

## Article

# Development- and Validation-Improved Metrological Methods for the Determination of Inorganic Impurities and Ash Content from Biofuels

Camelia Stratulat <sup>1</sup>, Raluca Elena Ginghina <sup>1,\*</sup> , Adriana Elena Bratu <sup>1</sup>, Alper Isleyen <sup>2</sup> , Murat Tunc <sup>2</sup>, Katarina Hafner-Vuk <sup>3</sup>, Anne Mette Frey <sup>4</sup>, Henrik Kjeldsen <sup>4</sup>  and Jochen Vogl <sup>5</sup> 

<sup>1</sup> Romanian Bureau of Legal Metrology, 11 Vitan Barzesti, 042122 Bucharest, Romania; camelia.stratulat@inm.ro (C.S.); adriana.bratu@nbce.ro (A.E.B.)

<sup>2</sup> TÜBİTAK UME National Metrology Institute, Gebze Yerleşkesi Barış Mah. Dr. Zeki Acar Cad. No:1, 41470 Gebze, Kocaeli, Turkey; alper.isleyen@tubitak.gov.tr (A.I.); tunc.murat@tubitak.gov.tr (M.T.)

<sup>3</sup> Institute of Metrology of Bosnia and Herzegovina, Branilaca Sarajeva 25, 71000 Sarajevo, Bosnia and Herzegovina; katarina.hafner@met.gov.ba

<sup>4</sup> Danish Technological Institute, Kongsvang Allé 29, DK-8000 Aarhus C, Denmark; amfr@teknologisk.dk (A.M.F.); hkje@teknologisk.dk (H.K.)

<sup>5</sup> Bundesanstalt für Materialforschung und-Prüfung, Richard-Willstätter-Straße 11, 12489 Berlin, Germany; jochen.vogl@bam.de

\* Correspondence: ginghinaraluca@gmail.com

**Abstract:** In this study, five laboratories, namely, BRML (Romania), TUBITAK UME (Turkey), IMBIH (Bosnia and Herzegovina), BAM (Germany), and DTI (Denmark), developed and validated analytical procedures by ICP-MS, ICP-OES, MWP-AES, WD-XRF, and ID-MS for the determination of inorganic impurities in solid and liquid biofuels, established the budget of uncertainties, and developed the method for determining the amount of ash in the measurement range 0–1.2% with absolute repeatability less than 0.1% and absolute reproducibility of 0.2% (according to EN ISO 18122). In order to create homogeneous certified reference materials, improved methodologies for the measurement and characterization of solid and liquid biofuels were developed. Thus, information regarding the precision, accuracy, and bias of the method, and identifying the factors that intervened in the measurement of uncertainty were experimentally determined, supplementing the information from the existing standards in the field.

**Keywords:** development; validate method; biodiesel; ICP-MS; ICP-OES; MW-AES; WD-XRF; ID-MS inorganic impurities; ash content; wood chips



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## 1. Introduction

The European Union Commission Communication of 22 January 2014 entitled “A Framework for Climate and Energy Policy 2020–2030” set a framework for the Union’s future energy and climate policies and promoted a common understanding of how to develop those policies after 2020. The Commission proposed that the Union’s 2030 target for the share of energy from renewable sources consumed in the Union should be at least 27% [1]. Therefore, it is appropriate to establish a mandatory Union target aiming at a share of at least 32% of energy from renewable sources.

A renewable source that can be used as a substitute for fossil fuels is biomass. Biomass consists of the biodegradable [2] part of products, waste and residues from agriculture (including plant and animal substances), from the forestry sector and related industrial branches, as well as the biodegradable part of industrial and municipal waste [3]. Biofuels represent any solid, liquid, or gas obtained from biomass, which can be used as fuel [4,5].

A qualitative evaluation of biofuels is given by the calorific value [6,7], which represents the most important evaluation parameter, being a measure of the heat developed by

burning them. The calorific value of biofuels is of great importance for the economic benefit for legal purposes, and it has an impact on the environment [8]. However, the Annex III Energy content of fuels of the European Directive (EU) 2018/2001 is not supported by traceable measurements [9]. In addition, the types and concentration of impurities in biofuels, i.e., organic and inorganic substances, the level of ash and moisture may have a negative impact on the calorific value and also a high ash level can also increase the cost of handling due to the need for ash waste removal. Therefore, controlling the process by measuring the impurities and ash content may lead to an accurate energy value [10–12].

The purpose of this study is to identify and quantify the content of impurities in solid and liquid biofuels and to determine the amount of ash in solid biofuels by several methods, and to evaluate the traceability of the results. Thus, five partner institutions, namely, BRML—Romanian Bureau of Legal Metrology, TUBITAK UME—Turkish National Metrology Institute, IMBIH—Institute of Metrology of Bosnia and Herzegovina, BAM—German Federal Institute for Materials Research and Testing, and DTI—Danish Technological Institute developed, validated various analytical methods, and performed the measurements of organic and inorganic impurities in solid and liquid biofuels.

It was decided to perform measurements with three solid biofuels and one liquid biofuel. The solid biofuels under investigation are high-quality wood chips (HQ-WCs), industrial-quality wood chips (IQ-WCs), and wood pellets (WPs). The origin of the wood chips was Denmark and the origin of the wood pellets was Poland. The samples were treated to reduce the moisture content to about 15% and were delivered by DTI (Denmark) to the other institutes in airtight bags, containing 1 kg of each type of sample.

For the investigation of liquid biofuels, biodiesel was chosen and the samples were delivered by BRML (Romania) in brown bottles of 1 L. In order to determine the inorganic impurities, the following techniques were used: inductively coupled plasma—mass spectrometry (ICP-MS), inductively coupled plasma—optical emission spectrometry (ICP-OES), microwave plasma atomic emission spectrometry (MWP-AES), and isotope dilution mass spectrometry (ID-MS), including the classic wet-chemical analysis (using the procedure to decompose a sample with a reagent, such as acids, to dissolve in a solvent) and the wavelength dispersive X-ray fluorescence spectroscopy WD-XRF analysis for the purpose of validating this method, which can be easily transferred to the portable XRF instruments used in the industry [13].

