

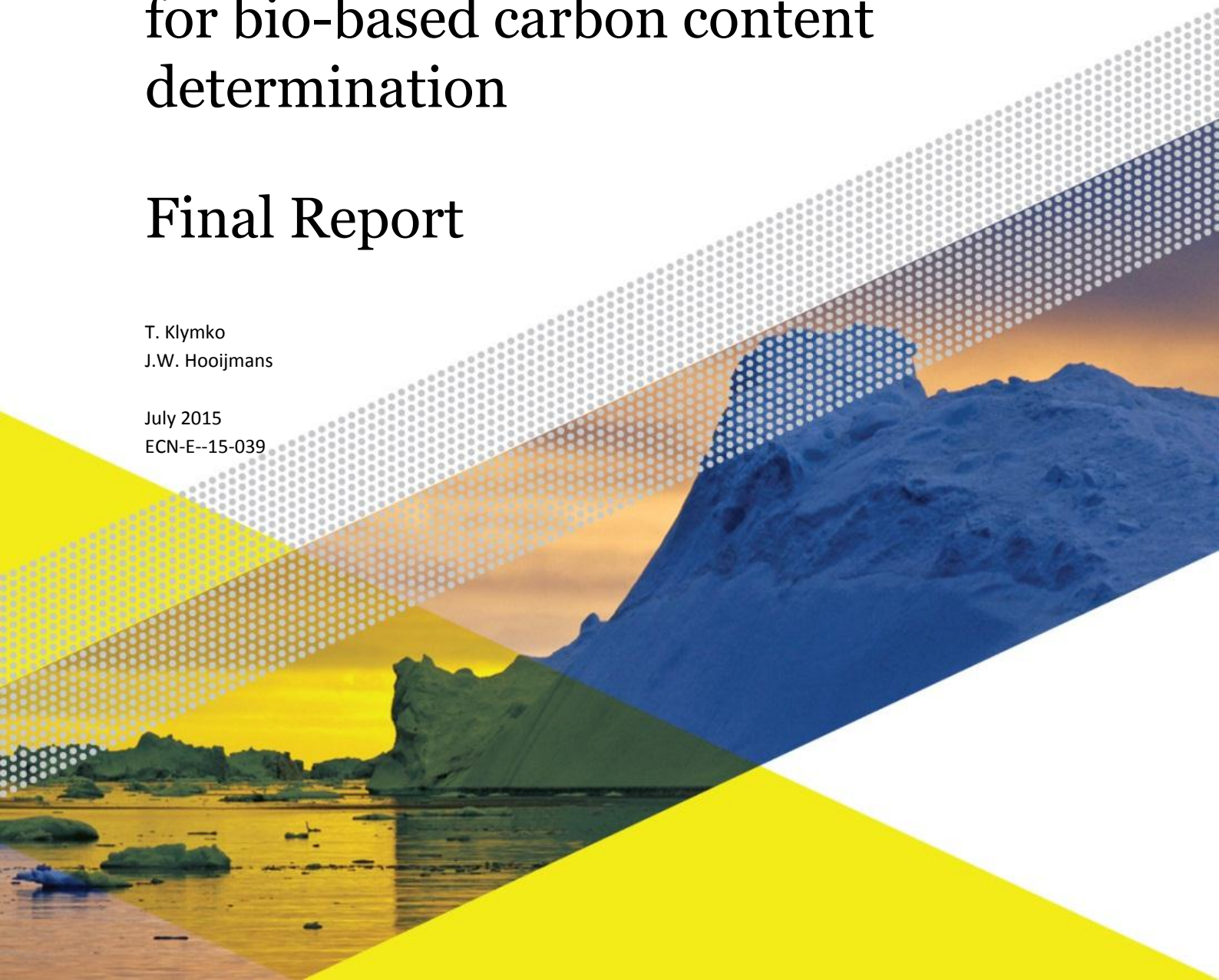
KBBPS

Knowledge Based Bio-based  
Products' Pre-Standardization  
Public report on horizontal standard  
for bio-based carbon content  
determination

Final Report

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# **KBBPPS**

## **Knowledge Based Bio-based Products’ Pre-Standardization**

**Work package 3**  
**Bio-based carbon content**

**Deliverable N° 3.6:**

**Public report on horizontal standard for  
bio-based carbon content determination**

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KBBPPS

Work Package 3: Bio-based carboncontent

Deliverable 3.6. Public report on horizontal standard for biogenic carbon determination

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## 1 Summary

The term “bio-based” refers to products that are fully or partly derived from biomass. The extent to which a product is derived from biomass is characterized by its bio-based carbon content. Generally the bio-based carbon content is expressed as a fraction of the biogenic carbon ( $^{14}\text{C}$ ) to the total amount of carbon in a product.

