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Bio-based products — Overview of methods to determine the bio-based content

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Bio-based products - Overview of methods to determine the bio-based content

Produits biosourcés - Vue d'ensemble des méthodes pour déterminer la teneur biosourcée

Biobasierte Produkte - Überblick über verfügbare und mögliche Methoden und Techniken zur Bestimmung des gesamten biobasierten Gehaltes von Produkten

This Technical Report was approved by CEN on 21 July 2014. It has been drawn up by the Technical Committee CEN/TC 411.

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Foreword

This document (CEN/TR 16721:2014) has been prepared by Technical Committee CEN/TC 411 “Bio-based products”, the secretariat of which is held by NEN.

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Introduction

Bio-based products from forestry and agriculture have a long history of application, such as paper, board and various chemicals and materials. The last decades have seen the emergence of new bio-based products in the market. Some of the reasons for the increased interest lie in the bio-based products' benefits in relation to the depletion of fossil resources and climate change. Bio-based products may also provide additional product functionalities. This has triggered a wave of innovation with the development of knowledge and technologies allowing new transformation processes and product development.

Acknowledging the need for common standards for bio-based products, the European Commission issued mandate M/492[1], resulting in a series of standards developed by CEN/TC 411, with a focus on bio-based products other than food, feed and biomass for energy applications.

The standards of CEN/TC 411 "Bio-based products" provide a common basis on the following aspects:

- Common terminology;
- Bio-based content determination;
- Life Cycle Assessment (LCA);
- Sustainability aspects;
- Declaration tools.

It is important to understand what the term bio-based product covers and how it is being used. The term "bio-based" means "derived from biomass". Bio-based products (bottles, insulation materials, wood and wood products, paper, solvents, chemical intermediates, composite materials, et cetera.) are products which are wholly or partly derived from biomass. It is essential to characterize the amount of biomass contained in the product by for instance its bio-based content or bio-based carbon content.

The bio-based content of a product does not provide information on its environmental impact or sustainability, which may be assessed through LCA and sustainability criteria. In addition, transparent and unambiguous communication within bio-based value chains is facilitated by a harmonized framework for certification and declaration.

The purpose of this Technical Report is provide an overview of methods for the determination of the bio-based content of solid, liquid and gaseous products.

The ability to determine the bio-based content of a product is an obvious prerequisite for developing the market for bio-based products. Currently, the bio-based content is usually derived from the determination of the bio-based carbon content by means of ^{14}C measurement (as described in ASTM D6866-12 [1]).This methodology is used because ^{14}C is measurable.

However, results based on the ^{14}C methodology are expressed as a fraction of bio-based carbon on the total (organic) carbon content of the sample. In some cases the bio-based content of a product can differ substantially from the bio-based carbon content. For example, for products in which a fraction of the raw materials has been replaced by bio-based materials/constituents containing other elements such as oxygen, nitrogen or hydrogen (e.g. carbohydrate-based products), the bio-based carbon content may be substantially lower than the fraction of the product that is derived from biomass. This Technical Report describes three different methodologies to determine the bio-based content in a product and proposes the development of standards.

It should be noted that the quantification of the bio-based content is not a measure of sustainability of a bio-based product.

[1] A Mandate is a standardization task embedded in European trade laws. M/492 Mandate is addressed to the European Standardization bodies, CEN, CENELEC and ETSI, for the development of horizontal European Standards for bio-based products.

1 Scope

This Technical Report gives an overview of methods which can be used for the determination of the bio-based content of solid, liquid and gaseous products. It describes more specifically:

a) a method using the radiocarbon analysis and elemental analysis: this method is based on a statement and a verification of the composition of the products;

b) methods based on measurement of stable isotopic ratio; and

c) a method based on the material balance.

This Technical Report gives guidance on the applicability of the different methods.

This Technical Report also gives recommendations for the further development of European Standards for the determination of the bio-based content.

2 Terms and definitions

For the purposes of this document, the terms and definitions given in FprEN 16575:2014 [2] and the following apply.

2.1
formulated product
product obtained by mixing of different constituents

2.2
material balance
comparison of physical quantities of inputs, outputs and inventory changes in a quantity centre over a specified time period

[SOURCE: ISO 14051:2011, 3.1]

3 Method using the radiocarbon analysis and elemental analysis

3.1 Background

Element carbon, C, has an isotope, ^{14}C, which allows for a clear distinction between carbon based substances derived from biomass and carbon based substances from fossil sources. The ^{14}C present in chemicals originates from recent atmospheric CO_2. Due to its radioactive decay, it is almost absent from fossil products older than 20 000 years to 30 000 years. The ^{14}C content may thus be considered as a tracer of chemicals recently synthesized from atmospheric CO_2 and particularly of recently produced products.