The impurity and ash content determination methods are validated to be used for producing homogeneous certified reference materials for biofuels according to ISO Guide 34, these CRMs being necessary for biofuel producers. Thus, in the existing ISO standards, there is no presented information regarding the precision, accuracy, and bias of the method, or the influencing factors that intervene in the measurement of uncertainty. In other words, the determination of the uncertainty components caused by the influencing factors that intervene in the calculation of the measurement uncertainty helps us to control the measurement and obtain the most accurate measurement results and with the least possible uncertainties.

## 2. Materials and Methods

### 2.1. Materials and Reagents

HNO<sub>3</sub> of an analytical grade was supplied by Merck (Darmstadt, Germany). Multi-element stock standard solutions containing all the analyzed chemicals toxic were supplied as follows: multi-element ICP-MS Calibration Std. 3, 10 µL/mL, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Ni, Pb, Rb, Se, Na, Ag, Sr, Ti, V, U, Zn, 5% HNO<sub>3</sub> by Merck, Germany; ICP multi-element standard solution IV, 1000 mg/L Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn 6.5% HNO<sub>3</sub> by Merck, Germany; and multi-element calibration standard 5, 10 µL/mL B, Ge, Mo, Nb, P, Re, S, Si, Ta, Ti, W, Zr H<sub>2</sub>O/0.2% HF/Tr. HNO<sub>3</sub> by PerkinElmer, United States.

Ultra-pure water was provided by a Stak Pure (Niederahr, Germany) water purification system, conductivity: 0.8–1.0 µS/cm, resistance: 18.2 MΩ·cm at 25 °C.

## 2.2. Instrumentation

### 2.2.1. Inorganic Impurities

The determination of impurities was performed using inductively coupled plasma mass spectrometry, ICP Mass Spectrometer ELAN DRC-e Axial Field Technology, PerkinElmer SCIEX (Waltham, MA, USA) by BRML and Thermo Element II ICP-MS, Thermo Fisher Scientific (Waltham, MA, USA) by TUBITAK. Spectro Arcos II ICP-OES, Spectro Ametek (Kleve, Germany) was used for the determination of elements in the biodiesel. IMBIH determined the inorganic impurities in the solid biofuel by a microwave plasma—atomic emission spectrometer, MWP-AES Agilent Technologies Inc. (Santa Clara, CA, USA), and wavelength dispersive X-ray fluorescence, Rigaku (Tokyo, Japan). BAM determined sulfur mass fractions in the wood chips and pellets by a high-resolution sector field ICP-MS-type Element 2, ThermoFisher Scientific (Waltham, MA, USA), with Jet-Interface using Jet cones.

START D and Ethos microwave digestion systems, Milestone Systems (Brøndby, Denmark), were used for digesting the samples.

All vessels, beakers, and glassware were soaked with 10% *v/v* HNO<sub>3</sub> for 24 h prior to their use to avoid cross-contamination, and further rinsed with de-ionized water.

### 2.2.2. Ash Content

The oven must ensure a uniform heat zone at the required temperatures and reach these temperatures in the specified time intervals, and the ventilation speed must ensure the oxygen for combustion. The equipment used was as follows: oven types: Caloris CD-1011 and ECV 50 (Bucharest, Romania), Protherm PFL110/10 PC442 (Brandon, FL, USA), Nabertherm LV 15/11 furnace (Lilienthal, Germany), Binder ED-240 (Tuttlingen, Germany); analytical balance AG 285 and XS 204, Mettler Toledo (Greifensee, Switzerland), Sartorius MSA 524S-100-DA (Goettingen, Germany).

## 2.3. Sample Preparation

### 2.3.1. Inorganic Impurities

Inorganic impurities for method development: ICP-MS—500 mg of the homogenized sample was mixed with 3 mL of H<sub>2</sub>O<sub>2</sub> 30%, 8 mL of HNO<sub>3</sub> 65%, and 1 mL of HF 40% in a closed Teflon digestion container. The mixture was allowed to react for 5 min before closing the container. The heating was performed using a microwave digestion system, according to the following temperature program: heating for 15 min to 190 °C; holding for 20 min at 190 °C. After cooling to room temperature, HF was neutralized by the addition of 10 mL of H<sub>3</sub>BO<sub>3</sub> 4%. After neutralization, the samples were re-digested into the microwave according to the following program: heating for 15 min to 150 °C and holding for 20 min at 150 °C. After cooling down to room temperature, the digestate was transferred into a 50 mL volumetric flask by gravimetric filtration. We carefully wash the digestion container with ultra-pure water and brought the samples to the mark.

The same procedure was applied for the ground sample from the wood pellets (WP-HQ), high-quality wood chips (HQ-WCs), industrial-quality wood chips (IQ-WCs), and biodiesel. Three preparation replicates were performed for each sample.

For the identification and quantification of the inorganic impurities from the bio-fuels, the laboratories used different sample preparations, each specific for the analysis technique used.

ICP-MS/ICP-OES—(a) peroxide digestion—0.2 g of wood samples were weighed into the microwave high-pressure vessels. A total of 4 mL H<sub>2</sub>O<sub>2</sub> was added to the vessels. (b) Acid digestion: 0.3 g of wood samples were weighed into the microwave digestion vessels. A total of 2.5 mL of HNO<sub>3</sub>, 1.5 mL of H<sub>2</sub>O<sub>2</sub>, and 0.2 mL of HF was added to the vessels. The following temperature program was used for both peroxide and acid digestions: heating for 30 min to 150 °C and holding for 20 min at 150 °C. The biodiesel samples were diluted with ICP solvent (1:2, *v:v*) and directly aspirated to ICP-OES oxygen (50 mL/min), which was used as an additional gas to prevent carbon deposition.