The procedure for determining the bio-based carbon content was proposed and validated by interlaboratory testing in CEN/TS 16640. This report is a public report that describes the approach proposed in CEN/TS 16640 (Bio-based products – Determination of the bio-based carbon content of products using the radiocarbon method) for the bio-based carbon content determination.

Accordingly to CEN/TS 16640, the bio-based carbon content determination consists of three subsequent steps: first material has to be sampled. Then the sample has to undergo a proper pre-treatment, i.e it has to be converted to the form that is suitable for the  $^{14}\text{C}$  measurements. Finally the  $^{14}\text{C}$  measurements can be done on the pre-treated sample. CEN/TS 16640 describes the complete method that is recommended to use for the conversion of samples for the  $^{14}\text{C}$  analysis. The method is based on the complete combustion of the samples and collection of the  $\text{CO}_2$  that is released during the combustion process. The collected  $\text{CO}_2$  is then analysed for the  $^{14}\text{C}$  content. Representativeness of a sample and its complete combustion are required in order to achieve reliable results on the  $^{14}\text{C}$  content. Combustion shall be carried out to achieve as high as possible recovery (at least 95%) of all carbon present in the sample into  $\text{CO}_2$  in order to yield valid results.

Special care shall be taken in case of products with high water content and therefore with possible combustion difficulties. In such cases the use of combustion aids are recommended. The true biogenic carbon content that originates from the sample itself than needs to be recalculated and corrected taking into account all the carbon and subsequently the  $^{14}\text{C}$  that originates from the combustion aid. For samples that contain volatile components it has to be ensured that all carbon that may originate from the volatile part is not lost before combustion. It can be achieved by using chromosorb material in order to absorb the sampled material and prevent leakage and loss of material before combustion.

Having ensured that proper sample preparation and proper sample pre-treatment was done, the interlaboratory testing revealed that both AMS and LSC techniques produce equally reliable results and both of them can be used for the  $^{14}\text{C}$  content determination.

For finalizing CEN/TS 16640, the performance characteristics have to be established. This will be done on a round robin.



## 2 Introduction

The term “bio-based” refers to products that are fully or partly derived from biomass: they can be plastic bottles, wood or wood products, various chemicals, cosmetic products, composite materials, etc. The extent to which a product is derived from biomass is characterized by its bio-based content or by its bio-based carbon content. Generally the bio-based carbon content is linked to the biogenic carbon ( $^{14}\text{C}$ ) that originates from recent atmospheric  $\text{CO}_2$ . Since the  $^{14}\text{C}$  isotope is not stable and undergoes radioactive decay with half-period of approximately 5730 years, it is absent in old fossil products and is present only in products that originate from recent biomass. Therefore the  $^{14}\text{C}$  isotope of carbon is used as a tracer for components that are derived from recent biomass. Determination of the bio-based carbon content and subsequently of total bio-based content (not only carbon but also oxygen and/or hydrogen and/or nitrogen can be bio-based) of a given product is therefore based on the  $^{14}\text{C}$  analysis of the product.

Previously (but also existing now) there were some product oriented standards - as for example CEN/TS 16137 “Measuring the bio-based carbon content of plastics and other polymers” - for determination of bio-based carbon content in plastics. However, such product devoted standards can pose some limitations when their methods are supposed to be applied to products of different nature than described in these standards.

Therefore, the horizontal method for bio-based carbon content determination was proposed with the idea to have a universal method that could be applicable to various products and that could allow both the producers and the consumers of the products to evaluate the bio-based content in their products. This idea was implemented in the European project KBBPPS (Knowledge Based Bio-based Products’ Pre-Standardization) where the development of a standard test method for bio-based carbon content measurements in different bio-based products was taken as subject for investigations. Besides developing the method, these investigations included also all validation data before completing the Technical Specification CEN/TS 16640 and subsequently the European Standard for the bio-based carbon determination.

Currently, ASTM D6866 “Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis” is also used to determine the bio-based carbon content in solids, liquids or gases. Despite ASTM D6866 and CEN/TS 16640 both aim for the determination of the bio-based carbon content, there are several parts (listed below) that will be different in CEN/TS 16640. Finally, it is expected that ASTM D6866 and CEN/TS 16640 will be harmonized.

At the start of the project, CEN/TS 16640 was different from ASTM D6866 in the following aspects:



- It provided more instructions on sampling;
- It is written in terms of bio-based carbon as related to Total Carbon (TC) and not to Total Organic Carbon (TOC). In recent version of ASTM D6866 biogenic carbon content is introduced (next to the original bio-based carbon content) as the amount of bio-based carbon as the weight (mass) percent of the Total Carbon (TC) in the product.
- Pre-treatment described in ASTM D6866 is with regard to TOC. This introduces large error since it is difficult to separate organic and inorganic carbon during pre-treatment. CEN/TS 16640 describes pre-treatment that is necessary to liberate all total carbon available in a sample.
- Contrarily to ASTM D6866, there will performance characteristics mentioned in CEN/TS 16640 based on the results of the validation of the method in a round robin testing.
- No LSC (Liquid Scintillation Counting) method was incorporated for the  $^{14}\text{C}$  determination in ASTM D6866. However, this method is again added to ASTM D6866 in its latest version.

