19ENG09 BIOFMET

D1: Report on required parameters and metrological methodologies for measuring calorific value of biofuels and qualifying impurities, moisture, and ash content.

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1 Introduction

The emission of greenhouse gases represents a major world threat as it causes the rise of average global temperature. The earth has recorded around 40 % increase in CO_2 emissions into the atmosphere since the industrial revolution. This increase is mainly caused by burning fossil fuels, razing the forests, and other industrial activities. Therefore, the need for green and clean alternative fuels became urgent. The European Union set a 10 % target for renewable energy use in transport for 2020, and a 14 % target for 2030. Renewable energy sources include wind power, solar power (thermal, photovoltaic, and concentrated), hydro power, tidal power, geothermal energy, ambient heat captured by heat pumps, and biofuels.

By 2030, the European Commission aims for biomass usage to be increased and represent over 27 % share of renewable energy consumption [1]. The main objective of the BIOFMET project is to research and develop online metrological methods to analyse solid and liquid biofuels. More specifically, the project focuses on methods to determine calorific value, moisture, ash content, and methods to quantify impurities. These parameters are important in process control wherever biofuels are used or produced and form the basis of accounting in biofuel trade. A decisive requirement is that the methods are metrologically traceable to basic SI units. In this way, this project aims to support the transition to clean CO_2 neutral energy and the independence of fossil fuels, where biofuels will have a crucial role to secure the stability of the future energy supply.

Biofuels can be categorized into liquid and solid fuels. Wood chips and wood pellets are the most common type of solid biofuels. Liquid biofuels are fuels derived from the direct conversion of solid biomass, biowaste, and agricultural residues (if the waste has a biological origin).

Different generations of biofuels have been developed during the last decades [2,3] depending on sugar, starch, vegetal oil, or animal fats using conventional technologies (by the action of microorganisms and enzymes through the fermentation of sugar, starches, or cellulose). Basic raw materials to produce first-generation biofuels include seeds (such as soya seeds, sunflower seeds), cereals (such as grains) also used in human food. The most common first-generation biofuels are vegetal oils, biodiesel, bio-alcohols (ethanol), and biogas.

Second generation biofuels, also called "olive green" or "cellulosic-ethanol" fuel, can be made from almost any form of biomass. If made from forest or crop-residues, they do not compete with food for feedstock. Waste vegetable oil, forest residue, industry residue, and sustainable biomass are the primary feedstock for second-generation biofuels. However, if made from dedicated energy crops, they compete with food for land and water resources.

Third generation biofuels, also known as "algae fuel" or "oilage", are produced from algae. Algae are used in the production of all types of biofuels such as biodiesel, gasoline, butanol, propanol, and ethanol with high yield; approximately ten times higher than the second-

generation biofuel. Cultivation of third generation biofuel biomass also helps to maintain environmental balance by consuming the CO_2 present in the atmosphere.

The fourth-generation biofuels combine genetically engineered feedstock with genomically synthesized microorganisms, such as cyanobacteria, to efficiently generate bioenergy, and they are made using nonarable land, similar to third-generation biofuels. The process utilizes bioengineering techniques to modify algal metabolism and properties to produce biofuel from photosynthetic organisms. They aim to simultaneously produce bioenergy and capture and store CO_2 during production stages. The geo-sequestered CO_2 stored in exhausted oil/gas fields, mineral storage (as carbonates), and saline aquifers reduces CO_2 emissions and makes the fourth-generation biofuel production carbon negative. Therefore, these biofuels require a minimum number of steps between sun providing energy and transforming this energy into biofuel, thereby avoiding fermentation and processing procedures. This is an emerging field, and extensive research is being undertaken to discover new solutions for the sustainable conversion of energy to fuel. The use of biofuel allowed for large-scale savings in the transport sector, alongside improvements in vehicle efficiency, the second great advantage of biofuels raised from their potential for greenhouse gas savings. Thus, biofuel promotion offered benefits both for the security of energy supply and for climate change policy.

This report is developed in the scope of Task 1.1 of the BIOFMET project and aims to assess the metrological needs of the biofuel industry. To accomplish this, a literature review and a stakeholders' survey about the requirements on methods for (traceable) measurement of moisture, ash, calorific value, and inorganic and organic impurities in biofuels were carried out.

After having the stakeholders' survey online on the project's website for over a month, about 58 responses were collected and analysed. Firstly, each participant had to answer general questions about which sector they represent and which kind of biofuel they use. Then, each participant had to answer independent sections one for each of the following parameters: calorific value, moisture, and impurities. The results of each section are analysed in the following chapters. The questions of the survey are presented in Annex A.

Most participants of the survey, around 45 %, are from research institutes. Adding to that, 22 % are from analysis laboratories and quality facilities, which confirms the need for a profound metrological procedure and analysis under defined uncertainty budget for the determination of the calorific value, moisture, and impurities of biofuels. Furthermore, around 31 % of the participants are from industry, divided between power plants and biofuel producers (Figure 1).

As shown in Figure 2, around 38 % of the respondents use solid biomass as wood chips and wood pellets. Then comes biodiesel with 37 %, followed by bioethanol (17 %) and algae (11

%). The use of a specific kind of biofuel will depend mainly on which sector. For example, in power plants the majority tend to use solid biomass as a fuel.
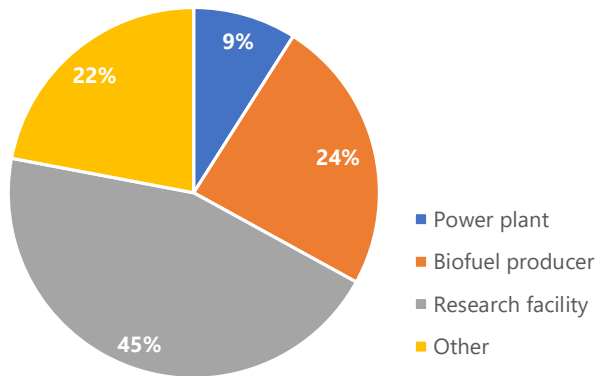

Figure 1. Distribution of the stakeholders' sector
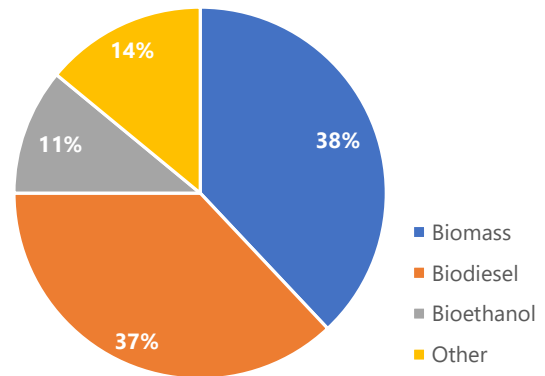
Figure 2. Distribution of the stakeholders' type of biofuel use

2 Calorific value and calorimetry

The determination of the physical properties of the different generations of biofuels is an important aspect to determine its suitability in a particular industry or field, since it is one of the quality control criteria that reflects a specific fuel's performance. For example, the current techniques for determining the calorific value of biomass show poor results in intercomparison between laboratories, and within this project, the goal is to improve the current methods to ensure a better interlaboratory reproducibility.

Calorific value can be defined as the total amount of heat energy released by a specified amount (mass) of the substance during complete combustion, whether in food or fuel. The SI unit for the calorific value is joule per kilogram (J/kg), but alternative units are often used (e.g., cal/g or MJ/ton). The calorific value can be measured by calorimetry.

Calorimetry is the science or act of measuring changes in a body to measure the heat transfer process released or absorbed, which is associated with changes of its state due to physical changes, chemical reactions, or phase transitions under specified constraints. Calorimetry is performed with a calorimeter.

A calorimeter is a special device used for measuring heat. It mainly consists of a metallic vessel (e.g., bomb) made of materials that are good conductors such as stainless steel and aluminium etc. Typically, there is also the function of stirring inside the bucket. An insulating jacket surrounds this metallic bucket with a stirrer to prevent any possible heat loss to the environment or gain heat, which affects the vessel's reaction. As a main part of the calorimeter, a thermometer measures the change in the bucket's thermal properties, mainly to determine the temperature rise of the sample caused by the ignition.

2.1 Types of calorimetry

Since heat cannot be measured directly, calorimetry takes place by detecting the change in the system by observing the energy (heat, Q) added to or removed from the system. There are two different common methods, constant pressure calorimetry and constant volume calorimetry. The constant-volume method is performed in a bomb calorimeter, and the bomb vessel employed has constant volume during the combustion process. The method is used to measure the internal energy change, ΔU, which equals to the heat of reaction under constant volume, Q_v. Measuring the change in enthalpy change, ΔH, would refer to calorimetry of a reaction occurring under constant pressure. This method is being used in reactions carried out in a solution. Under these conditions, the change in enthalpy of the reaction is equal to the measured heat at constant pressure, Q_P. This concept is being used in reactions carried out in a solution.

2.1.1 Adiabatic calorimetry

In this type, there is no temperature difference between the environment and the system. That occurs by continuously adjusting the environment's temperature by using heaters,

coolers, circulators, etc. The aim is to have identical temperatures in the reaction vessel and the surroundings. Therefore, theoretically, there would be no heat transfer between the calorimeter and the environment. The environment usually is a water bath that surrounds the calorimeter completely. The system (calorimeter) is the bomb vessel and the water bucket. Since the water bath temperature cannot be adjusted very quickly, this method is mainly suitable for slow processes.

2.1.2   Isothermal calorimetry

The isothermal calorimeter measures the impact that the environment has on the bucket and has been considered in both cases before and after the determination and analyse and corrects the results accordingly. That guarantees that the environment is highly stable during the measurements. To achieve stability a large body of water jacket surrounds the calorimetric vessel.

2.1.3   Isoperibol calorimetry

In the isoperibol calorimeter, a water jacket surrounds the vessel and the bucket (wherein the vessel is placed). Typically, the surrounding water jacket is controlled to be maintained at a specific constant temperature. Therefore, when the sample is burned, the heat from the calorimetric vessel is transferred to the water inside the bucket, and the temperature rise of the bucket water is measured to determine the calorific value of the sample.

2.2   Typical measurement methodology and procedure

An isoperibol or adiabatic bomb calorimeter is commonly used for the determination of the calorific value. Typically, the bomb calorimeter precision can vary based on the manufacturer specifications and design. An average RSD % of 0.1 – 0.2 % is normally achieved. Bomb calorimeters are calibrated by benzoic acid produced by some national metrology institutes and companies that are traceable to NIST Standard Reference Material (39J). Therefore, it is economically more feasible for laboratories to use benzoic acid.

Typically, the bomb/vessel is surrounded by a jacket that needs to pre-heat before running the experiment, and when a stable temperature reading is reached (around 10 mK or better), the experiment takes place. For the instrument's calibration, around 1 g of the benzoic acid should be weighted in the crucible and charged in the bomb. Note that the mass of the calibrant can vary based on which standard is being used. The sample should then be added to the bomb with 1 – 5 ml of water and under a pressure of around 30 bars of pure oxygen. After that, a 2000 ± 0.5 g of water is placed inside the bucket, and the charged bomb is placed inside it. By checking that no air bubbles come out of the bomb, it is ensured that the bomb is tightly sealed, and the ignition experiment can start. After the experiment, the residual

liquid in the bomb needs to be analysed by titration or IC to perform the required thermochemical corrections.

Figure 3 shows exemplarily an isoperibol calorimeter, from Parr Instrument Company.

Figure 3. Example of an isoperibol calorimeter (Parr Instrument Company)

2.3 Calibration

To calculate the calorific value of biofuels, a calibration of the calorimeter is needed. Calibration is carried out by adding a defined quantity of heat by burning a known mass of a reference material to form known quantities of combustion products or by applying a precise amount of electrical energy [4]. The purpose of calibration is to calculate the calorimeter's heat capacity, which includes all parts of the system such as the vessel, crucible, bucket water, and metal.

The most used reference material is benzoic acid due to its stable and well-known calorific value since it is a crystalline solid that can be obtained in high purity. One of the project aspects is to investigate the possibility of developing a reference material well suited to biofuels. The calculations of the calorific value can be done by different equations and techniques but mostly these equations are based on the Regnault-Pfaundler method. After calculating the temperature rise by the Regnault-Pfaundler method and before calculating the heat capacity, the mass of the samples needs to be corrected for the air buoyancy since it is known that calibrating the balance itself would not be sufficient to eliminate sources of uncertainty in used mass for calibration.

2.4 Analysis of the results of the stakeholder's survey

Table 1 presents an analysis of the results of the stakeholders' survey regarding the calorific value.

Table 1. Analysis of the results of the stakeholder's survey regarding the calorific value

Parameter	Stakeholders survey results
Type of biofuel	Biomass – Biodiesel-Bioethanol- Algae
Max uncertainty range	0.7 % - 5 % (average = 3 %)
Standards followed	ASTM D240:19 - BS EN ISO 18125:2017 - ISO15400 - ISO1928 - DIN 51900-01/02
Analytical instrument	Isoperibol bomb calorimeter – Adiabatic bomb calorimeter
Residual analysis	Ion chromatograph - N-elemental analyser -Carbon-Sulfur High Temp - gravimetric methods (Titration)
Instrument calibration	Varies from weekly to annually or when a significant change in the system takes place
Factors affect the calorific value	Moisture content - Ash content - Sample heterogeneity

Most users, around 60 %, use an isoperibol bomb calorimeter for the calorific value determination. Moreover, it has been found that the maximum accepted uncertainty range is relatively high, 3 %, while the target of the project would focus on having a lower range and taking into consideration the detailed uncertainty budget.

Furthermore, the instrument calibration mentioned by end users can vary from daily, weekly to annually or in case of any real change takes place in the system. Such factors can be concluded as following: changing any part of the instrument using a different crucible or bucket, changing the quantity of calibrant mass or water mass in the bucket, or altering the room temperature and humidity. Therefore, it is always recommended to fix the parameters and, most importantly, use the same conditions as calibration while determining the unknown sample.

In Figure 4, different standards have been mentioned, around 50 % of the participants use EN ISO 18125:2017 for solid biomass, while 40 % use ASTM D240 for liquid biofuels. Only 10 % use DIN 51900-01/02 for both solid and liquid fuels. In Figure 5, the maximum uncertainty tolerance has been stated by the participants, and it has been noticed that the average maximum uncertainty accepted is 3 %. Around 50 % of users accept a maximum uncertainty of up to 5 %, and only 11 % of the users tolerate a maximum uncertainty of 1 %.
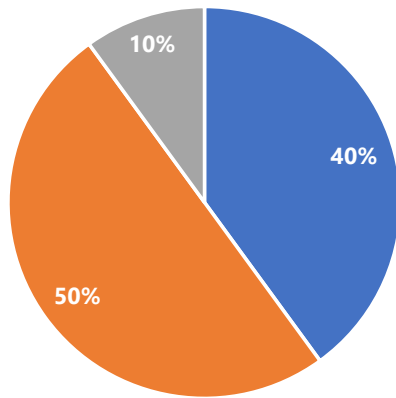
Figure 4. Standard usage
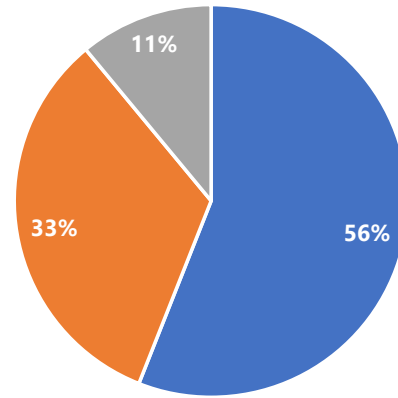
Figure 5. Uncertainty ranges

2.5 Standards

In the survey, many standards have been mentioned by the participants that are being used to determine the calorific value. Table 2 highlights each standard's main elements and gives an overview of how and why each standard is used [5–7].

Table 2. Comparison between different standards.