MWP-AES—raw wood pellet samples were prepared by milling. Subsamples for the microwave digestion technique using a mixture of acids were obtained from the mechanically homogenized sample. Roughly 0.5 g of raw wood samples were weighed accurately to the nearest 0.01 mg directly into microwave digestion Teflon vessels. A total of 9 mL of HNO<sub>3</sub> and 1 mL of H<sub>2</sub>O<sub>2</sub> were added in predetermined order by means of a digital pipet with clean plastic tips. The heating was performed using a microwave digestion system, according to the following temperature program: heating for 20 min to 210 °C; holding for 15 min at 190 °C. The samples were collected in plastic measuring vessels and the analysis was approached with the necessary dilutions for the elements of interest.

ID-MS—a sample of 0.25 g was accurately weighed into quartz vessels; then, 5 mL of concentrated HNO<sub>3</sub> (65%) and 1 mL of 30% H<sub>2</sub>O<sub>2</sub> were added, the vessels were closed, and the digestion was conducted using a high-pressure asher (Anton Parr, Graz, Austria) with  $T_{\max} \approx 300$  °C and  $p_{\max} \approx 130$  bar.

Ion-exchange chromatography with 1 mL of AG 1X8 resin filled in Eichrom columns: (1) sample loading with 2 mL of HNO<sub>3</sub> (0.028 mol/L); (2) elution of matrix with water; and (3) elution of S with 8 mL of HNO<sub>3</sub> (0.25 mol/L). The isotope ratios <sup>32</sup>S/<sup>34</sup>S were measured using the am Element 2 ICP-MS in medium mass resolution to remove plasma-based interferences; the mass fraction of the measured sample solutions was  $\approx 1$  µg/g.

### 2.3.2. Ash Content

Ash content: a laboratory sample for the determination of the ash content was prepared according to the ISO14778 standard [14], and from the laboratory sample, the general analysis sample was prepared according to ISO 14780 [15], with a nominal size of 1 mm or less. This type of sample for general analysis can be used both for the determination of ash content and the determination of other analyses that the laboratory needs (for example, humidity, different chemical elements, calorific value, etc.). The general analysis sample must include enough material to determine these analyses.

The sample must be wet before grinding to a maximum size of 1 mm. If it is very wet, then the sample is pre-dried in the oven at a maximum temperature of 40 °C to minimize the loss of moisture in the subsequent processes of dividing the sample and to facilitate the sample preparation processes. All samples (including those that were pre-dried) must be spread on a tray with a depth of a few particles and must be left for at least 4 h in the laboratory until they attain equilibrium with the environmental conditions in the laboratory (we monitored if a constant mass was obtained at an interval of 4 h by reweighing). Thus, from a minimum of 500 g of the laboratory sample with a size of 31.5 mm, we must obtain a minimum of 30 g of grinding with a size of 1 mm, according to ISO14780 [15]. After grinding, the ground material obtained was placed in trays with a depth of a few millimeters and left for at least 4 h in the laboratory to be in balance with the environmental conditions in the laboratory. We monitored if a constant mass was obtained every 4 h by reweighing the sub-sample; then, it was placed in hermetically sealed brown-glass containers. The general analysis sample must include enough material to determine the ash and moisture contents. Thus, the determination of the ash content must be conducted directly on a test portion from the general analysis sample of approximately 1 g, with the simultaneous determination of the moisture content on a similar test portion in accordance with ISO 18134-3 [16]. The procedure for determining the ash content is described in the ISO 18122 standard [17] and involves the slow heating of the sample in the oven to a temperature of  $250 \pm 10$  °C for 30 to 50 min, maintaining it at this temperature for 1 hour, to ensure the elimination of volatile substances up to calcination, slow heating to a temperature of  $550 \pm 10$  °C for 30 min, and holding at this temperature for at least 120 min.

The ash content was determined by calculating the residue left after the sample was heated in air under strictly controlled conditions regarding time, sample mass, and equipment specifications, at a controlled temperature of  $550 \pm 10$  °C with the formula presented in Section 2.4.2, Equation (3).

## 2.4. Method Development

### 2.4.1. Inorganic Impurities

The ICP-MS validation method for the identification of the inorganic impurities from biofuels was performed by developing and individually validate 4 methods, each one specific for a certain group of elements with their range of concentration characteristic to the biofuels: method I: specific for the identification and quantification of Na(23), Cr(52), Ni(60), Pb(208), Cu(63), and Cd(111) within the range of concentration of 1 to 50 ppb; method II: specific for the identification and quantification of Ca(40) within the range of concentration of 1 to 25 ppm; method III: specific for the identification and quantification of Mg(24), Al(27), K(39), Mn(55), Fe(57), and Zn(166) within the range of concentration of 0.08 to 1 ppm; and method IV: specific for the identification and quantification of S(32), Si(28), Ti(47), and P(31) within the range of concentration of 0.5 to 1.5 ppm. Five-point calibration curves were performed for each element from the methods.

To validate the analysis method, the following parameters were performed:

- Method detection limit represents the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from the method blank results; a. LOD (limit of detection) meaning the lowest concentration of an analyte in a sample that can be consistently detected with a stated probability; b. LOQ (minimum limit of quantification) meaning the lowest concentration of the calibration standard on the calibration curve, where the analyte response is reproducible, and the precision and accuracy are within 15% of the CV (coefficient of the variation) of the repeatability and reproducibility and 15% of the nominal concentration; and c. ULOQ (maximum limit of measurement) meaning the highest analyte concentration that can be determined.

For the detection limit determination, for each method, we performed 10 analyses of the standard for a value below the lower limit of the calibration curve (LOD) experiment chosen. After the 10 analyses of the standard, the medium concentration measured for each element was obtained for each method presented in Table 1 with the corresponding repeatability ( $SD_{\text{mediumconc.}}$ ). Thus the calculated detection of limit was:  $LOD_{\text{calculated}} = 0 + 3 \times SD_{\text{mediumconc.}}$ , where  $SD_{\text{mediumconc.}}$ —the repeatability of the medium concentration of the chemical element.