This report is a public report and gives an overview of the method that was proposed and confirmed by interlaboratory testing for the bio-based carbon content determination. This method is currently official method described in **CEN/TS 16640 “Bio-based carbon content determination of products using radiocarbon method”**.

The method consists of three main parts:

1. Sampling of a product where representativeness of the chosen sample compared to the whole product has to be guaranteed
2. Pre-treatment - conversion of available product sample to the form that is most suitable for the  $^{14}\text{C}$  analysis. Normally it implies conversion of a sample to  $\text{CO}_2$  via combustion. Complete combustion of the selected sample has to be ensured in order to have complete release of carbon available in the sample to its  $\text{CO}_2$  form
3. Determination of the  $^{14}\text{C}$  content in the collected  $\text{CO}_2$ . This step is standardized and well known AMS (Accelerated Mass Spectrometry) or LSC (Liquid Scintillation Counting) techniques are used for the  $^{14}\text{C}$  determination.

These three parts, followed by conclusions and recommendations, will be described further in this report. Since steps 1 and 3 are well known, most focus in this report will be on pre-treatment of the samples.



### 3 Horizontal method for bio-based carbon content determination

As it was already mentioned in the introduction part, the bio-based carbon content determination consists of three subsequent steps: first a material has to be sampled. Then the sample has to undergo a proper pre-treatment, i.e. it has to be converted to a form that is suitable for the  $^{14}\text{C}$  measurements. Finally  $^{14}\text{C}$  analysis shall be done on the pre-treated sample. Each of these steps has a defined set of requirements that need to be fulfilled in order to obtain reliable results on the bio-based carbon content. These requirements are described in the next sub-paragraphs.

#### 3.1 Sampling

The main purpose of sample preparation of a finished product is that a product is reduced to one or more test portions that are in general smaller than the original sample while at the same time maintaining the composition of the finished product. This is the main principle for sample reduction: the composition of the sample as taken on site shall not be changed during each stage of the sample preparation. Each subsample shall be representative of the original sample. To reach this goal every particle in the sample before sample division shall have an equal probability of being included in the sub-sample following sample division.

Both ASTM D7459 ("Standard Practice for Collection of Integrated Samples for the Speciation of Biomass (Biogenic) and Fossil-Derived Carbon Dioxide Emitted from Stationary Emissions Sources") and ISO 13833 ("Stationary source emissions -- Determination of the ratio biomass (biogenic) and fossil-derived carbon dioxide. Radiocarbon sampling and determination") and can be referred to for sampling guidelines.

In most cases, solid materials introduce no difficulties in obtaining a representative sample. However, practical difficulties can occur when sampling materials that are partially combustion resistant and therefore cannot be combusted completely (ceramics for example), or materials containing volatile components. Such materials are quite peculiar due to their inhomogeneity which cannot be removed by simple mechanical effects (crushing, shaking, centrifuging, mixing, etc.) Then a method of sampling has to be developed first on a laboratory scale.

All liquids, when sampling, should be either single phase or relatively homogeneous. The homogeneity in many cases can be achieved by stirring or centrifuging of a sample. Another approach is to separate the clear liquid and the sediment by centrifuging and then to examine them separately. In case of viscous liquids or materials with volatile components the transfer problems exaggerate weighing problems. Effort should be made to obtain the sample weight in the combustion tube, rather than transferring a previously weighed sample to the oxidation tube.





Independently of solid, liquid or gaseous state of a material or product to sample, attention should be paid to representativeness of a sample, its required minimal size and its homogeneity.

### 3.2 Pre-treatment accordingly to CEN/TS 16640

As it was already mentioned earlier in this report, CEN/TS 16640 describes the method for the bio-based carbon content determination in a wide range of material or product. Pre-treatment of the selected sample implies its complete combustion and collection of all carbon that is present in the sample in the CO<sub>2</sub> form.

Generally, to make all carbon free, material needs to be completely combusted, irrespectively of solid, liquid, or gaseous state of the material. After combustion procedure, all available carbon is gathered as CO<sub>2</sub> in some absorber: the CO<sub>2</sub> present in a representative stack gas sample is absorbed in an alkaline medium or transferred to a gas bag or lecture bottle. After sampling, the collected CO<sub>2</sub> is prepared for the <sup>14</sup>C analysis.