Standard	DIN 51900-01/02	ISO1928	SR EN ISO 18125:2017	ASTM D240-09
Water inside the bomb	5 mL	1 mL	1 mL – 5 mL	1 mL
Water in the bucket (recommended)	2000 ± 0.5 g	2000 ± 0.5 g	2000 ± 0.5 g	2000 ± 0.5 g
Calibration material	Benozoic Acid	Benozoic Acid	Benzoic Acid	Benzoic Acid
Recommended calibrant mass	1 g	0.7 – 1.3 g	0.7 – 1.3 g	0.9 – 1.1 g
Balance resolution	0.1 mg	0.01 mg	0.01 mg	0.1 mg
Types of materials	Solid – Liquid	Solid	Solid	Liquid hydrocarbon
Bomb volume	330 mL	250-350 mL	250-350 mL	350 ± 50 mL
Jacket water before experiment	20 – 30 °C	0.2 – 0.4 K Higher than expected temperature rise	0.2 – 0.4 K Higher than expected temperature rise	---
Temperature sensor resolution	0.004 K	0.001 K	0.001	0.001 °C
Temperature rise between calibration and determination	0.7 – 1.3 times calibration temp rise	---	---	1.6 – 2 °C above calorimeter temp

Temperature equalization and pre period end point	0.002 K/min – 0.001 K/min successively	0.002 K/min	0.002 K/min	5 min waiting
Main period – after period end point	0.002 K/min – 0.001 K/min respectively	0.001 K/min Or (10 min max)	0.001 K/min Or (10 min max)	---
Igniter material and diameter	Platinum wire 0.1 mm	Pt 0.05 – 0.1 mm. Or Nickel-Chrome 0.16-0.20 mm	Pt wire 0.05 – 0.1 mm	---
Pressure	30 - 40 bar	33 bar	30 bar	25 - 35 bar
Residual Analysis	IC	Titration	Titration - IC	Titration
Repeatability uncertainty	0.2 %	0.2 %	0.2 %	---

When comparing the standards side by side with the survey results, it can be concluded that choosing any of the standards would fulfill the requirements because the uncertainty requirements in the survey are higher than any of the standards suggest. One of the key differences between the standards is the way of calculating the temperature rise . Most of these standards follow the Regnault-Pfaundler method. The two standards ISO 1928 and BS EN ISO 18125:2017 are almost identical and follow the same basic concept in terms of the thermochemical corrections and calculations.

As can be noticed in Table 2, the main criteria of selecting a standard would be the type of the fuel, as the DIN 51900/01-02 gave more flexibility of use because it can be applied on both liquid and solid fuels. While the ISO standards are more commonly used but only for solid fuels, ASTM is only for liquid hydrocarbons as biodiesel.

Furthermore, the uncertainty mentioned in all the standards is only expressing the standard deviation of the repeatability, which shows and confirms the importantance to develope a detailed uncertainty budget that includes the key factors that affect the calorific value. Moreover, the literature review has shown clearly that there is a limitation in the number of publications that investigate the uncertainty of the calorific value measurements of biofuels and biomass.

3 Organic and inorganic impurities in liquid biofuels

This chapter is dedicated to the organic and inorganics impurities in liquid biofuels, that have a direct impact on their calorific value. Ash content has an impact on emissions of particulate matters and on residue management and utilization. Alkali metals, alkaline earth metals and phosphorous influence the ash behavior and utilization. Heavy metals impact ash utilization, heavy metal emissions, catalytic impacts (e.g., in polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F) formation) or particle emission.

3.1 Inorganic impurities

Metal contaminants in biofuels are carefully controlled as part of the quality assurance testing of the final product, and biofuel producers are required to adhere to various specifications. According to the specification given, several inorganic impurities maximum limits are allowed in liquid biofuels (cf. Table 6 in section 3.4).

Some of the inorganic impurities impact the combustion process and, consequently, the calorific value of the biofuel, the environment or proper functioning of the engine. Certain impurities come from the raw materials and are transferred to the end-product. Other inorganic impurities are formed in the production process.

3.1.1 Water

Water and ethanol form an azeotropic mixture at 95.63 % ethanol / 4.37 % water. The last water content is removed through an energy intensive dehydration process (azeotropic distillation - involving additives like benzene, cyclohexane or toluene, or extractive distillation - adding a solvent to break the azeotrope), in order to obtain most of the fuel grade ethanol dehydrated to a minimum purity of 99.6 % before blending or direct use as fuel. However, anhydrous bioethanol fuel is highly hygroscopic. The mixture of it with gasoline is somewhat less hygroscopic, with a tendency to absorb water. This is dependent on the ethanol content (the lower the ethanol content, the lower the tendency to absorb water), on the temperature of the mixture, and on the content of aromatic substances in the gasoline. In adverse circumstances, such as very low temperatures combined with low ethanol content, a separation of the gasoline and water into two phases can occur either in the stockpiling tanks or in vehicle fuel tanks, causing serious operational problems.

Water has a higher latent heat of vaporization and a higher specific heat capacity than ethanol. Because the stoichiometric air quantity decreases with higher water content, the latent heat of vaporization per kg air increases significantly, and this leads to an even bigger cooling effect of the intake charge. Adding water also results in an elevated knock resistance due to the cooling effect and the water vapor dilution, which both contribute to lower in-cylinder temperatures. The water vapor dilution of the air-fuel mixture yields a lower laminar burning velocity and lower adiabatic flame temperature. Because of the lower laminar

burning velocity, the combustion process takes more time to complete and is less isochoric [8].

Water is present in biodiesel as a result of the washing step. Higher content of water in biodiesel makes the fuel go rancid and alters the chemical structure of biodiesel. If moisture is allowed to accumulate for a long time, it will increase the free fatty acid level of biodiesel, and these fatty acids corrode metal parts or may react to form monoglycides. Water can also accumulate during transport and storage because the biodiesel is hygroscopic due to its polar molecular structure at one end. As temperature of storage increases, moisture also increases at a rate of 22.2 ppm/°C [9], more than 9 times higher than that of diesel. As the temperature drops, the adsorbed water precipitates and may accumulate at the bottom of storage tank and can promote algae growth that can clog fuel filters when transferred to vehicle and equipment tanks.

3.1.2 Sulfur

Bioethanol produced through the fermentation of sugars from plants such as corn or sugar cane does not contain significant amounts of sulfur. Mixing it with gasoline from various sources (including as a by-product of natural gas production), can however potentially introduce sulfur content into the finished product.

Sulfur may act as a lubricant in vehicle engines. When the fuel is combusted, sulfur combines with oxygen to create sulfur oxides (SOx) emissions that reduce air quality and have a negative impact on the environment and human health. The presence of sulfur in vehicle fuels can also cause an increase in the release of other environmentally damaging compounds such as NOx, CO etc. The major environmental concerns related to sulfur emissions are acid rain and the formation of particulate matter. Sulfur is also released from vehicles in the form of sulfate particles (SO_4). Along with NOx, these particles contribute to particulate matter formation.

Some process catalysts used in chemical refining can be poisoned, when trace amounts of sulfur-bearing materials are contained in the feedstocks.

Biodiesel made from virgin soybean oil does not contain any sulfur, since soybean oil does not contain sulfur. Canola, rapeseed, and mustard contain varying amounts of glucosinolates, which are sulfur-containing compounds. Canola, which has been cultivated to be low in glucosinolates, contains sulfur fatty acids. Canola oil contains from 3 to 25 ppm of sulfur. Some used vegetable oils, especially oil that has been used for cooking sulfur-rich foods such as onion rings, may also have a higher than 15 ppm level of sulfur. Biodiesel made from high sulfur oil may also contain a high level of sulfur. [9]

A comparison of the reviewed standardized methods for the determination of sulfur is presented in Table 3. More detailed information is presented in section B.1 of Annex B.

Table 3. Comparison of the standardized method for the determination of sulfur

Matrix	Principle of method	Maximum range	Indications of traceability
Biodiesel, diesel, motor gasoline, synthetic fuels	Ultraviolet fluorescence	(3 - 500) mg/kg with constrains for several impurities	CRMs indicated as alternatives
Ethanol		(5 - 20) mg/kg	CRMs produced in accordance with ISO 17034 indicated as alternatives
Biodiesel, diesel, motor gasoline, synthetic fuels	Wavelength dispersive X-ray fluorescence spectrometry (WDXRF)	(3 - 500) mg/kg with constrains for several impurities	
Ethanol		(7 - 20) mg/kg	Calibration of instrument
Ethanol	Inductively coupled plasma optical emission spectrometry (ICP-OES)	(2 - 15) mg/kg	Calibration of instrument

3.1.3 Phosphorous

Phosphorous is an essential plant nutrient, and it is present in limited amounts in bioethanol and biodiesel. Certain amounts of phosphorous improve biofuels' properties. However, high phosphorous content can damage catalytic converters, common on diesel powered equipment as emission standards.

A comparison of the reviewed standardized methods for phosphorous is presented in Table 4. More information is presented in section B.2 of Annex B.

Table 4. Comparison of the standardized method for determination of phosphorous

Matrix	Principle of method	Maximum range	Indications of traceability
FAME*	ICP-OES spectrometry	(4 -20) mg/kg	Calibration of instrument
ethanol		(0.13 - 1.90) mg/kg	Calibration of instrument
ethanol	Spectrophotometric method	(0.15 - 1.50) mg/L	Calibration curve

*Fatty acid methyl esters

3.1.4 Lead

Lead in petrol, due to concerns over air pollution and health risks, was slowly phased out from the late 1970s onwards and has been completely banned in the EU since 2000 (only traces of lead are found/allowed in petrol and diesel today). Lead can be released directly into the air as suspended particles. Nowadays, various antiknock agents (a petrol additive used to reduce engine knocking while increasing the fuel's octane rating by raising the pressure and temperature at which auto-ignition occurs) are used in petrol in place of lead. The EU Fuel Quality Directive (FQD) still allows petrol to contain trace amounts of lead up to 5 mg/l, to account for accidental cross-contamination with lead in the petrol distribution system.

Lead may be present in biodiesel samples due to the plant's raw material absorption from soil or be incorporated during production. Few studies reported the actual range of lead

content in bioethanol/biodiesel. On the other hand, the lead content in burned gases resulting from biofuels use have been studied.

Lead is not included in the requirements for liquid biodiesel, but a limit of 10 mg/kg is set for solid biofuels. Lead in biomass is due to pollution of soil and/or vegetation careful controlled in environment related directives.

3.1.5 Manganese

In the form of methylcyclopentadienyl manganese tricarbonyl (MMT), manganese is used as a metallic additive to increase the octane levels by 2-3 octanes and the antiknock of petrol fuel. MMT is responsible for the contamination of water, soil, and plants and can cause human health problems, such as headaches, nausea, chest tightness and breathing difficulties. Fine particles containing manganese can be absorbed by the blood through the lungs and transferred directly into the central nervous system and the brain. The FQD allows petrol to contain trace amounts of manganese up to 2 mg/l.

3.1.6 Other heavy metals and additives in biofuels

The metal content of refined fuels is critical to assessing their value, determining refining workflows, and ensuring appropriate functionality during combustion.

Heavy metals may be present in biofuels in very low concentrations, often originating from the raw materials used during the production process. Although there are no set limits for all possibly present metals, the determination of their content is important from the point of view of the effects of additives and chemicals on the physical and chemical characteristics of biodiesel [10]. Metal oxides of Cu, Fe, Ce, Pt, B, Al, and Co have been widely used as additives in diesel and biodiesel fuel blends.

Among the recent additives used in diesel and biodiesel fuels, nanoparticles have emerged as a novel and promising additive, which results in the reduction of exhaust emissions and enhancement in engine performance. The matter of concern with the addition of nanoparticles as fuel additives is their stability aspects. Nanoparticles tend to aggregate due to their large surface area and surface activity.

3.1.7 Alkali and Alkaline Earth Metals

In the esterification process of fatty acid methyl esters (FAMEs), residual amounts of sodium (Na) or potassium (K) from the catalyst can be left behind. In addition, small amounts of calcium (Ca) or magnesium (Mg) can be added to the fuel from the purification process. These metallic fuel contaminants are converted to oxides, sulfates, hydroxides, or carbonates in the combustion process and form inorganic ash that can be deposited onto the exhaust emission control devices found in modern diesel engines. Alkali metals are well known

poisons for catalysts and have been shown to negatively impact the mechanical properties of ceramic substrates. Furthermore, alkali metal hydroxides such as those from sodium and potassium are volatilized in the presence of steam and can therefore penetrate the catalyst washcoat or substrate, or be carried downstream of the diesel particulate filter (DPF), where the solid ash is captured. Of further concern, the increased ash from biodiesel combined with the normal ash from lube-oil could potentially result in excessive levels of ash in the DPF, increasing pressure drop, and the frequency required for filter maintenance.

3.2 Organic impurities

As in the case of inorganic impurities, the organic have an impact on the combustion process and, consequently, on the calorific value of the biofuel, on the environment, on the stability of the biofuel or on the proper functioning of the engine.

Certain impurities come from the raw materials and they are transferred into the end-product. Other organic impurities may remain as a by-product in the production process, such as glycerols.

Depending on the raw material and the production process, a wide range of organic impurities may be found in biofuels. These may lower the combustion efficiency, affect the performance of catalyst and/or engine, induce reactions with ethanol (thereby degrading the quality of bioethanol), or may produce harmful volatile organic compounds. Bioethanol samples have a complex matrix with variable water content ranging from 0 to 7 % [11,12].

The number of present organic impurities differs from the specific type of raw material (for instance lignocellulose or sugar), and it ranges between 8 to 130 components, such as: alcohols, aldehydes and ketones, esters, ethers, hydrocarbons, aromatic hydrocarbons, nitrogen compounds, organic acids, other organic compounds [13].

For instance, in lignocellulosic ethanol 29 impurities were identified, whereas in sugar- or starch-derived bioethanol 16 impurities were identified [14]. Thus, lignocellulosic ethanol might contain higher concentrations and a greater variety of organic impurities compared to sugar- or starch-derived bioethanol. Lignocellulosic ethanol contained high concentrations of acetic acid, acetaldehyde, methanol, and furan-related compounds such as furfural. In contrast, the concentrations of these components were lower in sugar- or starch-derived bioethanol samples – with the exception of molasses-derived bioethanol obtained by crude distillation. Lignocellulosic ethanol contained dimethyl-disulfide and thiazole, whereas the only organosulfur compounds found in sugar- or starch-derived bioethanol were dimethyl sulfide and dimethyl sulfoxide [15]. 130 organic compounds were reported as being identified in bioethanol in [14].

Alcohols and esters synthetized by the reaction of organic acids and alcohols seem to be the predominant groups of compounds in bioethanol. Although hydrocarbons and aromatic hydrocarbons are often present in trace amounts, they can affect the environment quality. Acetaldehyde was reported in a significant number of bioethanol samples of different origins

[16]. The same study concluded that the bioethanol originated from winemaking wastes yielded the highest number of compounds (37). Esters, especially FAEEs and 1,1-diethoxyethane are present in all bioethanol samples. Those organic compounds with lower or similar boiling points that of ethanol may appear in biofuel due to insufficient effectiveness of the distillation.

When cereals, wheat or beetroot are selected for bioethanol production (1st generation), fewer organic impurities were identified because of the simple fermentation process.

In general, the preparation of biodiesel starts from vegetable oils or animal fats, followed by trans-esterification reaction of triglycerides with short chain alcohols in the presence of a suitable catalyst, according to the following reaction:

$$
\begin{array}{ccc}
RCOO-CH_2 & & CH_2OH \\
| & \overset{catalyst}{} & | \\
RCOO-CH & + 3R'OH \; \rightleftarrows & 3\,RCOOR' \; + \; CHOH \\
| & & | \\
RCOO-CH_2 & & CH_2OH \\
\end{array}
$$
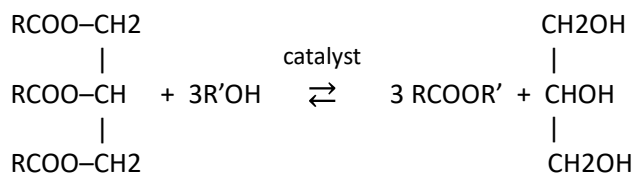
The type of raw material used for transesterification reaction and its quality (mostly regarding the acid value, free acids content, moisture content, viscosity, and fatty acid profile) influences the number and content of organic impurities.

In the stoichiometry of the vegetable oil transesterification reaction, three moles of methanol react with glycerides in three stages, in the presence of a catalyst, typically sodium hydroxide or potassium hydroxide, to produce methyl esters and glycerol. Note that 10 % (V/V) of the total biodiesel production is crude glycerol.

In the first stage, methanol reacts with triglycerides to form methyl esters and diglycerides.