The approach based on isotopic measurements to determine the bio-based content of a sample can be used for carbon but not for other elements, such as oxygen, nitrogen or hydrogen.

However the content of each element can be determined by an elemental analysis which leads to the total content of each element, but does not differentiate the elements according to their origin from bio-based resources or fossil resources. Therefore, the combination of the ^{14}C content determination and an elemental analysis does not give the bio-based content of a sample. To circumvent this difficulty, the method as given in 3.2 is proposed.

NOTE The bio-based content of a product can be derived from the bio-based carbon content if the composition of the biomass used is unchanged. Even for derivatives the bio-based carbon content can be used if the chemistry behind the conversion is well known and constant.

3.2 Principle

NOTE 1 This method is under development and at the end of experiment phase the results will be taken into account when drafting the European Standard dealing with this method.

This method, supported by rules described in 3.3, consists of the statement of the bio-based content and of the elemental content of the sample obtained by calculation. This statement is validated by means of a comparison with the same kind of data resulting from the ^{14}C analysis and the elemental analysis of the sample.

NOTE 2 The "statement" in the sense of this document is not to be confused with the "declaration" of the bio-based content, based on the results of this method.

Products can be classified into two groups, chemicals and formulated products depending on the type of analyses to be carried out:

a) Group 1: products obtained by chemical synthesis. A representative sample is analysed on the following criteria: ^{14}C content determination and elemental analysis of carbon, hydrogen, oxygen and/or nitrogen. If other elements are present, they may also be analysed. The validation process uses common rules of stoichiometry for these products. See 3.5;

b) Group 2: formulated products. A representative sample is analysed with the ^{14}C method only, if the bio-based content of the constituents (Group 1) of the product are analysed according to this method. The validation process uses a calculation by mass for these products. See 3.6.

NOTE 3 Since Group 2 formulated products can be made from several constituents, even in a large number, the complete method described for Group 1 may be difficult to implement. This is the reason why a simplified method was developed for the formulated products of Group 2.

3.3 Basic rules

3.3.1 Oxygen, hydrogen and nitrogen elements

As it is not possible to make a distinction between bio-based and non-bio-based elements such as oxygen, hydrogen or nitrogen, for the application of this method in this Technical Report, the following convention applies:

If oxygen (O) and/or hydrogen (H) and/or nitrogen (N) element(s) is(are) bound to a biomass carbon structure, it(they) is(are) considered to be part(s) of the bio-based content.

3.3.2 Chemical reactions

For products/constituents of products obtained by chemical synthesis, the following guidance is proposed:

a) in case that the chemical reaction occurs without release of by-products:

   1) if the reactants are exclusively derived from biomass, the bio-based content of the product/constituent of the product is 100 %; if none of the reactants is derived from biomass, the bio-based content of the product/constituent of the product is 0 %;

   2) if the reactants are derived from both biomass and fossil resource, the final product has a bio-based content proportional to the bio-based content of each reactant;

b) in case that the chemical reaction leads to the release of a molecule which is not part of the main product, the allocation of the main elements of the reactants follows the basic chemical rules.

EXAMPLE Esterification leads to the release of a water molecule, in which the oxygen will be considered as coming from the acid according to the usual chemical rules.

3.3.3 Natural products

The bio-based carbon content and the bio-based content of natural products [e.g. wood (including pulp), flax, hemp, bamboo] are each equal to 100 %. Therefore, it is not necessary to determine these contents by analytical methods.

3.4 Test methods

The bio-based carbon content of a sample can be determined according to FprCEN/TS 16640 [3], Method C (AMS). Alternatively, the bio-based carbon content can be determined according to EN 15440 [4] or CEN/TS 16137 [5], Method C, and declared according to CEN/TS 16295 [6] or ASTM D6866-12 [1] and the results can be reported according to ASTM D7026-04 [7].

NOTE CEN/TS 16137 is applicable to plastic material and products, but the test methods can be in principle applied to any other product.

For the elemental analysis, standard analytical methods should be used.

3.5 Products obtained by chemical synthesis (Group 1)

3.5.1 General

The statement (see 3.2) should include a detailed elemental composition of the bio-based part and the fossil part of the product, as well as the bio-based content.

EXAMPLE 1 Bio-ethyl acetate obtained by esterification between bio-ethanol from fermentation of sugar and acetic acid from fossil resources:

Fraction	**C** %	H %	O %	Total %
Fossil fraction (from acetic acid)	27,3	3,4	18,2	48,9
Bio-based fraction (from ethanol)	27,2	5,7	18,2	51,1
Total	54,5	9,1	36,4	100,0

Then, the data of the statement are compared with the results of the analysis.

