2Ca(CO_3)_2$), hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$), and a small amount of quartz (SiO_2). These crystalline phases may already be present in the initial biomass or they may have formed during the ashing process. As reported by Vassilev et al., the crystalline and semi-crystalline phases in biomass ashes are present in concentrations close to the XRD detection limit. They affirmed that many new

minerals can form from the carbonate, sulfate, silicate and phosphate in ashes (Vassilev et al. 2013).

CONCLUSIONS

The low content of some elements of wood biomass require the use of alternative dissolution methods to microwave if the determinations are to be carried out using an ICP-OES.

Among the considered dissolution methods, the wet digestion procedure determines accurately the elements considered with the exception of aluminum and silicon. So it was found to be a good alternative method to microwave digestion for the analysis of woody biomass. In fact, the woody biomass analysis after microwave digestion revealed that some elements, namely Cd, Co, Cr, Cu, Ni and Pb, were below the limit of quantification (LOQ). The wet dissolution method allows for the use of large sample quantities (in the range of grams), producing solutions that are measurable by ICP-OES. This is an advantage for laboratories that do not have an ICP-MS.

The dry digestion method was found to be an accurate method, but it is more susceptible to the matrix composition, and in some cases, it can lead to loss of volatile elements. The ash fusion digestion method was the most accurate method for Si determination also for these woody matrices.

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Table 1. Operating conditions of inductively coupled plasma - optical emission spectrometry.

Element	Wavelength (nm)	View
Al	396.153	Axial
Ca	317.933	Radial
Fe	238.204	Axial
K	766.490	Radial
Mg	285.213	Radial
Mn	257.610	Radial
Na	589.592	Axial/Radial
S	180.669	Axial
S	181.975	Axial
S	182.563	Axial
P	213.617	Axial
P	214.914	Axial
Si	251.611	Axial
Si	288.158	Axial
Cd	228.802	Axial
Co	228.616	Axial
Cr	267.716	Axial
Cu	324.752	Axial
Ni	231.604	Axial
Pb	220.353	Axial
Zn	206.200	Axial

Table 2. Limit of quantification (LOQ) for wood analysis by ICP-OES.

Element	Mw digestion mg/kg	Wet Digestion mg/kg	Dry digestion mg/kg	Ash fusion digestion mg/kg
Cd	0.24	0.05	0.01	0.02
Co	1.50	0.08	0.08	0.09
Cr	1.55	0.05	0.10	0.17
Cu	2.59	0.34	0.33	0.42
Ni	1.80	0.18	0.15	0.18
Pb	9.60	0.31	0.26	0.66

Table 3. Results of element contents of pellets and chips determined after microwave, wet, dry and ash fusion digestions (mg/kg), (n=4).

	Pellets					Chips			
Element	Mw digestion	Wet digestion	Dry digestion	Ash fusion digestion	Element	Mw digestion	Wet digestion	Dry digestion	Ash fusion digestion
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Al	131 ± 9	82 ± 4	83 ± 4	127 ± 4	Al	477 ± 38	166 ± 4	215 ± 9	479 ± 33
As[d]	not determined	0.006 ± 0.001	not determined	not determined	As[d]	not determined	0.077 ± 0.002	not determined	not determined
Ca	2572 ± 152	2720 ± 18	2831 ± 124	2139 ± 47	Ca	2091 ± 142	2422 ± 18	2043 ± 139	1730 ± 40
Cd	< 0.24	0.17 ± 0.01	0.10 ± 0.01	< 0.02	Cd	< 0.24	0.08 ± 0.01	0.08 ± 0.01	< 0.02
Co	< 1.50	0.09 ± 0.01	0.09 ± 0.01	< 0.09	Co	< 1.50	0.22 ± 0.01	0.22 ± 0.01	0.22 ± 0.01
Cr	< 1.55	0.52 ± 0.03	0.55 ± 0.04	0.77 ± 0.02	Cr	< 1.55	0.64 ± 0.01	0.60 ± 0.01	0.74 ± 0.02
Cu	< 2.59	1.84 ± 0.07	1.66 ± 0.05	1.84 ± 0.10	Cu	< 2.59	1.86 ± 0.02	1.93 ± 0.16	1.66 ± 0.12
Fe	101 ± 4	105 ± 4	107 ± 9	106 ± 2	Fe	223 ± 24	162 ± 4	198 ± 15	206 ± 18
Hg[c]	not determined	0.033 ± 0.003	not determined	not determined	Hg[c]	not determined	0.034 ± 0.001	not determined	not determined
K	1062 ± 46	1064 ± 37	1124 ± 74	1101 ± 83	K	1055 ± 41	1070 ± 37	611 ± 6	539 ± 36
Mg	214 ± 6	272 ± 6	266 ± 9	230 ± 10	Mg	264 ± 15	264 ± 6	261 ± 7	266 ± 5
Mn	35 ± 3	34 ± 2	35 ± 1	34 ± 1	Mn	55 ± 3	54 ± 2	54 ± 2	52 ± 1
Na	45 ± 9	52 ± 4	56 ± 5	47 ± 3	Na	87 ± 6	63 ± 4	93 ± 5	96 ± 8
Ni	< 1.80	0.47 ± 0.02	0.46 ± 0.02	0.54 ± 0.02	Ni	< 1.80	0.66 ± 0.04	0.68 ± 0.03	0.66 ± 0.04
P[b]	301 ± 15	290 ± 12	334 ± 14	313 ± 15	P[b]	179 ± 11	162 ± 12	165 ± 10	179 ± 8
Pb	< 9.60	0.34 ± 0.02	0.29 ± 0.01	0.64 ± 0.05	Pb	< 9.60	0.74 ± 0.04	0.53 ± 0.05	0.53 ± 0.04
S[a]	346 ± 10	378 ± 16	250 ± 11	42 ± 4	S[a]	455 ± 34	455 ± 16	215 ± 16	37 ± 8
Si	not determined	not determined	not determined	456 ± 29	Si	not determined	not determined	not determined	1259 ± 86
Zn	11.5 ± 1.7	11.6 ± 0.3	11.8 ± 0.5	10.8 ± 0.3	Zn	9.0 ± 0.8	9.2 ± 0.6	10.3 ± 0.7	9.15 ± 1.1

[a] Sulfur are expressed as sulfate.