**Total carbon content** of a sampled material can be determined in two ways:

- 1 from carbon dioxide that is formed during combustion and subsequently trapped into a washing bottle containing a sodium hydroxide solution or absorbent column. The sodium hydroxide solution is titrated with acid to determine the carbonate concentration. From this, total carbon concentrations can be calculated;
- 2 using an elemental analyser.

The **recovery of carbon during combustion** is calculated as a ratio between the carbon content determined from titration to the carbon content determined via elemental analyser. Generally, the achieved recovery rate is recommended to be at least 95%.

As it is described in CEN/TS 16640, **the pre-treatment (combustion) can be done in several ways:** in a calorimetric bomb, in a tube furnace, or in a laboratory scale combustion apparatus:

- Calorimetric bomb

When combustion is done in a calorimetric bomb, the carbon dioxide formed is subsequently led into a washing bottle containing a sodium hydroxide solution or through a cartridge containing a solid absorbent (e.g. Ascarite). From the solid absorbent the carbon dioxide is washed of into a sodium hydroxide solution. The sodium hydroxide solution is titrated with acid to determine the carbonate concentration. As an example, in one of the laboratories, the material is combusted with pure oxygen (30psi) in a closed steel container. The temperature inside the closed container can reach up to 1500°C. Combustion in a calorimetric bomb cannot be done for gaseous samples.



- Element analyser

An element analyser can be used for combustion as well. In an elemental analyser, the material is combusted (975°C) in a quartz tube containing chromium oxide, copper wires, and silvered cobaltous oxide with oxygen and helium carrier gasses. The carbon dioxide formed is collected in a washing bottle containing a sodium hydroxide solution or collected in a cartridge containing a solid absorbent (e.g. Ascarite). The sodium hydroxide solution is titrated with acid to determine the carbonate concentration. As an advantage, elemental analyser can also be used for the determination of the total carbon, hydrogen, nitrogen and oxygen content of the material.

- Tube furnace

A tube furnace with temperature controller capable of maintaining a stable furnace temperature of 1100°C and a quartz tube can be used for combustion. The inlet end of the quartz tube shall be large enough to accept a sample boat and to have side arms for introduction of oxygen and inert gas. The construction is such that the carrier gas sweep (200 ml/min oxygen plus 200 ml/min argon) the inlet zone transporting all of the volatilized sample into a high-temperature oxidation zone. The reaction product (carbon dioxide) is collected at the outlet of the quartz tube in a washing bottle containing a sodium hydroxide solution or in a cartridge containing a solid absorbent (e.g. Ascarite). The sodium hydroxide solution is titrated with acid to determine the carbonate concentration.

**Special care shall be taken in case of:**

- liquid sample preparation since possible presence of volatile liquid components can be a cause for concern.
- gaseous sample preparation during combustion of some gasses, due to the large amount of energy produced. Also care should be taken by combusting mixtures of gases to be sure that a good homogeneous sample is combusted. In order to have correct <sup>14</sup>C content of gaseous products, care should be taken to ensure that all CO<sub>2</sub> that is present in the sample, is part of the product and not the atmospheric CO<sub>2</sub>. This can be achieved by trapping of the CO<sub>2</sub> that does not belong to the product, before the combustion. Sampling of CO<sub>2</sub> in stack gas is in principle not different from sampling of other acid gaseous substances. As CO<sub>2</sub> is present in relatively high concentrations compared to other acidic gaseous substances, the capacity of the absorption media requires careful consideration and excess of alkaline media shall be used to ensure complete absorption during the sampling period. Deliverable 3.4 of KBBPPS is recommended as a reference for the description of installation that can be used for combustion of gaseous samples.
- solid/liquid/gaseous sample preparation: complete combustion of the material must be ensured (with use of combustion enhancers if necessary), so that all (also non-organic carbon) is transformed to CO<sub>2</sub>. In case combustion aids are used it is of necessity to know which part of carbon originates from the enhancer and which belongs to the product.



Below **several standards are listed that can be used for conversion of different samples to CO<sub>2</sub>**, depending of their state:

For solid samples pre-treatment, the following standards can be used:

EN 15104: Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen - Instrumental methods.

EN 15400: Solid recovered fuels – Determination of the calorific value.

EN 15440: Solid recovered fuels – Method for the determination of biomass content.

EN 15443: Solid recovered fuels – Methods for the preparation of the laboratory samples.

EN 15413: Solid recovered fuels – Methods for the preparation of the test sample from the laboratory sample.

CEN/TS 16137: Plastics – Determination of bio-based carbon content.

ISO 1928: Solid mineral fuels – Determination of gross calorific value by the bomb calorimetric method.

For liquid samples pre-treatment, the standards mentioned below can be used:

ASTM D7455: Standard practice and sample preparation for petroleum and lubricant products for elemental analysis.