If the data of the statement and the analytical results range within a defined error margin, as shown in Table 1, the bio-based content should be validated as stated or should be rounded down according to the rules given in 3.5.2.

The analytical results can differ from the stated values for the following reasons:

a) the composition of the product may show some variability due to its natural origin;

EXAMPLE 2 Natural fatty acids used in the production of fatty acid esters.

b) the production process may also to some extent be a cause of variability of the composition of the final product;

c) the analytical methods are also a source of uncertainty, as follows (values pertaining to the methods):

   1) ± 3 % of the measured value for the bio-based carbon content;

   2) ± 0,4 % of the measured value for the total carbon, total oxygen or total nitrogen content;

3) ± 0,2 % of the measured value for the total hydrogen content.

3.5.2 Validation criteria

The stated bio-based content of a sample can be validated by considering the bio-based carbon content obtained from the ^{14}C content determination and the analytical results of at least two more elements chosen among total carbon, total oxygen, total hydrogen or total nitrogen.

If nitrogen and/or oxygen element(s) is(are) not present in the molecule, it(they) is(are) not taken into account.

In case of bio-ethyl acetate in 3.5.1, EXAMPLE 1, nitrogen element is not present in the molecule; therefore nitrogen element cannot be taken into account. The validation is done by comparing the values of the bio-based carbon content as well as the total carbon content and the hydrogen content. The total oxygen content may also be considered instead of the total carbon content or total hydrogen content.

Three confidence levels are defined depending on the closeness between the stated values and the values obtained by analysis. The stated bio-based content of a sample is validated if the differences between the stated values and the values obtained by analysis comply with Table 1.

Table 1 — Decision process

Confidence level	Deviation between calculation and results of analysis				
	Bio-based carbon content %	Total carbon content %	Total hydrogen content %	Total oxygen content %	Total nitrogen content %
1 (High)	± 3,0	± 0,4	± 0,2	± 0,4	± 0,4
2 (Medium)	± 4,5	± 1,0	± 0.5	± 1,0	± 1,0
3 (Low)	± 6,0	± 2,0	± 1,0	± 2,0	± 2,0

If at least three of the values of the differences between the stated values and the values obtained by analysis are comprised within the uncertainties given in Table 1, then:

a) for confidence level 1, the stated value for the bio-based content is validated;

b) for confidence level 2, the stated value for the bio-based content is rounded down to the nearest "multiple of five" percentage (e.g. 52 % is rounded down to 50 %, 57 % is rounded down to 55 %);

c) for confidence level 3, the stated value for the bio-based content is rounded down to the second nearest "multiple of five" percentage in such a way that the difference between the stated value and the rounded value is > 5 % (e.g. 48 % is rounded down to 40 %, 45,2 % is rounded down to 40 %).

In addition, none of the values of the differences between the stated values and the values obtained by analysis should be higher than the values given in Table 1 for confidence level 3.

All calculations are based on results reported on a dry matter basis.

EXAMPLE 1:

	Bio-based carbon content %	Total carbon %	Total hydrogen %	Total oxygen %	Bio-based content %
Stated values	25,00	50,00	5,56	44,44	56
Measured values	25,86 ± 3	49,80 ± 0,4	5,68 ± 0,2	44,60 ± 0,4	-
Three values are within the maximum difference between stated value and the result of analysis defined for confidence level 1. "56 %" is validated.					

EXAMPLE 2:

	Bio-based carbon content %	Total carbon %	Total hydrogen %	Total oxygen %	Bio-based content %
Stated values	40,8	53,0	9,0	24,2	52
Measured values	40,1 ± 4,5	52,1 ± 1,0	8,82 ± 0,5	22,46 ± 1,0	-
Three values are within the maximum difference between stated value and the result of analysis defined for confidence level 2. "50 %" is validated.					

EXAMPLE 3:

	Bio-based carbon content %	Total carbon %	Total hydrogen %	Total oxygen %	Bio-based content %
Stated values	47,25	50,15	7,23	42,62	67
Measured values	42,2 ± 6	47,5 ± 2	7,86 ± 1	40,79 ± 2	-
Three values are within the maximum difference between stated value and the result of analysis defined for confidence level 3. "60 %" is validated.					

3.6 Formulated products (Group 2)

3.6.1 General

On the one hand, the bio-based carbon content (based on ^{14}C content) of the sample should be determined by analysis. On the other hand, the bio-based carbon content and bio-based content of the sample are calculated from data related to the constituents and stated. It implies that the constituents of the sample have been analysed and the statement of the bio-based content of each constituent has been validated according to 3.5.2.