In the second stage, methanol reacts again, this time with diglycerides to form monoglycerides and methyl esters. From the chemical point of view, oils from different raw sources used for biodiesel production have a different fatty acid composition in relation to the chain length, degree of unsaturation, or presence of other functions [15].

Glycerol is the main by-product of the process of producing biodiesel and a potential cause of biodiesel instability. Stoichiometrically, it has been calculated that for every 100 kg of biodiesel, 10 kg of glycerol is produced [14].

FAME are esters of fatty acids. There is no direct environmental harm linked to the use of FAME in diesel. However, the increase in FAME content is related to poor fuel oxidation stability that causes the fuel to biodegrade over time. The results of oxidation may include bacterial growth in gas tanks and the downing of engines, fuel filters and fuel injectors. The maximum percentage limit set by the FQD is 7 % (v/v). Free fatty acids due to incomplete

transesterification esterification cause instability of the biodiesel. Polyunsaturated fatty acids are susceptible to oxidation and polymerization reactions [16].

3.3 Analysis of the results of the stakeholder survey

The main inorganic components of interest for the stakeholders that answered the survey are summarized in Table 5.

Table 5. Status of the inorganic impurities of interest in liquid biofuels

Parameter		Stakeholder's survey	Literature data
Water	Indicated by 31 out of 37 respondents, mostly for solid fuels, but also for liquid biofuels		
	Ranges	Not specified in the survey	max. 0.300 % (m/m) (as specified in EN 15376:2011)
			max.500 mg/kg (as specified in EN 14214)
	Uncertainty	Not clearly specified in the survey	
	Standards followed	EN 15376:2011 'Automotive fuels. Ethanol as a blending component for petrol. EN 14214:2012+A2:2019 Liquid petroleum products. Fatty acid methyl esters (FAME) for use in diesel engines and heating applications. Requirements and test methods	Test methods:
			EN 15489, EN 15692 (as specified in EN 15376:2011)
			EN ISO 12937 (as specified in EN 14214)
Sulfur	Indicated in clear by 2 out of 12 respondents		
	Ranges	Not specified in the survey	
	Uncertainty	Between 5 % to 10 % for sample impurity	max.10.0 mg/kg (as specified in EN 15376)
			max.10.0 mg/kg (as specified in EN 14214)
	Standards followed	EN 15376:2011 'Automotive fuels. Ethanol as a blending component for petrol. Requirements and test methods EN 14214+A1: Automotive fuels – Fatty acid methyl esters (FAME) for diesel engine – Requirements and test methods	Test methods:
			EN 15485, EN 15486, EN 15837 (as specified in EN 15376)
			pEN ISO 20846, pEN ISO 20884 (as specified in EN 14214)
Phosphor	Indicated in clear by 3 out of 12 respondents		
	Ranges	Not specified in the survey	max.0.15 mg/L (as specified in EN 15376)
			max.10.0 mg/kg (as specified in EN 14214)
	Uncertainty	Between 5 % to 10 % for sample impurity	
	Standards followed	EN 15376:2011 'Automotive fuels. Ethanol as a blending component for petrol. Requirements and test methods EN 14214+A1: Automotive fuels – Fatty acid methyl esters (FAME) for diesel engine – Requirements and test methods	Test methods:
			EN 15487, EN 15837 (as specified in EN 15376)
			EN 14107 (as specified in EN 14214)
Lead	Indicated in clear by 1 out of 12 respondents.		

	Ranges	Not specified in the survey	max. 5.0 mg/L (as specified in EN 228 for gasoline/unleaded petrol, inclusive with ethanol blend)
		Not specified in the survey However, EN 14961-1:2010 is indicated	max.10 mg/kg (as specified in ISO 17255 series)
	Uncertainty	Between 5 % to 10 % for sample impurity	
	Standards followed	Not specified in the survey	Test method: EN 237:2004 (as specified in EN 228 for gasoline/unleaded petrol, inclusive with ethanol blend)
		EN 14961-1:2010 (replaced by ISO 17225-1)	Test method ISO 16968 (as specified in ISO 17255 series)

Parameter	Stakeholder's survey		Literature data
Copper	Indicated in clear by 1 out of 12 respondents. Two respondents indicated 'metal/metals'		
	Ranges	Not specified in the survey	max. 0.100 mg/kg (as specified in EN 15376)
			max. (10…20) mg/kg (as specified in ISO 17255 series)
	Uncertainty	Between 5 % to 10 % for sample impurity	
	Standards followed	EN 15376:2011 'Automotive fuels. Ethanol as a blending component for petrol. Requirements and test methods	EN 15488, EN 15837 (as specified in EN 15376)
		EN 14961-1:2010 is indicated	Test method ISO 16968 (as specified in ISO 17255 series)
Chloride	Indicated in clear by 1 out of 12 respondents.		
	Ranges	Not specified in the survey	Inorganic chloride: max.6.0 mg/kg (as specified in EN 15376:2011)
	Uncertainty	Between 5 % to 10 % for sample impurity	
	Standards followed	EN 15376:2011 'Automotive fuels. Ethanol as a blending component for petrol. Requirements and test methods	test method EN 15484, pEN 15492
Sodium	Indicated in clear by 4 out of 12 respondents. Two respondents indicated 'metal/metals'		
	Ranges	Not specified in the survey	Group I Metals (Na+K) max.5 mg/kg (as specified in EN 14214)
	Uncertainty	Between 5 % to 10 % for sample impurity	
	Standards followed	EN 14214+A1: Automotive fuels – Fatty acid methyl esters (FAME) for diesel engine – Requirements and test methods	test method EN 14108, EN 14109
Potassium	Indicated in clear by 3 out of 12 respondents. Two respondents indicated 'metal/metals'		
	Ranges	Not specified in the survey	Group I Metals (Na+K): max.5 mg/kg (as specified in EN 14214)
	Uncertainty	Between 5 % to 10 % for sample impurity	
	Standards followed	EN 14214+A1: Automotive fuels – Fatty acid methyl esters (FAME) for diesel engine – Requirements and test methods	test method EN 14108, EN 14109
	Standards followed	Not specified in the survey	
Magnesium	Indicated in clear by 3 out of 12 respondents. Two respondents indicated 'metal/metals'		
	Ranges	Not specified in the survey	Group II Metals (Ca+Mg) max.10 mg/kg (as specified in EN 14214)
	Uncertainty	Between 5 % to 10 % for sample impurity	
	Standards followed	EN 14214+A1: Automotive fuels – Fatty acid methyl esters (FAME) for diesel engine – Requirements and test methods	test method EN 14538
Calcium	Indicated in clear by 3 out of 12 respondents. Two respondents indicated 'metal/metals'		

	Ranges	Not specified in the survey	Group II Metals (Ca+Mg) max.10 mg/kg (as specified in EN 14214)
	Uncertainty	Between 5 % to 10 % for sample impurity	
	Standards followed	EN 14214+A1: Automotive fuels – Fatty acid methyl esters (FAME) for diesel engine – Requirements and test methods	test method EN 14538

Notes:

- Mn, sulfates and additives were not reported among the impurities tested for liquid biofuels. As, Cd, Hg, Ni and Zn are also mentioned with no clear reference to a certain type of biofuel.
- No indication is given for uncertainty at decision limits.
- For water/moisture content indication is given regarding the type of instruments, accuracy requirements, calibration, uncertainty of calibration or calibration interval. There is a wide range of accuracy values and uncertainty of calibration.
- No organic impurity is indicated in the survey as being of interest/analysed by the responding laboratories.
- Glycerides, glycerol, and polysaturated methyl esters in biodiesel need special attention in identifying and developing traceable methods in accordance with the requirements of CCQM.

3.4 Standards

There are many written standards (EN, ISO, ASTM) indicated as references in the FQD. The European Commission works with CEN to develop and improve biofuels' technical quality standards for biofuel blends for vehicle engines. The Technical Committee CEN/TC-19 'Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin' with its 19 sub-committees [17] has the main scope:

'Standardization of methods of sampling, analysis, and testing, terminology and specifications and classifications for petroleum related products, fuels, lubricants, and hydraulic fluids, that origin from mineral oil and biomass; including the standardization of gaseous and liquid fuels and bio-fuels for transport and stationary applications. It excludes bio-methane and natural gas. The standards include those for characterizing the product quality and for related aspects, e.g. a quality monitoring system for automotive fuel'.

Note that the European standards must be included in all national standards. A significant number of referenced written standards are joint European standards and international standards. The international standards are set up by the ISO, and they do not have to be implemented as national standards. As European standards of the CEN are mandatory to the EU member states, its standards on fuel/biofuels are also obligatory.

The European standards for automotive fuels and a fuel quality monitoring system are linked with Directive 98/70/EC, as amended and modified further. Standards for biofuels depend

on the European directive 2003/30/EC "Promotion of the use of biofuels or other renewable fuels for transport".

The European Commission has mandated CEN/TC 19 to produce a standard on ethanol for blending with gasoline early in 2006. This standard EN 15376 "Automotive fuels – Ethanol as a blending component for petrol – Requirements and test methods" had its first edition in 2007, amended in 2009. The document in force (2014) is at its third edition. If bioethanol is meant for use as an automotive fuel component, the standard applies. It is intended to call up EN 15375 in the European standard for gasoline, EN 228, to define the quality of bioethanol added/blended to petrol. The EN 228 has been adapted to allow a maximum content of 10 % ethanol.

Compared to ethanol, specifications for biodiesel are more advanced. There exists a common European standard for biodiesel: EN 14214 "Automotive fuels – Fatty acid methyl esters (FAME) for diesel engines – Requirements and test methods". Standard EN590 sets further limits for technical reasons and states that diesel must contain no more than 7 % biodiesel by volume (4.6 % in energy terms).

An important issue to fulfil the aims of the EU strategy on biofuels is the standardization of high-quality biofuels. As the development of biofuel production increases, also the need for standardization rises.

The standardized methods for the determination of organic and inorganic impurities in liquid biofuels are the following:

- Determination of sulfur:
    o EN 15485:2007 - Ethanol as a Blending Component for Petrol - Determination of Sulfur Content - Wavelength Dispersive X-ray Fluorescence Spectrometric Method
    o EN 15846:2007 Ethanol as a blending component for petrol - Determination of sulfur content - Ultraviolet fluorescence method
    o EN 15837:2009 Ethanol as a blending component for petrol - Determination of phosphorus, copper and sulfur content - Direct method by inductively coupled plasma optical emission spectrometry (ICP OES)
    o EN ISO 20846:2019 Petroleum products — Determination of sulfur content of automotive fuels — Ultraviolet fluorescence method
    o EN ISO 20884:2019 Petroleum products — Determination of sulfur content of automotive fuels — Wavelength-dispersive X-ray fluorescence spectrometry
    o SR EN ISO 13032:2012 Petroleum products — Determination of low concentration of sulfur in automotive fuels — Energy-dispersive X-ray fluorescence spectrometric method
    o EN 16997:2017 Liquid petroleum products - Determination of the sulfur content in Ethanol (E85) automotive fuel- Wavelength dispersive X-ray fluorescence spectrometric method
- Determination of phosphorus:

- o EN 15487:2009 Ethanol as a blending component for petrol - Determination of phosphorus content - Ammonium molybdate spectrometric method
- o EN 15837:2009 Ethanol as a blending component for petrol - Determination of phosphorus, copper and sulfur content - Direct method by inductively coupled plasma optical emission spectrometry (ICP OES)
- o SR EN 14107:2003 Fat and oil derivates. Fatty Acid Methyl Esters (FAME). Determination of phosphorus content by inductively coupled plasma (ICP) emission spectrometry
- o EN 16294:2012 Petroleum products and fat and oil derivatives - Determination of phosphorus content in fatty acid methyl esters (FAME) - Optical emission spectral analysis with inductively coupled plasma (ICP OES)
- Determination of heavy metals:
  - o EN 15488:2007 Ethanol as a blending component for petrol - Determination of copper content - Graphite furnace atomic absorption spectrometric method
  - o EN 15837:2009 Ethanol as a blending component for petrol - Determination of phosphorus, copper and sulfur content - Direct method by inductively coupled plasma optical emission spectrometry (ICP OES)
- Determination of alkali and earth alkali elements (sodium, potassium, calcium, and magnesium):
  - o SR EN 14108:2003 Fat and oil derivates. Fatty Acid Methyl Esters (FAME). Determination of sodium content by atomic absorption spectrometry
  - o SR EN 14109:2003 Fat and oil derivates. Fatty Acid Methyl Esters (FAME). Determination of potassium content by atomic absorption spectrometry
  - o EN 14538:2006 Fat and oil derivatives - Fatty acid methyl ester (FAME) - Determination of Ca, K, Mg and Na content by optical emission spectral analysis with inductively coupled plasma (ICP OES)
- Determination of inorganic chloride
  - o EN 15492:2012 Ethanol as a blending component for petrol – Determination of inorganic chloride and sulfate content – Ion chromatographic method
- Determination of water in bioethanol
  - o EN 15489:2007 Ethanol as a blending component for petrol - Determination of water content - Karl Fischer coulometric titration method
  - o EN 15692:2009 Ethanol as a blending component for petrol - Determination of water content – Karl Fisher potentiometric titration method
- Determination of water in biodiesel
  - o EN ISO 12937: Petroleum products – Determination of water – Coulometric Karl Fisher titration method
- Determination of organic impurities in bioethanol
  - o EN 15721:2013 'Ethanol as a blending component for petrol - Determination of higher alcohols, methanol and other impurities - Gas chromatographic method'

- Determination of organic impurities in biodiesel
  - EN 14103:2020 Fat and oil derivates. Fatty acid methyl esters (FAME). Determination of ester and linolenic acid methyl ester content
  - EN 15779:2009+A1:2013 Petroleum products and fat and oil derivates - Fatty acid methyl esters (FAME) for diesel engines - Determination of polyunsaturated (≥4 double bonds) fatty acid methyl esters (PUFA) by gas chromatography
  - EN 14110:2020 Fat and oil derivates. Fatty acid methyl esters (FAME). Determination of methanol content
  - EN 14105:2003 Fat and oil derivates. Fatty acid methyl esters (FAME). Determination of free and total glycerol and mon-, di-, triglyceride contents
  - EN 14106:2003 Fat and oil derivates. Fatty acid methyl esters (FAME). Determination of free glycerol content

These methods are detailed in Annex B.

Table 6 and 7 show, respectively, the inorganic and organic impurities' limits as mentioned in the FQD and its associated European Standards.