ASTM D5291: Standard test methods for instrumental determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants.

For conversion of gaseous samples to CO<sub>2</sub>, standards that are mentioned below can be used:

ISO 13833: Stationary source emissions - Determination of the ratio biomass (biogenic) and fossil-derived carbon dioxide. Radiocarbon sampling and determination.

ASTM D7459: Standard practice for collection of integrated samples for the specification of biomass (biogenic) and fossil-derived carbon dioxide emitted from stationary emission sources.

### **3.3 Bio-based carbon determination**

This paragraph describes the principles and the techniques that are used for bio-based carbon determination.



### 3.3.1 Background and principles

There are three naturally occurring isotopes of carbon: 99% of the carbon is carbon-12, 1% is carbon-13, and carbon-14 occurs in trace amounts, i.e. making approximately 1 atom per 1012 atoms of the carbon in the atmosphere.

The  $^{14}\text{C}$  is produced in the upper layers of atmosphere where thermal neutrons are absorbed by nitrogen atoms. When cosmic rays enter the atmosphere, they undergo various transformations, including the production of neutrons that participate in the reaction  $1n + ^{14}\text{N} \rightarrow ^{14}\text{C} + 1p$ , resulting in the  $^{14}\text{C}$  formation. The half-life of carbon-14 is  $5730 \pm 40$  years. Carbon-14 decays into nitrogen-14 through beta decay.

During their grow, plants absorb the  $\text{CO}_2$  from the atmosphere, thus the  $^{14}\text{C}$  that is present in biomass originates from recent atmospheric  $\text{CO}_2$ . Due to radioactive decay, it is almost absent in fossil materials older than 30 000 years. The  $^{14}\text{C}$  content may be thus considered as a tracer of products recently synthesized from atmospheric  $\text{CO}_2$  and particularly of recently produced bio-products. The only reliable determination of the biomass content in products is therefore based on the  $^{14}\text{C}$  measurements in bio-based products that allow calculation of the bio-based carbon fraction.

### 3.3.2 AMS and LSC techniques

Within the  $^{14}\text{C}$  determination method, three techniques are distinguished:

- 1) AMS - accelerator mass spectrometry
- 2) LSC - liquid scintillation counting
- 3) BI - beta-ionization technique

Since the BI measurements are not included in the normative part of CEN/TS 16640, but only in its informative part and besides its use is limited by only few laboratories in the world, it will also not be described in this report. When necessary, Annex D of CEN/TS 16640 can be referred to for the information on beta-ionization technique for the  $^{14}\text{C}$  determination.

AMS and LSC techniques are considered to be equivalent and are discussed further in this paragraph. Each of these techniques requires different amount of the  $\text{CO}_2$ : for AMS measurements the minimum amount of  $\text{CO}_2$  is 4 ml, and for LSC measurements the required amount of  $\text{CO}_2$  depends on the way the sample is prepared for measurement, but at least a few grams will be required.

After the  $^{14}\text{C}$  content is determined via AMS or LSC, the bio-based carbon content can be expressed as:

- Percentage of the total carbon of the product
- Percentage of the total mass of the product

The first way of representation is more common.



**Accelerator mass spectroscopy (AMS) / isotope ratio mass spectrometry (IRMS)**

This technique allows quantifying the bio-based content of a given product. Sample preparation methods include the production of CO<sub>2</sub> within a vacuum manifold system where it is ultimately distilled, quantified in a calibrated volume, transferred to a quartz tube, and torch sealed. This method represents a commonly used procedure to quantitatively combust the carbon fraction within product matrices of varying degrees of complexity. In this technique, sample atoms are ionized, accelerated to high energies, and then separated on basis of their momentum, charges and masses.

**Principle**

<sup>14</sup>C/<sup>12</sup>C and <sup>13</sup>C/<sup>12</sup>C isotopic ratios are determined using AMS. The AMS method determines the presence of the <sup>14</sup>C isotope directly. The atoms in the sample are converted into a beam of ions. The ions formed are accelerated in an electric field, and subsequently deflected in a magnetic field, and finally detected in ion detectors, resulting in the determination of the relative isotope abundances of these ions. AMS uses a high potential electrostatic field, which serves not only to accelerate but also to specifically form only C<sub>n+</sub> ions (n = 1 ... 4) that are allowed into the spectrometer, excluding all other ionic species. This enhances sensitivity without compromising selectivity. In most AMS systems, the <sup>14</sup>C is currently determined from graphite (carbon) sample targets. To obtain graphite sample targets, it is necessary to convert the CO<sub>2</sub> in each sample into graphite before analysing.