3.6.2 Calculation of the bio-based content of a sample

The bio-based content of a sample is calculated using Formula (1):

$$B_s = 100 \frac{\sum_{i=1}^{n} B_i \cdot m_i}{m_s} \quad (1)$$

Where

B_s is the bio-based content of the sample expressed as a percentage of the total mass of the sample;

B_i is the bio-based content of the constituent (i), expressed as a percentage of the mass of the constituent (i);

m_i is the mass of the constituent (i), expressed in grams;

m_s is the total mass of the sample, expressed in grams;

n is the number of constituents of the sample.

3.6.3 Calculation of the bio-based carbon content of a sample

3.6.3.1 Calculation as a fraction of total carbon (TC)

The bio-based carbon content of the sample is calculated using Formula (2):

$$B_{c,s}^{TC} = 100 \frac{\sum_{i=1}^{n} B_{c,i}^{TC} \cdot C_i^{TC} \cdot m_i}{\sum_{i=1}^{n} C_i^{TC} \cdot m_i} \quad (2)$$

Where

$B_{c,s}^{TC}$ is the bio-based carbon content, expressed as a percentage of the total carbon content of the sample;

$B_{c,i}^{TC}$ is the bio-based carbon content of the constituent (i), expressed as a percentage of the total carbon content of the constituent (i);

C_i^{TC} is the total carbon content of the constituent (i), expressed as a percentage of the mass of the constituent (i);

m_i is the mass of the constituent (i), expressed in grams;

n is the number of constituents of the sample.

3.6.3.2 Calculation as a fraction of total organic carbon (TOC)

The bio-based carbon content of the sample is calculated using Formula (3):

$$B_{c,s}^{TOC} = 100 \frac{\sum_{i=1}^{n} B_{c,i}^{TOC} \cdot C_i^{TOC} \cdot m_i}{\sum_{i=1}^{n} C_i^{TOC} \cdot m_i} \quad (3)$$

Where

$B_{c,s}^{TOC}$ is the bio-based carbon content, expressed as a percentage of the total organic carbon content of the sample;

$B_{c,i}^{TOC}$ is the bio-based carbon content of the constituent (i), expressed as a percentage of the total organic carbon content of the constituent (i);

C_i^{TOC} is the total organic carbon content of the constituent (i), expressed as a percentage of the mass of the constituent (i);

m_i is the mass of the constituent (i), expressed in grams;

n is the number of constituents of the sample.

3.6.4 Assessment of deviations of measured 14C values from theoretical values

The stated bio-based content of a sample is validated by comparing the bio-based carbon content determined by the analysis and the bio-based carbon content obtained by calculation.

Three confidence levels are defined depending on the closeness between the stated value obtained by calculation and the value obtained by analysis. The stated bio-based content of a sample is validated if the difference between these values complies with Table 2.

Table 2 — Decision process

Confidence level	Deviation between calculation and results of analysis for the bio-based carbon content %
1 (High)	± 3,0
2 (Medium)	± 4,5
3 (Low)	± 6,0

If the difference between the stated value and the value obtained by analysis for bio-based carbon content is comprised within the uncertainty given in Table 2, then:

a) for confidence level 1, the stated value for the bio-based content is validated;

b) for confidence level 2, the stated value for the bio-based content is rounded down to the nearest "multiple of five" percentage (e.g. 52 % is rounded down to 50 %, 57 % is rounded down to 55 %);

c) for confidence level 3, the stated value for the bio-based content is rounded down to the second nearest "multiple of five" percentage in such a way that the difference between the stated value and the rounded value is > 5 % (e.g. 48 % is rounded down to 40 %, 45,2 % is rounded down to 40 %).

If none of the above conditions are fulfilled, the stated value for the bio-based content is not validated.

EXAMPLE Stated value for the bio-based content: 51 %

Stated value for the bio-based carbon content: 48 %

Measured value for the bio-based carbon content: 44 %

Validated value for the bio-based content: 50 %

4 Methods based on measurement of stable isotopic ratio

4.1 General

4.1.1 Introduction

No method has been developed yet for the determination of the bio-based content by using stable isotopic forms of carbon, hydrogen, oxygen or nitrogen. The isotopic fingerprint of products is currently used to trace and authenticate food products (fruit juice, honey, etc.) or ingredients (e.g. vanilla).

It would certainly be worthwhile to evaluate the potential of such a method in the context of the determination of the bio-based content. It is conceivable that a data bank of the isotopic fingerprints of raw materials would need to be built up and that these materials could be traced in formulated products and their content determined. Of course this theory would need to be investigated and could be subject of future research work. The method will most probably not be usable for all types of products. It will be have to be adapted to each specific case and considered as an alternative method used in addition to the ^{14}C method, but faster to implement and economically affordable.