**Table 1.** Method detection limit. Values for LOD calculated, LOQ determined, and ULOQ measured.

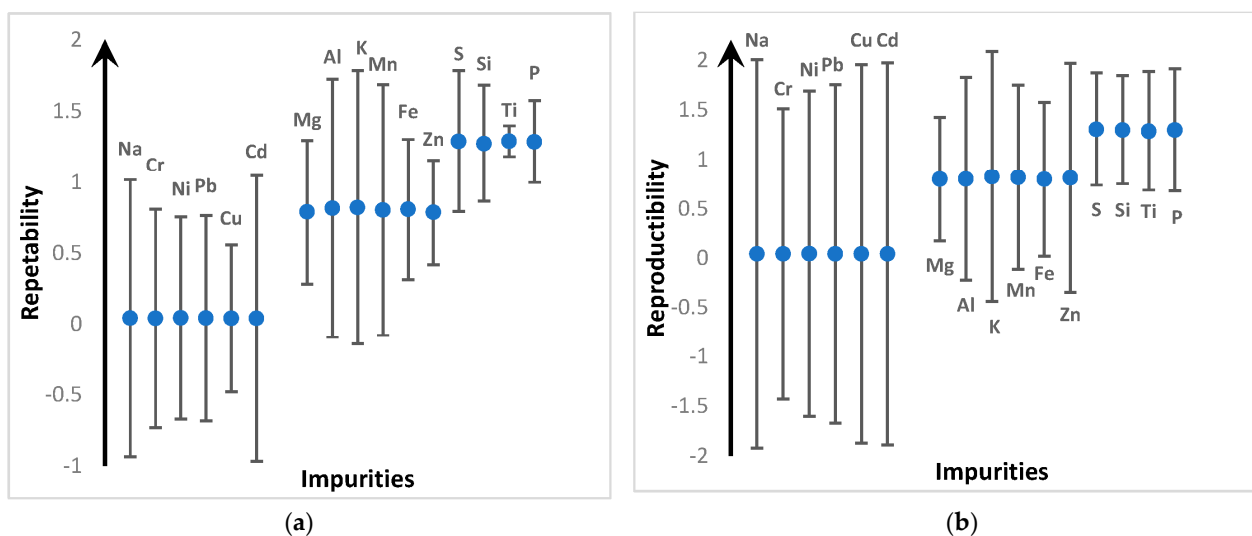
Method	Element	LOD (ppm) exp.	Medium Concentration Measured (ppm)	$SD_{\text{mediumconc.}}$ (ppm)	LOD (ppm) Calculated	LOQ (ppm)	ULOQ (ppm) exp.	ULOQ Measured (ppm)	$SD_{\text{ULOQ}}$ (ppm)
Method I	Na(23)	0.0005	0.00023	0.00029	0.00087	0.00261	0.06	0.057	0.0002
	Cr(52)		0.00019	0.00001	0.00003	0.001		0.059	0.0004
	Ni(60)		0.00026	0.00047	0.000141	0.001		0.058	0.0008
	Pb(208)		0.00055	0.00086	0.000258	0.001		0.056	0.0004
	Cu(63)		0.00089	0.00063	0.000189	0.001		0.058	0.0005
	Cd(111)		0.00093	0.00024	0.000072	0.001		0.059	0.0001
Method II	Ca(40)	0.5	0.5500	0.041231	0.123693	1	30	29.500	0.480
Method III	Mg(24)	0.06	0.0645	0.00046	0.00138	0.08	2	1.889	0.030
	Al(27)		0.0791	0.00104	0.00312	0.08		1.851	0.030
	K(39)		0.0946	0.00041	0.00123	0.08		1.820	0.041
	Mn (55)		0.0777	0.00087	0.00261	0.08		1.805	0.041
	Fe(57)		0.0582	0.00528	0.01584	0.08		1.864	0.013
	Zn(166)		0.0651	0.00063	0.00189	0.08		1.807	0.038
Method IV	S(32)	0.1	0.7433	0.05105	0.15315	0.50	2	2.080	0.165
	Si(28)		0.0099	0.00146	0.00438	0.50		1.493	0.015
	Ti(47)		0.0872	0.01589	0.04767	0.50		1.606	0.005
	P(31)		0.0682	0.02040	0.06120	0.50		1.610	0.010

To determine the maximum limit of measurement ( $ULOQ_{\text{measured}}$ ), we performed for each method 10 other analyses of the standard for a value higher than the upper limit of

the calibration curve (ULOQ) experiment chosen. The obtained  $ULOQ_{measured}$  values are presented in Table 1, together with the corresponding repeatability ( $SD_{ULOQ}$ ).

- Accuracy of the method (repeatability and reproducibility) represents the degree of agreement among individual test results when the procedure was applied repeatedly to multiple samplings.

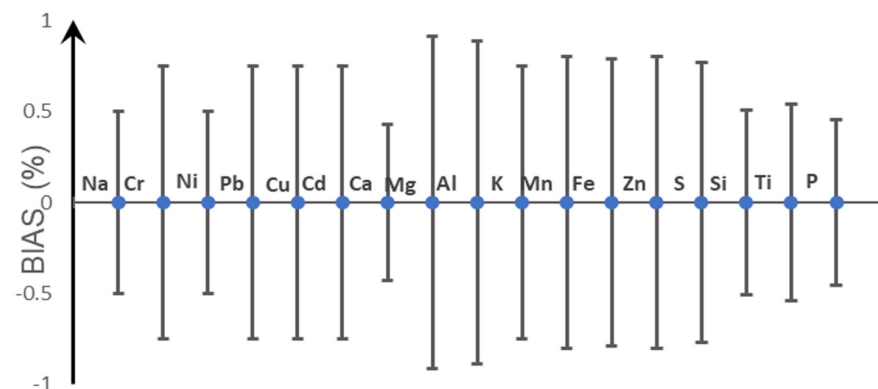
For the determination of the repeatability of the method, for each method, we chose a concentration of the standard within the calibration range, which was analyzed 10 times, in the same day, with the same conditions (operator, analytical equipment, measurement conditions, solvents, and room temperature) (Figure 1a). For the determination of the reproducibility of the method, for each method, we chose a concentration of the standard within the calibration range, which was analyzed 10 times, in different days, with the same conditions (operator, analytical equipment, measurement conditions, solvents, and room temperature) (Figure 1b).