With AMS the amount of <sup>14</sup>C atoms is measured relative to the amount of (one of) the more abundant carbon isotopes <sup>12</sup>C and/or <sup>13</sup>C. This measured <sup>14</sup>C/<sup>12</sup>C or <sup>14</sup>C/<sup>13</sup>C ratio is calculated relative to the measured isotope ratio in a reference material with standardized <sup>14</sup>C amount, to obtain standardized and normalized <sup>14</sup>C content (in pMC) for each sample.

**Sample analysis**

A zero percentage of <sup>14</sup>C represents the entire lack of <sup>14</sup>C atoms in a material thus indicating a fossil (for example, petroleum based) carbon source. One hundred percentage <sup>14</sup>C, after correction for the post-1950 bomb injection of <sup>14</sup>C into the atmosphere, likewise indicates an entirely bio-based carbon source. The percentage modern carbon can be slightly greater than 100 % due to the continuing, but diminishing, effects of the 1950s nuclear testing programs. However, all certified laboratories refer to pMC value determined from the atmosphere every year. Because all recent biomass is harvested within three years this yearly adopted value is used.

All percentage modern carbon (pMC) values obtained from radiocarbon analyses must be corrected for isotopic fractionation using stable isotope data (<sup>13</sup>C/<sup>12</sup>C ratios) obtained on CO<sub>2</sub> derived from combustion of the sample.



### Liquid scintillation counting (LSC)

This technique allows us to quantify the bio-based content of a product. LSC determines the isotope abundance of  $^{14}\text{C}$  indirectly, through its emission of beta-particles due to the radioactive decay of the  $^{14}\text{C}$  isotope. The beta-particles are observed through their interaction with a scintillator. This test method determines the bio-based content of a sample with a maximum total error of  $\pm 3\%$ . The test method directly discriminates between product carbon resulting from contemporary carbon input and that derived from fossil-based input.

#### Principle

There are three methods that can be used for the preparation of the collected  $\text{CO}_2$  for activity measurement.

- $\text{CO}_2$  extracted from the flue gas is converted to benzene. This benzene is mixed with an organic solution containing a scintillator. The  $^{14}\text{C}$  activity of the mixture is measured in a liquid scintillation counter.
- $\text{CO}_2$  extracted from the flue gas is trapped in an amine solution thus forming carbamates. This solution is mixed with the organic solution containing the scintillation reagent. The  $^{14}\text{C}$  activity of the mixture is measured in a liquid scintillation counter in Bq.
- Direct LSC measurements. These measurements are possible when a liquid sample can be directly mixed with the scintillation liquid without prior combustion.

In all cases, the measured activity of the sample is calculated relative to the known  $^{14}\text{C}$  activity of a standard reference material to obtain standardized and normalized  $^{14}\text{C}$  content (in pMC) for each sample.

#### Sample analysis

Significant  $^{14}\text{C}$  counts indicate the presence of  $^{14}\text{C}$  carbon. The lack of any  $^{14}\text{C}$  counts in a material indicates a fossil (for example, petroleum based) carbon source. A sample that has the same  $^{14}\text{C}$  activity level (after correction for the post-1950 bomb injection of  $^{14}\text{C}$  into the atmosphere) as the oxalic acid standard is 100% bio-based and signifies an entirely modern carbon source.

## 3.4 Ruggedness test and small interlaboratory test for CEN/TS 16640

### Ruggedness test

Ruggedness tests were performed in one laboratory (ECN) in order to investigate carbon recoveries that can be achieved by the methods described in CEN/TS 16640. To check the applicability of the method to various products, partly or fully bio-based products of various nature (paints, binders used in paints, cosmetic emulsions, bio-gas, wooden products, packaging film) were investigated. Carbon recovery rate (ratio between the total carbon from combustion and titration and the total carbon determined by an elemental analyser) was calculated for each sample. For most tested materials, the  $\text{CO}_2$  conversion results indicated a very high carbon recovery rate (in the range 90 % - 100 %) and thus proved the reliability of