At the time being and to the best of our knowledge no method is readily available.

4.1.2 Material and Methods

Isotopic analyses are performed using an elemental analyser (carbon nitrogen analyser or oxygen hydrogen analyser) linked to an isotope ratio mass spectrometer (IRMS). At first the samples are mineralized into gas: carbon and nitrogen are transformed into CO_2 and N_2 by combustion, and hydrogen and oxygen are converted into H_2 and CO by a pyrolysis reaction.

The determination of the isotopic ratios is carried out by using the different atomic masses of gas as follows:

— CO_2: atomic mass 44, 45 and 46;

— N_2: atomic mass 28, 29, and 30;

— H_2: atomic mass 2, 3;

— CO: atomic mass 28, 29, 30.

As the isotopic variations are very small, a relative scale (value δ) is used to express the isotopic ratio.

The isotopic ratios of samples for carbon, nitrogen, hydrogen and oxygen are expressed as values $\delta^{13}C$, $\delta^{15}N$, $\delta^{2}H$ and $\delta^{18}O$ respectively, using Formulas (4) to (7).

The STD ratio is given by the isotopic ratio of an international reference defined for each isotope.

$$\delta^{13}C = \left[\frac{\frac{^{13}C}{^{12}C}(sample)}{\frac{^{13}C}{^{12}C}(STD)} - 1 \right] \times 1000 \qquad (4)$$

Where

$\delta^{13}C$ is the delta value of ^{13}C isotope for the sample, expressed in parts per thousand (‰);

$\frac{^{13}C}{^{12}C}(STD)$ = 1,112 4 % is the isotopic ratio of Vienna Pee Dee Belemnite (VPDB) [26],

$\frac{^{13}C}{^{12}C}(sample)$ is the ratio $\frac{^{13}C}{^{12}C}$ of the sample.

$$\delta^{15}N = \left[\frac{\frac{^{15}N}{^{14}N}(sample)}{\frac{^{15}N}{^{14}N}(STD)} - 1 \right] \times 1000 \qquad (5)$$

Where

$\delta^{15}N$ is the delta value of ^{15}N isotope for the sample, expressed in parts per thousand (‰);

$\frac{^{15}N}{^{14}N}(STD)$ = 0,367 6 % is the isotopic ratio of atmospheric air;

$\frac{^{15}N}{^{14}N}(sample)$ is the ratio $\frac{^{15}N}{^{14}N}$ of the sample.

$$\delta^{2}H = \left[\frac{\frac{^{2}H}{^{1}H}(sample)}{\frac{^{2}H}{^{1}H}(STD)} - 1 \right] \times 1000 \quad (6)$$

Where

$\delta\,^{2}H$ is the delta value of ^{2}H isotope for the sample, expressed in parts per thousand (‰);

$\frac{^{2}H}{^{1}H}(STD)$ = 0,015 5 % is the isotopic ratio of Standard Mean Ocean Water (VSMOW), a water supplied by IAEA (Vienna);

$\frac{^{2}H}{^{1}H}(sample)$ is the ratio $\frac{^{2}H}{^{1}H}$ of the sample.

$$\delta^{18}O = \left[\frac{\frac{^{18}O}{^{16}O}(sample)}{\frac{^{18}O}{^{16}O}(STD)} - 1 \right] \times 1000 \quad (7)$$

Where

$\delta^{18}O$ is the delta value of ^{18}O isotope for the sample, expressed in parts per thousand (‰);

$\frac{^{18}O}{^{16}O}(STD)$ = 0,200 52 % is the isotopic ratio of Vienna Standard Mean Ocean Water (VSMOW), a water supplied by IAEA (Vienna).

$\frac{^{18}O}{^{16}O}(sample)$ is the $\frac{^{18}O}{^{16}O}$ of the sample.

The isotopic analysis is a fast method (duration less than 10 min) and needs only few milligrams of material. Furthermore, the cost of a isotopic analysis is not expensive, about 35 € per isotope.

The analysis error is about ± 0,3 ‰ for ^{13}C isotope and ^{15}N isotope, ± 1 ‰ for ^{18}O isotope and ± 5 ‰ for ^{2}H isotope. Although ^{2}H isotope error is high, the variations between the different origins are also greater than

others isotopes. Isotopic values range from -30 ‰ to +20 ‰ for ^{13}C isotope, ^{15}N isotope and ^{18}O and -300 ‰ to +100 ‰ for ^{2}H isotope.

4.2 $^{13}C/^{12}C$ isotope ratio

Three different metabolic pathways for carbon fixation in photosynthesis of plants exist:

a) the Calvin cycle or C3 cycle (C3 Plants);

b) the Hatch and Slack cycle or C4 cycle (C4 plants);

c) the Crassulacean acid metabolism or CAM cycle (CAM using plants).