**Figure 1.** Accuracy of the method: (a) repeatability and (b) reproducibility.

The trueness of the method was performed by determining the BIAS (%). For each method, the laboratory chose a concentration of the standard within the calibration range, which was analyzed 10 times, in different days, with the same conditions (operator, analytical equipment, measurement conditions, solvents, and room temperature) (Figure 2). BIAS was calculated with the following formula:

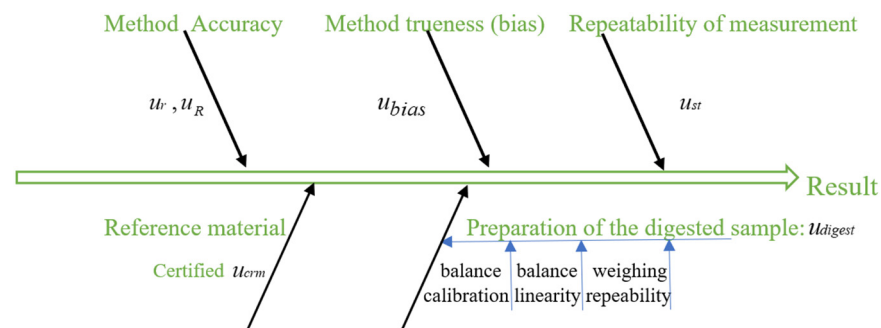
$$\text{BIAS (\%)} = 100 * ((\text{Value measured} - \text{Value reference}) / (\text{Value reference})) \quad (1)$$



**Figure 2.** The trueness of the method.



- Measurement uncertainty and uncertainties budget. The standard uncertainty for the determination of inorganic impurities in biofuel is composed of the precision components given by the repeatability ( $u_r$ ) and reproducibility ( $u_R$ ) of the the method and the laboratory, a systematic error ( $u_{BLAS}$ ) highlighted by the bias (difference between the reference and experimentally determined values) of the method and the laboratory, a component resulting from the preparation of the digested sample ( $u_{digest}$ ), a component given by the uncertainty of the certified reference material ( $u_{crm}$ ), and the repeatability component when measuring the concentration of inorganic impurities in biofuel ( $u_{st}$ ) (Figure 3). For the determination of the uncertainty for the prepared digested sample ( $u_{digest}$ ), we chose a standard concentration from each method. A total of 10 samples were analyzed by ICP-MS as they were, and each of them was digested into the microwave (blank method for sample preparation by microwave digestion) and analyzed again by ICP-MS. The uncertainty ( $u_{digest}$ ) represents the relative standard deviation of the repeatability of the differences between the experimentally determined values for the digested and undigested samples.



**Figure 3.** Sources of uncertainty for determining the concentration of inorganic impurities.

$$u = \sqrt{u_R^2 + u_r^2 + u_{bias}^2 + u_{digest}^2 + u_{crm}^2 + u_{st}^2} \quad (2)$$

#### 2.4.2. Ash Content

Ash content: the ash content  $A_d$  of the sample based on the dry product was calculated with the following formula:

$$A_d = \frac{(m_3 - m_1)}{(m_2 - m_1)} \times 100 \times \frac{100}{100 - M_{ad}} \quad (3)$$

$m_1$ —empty crucible mass in grams;

$m_2$ —crucible mass together with the test portion, in grams;

$m_3$ —crucible mass together with ash, in grams;

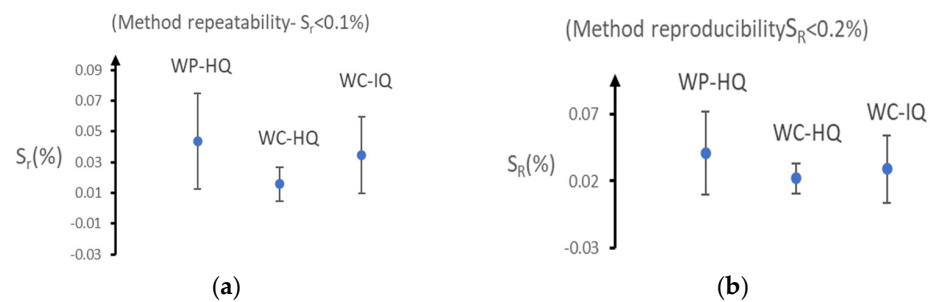
$M_{ad}$ —moisture content of the test portion used for the determination in percent (%).

Accuracy of the method was determined by the standard deviation of the repeatability and reproducibility of the differences between the experimentally determined values for a series of samples for each type of solid fuel analyzed. (Figure 4). The standard deviation of the repeatability of the differences between the experimentally determined ash values was calculated with the following relation:

$$S_r = \sqrt{\frac{\sum d_r^2}{n}} \quad (4)$$

$d_r$ —represents the differences between the experimentally determined values under repeatability conditions;

$n$ —the number of determinations.



**Figure 4.** Accuracy of the method: (a) repeatability and (b) reproducibility.

When determining the ash from the solid biofuel, the standard deviation of the repeatability of the differences between the experimentally determined values for the same sample must be less than 0.1% (absolute value), according to ISO 18122 [17] (Figure 4a). To determine the accuracy of the method, the laboratory analyzed 9 samples for each type of solid biofuel analyzed under repeatability conditions.

The standard deviation of the reproducibility of the differences between the values determined experimentally by the three laboratories under reproducibility conditions was calculated with the following formula:

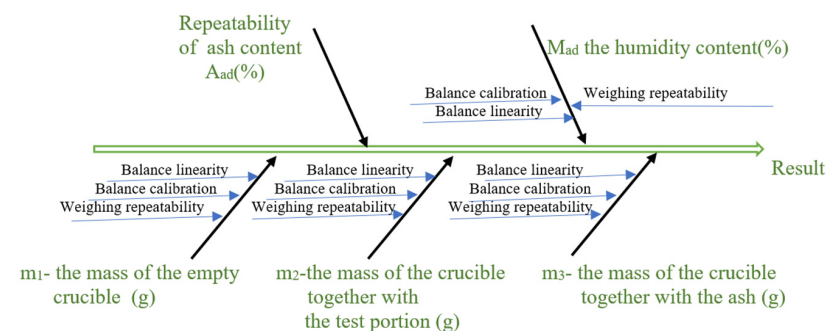
$$S_R = \sqrt{\frac{\sum d_R^2}{n}} \quad (5)$$

$d_R$ —represents the differences between the values experimentally determined by each laboratory under conditions of reproducibility;

$n$ —the number of determinations.