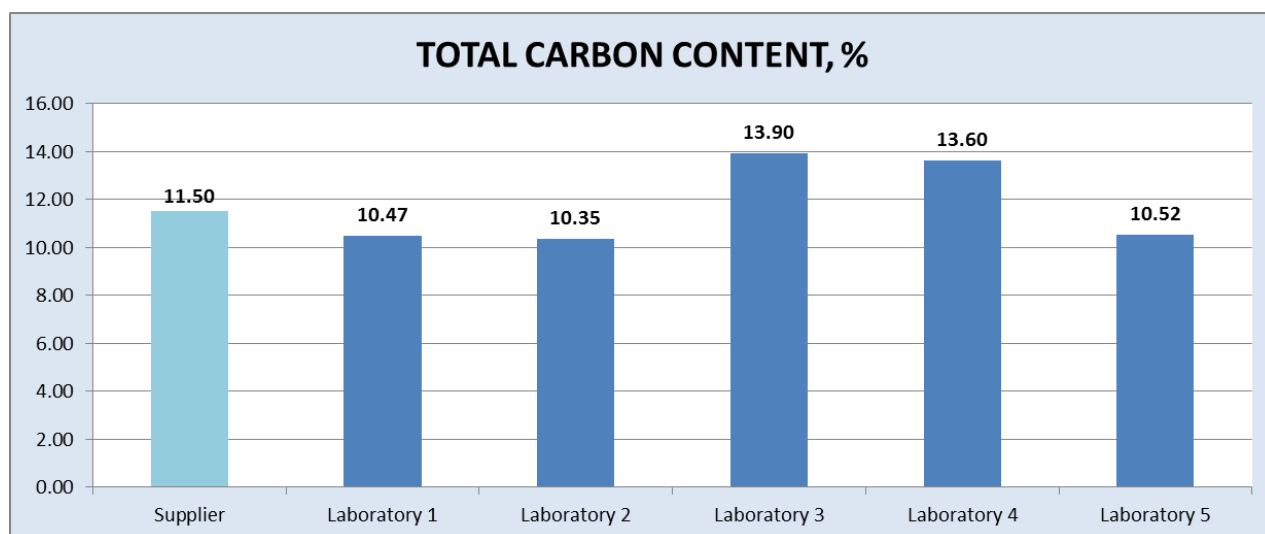


total carbon determination by combustion and titration. The results obtained on the total carbon fractions in each of the analysed materials were in good agreement with theoretical data (when known) and with data provided by products suppliers (when available). The results of measurements indicated a good accuracy (1.2% as a maximum relative standard deviation from the measured average when using an elemental analyser and 3.0% when using combustion and titration method for determining the total carbon content). Based on the results of the ruggedness testing, **95% of carbon recovery is recommended in order to have a reliable result on the total carbon content.**

### Small interlaboratory test

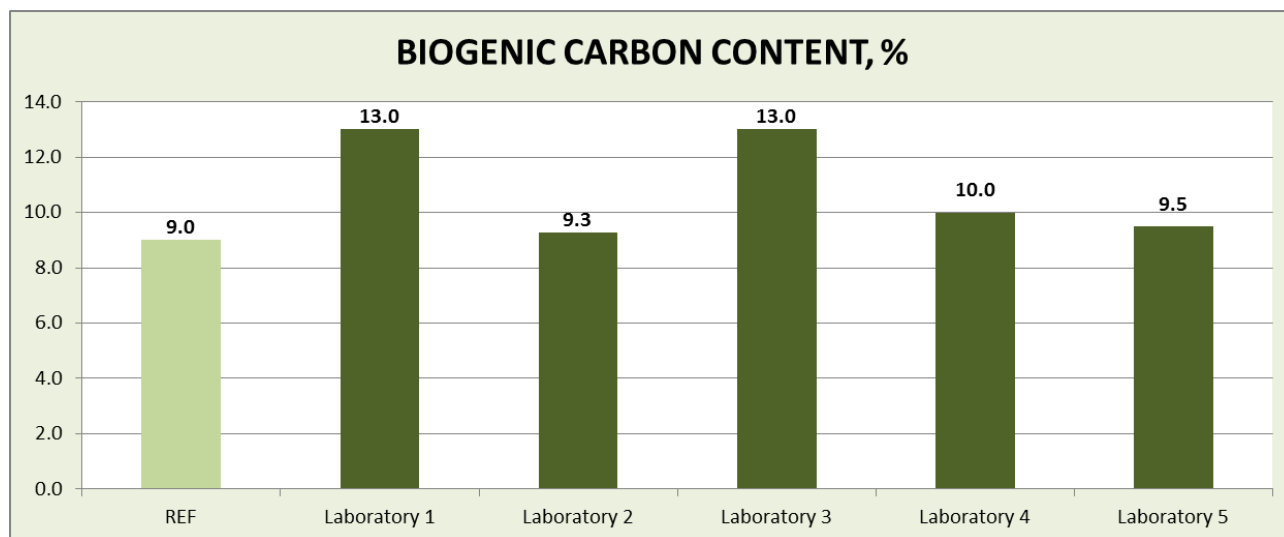
The most difficult product from the ruggedness test was distributed to 5 independent laboratories in order to check how the method will perform on the most challenging product. The selected product was matt paint with 35% volatile fraction and very low carbon content.

The results of the test are graphically presented in Figure 1 for the total carbon content in the sample and in Figure 2 for the biogenic carbon content in the sample.