Plants are divided in these classes according their different pathways.

In the Calvin cycle (C3 cycle) different plants and trees from temperate regions such as rice, orange, grape, plants found in honey. Their isotopic values are in the range -20 ‰ to -33 ‰.

In the Hatch and Slack cycle (C4 cycle) the rapidly growing plants such as cane sugar, maize, and amaranth are comprised. Their isotopic values are in the range -9 ‰ to -14 ‰.

The CAM cycle is reacting between the both C3 and C4 cycles and their isotopic values are in the range -10 ‰ to -24 ‰. In this class one can find pineapple and vanillin.

Vanillin, which is the more important flavour extracted in the world, has an isotopic value near -20 ‰ for bean origin that is far from the synthesis origin -28 ‰. This technique, which is over 30 years old, is currently used to check vanillin samples.

For the C4 plants (e.g. maize, cane sugar), isotopic values are in the range -9 ‰ to -14 ‰ that are different from the fossil oil origin where values range from -20 ‰ to -35 ‰. This means that products made from natural origins such as maize or cane sugar could be authenticated using ^{13}C isotopic measurements.

Recently, a method using the combustion module – cavity ringdown spectroscopy (CM-CRDS)[2)] consisting of the measurement of the stable carbon isotopes ^{12}C and ^{13}C, expressed as the $\delta^{13}C$, has been developed to determine the bio-based content of poly(ethylene terephthalate) (PET) material produced from bio-based C4 plant derived mono ethylene glycol.[3)]

4.3 $^{18}O/^{16}O$ isotope ratio

4.3.1 Isotopic measurement of water

$^{18}O/^{16}O$ measurements are used for checking the authentication of fruits juices. This method allows distinguishing between a pure juice and a concentrate with added water. The method is standardized for fruit juice [9].

4.3.2 Isotopic measurements of organic samples

$^{18}O/^{16}O$ isotopic ratio alone is not very useful to discriminate the origin of molecules as natural or synthetic. The determination of this isotope is used in addition of ^{13}C and ^{2}H (multi isotopic determinations).

2) Picarro Inc, Sunnyvale Canada.

3) BioPlastek, Forum Shotland organized by Business Research Inc. New York June 2011.

4.4 $^{2}H/^{1}H$ isotope ratio

Water is the only source of hydrogen for the natural compounds produced by photosynthesis. The hydrogen isotopic composition of water varies with geographical location, particularly latitude, altitude and distance from the ocean. $\delta\,^{2}H$ values for natural compounds are typically more negative that their synthetic analogues.

Deuterium isotope measurement is regularly used in order to check the origin of raw materials or flavours in order to differentiate between natural or synthetic. Differences between both origins are very high, more than 100 ‰.

EXAMPLES Linalool (natural: -307 ‰ to -265 ‰, synthesis -209 ‰ to -185 ‰) Linalyl acetate (natural: -280 ‰ to -276 ‰, Synthesis -181 ‰ to -172 ‰) [10].

α Ionone (synthesis > -45 ‰ ; natural: -203 ‰ to -257 ‰) ; β Ionone (synthesis > -43 ‰ natural: -160 ‰ to -235 ‰) [11].

Citral (synthesis: 14 ‰ to -200 ‰, natural: -273 ‰ to -303 ‰) [12].

NOTE The ^{3}H isotope (Tritium) is also present in living organism and is formed in the atmosphere by cosmic radiation, comparable with the formation of ^{14}C. Up till now no methods for the determination of 'biogenic' hydrogen based on the determination of ^{3}H are known. With a half-life ($^{1/2}T$) of ^{3}H = 12,3 year, and emitting a very weak beta particle, it's use for biogenic marker will not be as good as the ^{14}C isotope, but in fresh biomass it should be possible to be measured, however with a relative large error.

4.5 $^{15}N/^{14}N$ Isotope ratio

Nitrogen isotope ratios could not be used directly to determine the natural or synthetic origins of molecules However they can be linked to synthesis pathways or the sources of precursors.

IRMS analysis of nitrogen isotope ratios (often in combination with carbon) has shown the potential to characterise and distinguish illicit drugs of different batches including: cocaine [13], ecstasy [14] and marijuana [15].

4.6 Isotopes S

Sulfur isn't used in assessment of the origins of raw materials as its concentration is typically not high enough to allow isotopic analyses to be carried out.

4.7 Multi-isotopic determinations

Combination of multi-isotopic analysis (^{13}C, ^{2}H and ^{18}O determinations) is an efficient tool in order to characterize differences between industrial products in forensic interests, discriminate compounds, and is more and more used.