Table 6. Inorganic impurities considered for biofuels and their limits

Inorganic impurity	FQD	EN 228	EN 15376	EN 590	EN 14214	ISO 17225 series
water	NS	NS	≤ 0.300 % (m/m)	≤ 200 mg/kg	≤ 500 mg/kg	(moisture) 10 … 35 %
sulfur	≤ 50 mg/kg ≤ 10 mg/kg	≤ 10 mg/kg	≤ 10 mg/kg	≤ 50 mg/kg ≤ 10 mg/kg	≤ 10 mg/kg	0.04 … 0.2 % (m/m)
phosphorous	NS	NS	≤ 0.15 mg/L	NS	≤ 4.0 mg/kg	NS
lead	≤ 0.005 g/L	≤ 5.0 mg/L	NS	NS	NS	≤ 10 mg/kg
manganese	≤ 2 mg/L	≤ 2 mg/L	NS	NS	NS	NS
copper	NS	NS	≤ 0.100 mg/kg	NS	NS	10 … 20 mg/kg
chlorine	NS	NS	≤ 0.15 mg/kg	NS	NS	0.02 … 0.03 % (m/m)
sulfate	NS	NS	≤ 3.0 mg/kg	NS	≤ 0.02 % (m/m)	NS
additives	NS	NS	NS	NS	NS	≤ 2 % (m/m)
Group I (Na&K)	NS	NS	NS	NS	≤ 5.0 mg/kg	NS
Group II (Ca&Mg)	NS	NS	NS	NS	≤ 5.0 mg/kg	NS
arsenic	NS	NS	NS	NS	NS	≤ 1.0 mg/kg
cadmium	NS	NS	NS	NS	NS	0.05 … 2 mg/kg
chromium	NS	NS	NS	NS	NS	10 … 50 mg/kg
mercury	NS	NS	NS	NS	NS	≤ 0.1 mg/kg
nickel	NS	NS	NS	NS	NS	≤ 10 mg/kg
zinc	NS	NS	NS	NS	NS	≤ 100 mg/kg

Table 7. Organic impurities considered for biofuels and their limits

Organic impurity	FQD	EN 228	EN 15376	EN 590	EN 14214
benzene	≤ 1.0 % (V/V)	≤ 1.0 % (V/V)	NA	-	
polycyclic aromatic hydrocarbons	≤ 11.0 % (m/m)	NA	NA	≤ 11.0 % (m/m)	
methanol	≤ 3.0 % (V/V)	≤ 3.0 % (V/V)	NA	-	≤ 0.20 % (m/m)
ethanol	≤ 5.0 % (V/V)	≤ 10.0 % (V/V)	NA	-	-
iso-propyl alcohol	≤ 12.0 % (V/V)	≤ 12.0 % (V/V)	≤ 2.0 % (m/m) higher saturated (C3-C5) mono-alcohol content	-	-
tert-butyl alcohol	≤ 10.0 % (V/V)	≤ 15.0 % (V/V)		-	-
iso-butyl alcohol	≤ 7.0 % (V/V)	≤ 15.0 % (V/V)		-	-
ethers (>5 C/molec)	≤ 10.0 % (V/V)	≤ 22.0 % (V/V)	NA	-	-
polysaturated (≥4 double bonds) methyl esters					≤ 1.00 % (m/m)
other oxygenates	≤ 15.0 % (V/V)	≤ 15.0 % (V/V)	NA	-	-
FAME	NA	NA	NA	≤ 7.0 % (V/V)	Major compound
linoleic acid methyl ester					≤ 12.0 % (m/m)
monoglycerides					≤ 0.70 % (m/m)
diglycerides					≤ 0.20 % (m/m)
triglycerides					≤ 0.20 % (m/m)
free glycerol					≤ 0.02 % (m/m)
total glycerol					≤ 0.25 % (m/m)

4 Moisture content

Wood chips and wood pellets are mainly combusted in combined heat and power plants (CHPs) and district heating boilers, but also in much smaller installations, such as pellet stoves. Wood is an inhomogeneous and not specifically defined fuel. The chemical composition, as well as the physical properties of wood, depends mainly on plant species and location. Furthermore, wood from stem and branches differs from bark, twigs, and leaves. Burners and boilers for solid fuels are typically tolerant towards variations in the fuel. As a result, the detailed properties of these fuels are much less critical in comparison with those of liquid biofuels used in combustion engines.

Moisture is an important physical parameter of wood chips and wood pellets. This parameter, in combination with ash content, influences the heating value. Several approaches exist to estimate the heating value directly from moisture and inorganic content – based on the (implicit or explicit) assumption that the heating value of the combustible/organic fraction does not vary much for the different types of biomass considered.

4.1 Online measurement of moisture: state of the art

Several physical properties of water differ from that of the surrounding biomass, and these can in principle be used to measure water content online. Properties to distinguish components in solid-solid, solid-liquid and liquid-liquid mixtures have been reviewed in the context of industrial mixing. Water in biomass can be seen as a special case of a solid-liquid mixture. The following were identified as suitable for online and inline methods [18]:

- Absorption of near-infrared radiation (near-infrared spectroscopy/NIR/NIRS): O–H, C–H and N–H bonds absorb NIR at specific wavelengths. Water absorbs strongly in NIR-region;
- Attenuation of X-rays or gamma-rays (which depends on the density of the material tested);
- Nuclear Magnetic Resonance (NMR) of hydrogen atoms;
- Electric conductivity (especially for liquids in conductive bulk medium);
- Electric capacitance (especially for liquids in non-conductive bulk medium);
- Impedance;
- Optical image analysis: low-cost but requires controlled illumination;
- Acoustic methods, e.g., ultrasound: less disturbance from other sources;
- Acoustic emissions (passive);
- Active acoustics;
- Thermal effusivity (heat transfer coefficient);
- Interaction with microwaves.

Some of these methods, e.g., conductivity, capacitance, or impedance measurements, give a single parameter that can be interpreted to determine water amounts. Spectroscopic methods, such as NIR, use both the intensity and wavelength of the measured signal. Certain

wavelengths are attributed to water, and the intensity of the signal at that specific wavelength is a measure of the amount of water present.

Two- or three-dimensional spatial resolution can be achieved with several of the above methods, e.g., optical image analysis (2D), NIR (2D), MRI (3D) or electrical tomography based on conductivity, capacitance, or impedance (3D).

In an older review focusing on biomass in power plants, NIR and dual X-ray were identified as the optimal methods for measuring moisture in fuel flows (i.e., when the fuel is being transported on a conveyor or falling) and bulk fuels, respectively [19].

4.1.1   Near-infrared spectroscopy (NIR)

In the majority of works published in recent years, near-infrared spectroscopy (NIR or NIRS) is used to determine water content in solid biomass [20-29]. NIR has also been used to analyse liquid biofuels [20, 30]. Developments in the technique and its application to solid and liquid biofuels are summarized in Chadwick et al [20].

NIR typically refers to wavelengths between 800 – 2500 nm [19,20,21,23,24], where some researchers only use part of the spectrum (up to around 1700 nm [20,22,28]), and some extend it to lower wavelengths (around 400 nm [20,28]). Wavelength regions specific for water in biomass are reported as around 990 nm, 1400 nm or 1475 nm, and 1900 nm [19,21]. Comparison of published spectroscopic data for NIR spectra of wood do not necessarily exhibit sharp peaks or valleys [19,22,28]. Additionally, NIR absorption depends on density and chemical composition of the material [19]. This has been exploited by some authors, such as Lestander et al [22] and Feng et al [23] to determine the composition of the organic fraction, but it also means that instruments need calibration to determine water content. Spectroscopic data are typically fitted to or calibrated with moisture data determined by e.g., loss-on-drying. Fitting is carried out by e.g., partial-least squares regression [29] or slightly more sophisticated data analysis techniques [22, 28].

Authors typically report the quality of the thus found moisture models by a coefficient of determination (R^2). Values for R^2 are typically above 0.9 (0.94 [22]; 0.995 [24]; a range of 0.84 – 0.99 is reported in Jensen et al [21]). Some authors split their data set into a model training and a validation set and report coefficients of determination for cross validation. The reported values for cross-validation R^2 are slightly lower (0.814 [23], 0.88 [29]), but validation with data not used in the creation of the model gives more information on the usefulness of the respective model in practical applications.

An older study concluded that calibration equations are affected by laboratory and fuel type, suggesting individual calibration routines for each fuel at each facility [21]. Though not explicitly reported by other authors, this observation suggests some care be taken when transferring models.

Ranges in which NIR-models have been calibrated span wide. Individual authors report such diverse intervals as 6.0 – 13.3 % moisture [22], 3 – 21.9 % moisture [23], and 31.9 – 61.5 % moisture [29].

4.1.2 Microwave

The use of microwaves to detect moisture in biomass has previously been published [31-34]. Microwaves were used to measure dielectric properties of pellets from pine, a hardwood (oak and hickory in undefined proportions) and peanut hulls [31,32]; as well as pulp or pulp slush (in a papermill) [33], and sawdust [34]. As with NIR, quality of the measurements is reported in terms of the model quality when comparing (modelled) microwave data to loss-on-drying reference data.

Ranges of moisture considered varied broadly from 4.9 – 16.0 % [31,32] to 47 – 67 % [33]. Authors generally focused on moving samples, e.g., in chutes [32] and on conveyors [33,34]. Predicted moisture contents under static and flowing conditions were, however, found comparable [32], although some authors report lower standard errors of calibration at higher conveyor speeds (1.75 % at 0.15 m/s vs. 1.28 % for at 0.35 m/s) [34].

An effect of sample temperature on the predicted moisture content was found, and temperature-compensated models were developed [31]. For moisture content between 4.9 – 16.0 % and a temperature range of 10 – 50 °C, standard errors of calibration were between 0.50 % and 1.04 %. A unified calibration for pine, peanut-hull, and hardwood pellets at 20 °C was developed that provides moisture content for the materials with a standard error of calibration between 0.48 % and 0.56 % [31].

4.1.3 Capacitance

Capacitance-based online moisture measurement of wood chips is presented in both Fridh et al [35] and Kandala et al [36]. Fridh focuses on handheld capacitance sensors with an emphasis on speed compared to the standard loss-on-drying method. The sensors were found to underestimate moisture content by 6 percentage points. The authors give a precision of ±3.8 percentage points in the 95 % confidence interval. At moisture contents above 50 %, accuracy and precision were found to decrease [35].

Simple/low-cost sensors were also studied Kandala et al [36], using wood chips with 6 – 50 % moisture as samples. Samples tested were classified into moisture groups. A model calibrated on eight of these groups could predict 79 % of the samples from the validation set (six groups) within 3 %. The authors further stress the need for proper calibration of the instrument [36].

4.1.4 Magnetic resonance

Magnetic resonance has been used to measure moisture in wood chips [37,38]. Moisture ranges tested vary broadly (17 – 65 % [37], 24 – 60 % [38]), corresponding to the large variations in moisture seen in wood chips, as opposed to more homogenous fuels (e.g., wood pellets). Magnetic resonance measurements were found to reproduce loss-on-drying data quite accurately. In Fridh et al [37], magnetic resonance data agreed with loss-on-drying values within -1.84/+0.23 percentage points. Repeatability experiments showed 95 % of the measurements to be within ±1.9 percentage points of the mean. Aminti et al [38] showed that 95 % of values deviated within ±2.5 % of the reference value, while the standard error of performance was 1.2 %.

4.1.5 X-ray

X-rays have been used to determine moisture content, e.g., by combination of X-ray transmission imaging and X-ray fluorescence spectroscopy to determine several biomass parameters at once [39], or as X-ray absorptiometry specifically targeted at moisture [40]. Samples tested included wood chips [39,40], logging residues [39] and sawdust [39]. Using the combined method, mean absolute errors are given in a range of 1.1 % – 3.4 % for 5 – 65 % moisture [39].

For wood chips from pine, spruce, and mixtures of the two, a standard error of estimation of 2.24 % is given (for samples varying between 8 – 59 % moisture) [40]. No relevant difference was found by comparing samples analysed at room temperature and frozen samples [40].

4.1.6 Other methods

As a less frequent solution, some authors have proposed methods to measure moisture indirectly by measuring water content (humidity) in flue gases [41,42]. This information can be used to calculate the moisture content of the fuel, provided that the fuel hydrogen content is also known or can be estimated with reasonable accuracy.

4.2 Analysis of the results of the stakeholder survey

The survey resulted in about 30 answers related to the moisture and ash contents of solid biofuels. The answers support the importance of moisture measurements. In almost all cases, "moisture" is stated as the most significant factor in determining the energy content, but also "ash content" and "heterogeneity" are indicated. The latter refers to the fact that chipped wood is a very heterogeneous material, and consequently, sampling issues play a critical role in the total uncertainty of the measurements process.

The survey provides an approximate goal for the accuracy of moisture measurements between 1.6 % to 5 %. However, in one case the answer is accompanied by the comment

that the mean error must be zero; that is, 5 % precision is sufficient, provided that the accuracy is much better. These answers illustrate that moisture measurements have a very significant economic impact (in accounting deliveries). However, high precision is not an operational requirement.

The range of moisture content relevant was not addressed in the survey. However, it is a well-known fact that the moisture content of wood chips varies in a wide range, and thus the Grant Agreement of this project include "measurement ranges 5 % – 12 % (wood pellets) and 20 % – 75 % (wood chips)" in the specific goals.

Survey participants were queried about the importance of online measurements. However, the corresponding answers span from "not at all" to "to a large/great extent". The reason for this may partly be due to the different roles of the respondents (research facilities, biomass providers, power plants etc.) but also to different structures and sizes of individual plants. Furthermore, it is not clear whether the answers deal with moisture or ash content.

4.3 Standards

For a lack of standardized online methods to determine moisture content, relevant offline methods are listed instead.

- EN ISO 18134-1,2,3 – Solid biofuels – Determination of moisture content – Oven dry method. (Replaces EN 14774-1,2,3 – Solid biofuels – Determination of moisture content – Oven dry method)
- ASTM E871-82 – Standard Test Method for Moisture Analysis of Particulate Wood Fuels. (compare ASTM E1756-08 for non-woody biomass)
- ASTM E1358-97 – Standard Test Method for Determination of Moisture Content of Particulate Wood Fuels Using a Microwave Oven.
- ASTM E1756-08 – Standard Test Method for Determination of Total Solids in Biomass (note: for biomass other than particulate wood – compare ASTM E871-82)
- ASTM D4442-20 – Standard Test Methods for Direct Moisture Content Measurement of Wood and Wood-Based Materials.
- GOST 32975.1,2,3 – Solid biofuels. Determination of moisture content. Oven dry method. (Russian number, but refers to EN 14774)

Further relevant standards related to or containing moisture measurements are:

- ISO 331:1983 Coal - Determination of moisture in the analysis sample — Direct gravimetric method and ISO 687:1974 Coke — Determination of moisture in the analysis sample
- EN 13229 – Inset appliances including open fires fired by solid fuels – Requirements and test methods, EN 13240 – Room heaters fired by solid fuel – Requirements and test methods, EN 12815 – Residential cookers fired by solid fuel – Requirements and test methods, EN 12809 – Residential independent boilers fired by solid fuel – Nominal heat output up to 50 kW – Requirements and test methods, EN 14785 –

Residential space heating appliances fired by wood pellets – Requirements and test methods.

Oven dry methods, also referred to as loss-on-drying, rely on weight measurements before and after drying, where the mass loss is attributed to water evaporation. Drying is carried out at 105 C for a maximum 24 hours (EN 18134). Mass loss can be measured accurately (e.g., EN 18134 prescribes balances with 0.1 g accuracy for 300 g samples). Uncertainty of loss-on-drying is therefore mainly conceptual. However, a comparison with an SI-traceable method showed loss-on-drying to be accurate within the measurement uncertainty of the traceable method, 2 % of the measured moisture, for wood pellets [43].

More information on EN ISO 18134-1,2,3 is presented in Section C.1 of Annex C.

EMPIR
The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

5 Ash content

The elements Al, Ca, Fe, Mg, P, K, Si, Na, Ti present in solid biofuels, are in fact, major elements of the fuel ashes more than of the fuels. The determination of these elements can be used to assess ash behaviour in a thermal conversion process or to assess the utilization of ashes. Moreover, fuel contamination or process additives are indicated by high concentration of certain elements. Contamination of fuel with sand or soil also leads to high concentrations of several elements.

The minor elements present in solid biofuels can, in some cases, be of environmental concern. It has been shown that certain energy crops concentrate cadmium and, in polluted areas, other toxic elements, which then may be found at elevated concentrations in the biofuels. This can be a problem if, for example, the ash from the combustion is to be put back in the forest as fertilizer. The more volatile heavy metals cadmium, lead and zinc are listed as major aerosol-forming elements increasing the emissions of particulate matter during combustion. Trace elements in biofuels are often present at very low concentrations. From an analytical point of view, this requires great care to avoid contamination in the sample preparation and decomposition steps. Note that some heavy metals such as Cu and Fe can be used as good catalysts. The typical concentrations of minor elements in sold biofuels can be found in ISO series 17225 standards.

The elements chlorine, sodium, and potassium present in solid biofuels can contribute significantly to corrosion, fouling or slagging in furnaces. Also, they affect the gaseous emissions from the thermal processes.

The chlorine content in solid biofuels may be significant, and it is mainly present as water-soluble inorganic salts such as sodium and potassium chlorides or other ion-exchangeable forms. The significance of chlorine in a thermochemical conversion process is manifold. For instance, chlorine is participating in the formation of HCl and dioxin/furan. Although 40 to 95 % of chlorine embeds into the ash, the HCl emissions can be critical for certain Cl-rich fuels, requiring then secondary flue gas treatment. Furthermore, chlorine acts corrosive at the surface of heat exchangers [44].

In solid biofuels, sodium and potassium can be present as both minerals and salts. The salts of these elements are extractable with water and are readily volatile during thermal conversion. By determination of the water-soluble content of sodium and potassium, an estimate of the aggressive content of the elements in relation to potential slagging and fouling problems can be achieved. For some biofuels, such as straw, experience has shown that the water-soluble content of sodium and potassium corresponds to the total content of the elements.