The reproducibility value of the method must be less than 0.2% (absolute value) according to ISO 18122:2015 [17] (Figure 4b).

- Measurement uncertainty and uncertainties budget. The formula for calculating the ash content (3) resulted in the following sources of uncertainty (Figure 5):



**Figure 5.** Sources of uncertainty for determining the concentration of ash content in solid biofuel.

$m_1$ —the mass of the empty crucible in grams;

$m_2$ —the mass of the crucible together with the test portion, in grams;

$m_3$ —the mass of the crucible together with the ash, in grams;

$M_{ad}$ —moisture content in (%) of the test portion used for determining the repeatability of the values obtained when determining the ash content.

The standard uncertainty for the determination of ash content was composed of the precision component given by the repeatability of ash content ( $S_{A_d}$ ), an uncertainty of humidity content ( $u_{M_{ad}}$ ), a component given by the mass of the empty crucible ( $u_{m_1}$ ), a component given by the mass of the crucible together with the test portion ( $u_{m_2}$ ), and a component given by the mass of the crucible together with the ash content ( $u_{m_3}$ ). Each



component of the mass was influenced, in turn, by the calibration of the balance, the precision and linearity of the balance, and the repeatability of the weighing (Figure 5). The values of the uncertainties that contributed to the composed standard uncertainty of the ash content are presented in Table 2.

**Table 2.** Measurement uncertainty of the ash content.

Parameter	Notation	Unit	Value HQ-WP	Value HQ-WC	Value IQ-WC	Contribution to Composed Standard Uncertainty				
						Notation	Unit	Value HQ-WP	Value HQ-WC	Value IQ-WC
The moisture content of the test portion	$M_{Ad}$	%	6.37	7.46	7.87	$u_{Mad}$	%	0.1122	0.0726	0.0771
The mass of the empty crucible	$m_1$	g	13.2212	13.4741	13.9010	$u_{m1}$	g	0.3232	0.3392	0.2601
The crucible mass with the test portion	$m_2$	g	14.2708	14.4991	14.9327	$u_{m2}$	g	0.3241	0.3375	0.2663
The crucible mass with ash	$m_3$	g	13.2235	13.4761	13.9117	$u_{m3}$	g	0.3232	0.3392	0.2601
Repeatability of ash content	$A_{Ad}$	%	0.22982	0.2099	1.1326	$S_{Ad}$	%	0.0290	0.0145	0.0527
Result of ash content		%	0.23	0.21	1.13	$U (k = 2)$	%	0.06	0.03	0.13

### 3. Results

BRML (Romania), TUBITAK UME (Turkey), IMBIH (Bosnia and Herzegovina), and BAM (Germany) determined the inorganic impurities in solid and liquid biofuel by ICP-MS, ICP-OES, MWP-AES, WDXRF, and ID-MS methods.

For this purpose, wood pellets, high-quality wood chips, and industrial-quality, biodiesel, and reference materials were analyzed using several digestion and determination methods. The digestion methods investigated included wet-digestion in closed vessels with different acid mixtures.

The qualitative investigation involved the identification of 17 elements as inorganic impurities: Na, Cr, Ni, Cu, Cd, Pb, Ca, Mg, Al, K, Mn, Fe, Zn, S, Si, Ti, and P. The results for the obtained inorganic impurities' contents for each type of biofuel, high-quality wood pellets (HQ-WPs), high-quality wood chips (HQ-WCs), industrial-quality wood chips (IQ-WCs), and biodiesel are presented in Tables 3 and 4.

**Table 3.** High-quality wood pellets (HQ-WPs) and biodiesel inorganic impurities analyses.

Impurity	HQ-WP								BIODIESEL			
	BRML		TUBITAK		IMBIH		BAM		BRML		TUBITAK	
	ICP-MS		MWP-AES		Quantity (mg/kg)		ID-MS		ICP-MS		ICP-OES	
	Value	$U (k = 2)$	Value	$U (k = 2)$	Value	$U (k = 2)$	Value	$U (k = 2)$	Value	$U (k = 2)$	Value	$U (k = 2)$
Na	49.68	0.102	-	-	-	-	-	-	0.25	0.0634	0.33	0.03
Cr	4.60	0.006	0.10	0.020	-	-	-	-	0.47	0.0061	-	-
Ni	0.15	0.010	0.02	0.011	0.70	22.2	1.33	0.0002	-	-	-	-
Pb	0.12	0.009	0.08	0.025	2.94	2.370	4.00	0.001	-	-	-	-
Cu	0.83	0.008	0.66	0.014	8.89	0.140	7.67	0.0002	-	-	-	-
Cd	0.20	0.010	0.22	0.005	-	-	-	-	0.009	0.0049	-	-
Ca	127.90	1.201	674	4	-	-	968.00	0.002	-	-	0.47	0.2551
Mg	156.40	0.103	175	2	-	-	296.00	0.006	-	-	0.11	0.0549
Al	8.19	0.073	16.10	0.600	-	-	-	-	-	-	35.4	0.0730
K	324.80	0.137	251	10	-	-	396.00	0.002	-	-	0.15	0.0764
Mn	63.70	0.065	71.20	0.200	-	-	72.00	0.001	-	-	0.14	0.0645
Fe	12.15	0.070	9.50	1.200	8.94	1.320	14.33	0.001	-	-	3.68	0.0696
Zn	5.86	0.069	8.80	0.100	8.89	1.560	7.67	0.0002	-	-	3.65	0.0685
S	26.35	0.275	73	1.00	-	-	91.00	0.001	69	3.5	1.1	0.2332
Si	317.40	0.100	-	-	86.20	0.120	154.00	0.001	-	-	405.6	0.1241
Ti	0.88	0.096	-	-	-	-	-	-	-	-	0.59	0.0956
P	8.57	0.098	60	2	-	-	744	0.001	-	-	0.03	0.0199