EXAMPLE White paints [16], PVC tape backings [17], cotton fibres [18] and adhesives [19].

A compilation of isotope ranges is given in Annex A.

5 Method based on material balance

5.1 General

For companies which produce a wide range of products, possibly in very low quantities, or products made from heterogeneous constituents, or for which the analysis methods described in Clauses 3 and 4 can be difficult or too costly to implement, the following method is proposed.

A material balance based on inflow and outflow of bio-based material(s) is to be established. It is a cost effective alternative to the methods described in Clause 3 and 4.

The bio-based content for a single product can be verified through chemical analysis.

This method is applicable to mixing of materials with or without chemical reaction.

5.2 Principle

This method consists, for a given product, in quantifying the inputs in mass of the bio-based materials which enter the manufacturing unit and to identify by means of calculation and traceability these mass quantities in each of the compositions of products put on the market. See Formula (8).

$$\sum M_{b,in} = \sum M_{b,out} + \sum M_{b,loss} \quad (8)$$

Where

$\sum M_{b,in}$ is the sum of the inputs of total bio-based materials, by mass (by origin);

$\sum M_{b,loss}$ is the sum of the bio-based materials, by mass, lost during processing (by origin);

$\sum M_{b,out}$ is the sum of the outputs of total bio-based materials, by mass (by origin) distributed among the manufactured or semi-finished products.

5.3 Examples

5.3.1 Paint formulation

Paints are produced by mixing raw materials in a vessel according to a precise and fixed formulation by weight. There is no covalent chemical reaction but only dissolution and mixing operations. They are produced in an individual and identified batch. Raw materials are characterized (code, producer, technical characteristics including bio-based content) and weighted very precisely. The bio-based content of each raw material is certified by the producer.

The quantities and proportions of raw materials introduced in the mixing vessel are guaranteed by the quality assurance process (production procedures, weights records, quality control).

The produced paint is packaged in individual cans and identified.

The wastes of the process occur during the packaging process; they do not affect the bio-based content of the paint.

The typical formulation of a water based decorative flat paint is given in Table 3.

Table 3 —Typical formulation of a water based decorative flat paint

Raw material	Bio-based content of the raw material % (by mass)	Mass of raw material kg	Mass of the bio-based constituents in the paint kg
Water	0	300	0
Biocide	0	2	0
Dispersing agent	50	5	2,5
Rheological agent	80	3	2,4
White pigment	0	150	0
Wood filler	95	120	114,0
Calcium carbonate	0	120	0
Alkyd emulsion	94	300	282,0
Total		1 000	400,9

Bio-based content of the paint = 100 $\frac{400.9}{1000}$ = 40,09 %

5.3.2 Flexible insulation panel made from wood fibres

Characteristics of a panel:

— Size: 100 mm x 1 220 mm x 575 mm

— Mass: 3,50 kg

— Constituents: wood fibres, polyolefin fibres

Example for one batch production: 1 425 panels (997 m^2)

— Mass of bio-based constituents introduced in the process: $M_{b,in}$ = 3 852 kg (75 %)

— Mass of fossil raw material introduced in the process: $M_{nonb,in}$ = 1 284 kg (25 %)

— Mass of bio-based constituents lost during processing: $M_{b,loss}$ = 112 kg

— Mass of fossil constituents lost during processing: $M_{b,loss}$ = 36,5 kg

— Total mass of the final product for one batch: $M_{mass,\ prod}$ = 4 987,50 kg

Bio-based content (by total mass):

$$x_{bio}^{mass} = 100 \cdot \frac{M_{bio,in} - M_{bio,loss}}{M_{mass,prod}} = 100 \cdot \frac{3852 - 112}{4987.50} = 74{,}9 \ \%$$

6 Applicability of the different methods

The C14 content (see FprCEN/TS 16640) is directly measurable on any sample but does not lead to the determination of the bio-based content.

As the bio-based content is not directly measurable, the method using the radiocarbon analysis and elemental analysis (Clause 3) needs a statement giving the bio-based content and the elemental analysis obtained by calculation.

The methods based on stable isotopic ratio (Clause 4) are only applicable to specific cases depending on the nature of the feedstock used.

The method based on the material balance (Clause 5) is easy to implement but requires knowing the bio-based content of the feedstock used.

7 Recommendations

On the basis of this Technical Report, CEN/TC 411/WG 3 recommends preparing the following European Standards:

— a method for the determination of the bio-based content using the radiocarbon analysis and elemental analysis;

— a method based on the material balance, and

— methods for the determination of the bio-based content using stable isotopic ratio, once investigations and research works will demonstrate the relevance of these methods.