Within the combustion process, calcium present in solid biofuels improves the ash-softening behaviour by increasing the melting temperature of the ash. Therefore, it can be used as an additive. Also, high contents of calcium can lead to a higher embedding of sulfur into ash, preventing the emission of sulfur dioxide.

Ash is an important property for fuel deliveries, since ash is a by-product of combustion and ends up as bottom ash or fly-ash and needs to be removed. Depending on the jurisdiction, ash may be deposited or used for the production of other products. Knowing how much ash comes with fuel may have economic consequences and impact in the technological process as well as environmental protection. In addition, the chemical composition of ash contributes to slagging and corrosion in the combustion equipment, and it is therefore important to know the amount of ash contained in fuel.

Analysis of the elemental composition of ash with a focus on heavy metals in terms of conducting product conformity assessment procedures is one of the objectives of this project. Methods that enable these types of analyses include "wet chemistry" methods with microwave digestion of ash samples with metal detection by spectroscopic methods, optical and mass spectrometry. Other types of techniques used allow the analysis of samples without destroying the sample, such as various XRF methods that are divided into energy and wave dispersion.

Standardized ISO, ASTM and EPA methods are routinely used in the elemental analysis of liquid and solid minerals and biofuels with a focus on sulphur, phosphorus, manganese, lead and some other elements. However, there is a need to develop XRF spectrometric methods adapted for direct analysis of heavy metals and other elements in the ash generated after the combustion of solid biofuels. Depending on the type of instrument and the level of selectivity and sensitivity, these methods can be successfully used for the certification of matrix reference materials - reference ash for the calibration of online and mobile XFR devices to be used to assess product compliance on site, hence in industry and by control laboratories.

5.1 Online measurement of ash: state of the art

This section describes the methods used for the online measurement of ash.

5.1.1 Near-infrared spectroscopy (NIR)

As outlined above, NIR can be used to determine other properties of solid biomass besides water content [20]. Several authors [23, 24, 27, 29] have linked NIR-data to ash content. Ash amounts investigated spanned relatively broad, up to 15.9 % [23] or even up to 24.7 % [24]. Coefficients of determination (R^2) of the ash-prediction models are about the same as, or slightly lower than those for moisture (see above): 0.92 [23], 0.99 [24], 0.77 [27] and 0.69 [29]. Despite using the same metric, models of different authors are difficult to compare owing to the different modelling/model fitting strategies, different model validation (size of training vs. size of validation data set), and different materials studied (narrow or broad range of ash content).

5.1.2 Other methods

Other spectroscopic methods can be applied to determine ash content as well, such as the combination of X-ray transmission imaging and X-ray fluorescence spectroscopy [39] or laser

induced breakdown spectroscopy (LIBS) [45]. In the LIBS study, the range of ash content was rather narrow and low (0.48 – 1.39 %). The authors give a limit of detection of 0.026 % and a coefficient of determination (R²) of 0.99 [45]. The X-ray study had a slightly broader range of calibration (0.2 – 4.5 % ash), with mean absolute errors given as 0.15 % – 0.49 % [39].

The WDXRF method with the use of laboratory instruments with higher X-ray tube power allows the analysis of samples with high sensitivity in Helium and vacuum atmospheres. In order to increase the sensitivity of the analysis and enable the detection and quantification of elements in low concentrations, various techniques are used to prepare ash samples that involve forming tablets or packaging pure ash in transparent foils, which allows analysis of the concentrated sample in vacuum.

Besides ash content, the composition of the inorganic fraction can also be of interest to boiler operators. Knowledge of the concentration of different metals present may allow to predict slagging and corrosion behaviour. No studies were found reporting an online analysis of these concentrations. However, a fast method (≈3h) to determine ash-forming elements K, Ca, Na, Mg, Al, using scanning electron microscopy with energy dispersive X-ray fluorescence spectrometry (SEM–EDX) and X-ray diffraction (XRD) has been described in the literature [46]. Focus of the work appears to be determining metal species problematic for boiler operation, rather than total inorganic amount. Accuracy evaluated by comparison of recovery of metals in different solutions vs microwave digestion. Due to the resources required for this kind of measurements it is only relevant in very special cases.

5.2   Analysis of the results of the stakeholders' survey

As previously mentioned, answers from the survey related to the moisture and ash contents of solid biofuels have been received. It is evident from the answers that the importance of the ash content is less than that of the moisture. 53 % of the respondents answer that they measure the ash content, whereas 34 % reply that they do not. Furthermore, one respondent indicates "ash content" as the most significant parameter for the calorific values. With respect to the method employed, "muffle furnace" is by far the dominating.

Two respondents addressed the required accuracy of the ash-content measurements. In one case, the required accuracy is given as ±10 % for ≥ 1 % ash content, and in the other ±15 %.

As stated in the corresponding section regarding the moisture content, the impact of online measurements is addressed in the survey, and the corresponding answers span from "not at all" to "to a large/great extent". The reason for this may partly be due to the different roles of the subjects (research facilities, biomass providers, powerplants etc.) but also to different structures and sizes of individual plants. Furthermore, it is not clear whether the answers deal with moisture or ash content.

The main inorganic components, besides ash, of solid biofuel of interest for the stakeholders that answered the survey are summarized in Table 8.

Table 8. Status of the inorganic impurities of interest, besides ash, in solid biofuels

Parameter		Stakeholder's survey	Literature data
Arsenic	Indicated in clear by 1 out of 12 respondents with no reference to the matrix. Two respondents indicated 'metal/metals'		
	Ranges	Not specified in the survey However, EN 14961-1:2010 is indicated	max.1.0 mg/kg (as specified in ISO 17255 series)
	Uncertainty	Not clearly specified, 5-10 % of the impurity content	
	Standards followed	EN 14961-1:2010 (replaced by ISO 17225-1)	Test method ISO 16968 (as specified in ISO 17255 series)
Cadmium	Indicated in clear by 1 out of 12 respondents with no reference to the matrix. Two respondents indicated 'metal/metals'		
	Ranges	Not specified in the survey However, EN 14961-1:2010 is indicated	max. (0.5 … 2.0) mg/kg depending on the type (as specified in ISO 17255 series)
	Uncertainty	Not clearly specified, 5-10 % of the impurity content	
	Standards followed	EN 14961-1:2010 (replaced by ISO 17225-1)	Test method ISO 16968 (as specified in ISO 17255 series)
mercury	Indicated in clear by 1 out of 12 respondents with no reference to the matrix. Two respondents indicated 'metal/metals'		
	Ranges	Not specified in the survey However, EN 14961-1:2010 is indicated	max.0.1 mg/kg (as specified in ISO 17255 series)
	Uncertainty	Not clearly specified, 5-10 % of the impurity content	
	Standards followed	EN 14961-1:2010 (replaced by ISO 17225-1)	Test method ISO 16968 (as specified in ISO 17255 series)

5.3 Standards

As with moisture, there are no established, standardized methods to determine ash content online. Relevant offline methods are therefore listed instead.

- EN ISO 18122 – Solid biofuels – Determination of ash content. (Replaces: EN 14775 – Solid biofuels – Determination of ash content.)
- ASTM E1534-93 – Standard Test Method for Determination of Ash Content of Particulate Wood Fuels.
- ASTM D1102-84 – Test Method for Ash in Wood
- ASTM E1755-01 – Standard Test Method for Ash in Biomass.
- GOST 32988 – Solid biofuels – Determination of ash content. (Russian number, but refers to EN 14775)

Typical ash measurement methods are based on incinerating the sample and determining the residual mass. EN 18122 requires at least 0.1 mg accuracy of the balance for 1 g of (original) sample. Combustion of the sample is carried out at 550 °C. As with moisture measurement, the accuracy of the method is likely not limited by the instrument used, but

by the conceptual uncertainty (oxidation of all organic matter, while avoiding the release of inorganic matter).

Further relevant standards for the determination of impurities in solid biofuels are:

- EN ISO 16994:2016 - Solid biofuels — Determination of total content of sulfur and chlorine
- EN ISO 16967:2015 Solid Biofuels – Determination of major elements - Al, Ca, Fe, Mg, P, K, Si, Na, and Ti
- EN ISO 16968:2015 Solid biofuels — Determination of minor elements
- SR EN ISO 16995:2015 Solid biofuels – Determination of water-soluble chloride, sodium and potassium content

More information on these standards is presented in section C.2 of Annex C.

6 Conclusions

The project BIOFMET aims to research and develop online metrological methods to analyse solid and liquid biofuels. More specifically, the project focuses on methods to determine calorific value, moisture, ash content, and methods to quantify impurities. This report aims to specify and provide a framework each parameter's targeted range. Based on the information gathered during the stakeholder's survey and from the literature review, several conclusions and considerations can be drawn.

The estimation of the energy content of a solid biofuel based on non-ideal, slow, or offline methods can have a major economic consequence if this estimated value contains errors due to the heat production taxes calculations. From the results of the stakeholders' survey, it can be concluded that any of the standards would fulfill the requirements, since the uncertainty requirements presented in the survey are less strict than any of the standards' suggestions. The type of fuel should be the main criteria for the selection a standard. DIN 51900/01-02 gives more flexibility of use because it can be applied on both liquid and solid biofuels. On the other hand, ISO standards are more commonly used (but only for solid fuels) while ASTM applies only to liquid hydrocarbons such as biodiesel.

Furthermore, the uncertainty mentioned in all the standards only expresses the standard deviation of the repeatability, which shows and confirms the important need for developing an uncertainty budget that includes the key factors that affect that calorific value. Moreover, the literature review has shown clearly that there is a limitation in the number of publications that investigate the uncertainty of the biofuels and biomass heating value.

Quoting from the Grant Agreement, specific objective number 4 of the project is:

'To develop validated methods to determine the amount and nature of impurities in liquid biofuels, including quantifying and qualifying inorganic (i.e., Na, Ca, K, Mg, P) for a measurement range of 0.5 mg/kg to 2.5 mg/kg with a relative target uncertainty of 5-10 % (k=1) and organic by-products (i.e., total glycerol) < 5 % relative repeatability for 0.1 - 0.3 % range as per EN ISO 14105. In addition, to develop a traceable method for the online determination of the calorific value of liquid biofuels.'

For liquid biofuels, a wide range of inorganic impurities was indicated as being of interest (water, S, P, Pb, Cu, Cl, Na, K, Ca, Mg, As, Cd, Hg) in the survey's answers, and a target uncertainty of 5-10 % is supported. Additionally, there is no organic impurity indicated in the survey as being of interest and/or analysed. However, glycerides, glycerol, and polysaturated methyl esters in biodiesel need special attention in identifying and developing traceable methods in accordance with the requirements of CCQM. In regard to this issue, there are several areas where there is still need for research, namely, IDMS traceable measurements of metal traces in biofuels, with a focus on Mn. Additionally, there is still the need to develop a higher order of measurements methods for tracing organic impurities, clearly identify traceability chains for regulated measurement results, certified reference materials for critical and relevant impurities, and further research attention in nano-additives.

Quoting from the Grant Agreement, specific objective number 1 of the project is:

'To develop traceable online measurements for water content in solid biofuels, for the measurement ranges 5 % – 12 % (wood pellets) and 20 % – 75 % (wood chips) with a target uncertainty of 5 %.'

Regarding moisture, the survey supports the target uncertainty of 5 %, although requirements are also made for better uncertainty (2 % – 3 %). It does not provide new information on the range. Interpretation of the survey results is further complicated by the fact that most answers came from research institutions. A higher response rate among industrial/commercial users and manufacturers of solid biofuels would have allowed a better assessment of the needs and demands in the industry.

Quoting from the Grant Agreement, specific objective number 3 of the project is:

'To traceably determine the calorific value of the solid biofuels by developing validated methods for the online measurement of ash content. In addition, to develop accurate methods < 0.1 % absolute repeatability and 0.2 % absolute reproducibility for determining the amount and composition of ash content in the measurement range 0 % – 1 %.'

Regarding the ash content, the survey supports the same targets and ranges as the moisture content. Similarly, to the moisture content, the survey does not provide new information on the range. It does not provide new information on the range. Interpretation of the survey results is further complicated by the fact that most answers came from research institutions. A higher response rate among industrial/commercial users and manufacturers of solid biofuels would have allowed a better assessment of the needs and demands in the industry.

Both moisture and ash can be measured online with a variety of methods. Several of these are spectroscopic and require a numerical model to translate measured spectra to moisture or ash content. Some methods, such as NIR or X-ray transmission imaging/X-ray fluorescence spectroscopy, can be used to determine moisture and ash content simultaneously. Overall, technology for online moisture measurements appear to be more thoroughly researched than those for ash content. This may be due to the large variations in moisture seen in some solid biofuels, such as wood chips.

In the studies cited, only few authors give a direct estimate of the uncertainty of the measurement method in question (and none hold this up against a desired/demanded uncertainty). Instead, metrics such as the coefficient of determination are used to compare models of online data to data from e.g., loss-on-drying (which is implicitly assumed to represent the true moisture content) or other offline methods to determine ash and moisture.

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Annex A – Questions of the stakeholders' survey

1. Stakeholder's sector (power plant, biofuel producer, research, etc)

2. Type of biofuel used (bioethanol, biodiesel, wood pellets, chips, etc)

3. Do you measure energy content (**calorific value**)?

- To which extent plays the uncertainty a role in your measurements (small → great)
- What is the maximum tolerance in uncertainty of the sample's energy content you can accept?
- Which factors affects your sample's energy content the most? (moisture, ash, others)
- Which standard procedure (ISO, ASTM etc.) do you follow for the determination of the energy content?
- Which analytical instrument do you use for the determination of the energy content? (Adiabatic bomb calorimeter, Isoperibol bomb calorimeter, other)
- Which analytical instruments do you use for the analysis of the combustion residuals?
- How frequent do you calibrate your analytical instruments for energy content measurements? (Weekly, Monthly)
- Do you participate in interlaboratory proficiency or comparison tests regarding energy content measurements? (Yes, No)
- What is the frequency of your participation?
- Organiser and country

4. Is the **impurity** of the raw material important to you?

- What impurities present in the biofuel raw material are relevant for your purpose? (Inorganics (please specify), Organics (please specify), Others (please specify))
- Which standard procedure (ISO, ASTM etc.) do you follow for the quality confirmation of the biofuel raw material you are using?
- Do you ask for a Quality Certificate/Testing Report when purchasing biofuel raw material? (Yes, No)
- What are your traceability requirements for the determination of impurities in your biofuel raw material?
- What is the maximum tolerance in the uncertainty of the sample's impurity content?

5. Do you measure **moisture** content in your fuel?

- What instrument for measuring moisture do you use? (Loss on drying method, Microwave, NIR, Karl Fischer titration, other)
- Could you specify the model of your measurement device?
- Have you made any demands for accuracy of your measurement?
  - What is your accuracy requirement?

- Do you calibrate your equipment regularly?
  - How frequent do you calibrate your equipment (Every month, Twice a year, Once a year)
  - Do you have uncertainty requirements for the calibration? (Yes, + which requirement, No)
- Which standard procedure /national guidelines regarding moisture measurement do you follows? (EN ISO 18134 – Solid biofuels – Determination of moisture content – Oven dry method, EN 14774 – Solid biofuels – Determination of moisture content – Oven dry method, ASTM E871-82 – Standard Test Method for Moisture Analysis of Particulate Wood Fuels, National guideline (please write name of guideline))

6. Do you measure **ash content**?

- If <u>yes</u>, what method for measuring ash content do you use? (Thermogravimetric analysis (TGA), Muffle furnace, Other)
- Have you made any demands for accuracy of your measurement? (Yes, No)
  - What is your accuracy requirement?
- If <u>no</u>, what is the reason why you do not measure ash content?
- Do you calibrate your equipment regularly?
  - How frequent do you calibrate your equipment (Every month, Twice a year, Once a year)
  - Do you have uncertainty requirements for the calibration? (Yes, + which requirement, No)
  - Which standard procedures / national guidelines regarding ash content do you follow? (EN ISO 18122 – Solid biofuels – Determination of ash content, EN 14775 – Solid biofuels – Determination of ash content, ASTM E1534-93 – Standard Test Method for Determination of Ash Content of Particulate Wood Fuels, National Guideline and name of this)

7. To which degree are **online measurements** important for the operation of your plant? (small --> great)

8. Are there any issues regarding **moisture** and **ash** measurements which you would like to share?

Annex B – Relevant standardized methods for liquid biofuels

This annex presents the review of the standardized methods for the determination of inorganic and organic impurities in liquid biofuels.