[b] Phosphorous are expressed as phosphate.

[c] Cold vapor atomic absorption spectrometry analysis.

[d] Hydride generation atomic absorption spectrometry analysis.

Table 4. Inductively coupled plasma - optical emission spectrometry analysis of BCR 100 after microwave, wet, dry and ash fusion digestions (mg/kg), (n=4).

Element	Certified value mg/kg	Confidence range[a] mg/kg	Mw digestion mg/kg	Wet digestion mg/kg	Dry digestion mg/kg	Ash fusion digestion mg/kg
Al	435	424-446	427 ± 16	294 ± 4	189 ± 14	426 ± 10
Ca	5300	5166-5434	5199 ± 108	5367 ± 182	4731 ± 218	4797 ± 45
Cd	(0.34 ± 0.01)		0.36 ± 0.02	0.31 ± 0.01	not determined	< 0.02
Cr	8.0	6.6-9.4	8.2 ± 0.2	7.5 ± 0.4	4.6 ± 0.3	8.3 ± 0.3
Cu	(11.8 ± 0.4)		11.5 ± 0.6	12.3 ± 0.4	not determined	11.7 ± 1.8
Fe	(550 ± 30)		553 ± 17	547 ± 8	475 ± 28	552 ± 21
Hg[b]	(0.26 ± 0.01)		0.28 ± 0.02	0.24 ± 0.01	not determined	not determined
K	9940	9464-10416	9465 ± 335	10236 ± 131	9200 ± 283	10238 ± 251
Mg	878	843-913	907 ± 16	887 ± 5	826 ± 19	913 ± 6
Mn	(1330 ± 40)		1283 ± 29	1354 ± 17	1124 ± 83	1336 ± 13
P	1550	1453-1647	1538 ± 52	1602 ± 22	1339 ± 107	1548 ± 17
Pb	(16 ± 0.7)		16 ± 0.6	16 ± 0.3	not determined	7.3 ± 1.9
S	2690	2570-2810	2590 ± 57	2754 ± 39	1173 ± 97	41 ± 11
Si	(13000 ± 200)		8033 ± 652	not determined	not determined	13024 ± 1210
Zn	(69 ± 5)		68 ± 3	66 ± 8	not determined	61 ± 4

Values and standard deviations in parentheses are not certified (indicative values).

[a] Range calculated according to the BCR instructions.

[b] Cold-vapor atomic absorption spectrometry analysis.

Table 5. Inductively coupled plasma - optical emission spectrometry analysis of BCR 62 after wet, dry and ash fusion digestions (mg/kg), (n=4).

Element	Certified value	Confidence range[a]	Mw digestion	Wet digestion	Dry digestion	Ash fusion digestion
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Al	448	394 - 502	495 ± 31	371 ± 18	382 ± 38	459 ± 35
Ca	(17510)		16765 ± 581	18048 ± 182	17564 ± 521	16033 ± 319
Cd	0.10	0.06 - 0.14	< 0.24	0.08 ± 0.01	0.07 ± 0.01	< 0.02
Co	(0.2)		< 1.50	0.21 ± 0.01	0.20 ± 0.01	< 0.09
Cr	(2)		2.1 ± 0.1	1.4 ± 0.1	1.8 ± 0.2	1.8 ± 0.3
Cu	46.6	41.4 - 51.8	45.9 ± 1.3	51.7 ± 1.2	48.2 ± 1.9	47.1 ± 2.1
Fe	(280)		307 ± 6	273 ± 14	277 ± 8	341 ± 30
Hg[b]	0.28	0.22 - 0.34	0.26 ± 0.01	0.29 ± 0.01	not determined	not determined
K	(3072)		5205 ± 165	5336 ± 50	4310 ± 221	4051 ± 219
Mg	(1206)		1111 ± 39	1127 ± 96	1094 ± 71	1057 ± 19
Mn	57.0	50.3 - 63.7	55.9 ± 1.3	53.8 ± 2.3	53.1 ± 1.3	56.5 ± 2.5
Ni	(8)		< 1.80	1.2 ± 0.1	1.8 ± 0.2	1.7 ± 0.2
P	(1047)		1053 ± 13	1046 ± 64	910 ± 42	1096 ± 43
Pb	25.0	20.7 - 29.3	25.5 ± 1.2	23.9 ± 0.9	22.1 ± 2.0	19.2 ± 1.7
S	(1600)		1576 ± 37	1510 ± 93	744 ± 31	97 ± 17
Si	(1262)		902 ± 209	not determined	not determined	1277 ± 27
Zn	16.0	13.8 - 18.2	17.7 ± 0.6	15.2 ± 0.6	16.6 ± 0.3	16.7 ± 0.9

Values in parentheses are not certified (indicative values), standard deviations are not given.

[a] Range calculated according to the BCR instructions.

[b] Cold-vapor atomic absorption spectrometry analysis.

Captions

Figure 1. X-ray diffraction profiles of BCR 100 ash.

Figure 2. X-ray diffraction profiles of BCR 62 ash.