**Table 4.** High-quality wood chips (HQ-WCs) and industrial-quality wood chips (IQ-WCs) inorganic impurities analyses.

Impurity	HQ-WC										IQ-WC									
	BRML		TUBITAK		IMBIH		BAM		BRML		TUBITAK		IMBIH		BAM					
	Quantity (mg/kg)				MWP-AES		WDXRF		ID-MS		Quantity (mg/kg)				MWP-AES		WDXRF		ID-MS	
	Value	U(k = 2)	Value	U(k = 2)	Value	U(k = 2)	Value	U(k = 2)	Value	U(k = 2)	Value	U(k = 2)	Value	U(k = 2)	Value	U(k = 2)	Value	U(k = 2)	Value	U(k = 2)
Na	62.01	0.22	-	-	-	-	-	-	-	65.20	0.04	-	-	-	-	-	-	-	-	-
Cr	3.43	0.01	0.198	0.06	-	-	-	-	-	2.99	0.31	0.589	0.15	-	-	-	-	-	-	-
Ni	0.15	0.01	0.105	0.02	0.22	71.1	4.00	0.01	-	0.16	0.01	0.400	0.27	1.03	27.3	3.00	0.01	-	-	-
Pb	0.48	0.01	0.236	0.01	1.92	10.4	0.01	0.01	-	0.62	0.01	0.383	0.04	3.54	2.43	0.33	0.01	-	-	-
Cu	0.89	0.01	0.754	0.13	-	-	-	-	-	1.17	0.01	1.25	0.19	-	-	-	-	-	-	-
Cd	0.11	0.01	0.104	0.01	-	-	6.33	0.01	-	0.11	0.01	0.136	0.01	-	-	-	-	-	-	-
Ca	176.8	1.19	301	18	-	-	-	-	-	1727	1.58	2455	32	-	-	-	-	-	-	-
Mg	178.6	0.10	96	2	-	-	-	-	-	632.4	0.09	300	3	-	-	-	-	-	-	-
Al	69.27	0.07	15	1	-	-	-	-	-	152.2	0.08	86	4	-	-	-	-	-	-	-
K	415.1	0.12	473	25	-	-	-	-	-	1743	0.29	1134	34	-	-	-	-	-	-	-
Mn	68.85	0.06	64	1	-	-	-	-	-	66.25	0.07	41	1	-	-	-	-	-	-	-
Fe	21.30	0.07	20	2	18.4	1.66	34.33	0.01	-	260.1	0.07	51	6	72.1	0.33	91	0.01	-	-	-
Zn	9.74	0.06	5.4	0.8	14.3	2.71	10.33	0.01	-	28.96	0.07	19.2	0.2	69.6	0.08	17.33	0.01	-	-	-
S	99.38	0.08	72	2	-	-	-	-	58	2.2	159.0	0.11	152	1	-	-	-	-	124	5.3
Si	727	0.09	-	-	-	-	286.3	0.01	-	837.4	0.09	-	-	346	0.04	1720	0.02	-	-	-
Ti	3.32	0.09	-	-	-	-	-	-	-	11.88	0.09	-	-	-	-	-	-	-	-	-
P	107	0.10	81	13	-	-	-	-	-	234.3	0.11	143	5	-	-	-	-	-	-	-

BRML, TUBITAK, and DTI determined the ash content for three types of solid bio-fuel (wood pellets, high-quality wood chips, and industrial-quality wood chips) in the measurement range of 0–1.2% with absolute repeatability values less than 0.1% and reproducibility less than 0.2% using the method described above. The results are presented in Tables 5 and 6.

**Table 5.** The amount of ash in the measurement range of 0–1.2% with absolute repeatability values less than 0.1% (according to EN ISO 18122 [17]).

	High-Quality Wood Pellets (HQ-WPS)		High-Quality Woodchips (HQ-WCS)		Industrial-Quality Wood Chips (IQ-WCS)	
	Quantity (%)					
	Value	SD	Value	SD	Value	SD
BRML	<1%	<0.1%	<1%	<0.1%	<1.1%	<0.1%
TUBITAK	0.23	0.029	0.21	0.015	1.13	0.053
DTI	0.28	0.028	0.24	0.006	1.10	0.032
	0.27	0.015	0.22	0.029	1.02	0.188

**Table 6.** The amount of ash in the measurement range of 0–1.2% with reproducibility values less than 0.2% (according to EN ISO 18122 [17]).

	High-Quality Wood Pellets (HQ-WPS)		High-Quality Wood Chips (HQ-WCS)		Industrial-Quality Wood Chips (IQ-wcs)	
	Quantity (%)					
	Medium value	S <sub>R</sub>	Medium value	S <sub>R</sub>	Medium value	S <sub>R</sub>
BRML	<1%	<0.2%	<1%	<0.2%	<1%	<0.2%
TUBITAK	0.26	0.041	0.22	0.022	1.08	0.029
DTI						

### 4. Discussion

The partners involved in this study developed and validated analytical procedures for the determination of inorganic impurities in solid and liquid biofuels. They established the uncertainty budget and developed a method for determining the amount of ash in the

measurement range of 0–1.2% with absolute repeatability values less than 0.1% and absolute reproducibility values of 0.2% (according to EN ISO 18122 [17]). Improved methodologies for the measurement and characterization of solid and liquid biofuels were developed.

The solid biofuels investigated were high-quality wood chips (HQ-WCs), industrial-quality wood chips (IQ-WCs), and wood pellets (WPs), and biodiesel was chosen for the liquid biofuels to be investigated. The methods were validated by evaluating some parameters, such as detection limit, precision, accuracy, and uncertainty. The methods demonstrated good parameters for precision, accuracy, and trueness; the coefficients of variation were lower than 2%. The limits of detection and quantification also showed good results.