B.1 Sulfur

Six standardized method for sulfur content determination are indicated in EN 15376 and in EN 14214, respectively as follows:

EN 15485:2007 - Ethanol as a Blending Component for Petrol - Determination of Sulfur Content - Wavelength Dispersive X-ray Fluorescence Spectrometric Method

The document, based on EN ISO 20884, specifies a wavelength-dispersive X-ray fluorescence (WDXRF) test method for the determination of sulfur content of ethanol from 7 mg/kg to 20 mg/kg.

Principle of the method: The sample is exposed in a sample cell to the primary radiation of an X-ray tube. The count rates of the S-Kα - Siegbahn X-ray line (corresponding to S K-L2,3 in IUPAC notation for the X-ray line) X-ray fluorescence and the count rate of the background radiation are measured. The sulfur content of the sample is determined against a calibration curve defined for the relevant measuring range.

Dibutylsulfide of nominal sulfur content 21.92 % (m/m) or dibutyldisulfide of nominal sulfur content 35.95 % (m/m) are indicated to gravimetrically prepare calibration standards. Ethanol of 99 % purity with less than 1 mg/kg S content is used for blank.

No indication is given for the uncertainty of the gravimetric stock solution/calibration standards. No requirements for traceability. Balance capable of weighing to the nearest 0.1 mg is indicated. The calibration of the instrument is described.

Repeatability should not exceed r=0.04 X + 1.82 and the reproducibility should not exceed R=0.07 X + 3.26.

EN 15846:2007 Ethanol as a blending component for petrol - Determination of sulfur content - Ultraviolet fluorescence method

Based on EN ISO 20846, the document specifies an ultraviolet (UV) fluorescence test method for the determination of the sulfur from 5 mg/kg to 20 mg/kg. Other products may be analysed, and higher contents may be determined according to this test method. However, no precision data for products other than ethanol and for the results outside the specified

range has been established for this document. Halogens interfere with this detection technique at concentrations above approximately 3.5 g/kg.

Principle of the method: An ethanol sample is directly injected into a UV fluorescence detector. Then, it enters in a high temperature (1000 … 1100) °C combustion tube, where the sulfur is oxidized to sulfur dioxide (SO_2) in an oxygen-rich atmosphere. Water produced during the sample combustion is removed. Sample combustion gases are exposed to UV light. The SO_2 absorbs the UV light's energy and is converted to excited sulfur dioxide (SO_2^*). The fluorescence emitted from the excited SO_2^* as it returns to a stable state SO_2 is detected by a photomultiplier tube and the resulting signal is a measure of the sulfur content in the sample. Compounds with a minimum purity of 99 % (m/m) – i.e., dibezothiofene with a nominal sulfur content of 17.399 % (m/m), dibutylsulfide of nominal sulfur content 21.915 % (m/m) or thionaphthene with a nominal sulfur content of 23.89 % (m/m) - are indicated to gravimetrically prepare calibration standards. CRMs produced in accordance with ISO 17034 are indicated as suitable alternatives. No indication is given for the uncertainty of the gravimetric stock solution/calibration standards. No requirements for traceability. Balance capable of weighing to the nearest 0.1 mg is indicated. Class A volumetric flask is indicated.

EN 15837:2009 Ethanol as a blending component for petrol - Determination of phosphorus, copper and sulfur content - Direct method by inductively coupled plasma optical emission spectrometry (ICP OES)

The document specifies an ICP-OES method for direct determination of elements content in ethanol, namely P in the range (0.13 - 1.90) mg/kg, Cu in the range of (0.050 - 0.300) mg/kg and sulfur in the range (2.0 - 15.0) mg/kg.

Principle of the method: A portion of a sample is directly injected into the spray-chamber of an inductively coupled plasma emission spectrometer. The element content is determined by comparing the emission of the element in the test portion with the calibration solutions' emission at the same wavelength. Commercially available sulfur standard solution or gravimetrically prepared ones are indicated.

EN ISO 20846:2019 Petroleum products — Determination of sulfur content of automotive fuels — Ultraviolet fluorescence method

This document specifies an UV fluorescence test method for the determination of the sulfur content of the following products:

- having sulfur contents in the range 3 mg/kg to 500 mg/kg,
- motor gasolines containing up to 3.7 % (m/m) oxygen [including those blended with ethanol up to about 10 % (V/V)],

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

- diesel fuels, including those containing up to about 30 % (V/V) FAME,
- having sulfur contents in the range of 3 mg/kg to 45 mg/kg,
- synthetic fuels, such as hydrotreated vegetable oil (HVO) and gas to liquid (GTL).

Other products can be analysed and other sulfur contents can be determined according to this test method. However, no precision data for products other than automotive fuels and for results outside the specified range have been established for this document. Halogens interfere with this detection technique at concentrations above approximately 3500 mg/kg. The test method can be used to determine sulfur in process feeds and can also be used to control sulfur in effluents. Sulfate species in ethanol do not have the same conversion factor as organic sulfur in ethanol. Nevertheless, sulfates have a conversion factor close to that of organic sulfur. Nitrogen interference can occur.

Principle of the method: A hydrocarbon sample is either directly injected or placed in a sample boat. Then, it enters in a high temperature (1000 … 1100) °C combustion tube, where the sulfur is oxidized to SO_2 in an oxygen-rich atmosphere. Water produced during the sample combustion is removed. Sample combustion gases are exposed to UV light. The SO_2 absorbs the UV light's energy and is converted to SO_2^*. The fluorescence emitted from the excited SO_2^* as it returns to a stable state SO_2 is detected by a photomultiplier tube and the resulting signal is a measure of the sulfur content in the sample.

Compounds with a minimum purity of 99 % (m/m) – i.e., dibezothiofene with a nominal sulfur content of 17.399 % (m/m), dibutylsulfide of nominal sulfur content 21.915 % (m/m) or thionaphthene with a nominal sulfur content of 23.89 % (m/m) - are indicated to gravimetrically prepare calibration standards. CRMs produced in accordance with ISO 17034 are indicated as suitable alternatives. No indication is given for the uncertainty of the gravimetric stock solution/calibration standards. No requirements for traceability. Balance capable of weighing to the nearest 0.1 mg is indicated. Class A volumetric flask is indicated. Repeatability and reproducibility between two independent results are given in Table B1, based on two studies.

Table B1. Precision data for determination of sulfur using UV method

Sulfur content, mg/kg	Repeatability, r		Reproducibility, R	
	gasoline	Diesel/HVO/GTL	Gasoline	Diesel/HVO/GTL
(3 - 60)	r=0.063 1 X+0.35	r=0.055 3 X+0.55	R=0.174 9 X+0.96	R=0.112 0 X+1.12
10	1.0	1.1	2.7	2.2
30	2.2	2.2	6.2	4.5
50	3.5	3.3	9.7	6.7
(>60 - 500)	r=0.041 7 X+1	r=0.028 5 X+2	R=0.157 3 X+2	R=0.108 0 X+2
100	5	5	18	13
350	16	12	57	40
500	22	16	81	56

Notes: X is the average of the results being compared, expressed in mg/kg. Precision for HVO and GTL applies only between (3 - 45) mg/kg.

EN ISO 20884:2019 Petroleum products — Determination of sulfur content of automotive fuels — Wavelength-dispersive X-ray fluorescence spectrometry

The document specifies a wavelength-dispersive X-ray fluorescence (WDXRF) test method for the determination of the sulfur content of liquid, homogeneous automotive fuels from 5 mg/kg to 500 mg/kg, which have a maximum oxygen content of 3.7 % (m/m). This product range covers:

- diesel fuels containing up to about 30 % (V/V) FAME,
- motor gasolines containing up to about 10 % (V/V) ethanol,
- synthetic fuels such as HVO and GTL have sulfur contents ranging from 5 mg/kg to 45 mg/kg.

Products with higher oxygen content show significant matrix effects, e.g. pure FAME used as biodiesel. Nevertheless, pure FAME can be analysed when the corresponding procedures are followed. Other products can be analysed with this test method, though precision data for products other than those mentioned have not been established for this document. Sulfur contents higher than 500 mg/kg can be determined after sample dilution. However, the precision was not established for diluted samples.

Principle of the method: The sample is exposed in a sample cell to the primary radiation of an X-ray tube. The S-K count rates α - Siegbahn X-ray line (corresponding to S K-L2,3 in IUPAC notation for the X-ray line) X-ray fluorescence and the count rate of the background radiation are measured. The sulfur content of the sample is determined against a calibration curve defined for the relevant measuring range. Dibutylsulfide of nominal sulfur content 21.92 % (m/m) or dibutyldisulfide of nominal sulfur content 35.95 % (m/m) is indicated gravimetrically prepare calibration standards. CRMs produced in accordance with ISO 17034 are indicated as suitable alternatives. No indication is given for the uncertainty of the gravimetric stock solution/calibration standards. No requirements for traceability. Balance capable of weighing to the nearest 0.1 mg is indicated. Repeatability and reproducibility between two independent results are given in Table B2, based on two studies.

Table B2. Precision data for determination of sulfur using UV method

Sulfur content, mg/kg	Repeatability, r in mg/kg	Reproducibility, R in mg/kg
5 - 60	1.7 + 0.024 8 X	1.9 + 0.120 1 X
> 60 - 500	4.0	4.6 + 0.075 X

Notes: X is the average of the results being compared, expressed in mg/kg. Precision for HVO and GTL applies only between (3 - 45) mg/kg

SR EN ISO 13032:2012 Petroleum products — Determination of low concentration of sulfur in automotive fuels — Energy-dispersive X-ray fluorescence spectrometric method

An energy dispersive X-ray fluorescence (EDXRF) test method is specified for the determination of sulfur content in automotive gasoline containing up to 3.7 % (m/m) oxygen [including those blended with ethanol up to 10 % (V/V)], and in diesel fuels [including those containing up to about 10 % (V/V) FAME] having sulfur contents in the range 8 mg/kg to 50 mg/kg. Other products can be analysed, and other sulfur contents can be determined according to this test method; however, no precision data for products other than automotive fuels and results outside the specified range have been established for this International Standard. For reasons of spectral overlap, the written standard is not applicable to leaded automotive gasoline, gasoline having a content of greater than 8 mg/kg lead replacement, or to product and feedstock containing lead, silicon, phosphorus, calcium, potassium, or halides at concentrations greater than one tenth of the concentration of sulfur measured or more than 10 mg/kg, whichever is the greater.

Principle of the method: The test portion, in a cup fitted with an X-ray transparent windows, is placed in a beam of exciting radiation from an X-ray tube. The exciting radiation can be either direct or indirect via a polarizing or secondary target. The intensity of the sulfur K-L2,3 characteristic X-radiation is measured, and the accumulated count is compared with a calibration curve plotted based on the sulfur standards covering the range of sulfur contents under examination. Sulfur compounds of known content are to be used for the preparation of the primary standards. When these components' purity is less than 99 % (m/m), either the concentration and nature of all impurities are to be known or certified reference materials shall be used instead. A performance characteristic is given for the energy dispersive X-ray fluorescence instrument in terms of variation coefficient for the gross count rate for the sulfur region of interest for a 10 mg/kg sulfur standard.

Apart from the above indicated test methods, the written standard:

EN 16997:2017 Liquid petroleum products - Determination of the sulfur content in Ethanol (E85) automotive fuel- Wavelength dispersive X-ray fluorescence spectrometric method

Specifies a wavelength-dispersive X-ray fluorescence (WDXRF) test method for the determination of sulfur content in ethanol (E85) automotive fuel, containing ethanol between 50 % (V/V) and 85 % (V/V), from 5 mg/kg to 20 mg/kg, using instruments with either monochromatic or polychromatic excitation. Sulfur contents higher than 20 mg/kg can be determined after sample dilution with an appropriate solvent. However, the precision was not established for diluted samples.

<u>Principle of the method</u>: The sample is exposed in a sample cell to the primary radiation of an X-ray tube. The count rates of the o S K-L2,3 (in IUPAC notation for the X-ray line) X-ray fluorescence and the background radiation count rate are measured. The correlation between the pulse rate and the concentration is calculated by the software. The matrix effects are compensated either on the basis of fundamental parameters or using a correction table. The sulfur content in then determined using this calibration. Compounds with a minimum purity of 99 % (m/m) – i.e. dibutylsulfide of nominal sulfur content 21.92 % (m/m) or dibutyldisulfide with a nominal sulfur content of 35.95 % (m/m) - are indicated to gravimetrically prepare calibration standards. CRMs produced in accordance with ISO 17034 are indicated as suitable alternatives. Ethanol of 99 % purity with less than 1 mg/kg S content is used for blank. No indication is given for the uncertainty of the gravimetric stock solution/calibration standards. No requirements for traceability. Balance capable of weighing to the nearest 0.1 mg is indicated.

B.2 Phosphorus

Four standards are indicated for the determination of phosphorous in liquid biofuels, as following:

EN 15487:2009 Ethanol as a blending component for petrol - Determination of phosphorus content - Ammonium molybdate spectrometric method

The standard specifies a procedure for the determination of phosphorous content measured as orthophosphate, in ethanol from 0.15 mg/L to 1.50 mg/L by ammonium molybdate spectrometric method. The phosphorous content is determined in an aqueous solution after the dissolution of the evaporation residue of ethanol sample.

<u>Principle of method</u>: After evaporation of the ethanol sample, the dry residue is dissolved in water. The aqueous solution is treated with an acid solution containing molybdate and antimony ions to obtain an antimony phosphor-molybdate complex. The complex is treated with ascorbic to form an intensely coloured molybdenum blue complex. The content of phosphorous is obtained by measuring the absorbance of the complex at 880 nm.

EN 15837:2009 Ethanol as a blending component for petrol - Determination of phosphorus, copper and sulfur content - Direct method by inductively coupled plasma optical emission spectrometry (ICP OES)

SR EN 14107:2003 Fat and oil derivates. Fatty Acid Methyl Esters (FAME). Determination of phosphorus content by inductively coupled plasma (ICP) emission spectrometry

The European standard specifies an inductively coupled plasma (ICP) emission spectrometry method to determine phosphorous content between 4 mg/kg and 20 mg/kg in FAME. The

method aims to evaluate the FAME quality in terms of transesterification by-products, such as phosphorous, whose concentration may affect the fuel behaviour.

Principle of the method: A weighted test portion of the sample is diluted at least ten times in xylene. Ten times dilution is needed to allow a proper introduction of the aerosol into the plasma. Xylene may be replaced by other suitable solvents in the case of unstable plasma. The standards are prepared from organic phosphorous compounds dissolved in mineral oil and diluted in a mixture of xylene and stock oil. The addition of stock oil makes it possible to reduce the difference in viscosity between samples and standards and improves their storage. The solutions are introduced in aerosol form into an inductively coupled argon plasma. The phosphorous content is determined by comparing the emission of the element in the solution of the test portion of the sample with the emission standards at the same wavelength. The commonly used wavelengths are 213.6 nm and 178.3 nm. The calibration of the instrument is in the range 0.0 - 4 mg/L.

Performance data:

- repeatability: < 0.6 mg/kg for maximum one determination out of 20,
- Reproducibility: $R = 0.1923\,X + 0.025$.

As a result of a European collaborative test involving 12 laboratories, the obtained performance data EN ISO 4259 are presented in Table B3.

Table B3. Precision data for phosphorous content

Average content, mg/kg	r, mg/kg	r_{limit}, mg/kg	R, mg/kg	R_{limit}, mg/kg
7.71	0.24	0.74	0.39	1.22
11.5	0.12	0.38	0.81	2.53
4.47	0.17	0.54	0.50	1.54
19.53	0.22	0.68	0.66	2.05
0.39	0.06	0.22	0.24	0.96

EN 16294:2012 Petroleum products and fat and oil derivatives - Determination of phosphorus content in fatty acid methyl esters (FAME) - Optical emission spectral analysis with inductively coupled plasma (ICP OES)

The European Standard specifies an inductively coupled plasma optical emission spectrometry (ICP OES) method to determine phosphorus content of FAME in the range of 2.5 mg/kg to 8.0 mg/kg.

Principle of the method: A weighted amount of FAME sample is diluted with kerosene. The solution is then introduced directly into an ICP-OES spectrometer. Phosphorous content is determined by comparison with calibration solutions. An internal standard is used to correct viscosity effects. Calibration of instrument and calibration solutions are required.