Annex A
(informative)

Isotope ratio tables

Table A.1 — Isotope ratio

Element	Isotope	Abundance	Biomass		Fossil	
			from	to	from	to
		%	δ	δ	δ	δ
C	12	98,93				
	13	1,07	-75	35	-20	-35
H	1	99,98				
	2	0,015	-300	100		
O	16	99,759				
	17	0,037				
	18	0,204				
N	14	99,634				
	15	0,366				
S	32	95,02				
	33	0,75				
	34	4,21				
	36	0,02				

Table A.2 — Isotope ratio table

Process	Material or compound	Location	$\delta^{13}C$, ‰		$\delta^{15}N$, ‰		$\delta^{18}O$, ‰		$\delta^{2}H$, ‰		$\delta^{34}S$, ‰		Ref.
			from	to	from	to	from	to	from	to	from	to	
C3			-20	-33									
C4			-9	-14									
CAM			-10	-24									
	Biomass		-75	35					-300	100			
	Fossil		-20	-35									
C3	Cellulose from C3 plants	Texas	-24,6±1,3				+26,8±1,9		-42±16				1
C4	Cellulose from C4 plants		-12,0±0,5				+34,6±1,4		-33±12				
CAM	Cellulose from CAM plants		-12,1±0,1				+29,7±3,1		+51±10				
C3	Plant cellulose nitrate		-26	-22					-70	-15			7
C4			-13	-11					-50	-3			
CAM			-14	-10,5					32	63			
	C3 plants				-8	+4							5
	Atmospheric N2				0								
	Ocean plankton				-3	18							
	NH4				+4	+20							
	Non-organic synthetic fertilizers				-4	+4							
	Organic fertilizers				+6	+30							
	Cow milk				+1	+3							
	Equatorial waters						0						
	Temperate and near-polar waters						-15	-5					
	Polar ice *						-55	-20					
	Surface ocean water						-2	0					
	Deep ocean water						3	4					

*(-55) – for Antarctica, (-20) for Greenland

Table A.2 *(continued)*

Process	Material or compound	Location	$\delta^{13}C$, ‰		$\delta^{15}N$, ‰		$\delta^{18}O$, ‰		$\delta^{2}H$, ‰		$\delta^{34}S$, ‰		Ref.
			from	to	from	to	from	to	from	to	from	to	
	Atmospheric sulfur										-5	25	9
	Lithospheric sulfur										-10	35	
	Marine sulfur										Modern 21‰		
	Groundwater sulfur										-10	35	
	Most terrestrial materials				-20	+30							10 10
	Fertilizers produced from atmospheric N				0±3								
	Animal manure				10	25							
	Atmospheric NO3 andNH4				-15	15							
	NH4	Germany			-12,0±1,9								
	NO3				-2,5±3,0								
	Nitric acid vapour from anthropogenic sources				-2,7								
	NH4	Tennessee, USA			3,4±2,1								
	NO3				2,3±2,4								
	Nitric acid vapour from anthropogenic sources				+6,0±2,3								
	NO_x emitted from coal combustion	South Africa			+6	+9							
	NO_x emitted from automobiles				-13	-2							
	Anthropogenic fertilizers: Usually				-4	+4							
	Some of them				-8	+7							
	Organic fertilizers				+2	+30							
	Most plants				-5	+2							
	Plants fixing N2 from atmosphere				0	+2							
	Soils, total range				-10	+15							

	Most soils				+2	+5							
	Cultivated soils				0,65±2,6								
	Uncultivated soils				2,73±3,4								
	Atmospheric nitrate	Bavaria, Germany					+55	+75					10
		Germany, Dortmund					+23	+58					
		USA					+18	+70					
		Canada, east-central					+28	+51					
	Synthetic nitrate formed from atmospheric O2						+18	+22					
	Meteorites										-1	+1	6
	Basic sills										-4	+4	
	Igneous rocks Total: Most:										-45 -10	+35 +12	
	S of volcanic origin										-17	+17	
	Sea water										+18	+20	
	Evaporites										+4	+35	
	Rain and snow										+3	+8	
	Sedimentary sulphides										-48	+10	
	Petroleum										-9	+30	
	Coal										-32	+23	
C3	C3 plants legumes		-27,5	-25	0.5	3,5							8
C3	C3-based terrestrial fauna		-25,7	-22,2	3,5	7,75							
C3	Freshwater fish		-31,5	-24	10	12,6							
C4	Maize		-13,5	-9,5	1,25	2,75							
CAM	Reef shellfish		-15,7	-13,9	2,5	6,5							
CAM	Marine mammals and fish		-17,5	-13,8	12	17,75							
C4/CAM	Tropical reef fish		-12,2	-7,3	5,3	9							

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