BRML (Romania), TUBITAK UME (Turkey), IMBIH (Bosnia and Herzegovina), and BAM (Germany) through complementary validated methods (ICP-MS, MWP-AES, WDXRF, and ICP-OS, ID-MS) obtained traceable measurement results.

The qualitative investigation involved the identification of 17 elements as inorganic impurities: Na, Cr, Ni, Cu, Cd, Pb, Ca, Mg, Al, K, Mn, Fe, Zn, S, Si, Ti, and P. All impurities were evaluated quantitatively.

Thus, by analyzing the results obtained by the partners for both pellets and wood chips, it can be seen that these results are scattered. The main reason why these results are scattered is the heterogeneity of the biofuel samples. This heterogeneity was given by the chemical composition of the biomass (the raw material from which the biofuel is obtained). Thus, the biomass is composed of cellulose molecules (C6 polymer), surrounded by hemicellulose (predominantly C5 polymers with inclusions C6) and the lignin that is deposited between the fibers. The contents of cellulose, hemicellulose, and lignin in plant biomass is different and, as a result, the energy potential of different types of biomasses is quite varied [18].

The calorific value of woody biomass is higher because it has a higher percentage of lignin compared to biomass from agricultural residues and herbaceous energy crops that have a lower percentage of lignin. At the same time, a complete characteristic of biomass, used for the production of solid biofuels, requires a more detailed analysis of the chemical composition, especially of the elements that influence the combustion process. The chemical elements include major ash-forming elements (Al, Ca, Fe, Mg, P, K, Si, Na, and Ti), volatile minor elements (Cd, Pb, and Zn), and non-volatile or partially volatile elements (Cr, Cu, and Mn) [18]. All these elements were determined and presented in Tables 3 and 4.

Another cause that determined the dispersion of the results obtained for the determination of inorganic impurities in high-quality wood pellets (HQ-WPs) and high-quality and industrial-quality wood chips (HQ-WCs and IQ-WCs) was the humidity of the environment. The measurements of these impurities were performed in different laboratories, in different countries, in different environmental conditions with different methods. Pellets and wood chips are hygroscopic materials; therefore, the humidity of the environment played an important role in the accuracy of the results.

Finally, the other reasons that contributed to the spread of the results was the preparation of the samples for the analyses (how to take samples from the batch, the grinding tools, and grinding granulation) and different experimental practices (different sample digestion methods, different equipment, and different sample analysis methods).

The purpose of this study was to present and develop valid methods for determining inorganic impurities and the ash content generated by these impurities, and to obtain traceable measurement results. All the results obtained by the partners and presented in Tables 3 and 4 fall within the limits presented in the quality standards corresponding to wood pellets and chips, ISO 17225-2,4 and EN 14214, respectively, for biodiesel.

In order to solve the scattered results obtained by the partners (Tables 3 and 4), candidate reference materials for biofuels were established within the Biofmet project. The validated methods mentioned above were used for the certification of candidate reference materials (including homogeneity, stability, and characterization tests) [19]. These

homogenous candidate reference materials were intended to establish traceability for the calorific value and ash/impurity content.

At the same time, knowing the ash content (in combination with the water content) is crucial for determining the calorific value and thus the energy content of the biofuel. Ash content quantification and characterization were necessary to gain an insight into the possibility of slag formation [9]. Knowing how much ash is present with biofuel may have economic consequences and impacts on the technological process, as well as environmental protection [9].

The ash content represents a very important quality characteristic of solid biofuels being an important parameter for biofuel deliveries. Thus, the amount of ash from high-quality wood chips (HQ-WCs), industrial-quality wood chips (IQ-WCs), and wood pellets (WPs) was determined, and the values in the range of 0.2–1.1% were obtained with absolute repeatability values of less than 0.1% and absolute reproducibility values of 0.2%, according to Tables 5 and 6.

Additionally, during handling waste and deposition as such, it was important to have measurement techniques that provided information on the total amount and composition of the ash [9]. The elements Al, Ca, Fe, Mg, P, K, Si, Na, and Ti present in the solid biofuels were, in fact, major elements in biofuel ash compared to the biofuels. The determination of these elements can be used to assess ash behavior in a thermal conversion process or to assess the utilization of ash [9]. This study provided and developed a metrological framework for online methods by first understanding the parameters needed to define the methodologies required for traceability. This included the identification and quantification of inorganic impurities and the determination of ash content. The improved methodologies will be used to ensure the traceability of the results of measurements in the field and validation of online methods. The online analysis of industrial processes shows an increasing interest because of the reduction in the time delay for offline sample preparation and the subsequent analyses via conventional methods. The continuous monitoring of materials' characteristics is a prerequisite for the direct control of the process.

The dissemination of the traceability concept to field laboratories through the implemented metrology infrastructure is very important for industrial validation. The determination of all these chemical and physical parameters aims at harmonizing the measurement standards, which is obviously essential for the confidence in international quality assurance needed to facilitate global trade and conformity assessments of such products [19].

## 5. Conclusions

The present study showed several developed methods for the determination on impurities and ash content in solid and liquid biofuels, in order to create a homogeneous certified reference material, which can be characterized by any of these methods and with traceable results. The methods were developed following the ISO standards in the field, which were additionally completed with experimental information about the precision, accuracy, and bias of the methods, and the factors that intervened in the measurement of uncertainty.

Considering the technique used, working conditions within the laboratory, different sample preparation methods, and different equipment used, the few scattered results obtained by the laboratories were expected. The results obtained for ash content are very similar between the laboratories; however, in the case of the quantification of the impurities, the range of similarities was greater. Apart from the different conditions for working in laboratories, the most important factor was determined by the sensibility of the equipment used for analyzing the samples. Further studies will focus on the interlaboratory characterization of the certified reference material.

This study had a great impact on both the producers of solid biofuels and the users of these products. The development of the validated methods to determine the amount and nature of the impurities in solid and liquid biofuels brings us one step closer to achieving a reduction in greenhouse gas emissions.

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