B.3 Heavy metals

Copper is limited in ethanol, and manganese in fuel samples. The indicated standardized methods are as follows:

EN 15488:2007 Ethanol as a blending component for petrol - Determination of copper content - Graphite furnace atomic absorption spectrometric method

This standard specifies a procedure for determining copper content in ethanol from 0.07 mg/kg to 0.20 mg/kg using graphite furnace atomic absorption spectrometry.

Principle of method: The graphite furnace is aligned in the optical path of the atomic absorption spectrometer. A test portion is pipetted onto the platform or at the wall of the graphite furnace. The furnace is heated in consecutive thermal stages, firstly to dry the test portion completely without spattering, eliminating excess sample matrix, and finally volatilizing the analyte of interest. During this final stage, the amount of light absorbed by the copper atoms is measured over a specified period. The integrated absorbance A_i, produced by the copper in the test portion, is compared to a calibration curve constructed from copper standards in ethanol solution. The second heating stage is used to eliminate as much of the sample matrix as possible before the atomization step, as non-dissociated molecular species are the most common form of interference. Spectrometers are equipped with background correction capabilities to control further possibilities of erroneous results due to molecular absorption. Copper standard and calibration of the instrument are required.

EN 15837:2009 Ethanol as a blending component for petrol - Determination of phosphorus, copper and sulfur content - Direct method by inductively coupled plasma optical emission spectrometry (ICP OES)

The document specifies an ICP-OES method for the direct determination of elements content in ethanol, namely phosphorus in the range (0.13 to 1.90) mg/kg, copper in the range (0.050 to 0.300) mg/kg, and sulfur in the range (2.0 to 15.0) mg/kg.

Principle of method: A portion of a sample is directly injected into the spray-chamber of an inductively coupled plasma emission spectrometer. The element content is determined by comparing the emission of the element in the test portion with the calibration solutions' emission at the same wavelength.

In accordance with the FQD, the standardized method for manganese is under development and only limits are required. For different other matrices, the manganese is widely determined using ICP-OES, FAAS or ICP-MS.

Lead is determined in accordance with EN 237:2004; the petroleum sample diluted with methyl isobutyl ketone and treated with iodine in determined using flame atomic absorption

B.4 Alkali and earth alkali elements (sodium, potassium, calcium, and magnesium)

SR EN 14108:2003 Fat and oil derivates. Fatty Acid Methyl Esters (FAME). Determination of sodium content by atomic absorption spectrometry

The European Standard specifies a method for the determination of sodium contents equal to or greater than 1 mg/kg. This method is applicable to fatty acid methyl esters intended for addition to mineral oil.

Principle of the method: The vegetable oil methyl ester sample is diluted with a xylene solution. Xylene can be replaced by cyclohexane or light petroleum in those laboratories that are not authorized to use aromatic solvents. FAAS directly determines the sodium content in the sample at the wavelength of 589 nm. The calibration solutions used are prepared from an organometallic sodium salt dissolved in a mixture of xylene and stock oil. The addition of stock oil to the calibration solutions is necessary to improve their storage (the low element contents are unstable) and the calibration's linearity. The ester sample shall be diluted at least 25 times with xylene, so comparing the measurements of the sample solution and standards is valid. The calibration of the instrument is in the range 0.1 … 0.3 mg/L.

Performance data:

- repeatability: $r = 0.086\,X + 0.242$;
- Reproducibility: $R = 0.263\,X + 1.355$.

As a result of a European collaborative test involving 13 laboratories, the obtained performance data are presented in Table B4.

Table B4. Performance data for sodium determination

Average content, mg/kg	r, mg/kg	r_{limit}, mg/kg	R, mg/kg	R_{limit}, mg/kg
4.96	0.23	0.70	0.88	2.70
1.14	0.10	0.32	0.53	1.64
3.14	0.21	0.64	0.69	2.10
1.00	0.13	0.39	0.54	1.67
3.01	0.11	0.32	0.69	2.13

SR EN 14109:2003 Fat and oil derivates. Fatty Acid Methyl Esters (FAME). Determination of potassium content by atomic absorption spectrometry

The European Standard specifies a method for determining potassium contents equal to or greater than 0.5 mg/kg. This method applies to fatty acid methyl esters intended for addition to mineral oil.

<u>Principle of the method</u>: The vegetable oil methyl ester sample is diluted with a xylene solution and a stabilizer. Xylene can be replaced by cyclohexane or light petroleum in those laboratories that are not authorized to use aromatic solvents. FAAS directly determines the potassium content in the sample at the wavelength of 766.5 nm. The calibration solutions used are prepared from an organometallic potassium salt dissolved in a mixture of xylene and stabilizer. The addition of a stabilizer to the calibration solutions is necessary to improve their storage (the low element contents are unstable) and the calibration's linearity. The ester sample shall be diluted at least 10 times with xylene, so comparing the measurements of the sample solution and standards is valid. Calibration of the instrument is in the range 0.1 ... 0.3 mg/L.

Performance data:

- repeatability: r = 0.3 mg/kg;
- Reproducibility: R = 0.505 X + 0.522.

As a result of a European collaborative test involving 13 laboratories, the obtained performance data are presented in Table B5.

Table B5. Performance data for potassium determination

Average content, X, mg/kg	r, mg/kg	r_{limit}, mg/kg	R, mg/kg	R_{limit}, mg/kg
0.15	0.13	0.43	0.14	0.45
0.50	0.07	0.21	0.26	0.80
5.60	0.08	0.23	1.04	3.21
4.42	0.09	0.28	0.92	2.83
2.49	0.06	0.19	0.64	1.98

Note that a mass fraction of 0.50 mg/kg reproducibility is 52 %, and NMI's capability is almost 2.5 times lower.

EN 14538:2006 Fat and oil derivatives - Fatty acid methyl ester (FAME) - Determination of Ca, K, Mg and Na content by optical emission spectral analysis with inductively coupled plasma (ICP OES)

This document establishes the method to determine direct the elements that form soaps, calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K), from the methyl esters of fatty acids (EMAG), by ICP-OES spectrometry, in the range from 1 mg/kg to 10 mg/kg.

Principle of the method: An exact weighed test portion is diluted with kerosene using a 1:1 weight ratio. The resulting solution is directly injected into the plasma of the ICP-OES spectrometer. For reference and calibration purposes, calibration samples with known contents of the element(s) under investigation in the range of 0.5 mg/kg to 10 mg/kg are used. The sum of the content of calcium and the content of magnesium and the sum of the content of sodium and the content of potassium is reported. Calibration of the instrument is required. Standard solutions are indicated for the preparation of calibration solutions. Alkali and earth alkali metals present in liquid samples are determined using either optical emission spectrometry or atomic absorption spectrometry. Applying these methods, instrument calibration, and the use of suitable certified references are critical for ensuring the traceability of the reported result.

B.5 Inorganic chloride

EN 15492:2012 Ethanol as a blending component for petrol – Determination of inorganic chloride and sulfate content – Ion chromatographic method

This European Standard specifies an ion chromatographic (IC) method to determine inorganic chloride content in ethanol from about 1 mg/kg to about 30 mg/kg and of sulfate content in ethanol from about 1 mg/kg to about 20 mg/kg. Sulfate content can be determined from 0.5 mg/kg to 1.0 mg/kg. However, the precision was not established as no samples with sulfate content in this range were included in the interlaboratory test.

Principle of the method: A test portion of the ethanol sample is evaporated on a water bath. The dry residue is dissolved in water. The chloride and sulfate ion contents are determined by comparing the peak area in the chromatogram of the aqueous solution of the test portion with the calibration standards curve. The calibration standards are prepared from suitable compounds in an aqueous solution. Applying these methods, instrument calibration, and suitable certified references is critical for ensuring the traceability of the reported result.

B.6 Water

B.6.1 In bioethanol

EN 15489:2007 Ethanol as a blending component for petrol - Determination of water content - Karl Fischer coulometric titration method

The document specifies a method for the direct determination of water in ethanol to be used in gasoline blends. It is applicable to ethanol having water contents (mass faction) in the range 0.039 % (m/m) to 0.500 % (m/m).

Principle of the method: A weighted test portion is injected into the titration vessel of a coulometric Karl Fisher apparatus in which iodine for the Karl Fisher reaction is generated coulometrically at the anode. When all the water has been titrated, excess iodine is detected by an electrometric end-point detector, and the titration is terminated. Based on the stoichiometry of the reaction, one mole of iodine reacts with one mole of water. Thus, the quantity of water is proportional to the total integrated current according to Faraday's Law. Instrument method verification is given

Performance data:

- repeatability: $r = 0.011\ 16\ (X +1)$, % (m/m);
- Reproducibility: $R = 0.018\ 80\ (X +1)$, % (m/m).

Typical values for repeatability and reproducibility are given in Table B6.

Table B6. Performance data

Water mass fraction, %	repeatability, % (m/m)	Reproducibility, % (m/m)
0.020	0.0114 (57 % rel)	0.0192 (96 % rel)
0.050	0.0117 (23 % rel)	0.0197 (39.4 %rel)
0.100	0.0123 (12.3 % rel)	0.0207 (20.7 %rel)
0.200	0.0134 (6.7 % rel)	0.0226 (11.3 %rel)
0.300	0.0145 (4.8 %rel)	0.0244 (8.13 %rel)
0.500	0.0167 (3.34 % rel)	0.0282 (5.64 %rel)

Note that the limit of mass fraction 0.300 % water in bioethanol is maximum admitted.

EN 15692:2009 Ethanol as a blending component for petrol - Determination of water content – Karl Fisher potentiometric titration method

The European Standard, developed as an alternative to EN 15489, specifies a method for determining water in ethanol to be used in gasoPline blends. It is applicable to ethanol having water contents (mass faction) in the range 0.05 % (m/m) to 0.54 % (m/m).

Principle of the method: A weighted test portion is injected into the potentiometric Karl Fisher apparatus's titration vessel. The water present is titrated to a potentiometric endpoint using a Karl Fisher reagent. Iodine (I_2) with the presence of anhydride sulfur (SO_2) of methanol (CH_3OH) and of an appropriate nitrogen base (RN) is introduced for the Karl Fisher reaction. Based on the stoichiometry of the reaction, one mole of iodine reacts with one mole of water. Thus, the quantity of water is proportional to the total integrated current according to Faraday's Law.

B.6.2 In biodiesel

EN ISO 12937: Petroleum products – Determination of water – Coulometric Karl Fisher titration method

A method is specified for the direct determination of water in petroleum products boiling below 390°C. It covers the mass fraction range 0.003 % (m/m) to 0.100 % (m/m). It is not applicable to products containing ketones or to residual fuel oils.

This International Standard may be applicable to lubricating base oils. However, precision has not been established for these materials.

Several substances and classes of compounds associated with condensation or oxidation-reduction reactions interfere in the determination of water by Karl Fischer titration. In petroleum products, the most common interferences are hydrogen sulfide and mercaptan sulfur, however, mass fractions of these below 0.003 % (*m/m*) as sulfur will not cause significant interference over the range 0.003 % (*m/m*) to 0.100 % (*m/m*) water. Other organic sulfur compounds commonly present such as sulfides, disulfides and thiofenes, do not interfere.

<u>Principle of the method</u>: A weighted portion of clear and bright, and free from both water droplets and particulate matter on swirling is injected into the titration vessel of a coulometric Karl Fisher apparatus in which iodine for the Karl Fisher reaction is generated coulometrically at the anode When all the water has been titrated, excess iodine is detected by an electrometric end-point detector and the titration is terminated. Based on the stoichiometry of the reaction, one mole of iodine reacts with one mole of water, thus the quantity of water is proportional to the total integrated current according to Faraday's Law. For samples not fulfilling the above-mentioned criteria, a solution of sodium dioctylsulfosuccinate is added before homogenization with a mixer.

The precision based upon data obtained using dual-cell, dual-electrolyte systems, are:

- repeatability, $r = 0.0187\,X^{0.5}$;
- Reproducibility, $R = 0.06877\,X^{0.5}$.

Note that only coulometric or potentiometric Karl Fischer titration is used for the determination of water in liquid biofuels. Coulometric KF is used for lower water content ranges.

B.7 Organic impurities

B.7.1 In bioethanol

Methanol and higher saturated monoalcohols are limited in bioethanol, and only one standardized method is indicated:

EN 15721:2013 'Ethanol as a blending component for petrol - Determination of higher alcohols, methanol and other impurities - Gas chromatographic method'

The document specifies a gas chromatographic (GC) method for ethanol, in which higher alcohols (propan-1-ol, butan-1-ol, butan-2-ol, 2-methylpropan-1-ol (isobutanol), 2 methylbutan 1 ol, and 3 methylbutan 1 ol) from 0.1 % up to 2.5 % (*m/m*), methanol from 0.1 % up to 3 % (*m/m*) and other impurities, in the range from 0.1 % up to 2 % (*m/m*) are determined. Impurities are all the compounds not attributed to the groups of higher alcohols or methanol. Due to possible interferences, the method is not applicable to denatured ethanol samples. If present in the sample, water is not included in this analysis because a signal for water is not visible in the chromatogram. Therefore, if "alcohol content" is called up in a specification, water needs to be considered separately in the calculations. The compounds specified in the scope are determined by direct injection of a test portion into a gas chromatograph (GC) system. An internal standard is added to the sample before the injection. The compounds are separated with suitable GC equipment using temperature programming with the option also to use flow programming on a suitable column. They are detected using a flame ionisation detector (FID). The concentration of each compound is determined from response factors with respect to the internal standard. The response factors are obtained during calibration using the same chromatographic conditions as those for the ethanol samples analysis. Two procedures ("Procedure A" and "Procedure B") are specified, which differ mainly in the optional use of a water dilution step prior to the analysis. Both variants have been validated to produce identical results and precision in extensive RR tests.

B.7.2 In biodiesel

Several organic components are restricted in biodiesel. Almost for each type a standardized method is indicated.

EN 14103:2020 Fat and oil derivates. Fatty acid methyl esters (FAME). Determination of ester and linolenic acid methyl ester content

A procedure is described for the determination of the esters content in FAME intended for incorporation into diesel oil. It also allows determining the linoleic acid ester content. It allows verifying that the ester content of FAME is greater than 90 % (m/m) and that the linoleic acid methyl ester content is between 1 % (m/m) and 15 % (m/m). The method is suitable for FAME, which contains methyl esters between C6 and C24. The method was elaborated for FAME

samples from the usual raw material. For FAME sample from unidentified raw material, a solution of test sample is prepared without any standard internal addition in order to verify the absence of natural nonadecanoic methyl ester or other unknown substances co-eluting with the internal standard.

<u>Principle of the method</u>: Determination of mass percentage of total methyl esters of fatty acids and the mass percentage of linolenic acid ester present in the sample, by GC according to a procedure using internal standard. The precision was established using FAMEs with an ester content of 95 % (*m/m*) and 100 % (*m/m*) only, thus covering the limit value range. The method is also suitable outside of this range. However, precision for lower concentration is subject to further work. The precision was determined in accordance with EN ISO 4259 Petroleum products – determination and application of precision data in relation to methods of tests.

repeatability: for ester content:

- r = 1.65, % (m/m); for linoleic acid methyl ester:
- r = 0.0092 * (x + 3.9180), % (m/m).

Reproducibility: for ester content:

- R = 2.45, % (m/m); for linoleic acid methyl ester:
- R = 0.0185 * (x + 3.9180), % (m/m).

As a result of a European collaborative test involving 16 laboratories, the obtained performance data were as follows:

- repeatability:
  - for ester content: r = 1.6500, % (m/m), for 55 degrees of freedom;
  - for linoleic acid methyl ester: r = 0.0092 * (x + 3.9180), % (m/m),), for 52 degrees of freedom
- Reproducibility:
  - for ester content: r = 2.4520, % (m/m), for 61 degrees of freedom;
  - for linoleic acid methyl ester: r = 0.0185 * (x + 3.9180), % (m/m), for 65 degrees of freedom.