**Figure 1** Total carbon content of the selected material. An elemental analyser was used by each laboratory for the determination of total carbon





**Figure 2** Biogenic carbon content of the selected material, as a fraction of total carbon

Total carbon content was determined with an elemental analyser by each participating laboratory. For determination of the biogenic carbon content, the  $\text{CO}_2$  of the combusted sample was captured in NaOH solutions and analysed by Accelerated Mass Spectrometry (AMS) by Laboratories 1 - 4 and by Liquid Scintillation Counting (LSC) by Laboratory 5. REF is the number obtained by an accredited AMS laboratory when a raw product was sent to the laboratory for the  $^{14}\text{C}$  analysis in "as received" condition. Laboratories 1, 3 and 4 used combustion enhancers in order to facilitate better combustion of the samples. The true biogenic carbon that originates only from the sample was recalculated accordingly, with the subtraction of the biogenic carbon that could originate from the combustion aids. Figure 2 presents the results on the true bio-based carbon content of the sample.

Based on the results of the interlaboratory test for the matt paint, relative standard deviation for the total carbon content measured among 5 different laboratories was 15% ( $11.77 \pm 1.81$ , % of total C). For the biogenic carbon content measured among 5 different laboratories, the relative standard deviations is 17% ( $11.0 \pm 1.9$ , % of  $^{14}\text{C}$ ). There was no correlation observed between the use of combustion enhancers, total carbon content and the biogenic carbon content. Since the selected material was the most challenging, it will be also checked in round robin testing, that will involve more laboratories, in order to see whether some tendencies can be observed.

### 3.5 Recommendations based on the ruggedness test and interlaboratory testing

1. In order to have a reliable result on the  $^{14}\text{C}$  content, it is recommended to achieve high carbon recovery (at least 95%) during the pre-treatment process.





2. For samples that are difficult combustible, the use of combustion enhancers is recommended. Sample is combusted then together with combustion aid. The true biogenic carbon content that originates from the sample itself has to be recalculated and corrected taking into account the  $^{14}\text{C}$  that originates from the combustion aid.
3. For samples that contain volatile components it has to be ensured that the carbon that originates from the volatile part is also taken into account and not lost before the combustion. It can be achieved by using chromosorb material in order to absorb the sampled material and prevent leakage and loss of material before combustion.



## 4 Conclusions

To summarize, the  $^{14}\text{C}$  isotope method is applied in a variety of samples to determine the ratio of biogenic and fossil carbon.

The procedure for determining the bio-based carbon content was proposed and validated by interlaboratory testing in CEN/TS 16640. Bio-based content determination consists of three subsequent steps: first a material has to be sampled. Then the sample has to undergo a proper pre-treatment, i.e. it has to be converted to the form that is suitable for the  $^{14}\text{C}$  measurements. Finally the  $^{14}\text{C}$  measurements can be done on the pre-treated sample.

CEN/TS 16640 describes the method that is recommended to use for the conversion of samples for the  $^{14}\text{C}$  analysis. The method is based on complete combustion of the samples and collection of the  $\text{CO}_2$  that is released during the combustion process. The collected  $\text{CO}_2$  is then analysed on the  $^{14}\text{C}$  content. Representativeness of a sample and its complete combustion are required in order to achieve reliable results on the bio-based carbon content.

As it followed from the ruggedness test, complete combustion (that results in at least 95% of recovery rate) shall be carried out to have all the carbon present in the sample in its  $\text{CO}_2$  form, in order to yield valid results.

To establish performance characteristics of the method described in CEN/TS 16640 for the bio-based carbon content determination, a round robin assessment will be organized.



## Appendix A. List of standards

A list of standards that can be helpful for the bio-based carbon content determination.

ASTM D6866

Standard Test Methods for Determining the Bio-based Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis

ISO 13833

Stationary source emissions -- Determination of the ratio biomass (biogenic) and fossil-derived carbon dioxide. Radiocarbon sampling and determination

CEN/TS 16137

Measuring the bio-based carbon content of plastics and other polymers

CEN/TR 15591

Solid recovered fuels – determination of the biomass content based on the <sup>14</sup>C method

EN 15440

Solid recovered fuels – method for the determination of biomass content

EN 15104

Solid biofuels – determination of total content of carbon, nitrogen and hydrogen

ISO DIS 16948

Solid biofuels – determination of total content of carbon, nitrogen and hydrogen

ISO 29541

Solid mineral fuels – determination of total carbon, hydrogen and nitrogen – instrumental methods

ISO 21068

Chemical analysis of silicon carbide containing raw materials and refractory products. Part 2: determination of loss on ignition, total carbon, free carbon and silicon carbide, total and free silica and total and free silicon

ASTM D5291

Standard test methods for instrumental determination of carbon, hydrogen and nitrogen in petroleum products and lubricants

EN 1484

Water analysis -- Guidelines for the determination of total organic carbon and dissolved organic carbon

EN 13137

Characterization of waste. Determination of total organic carbon content in wastes, sludge and sediments



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