EN 15779:2009+A1:2013 Petroleum products and fat and oil derivates - Fatty acid methyl esters (FAME) for diesel engines - Determination of polyunsaturated (≥4 double bonds) fatty acid methyl esters (PUFA) by gas chromatography

Based on A.O.C.S Official Method Ce 1b-89, a method is specified for the determination of the polyunsaturated (≥ 4 double bonds) fatty acid (PUFA) methyl esters content of FAME as a whole between 0.6 % (m/m) and 1.5 % (m/m). The method covers the predominant four polyunsaturated fatty acid methyl esters of eicosatetraenoic acid (C 20:4 (n-6)),

eicosapentaenoic acid (C 20:5 (n-3)), docosapentaenoic acid (C 22:5 (n 3), and docosahexaenoic acid (C 22:6 (n 3)). Studies have indicated that based on the linearity of results from this European Standard, PUFA methyl esters can be determined in FAME in the range between 0.3 % (m/m) to 3.0 % (m/m). However, the precision was not established in that range, as no samples within the upper ranges were included in the final interlaboratory test. Although the method is applicable to all uses, it is predominantly for FAME for use in diesel engines.

Principle of the method: Determination of the percentage of polysaturated (more than or equal to 4 double bonds) fatty acid methyl ester (PUFA) present in FAME is performed GC with FID detection using internal calibration with C 23:0 methyl ester. The theoretical detector correction factors are relative to C 23:0 internal standard for different poly-unsaturated ester types are applied to the analytical data for optimum accuracy.

A reference chromatogram based on salmon oil methyl ester is given. Reagents of high purity are required.

EN 14110:2020 Fat and oil derivates. Fatty acid methyl esters (FAME). Determination of methanol content

A procedure is described for the determination of the methanol content in FAME for use as diesel fuel and heating fuel. The method is applicable for a concentration range from 0.01 to 0.5 % (m/m) methanol. The method is not applicable to mixtures of FAME, which contain other low boiling components.

Principle of the method: The sample is heated at 80°C in a hermetically sealed vial to allow desorption of contained methanol into the gas phase. When the equilibrium is reached, a defined part of the gas phase is injected into a gas chromatograph where methanol is detected with a flame ionization detector. Normally methanol is the only peak in the chromatogram. The amount of methanol is calculated by reference to an external calibration. Methanol can also be determined after the addition of an internal standard to the sample before heating, followed by calculation with the use of an internal calibration factor. Standards and internal standard are gravimetrically prepared from high purity reagents. No traceability and no measurement uncertainty indication.

Performance of the method:

- repeatability: $r = 0.056\,X + 0.001$
- Reproducibility: $R = 0.221\,X + 0.003$

As a result of a European collaborative test involving 10 laboratories, the obtained performance data are presented in Table B7.

Table B7. Performance data for methanol determination

Average content, % (m/m)	r, % (m/m)	r_{limit}, % (m/m)	R, % (m/m)	R_{limit}, % (m/m)
Internal standard				
0.071	0.002	0.005	0.007	0.018
0.105	0.003	0.008	0.013	0.037
0.008	0.000	0.001	0.001	0.003
0.020	0.001	0.002	0.003	0.007
0.136	0.030	0.008	0.011	0.030
External standard				
0.063	0.001	0.004	0.006	0.016
0.097	0.003	0.008	0.009	0.025
0.007	0.001	0.002	0.002	0.004
0.017	0.001	0.002	0.003	0.008
0.122	0.002	0.006	0.010	0.027

EN 14105:2003 Fat and oil derivates. Fatty acid methyl esters (FAME). Determination of free and total glycerol and mon-, di-, triglyceride contents

It describes the method to determine the free glycol and residual mon-, di-, triglyceride content in FAME intended for mineral oil. The total glycerol content is then calculated from the obtained results. Under the conditions described, the quantification limits are 0.001 % (m/m) for free glycerol, 0.10 % (m/m) for all glycerides (mono-, di-, and tri-). This method is suitable for FAME prepared from rapeseed, sunflower, soybean, palm, animal oils and fats, and a mixture. It is not suitable for FAME produced from or containing coconut and palm kernel oils derivatives because of the overlapping of different glyceride peaks.

Principle of the method: Transformation of the glycerol and of the mono- and diglycerides into more volatile and stable silyl derivatives in the presence of pyridine and of N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA). Analysis of the sample after silylation by GC on short capillary column with thin film thickness, with an on-column injector or equivalent device, and flame ionization detection. After a calibration procedure, the quantification of glycerol is carried out in the presence of the internal standard 1,2,4-butanetriol. Mono-, di-, and triglycerides are directly evaluated in presence of an internal standard for each glyceride category:

- glyceryl monononadecanoate (Mono C19) for monoglycerides;
- glyceryl dinonadecanoate (Di C38) for diglycerides;
- glyceryl trinonadecanoate (Tri C57) for triglycerides.

Commercial standards are indicated.

The performance of the method is presented in Table B8.

Table B8. Performance of the method

	repeatability	Reproducibility
Free glycerol	0.1615 X + 0.0003	0.1833 X + 0.0061
monoglycerides	0.0787 X + 0.0059	0.1867 X + 0.0654
diglycerides	0.0989 X + 0.0042	0.1885 X + 0.0289
triglycerides	0.0469 X + 0.0128	0.3180 X + 0.0520
Total glycerol	0.1092 X + 0.0034	0.1902 X + 0.0115

As a result of a European collaborative test involving 16 laboratories, the obtained performance data are presented in Table B9.

Table B9. Performance data for glycerides determination

Mean value, % (m/m)	r, % (m/m)	r_{limit}, % (m/m)	R, % (m/m)	R_{limit}, % (m/m)
monoglyceride				
0.42654	0.01325	0.04009	0.05286	0.15999
0.43379	0.01272	0.03849	0.06011	0.18193
0.61554	0.02208	0.06683	0.06355	0.19142
0.76120	0.02685	0.08088	0.07516	0.22533
0.30308	0.00792	0.02320	0.02564	0.07833
0.81008	0.01577	0.04862	0.05869	0.18094
diglycerides				
0.14203	0.00619	0.01864	0.02123	0.06395
0.15967	0.00603	0.01817	0.01872	0.05614
0.17237	0.00713	0.02148	0.01961	0.05880
0.30508	0.01127	0.03441	0.02977	0.09010
0.18457	0.00767	0.02309	0.01857	0.05540
0.08077	0.00414	0.01246	0.01527	0.04601
triglycerides				
0.18181	0.00755	0.02305	0.03785	0.11670
0.05339	0.00570	0.01726	0.02023	0.06121
0.07250	0.00529	0.01601	0.02290	0.06932
0.015479	0.00707	0.02140	0.04819	0.14721
0.31533	0.00859	0.02649	0.04274	0.13299
0.07189	0.00408	0.01236	0.01817	0.05499
Free glycerol				
0.00744	0.00050	0.00150	0.00251	0.00754
0.00600	0.00035	0.00106	0.00231	0.00695
0.01393	0.00082	0.00246	0.00253	0.00758
0.00931	0.00079	0.00237	0.00258	0.00775
0.00353	0.00026	0.00078	0.00220	0.00666
0.01210	0.00066	0.00198	0.00321	0.00967
Total glycerol				
0.15423	0.00520	0.01590	0.01452	0.04393
0.14582	0.00534	0.01617	0.01483	0.04468

0.20271	0.00781	0.02364	0.01700	0.05096
0.26192	0.00922	0.02818	0.02224	0.06732
0.13925	0.00171	0.00527	0.01008	0.03136
0.23833	0.00492	0.01518	0.01556	0.04797

EN 14106:2003 Fat and oil derivates. Fatty acid methyl esters (FAME). Determination of free glycerol content

It specifies a GC method for the determination of free glycerol content in FAME in the range of (0.005 … 0.070) %. The method aims to evaluate the FAME quality in terms of transesterification by-products content such as glycerol, whose concentration may affect the fuel behaviour.

<u>Principle of the method</u>: Ethyl alcohol, water and a known amount of internal standard are added to a known quantity of sample. The addition of these solvents causes the formation of two phases, and free glycerol is quantitatively transferred into a lower one. The GC analysis of the lower phase allows to quantify the concentration of free glycerol. Standards and internal standard are gravimetrically prepared from high purity reagents. No traceability and no measurement uncertainty indication.

Performance of the method:

- repeatability, $r = 0.4664\,X - 0.0012$
- Reproducibility, $R = 0.7812\,X + 0.0032$

As a result of a European collaborative test involving 7 laboratories, the obtained performance data are presented in Table B10.

Table B10. Performance data

Average content, % (m/m)	r, % (m/m)	r_{limit}, % (m/m)	R, % (m/m)	R_{limit}, % (m/m)
0.018	0.001	0.004	0.003	0.011
0.014	0.001	0.004	0.004	0.015
0.032	0.005	0.018	0.007	0.025
0.001	0.000	0.001	0.002	0.006
0.048	0.006	0.020	0.012	0.042

Note that mostly gas-chromatographic methods are used with FID and MS detectors to determine the organic impurities. Also, all performance date are statistically determined according to EN ISO 4259.

Annex C – Relevant standardized methods for solid biofuels

This annex presents the review of the standardized methods for the determination of moisture content and inorganic impurities in solid biofuels.

C.1 Moisture content in solid biofuels

EN ISO 18134-1:2015 Determination of moisture content — Oven dry method — Part 1: Total moisture — Reference method

This part of ISO 18134 describes the method of determining the total moisture content of a test sample of solid biofuels by drying in an oven and may be used when high precision of the determination of moisture content is necessary. The method described in this International Standard applies to all solid biofuels. The moisture content of solid biofuels (as received) is always reported based on the test sample's total mass (wet basis).

The term moisture content, when used with biomass materials, can be misleading since untreated biomass frequently contains varying amounts of volatile compounds (extractives), which might evaporate when determining moisture content by oven drying. Thus, the moisture content refers to all extractives in the sample, whereas the water content refers to the water in the sample.

Part 2 of this written standard describes the method of determining the total moisture content of a test sample of solid biofuels by drying in an oven and is used when the highest precision is not needed, e.g. for routine production control on site. The method described in ISO 18134 (all parts) applies to all solid biofuels. The moisture content of solid biofuels (as received) is always reported based on the test sample's total mass (wet basis).

C.1 Inorganic impurities on solid biofuels

EN ISO 18122:2015 Solid biofuels — Determination of ash content

EN 14775:2009 Solid biofuels — Determination of ash content

A method for the determination of ash content of all solid biofuels is described.

Principle of method: The ash content is determined by calculation from the residue's mass remaining after heating the sample under rigidly controlled conditions of time, sample weight, and equipment specification. Heating is controlled at (550 ±10).

Automatic equipment validated with biomass reference samples of adequate type may be used. Also, requirements for sample size, heating procedure, atmosphere, temperature and weighing accuracy apply.

Differences in the ash content determined at a higher temperature (such as 815 °C) are explained by the decomposition of carbonates, by losses of volatile inorganic compounds, and further oxidation of inorganic compounds to a higher oxidation stage.

EN ISO 16994:2016 Solid biofuels — Determination of total content of sulfur and chlorine

This International Standard describes methods for determining the total sulfur and total chlorine content in solid biofuels, specifying two methods for decomposition of the fuel and different analytical techniques for the quantification of the elements in the decomposition solutions. The use of automatic equipment is also included, provided that validation is carried out as specified and that the performance characteristics are similar to those of the method described in this International Standard.

Principle of the method: The determination of total S is performed in two steps or by using automatic equipment. Decomposition of the biofuel is accomplished either by

- combustion in an oxygen atmosphere in a combustion vessel and absorption of the acidic gas components in an absorption solution (method A), or
- digestion in closed vessels in a microwave oven with a mixture of H_2O_2 (3/12 parts), HNO_3 (8/12 parts), and HF (1/12 parts).

The sulfate in the decomposition solution is determined either by Ion Chromatography (ISO 10304-1) or by ICP (ISO 11885). Use of Certified Reference Materials is documented to check if the calibration accuracy meets the required performance characteristics. Examples of CRMs are given (SRM NIST 1570 spinach leaves, SRM 1571 orchard leaves, SRM tomato leaves). When due to matrix effects or concentration range limitations, no good recoveries for the CRMs can be obtained, calibration with at least two CRM or SRM materials is recommended (for example, CRM 101 spruce needles and CRM 100 beech leaves). By indicating the use of CRMs and/or SRMs information on measurement uncertainty and traceability may be deduced.

EN ISO 16967:2015 Solid Biofuels – Determination of major elements - Al, Ca, Fe, Mg, P, K, Si, Na, and Ti

The document describes methods for determining major elements of solid biofuels respectively of their ashes, which are Al, Ca, Fe, Mg, P, K, Si, Na, Ti. Other elements such as barium (Ba) and manganese (Mn) may also be determined with the methods described.

This International Standard includes two parts: Part A describes the direct determination on the fuel, this method is also applicable for sulfur and minor elements, Part B gives a method of determination on a prepared 550°C ash.

Principle of method: The sample is digested in a close vessel with reagents, temperature, and pressure. The digestion is realized either direct on the biofuel (part A) or on the ash prepared

at 550 °C (part B). The detection of the elements may be realized by ICP-OES, ICP-MS, FAAS, or FES. The use of CRMs or SRMs is documented. Examples of such materials used in the standardized procedure are SRM NIST 1570 spinach leaves, SRM NIST 1571 orchid leaves, SRM NIST 1573 tomato leaves, SRM NIST 1575 pine needles.

Performance data are given for elements, as shown in Table C1.

Table C1. Precision data for major elements determination in solid biofuels

	Overall average, mg/kg	repeatability, r, mg/kg	Reproducibility, R, mg/kg
Aluminium			
Wood chips	47	2	8
Exhausted olive cake	2360	110	170
Calcium			
Wood chips	1500	24	100
Exhausted olive cake	14200	607	1040
Iron			
Wood chips	54	4	6
Exhausted olive cake	1600	81	165
Magnesium			
Wood chips	194	3	14
Exhausted olive cake	3140	149	243
Phosphor			
Wood chips	74	2	5
Exhausted olive cake	1490	58	127
Potassium			
Wood chips	691	12	77
Exhausted olive cake	24500	468	1560
Silica			
Wood chips	320	36	106
Exhausted olive cake	10040	769	1230
Sodium			
Wood chips	13	2	6
Exhausted olive cake	171	9	40
Titan			
Wood chips	5.5	0.32	0.40
Exhausted olive cake	136	6	11

EN ISO 16968:2015 Solid biofuels — Determination of minor elements

This standard is intended to determine the minor elements As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V and Zn in all solid biofuels. Further, it describes methods for sample decomposition and suggests suitable instrumental methods for determining the elements of interest in the digests. The determination of other elements such as Se, Sn and Tl is also possible with the method described.

Principle of method: The analysis sample is digested in a closed vessel made from fluoropolymer using HNO_3, H_2O_2 and HF in a microwave oven or a resistance owe or heating block. The digest is then diluted, and the elements are determined with suitable instruments.

Indicated methods include CV-AAS, GF-AAS, HG-AAS, ICP-OES ICP-MS. Calibration of instrument and MRC & SRMs (1570, 1571, 1573, 1575) are requested. Heavy metals present/processed in liquid samples are determined using either optical emission spectrometry or atomic absorption spectrometry. Basically, two main procedures are indicated for sample decomposition: either by microwave digestion or ashing followed by dissolving the ash in an appropriate mixture of acids. Applying these methods, the instrument calibration and the use of suitable certified references are critical for ensuring the traceability of the reported result.

SR EN ISO 16995:2015 Solid biofuels – Determination of water-soluble chloride, sodium and potassium content

A method for the determination of the water-soluble chloride, sodium and potassium content in solid biofuels by extraction with water in a closed container and their subsequent quantification by different analytical techniques is described.

Principle of the method: The biofuel sample is heated with water in a close vessel at 120 °C for 1 h. The contents of chloride, sodium and potassium from the obtained water extract are determined by one of the followings techniques:

- chloride – ion chromatography or potentiometric titrimetry with Ag NO_3;
- sodium and potassium – flame emission spectrometry (FES) or flame atomic absorption spectrometry (FAAS) or
- optical emission spectrometry with inductive coupled plasma (ICP-OES)

As a result of a European collaborative test involving laboratories from 14 countries, the obtained performance data are presented in Table C2.

Table C2. Performance data

	Overall average, mg/kg	repeatability, r, mg/kg	Reproducibility, R, mg/kg
Soluble chloride			
Wood chips	26	5	13
Exhausted olive cake	2100	49	150
Soluble sodium			
Exhausted olive cake	99	8	16
Soluble potassium			
Wood chips	634	9	20
Exhausted olive cake	22400	524	1060