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Bio-based products — Bio-based carbon content — Determination of the bio-based carbon content using the radiocarbon method

National foreword

This British Standard is the UK implementation of EN 16640:2017. It supersedes PD CEN/TS 16640:2014 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee MI/2, Bio-based products.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Produits biosourcés - Teneur en carbone biosourcé - Détermination de la teneur en carbone biosourcé par la méthode au radiocarbone

Biobasierte Produkte - Gehalt an biobasiertem Kohlenstoff - Bestimmung des Gehalts an biobasiertem Kohlenstoff mittels Radiokarbonmethode

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Contents

European foreword

This document (EN 16640:2017) has been prepared by Technical Committee CEN/TC 411 “Bio-based products”, the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by August 2017, and conflicting national standards shall be withdrawn at the latest by August 2017.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

This document supersedes CEN/TS 16640:2014.

This document has been prepared under Mandate M/492 “Mandate addressed to CEN, CENELEC and ETSI for the development of horizontal European Standards and other standardization deliverables for bio-based products”.

According to the CEN-CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

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, etc.) 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.

This European Standard has been developed with the aim to specify the method for the determination of bio-based carbon content in bio-based products using the ^{14}C method. This method using the ^{14}C method is based on the analytical test methods used for the determination of the age of objects containing carbon.

This European Standard provides the reference test methods for laboratories, producers, suppliers and purchasers of bio-based product materials and products. It may be also useful for authorities and inspection organizations.

Part of the research leading to this document has been performed under the European Union Seventh Framework Programme (see http://www.biobasedeconomy.eu/research/kbbpps/).This document is based on EN 15440 [1] prepared by CEN/TC 343, "Solid recovered fuels", EN ISO 13833 [2], prepared by ISO/TC 146 "Air quality" and CEN/TC 264 "Air quality", and CEN/TS 16137 [3], prepared by CEN/TC 249, "Plastics".

The analytical test methods specified in this European Standard are compatible with those described in ASTM D 6866-12 [4].

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[1]) A mandate is a standardization task embedded in European trade laws. Mandate M/492 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 European Standard specifies a method for the determination of the bio-based carbon content in products, based on the ^{14}C content measurement.

This European Standard also specifies two test methods to be used for the determination of the ^{14}C content from which the bio-based carbon content is calculated:

— Method A: Liquid scintillation-counter method (LSC) ;

— Method B: Accelerator mass spectrometry (AMS).

A third method, Method C: Beta ionization (BI) can also be used for the determination of the ^{14}C content and is described in Annex D (informative)

The bio-based carbon content is expressed by a fraction of sample mass or as a fraction of the total carbon content. This calculation method is applicable to any product containing carbon, including bio composites.

NOTE This European Standard does not provide the methodology for the calculation of the biomass content of a sample see prEN 16785–1 [5] and prEN 16785–2 [6].

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 15400, *Solid recovered fuels - Determination of calorific value*

EN ISO 1716, *Reaction to fire tests for products - Determination of the gross heat of combustion (calorific value) (ISO 1716)*

ISO 1928, *Solid mineral fuels — Determination of gross calorific value by the bomb calorimetric method and calculation of net calorific value*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
organic material
material containing carbon-based compound in which the element carbon is attached to other carbon atoms, hydrogen, oxygen, or other elements in a chain, ring, or three-dimensional structure

3.2
isotope abundance
fraction of atoms of a particular isotope of an element

3.3
percentage modern carbon
pMC
normalized and standardized value for the amount of the ^{14}C isotope in a sample, calculated relative to the standardized and normalized ^{14}C isotope amount of oxalic acid standard reference material, NIST SRM 4990b or NIST SRM 4990c or Sucrose (NIST SRM 8542)

Note 1 to entry: In 2016, the value of 100 % bio-based carbon was set at 101,5 ± 0,5 pMC.

Note 2 to entry: SRM 4990c, SRM 4990b and SRM 8582 are the trade name of products supplied by the US National Institute of Standards and Technology. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of this product. Equivalent products may be used if they can be shown to lead to the same results.

3.4
laboratory sample
sub-quantity of a sample suitable for laboratory tests

3.5
sample
quantity of material, representative of a larger quantity for which the property is to be determined

3.6
sample preparation
all the actions taken to obtain representative analysis samples or test portions from the original sample

3.7
beta- particle
electron emitted during radioactive decay

4 Symbols and abbreviations

^{14}C	carbon isotope with an atomic mass of 14
AMS	accelerator mass spectrometry
BI	beta-ionization
Bq	Bequerel (disintegrations per second)
C	symbol for element carbon
Cpm	counts per minute
dpm	disintegrations per minute
GM	Geiger-Müller
LLD	lower limit of detection
LSC	Liquid Scintillation Counter or Liquid Scintillation Counting
m	dry mass of a sample expressed in grams
MOP	3-methoxy 1-propyl amine
PE	Polyethylene
PLA	poly(lactic acid)
pMC	percentage of modern carbon
REF	reference value, expressed in pMC, of 100 % bio-based carbon depending on the origin of organic carbon
TC	total carbon
x_{B}	bio-based carbon content by mass, expressed as a percentage of the mass of the sample (dry)
x^{TC}	total carbon content, expressed as a percentage of the mass of the sample (dry)
x_{B}^{TC}	bio-based carbon content by total carbon content, expressed as a percentage of the total carbon content

5 Principle

The ^{14}C present in products is originating 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 products recently synthesized from atmospheric CO_2 and particularly of recently produced bio-products.

The determination of the biomass content is based on the measurement of ^{14}C in bio-based products, which allows the calculation of the bio-based carbon fraction.

A large experience in ^{14}C determination and reference samples is available from dating of archaeological objects, on which the three methods described in this European Standard are based:

— Method A: Proportional scintillation-counter method (LSC),

— Method B: Accelerator mass spectrometry (AMS); or

— Method C: Beta-ionization (BI).

NOTE 1 The advantages and disadvantages of these test methods are given in Table 1.

Table 1 — Advantages and disadvantages of the methods

Method	**Additional requests**	**Duration needed for measurement**	**Relative standard deviation**	**Instrumental costs**
Method A (LSC)	Normal laboratory	4 h to 12 h	0,2 % to 5 %	Low
Method B (AMS)	- Low background laboratory - Gas purification device	8 h to 24 h	0,2 % to 5 %	Low
Method C (BI)	- Large installation - Graphite Conversion device	10 min to 30 min	0,2 % to 2 %	High

For the ^{14}C LSC measurement a Low Level Counter shall be used. The statistical scattering of the radioactive decay sets a limit, both for method A and B. Thereby both methods need a purified carbon dioxide, otherwise oxides of nitrogen from the combustion in the calorific bomb will result in counting losses by quenching and adulteration of the cocktail in case of LSC measurement. When using method A (LSC), samples with low bio-based carbon content (<10 %) can only be measured with sufficient precision using the benzene conversion procedure or, if applicable, direct LSC measurement, as described in Annex B.

NOTE 2 At this moment compact new AMS equipment has become available. In a number of cases, no graphite conversion is required anymore.

6 Determination of the ^{14}C content

6.1 General

A general sample preparation and three test methods for the determination of the ^{14}C content are described in this European Standard. With this modular approach, it will be possible for normally equipped laboratories to prepare samples for the ^{14}C content, and determine the ^{14}C content with own equipment or to outsource the determination of the ^{14}C content to laboratories that are specialized in this technique.

For the collection from the sample of the ^{14}C content, generally accepted methods for the conversion of the carbon present in the sample to CO_2 are described.

For the measurement of the ^{14}C content, methods are selected that are already generally accepted as methods for the determination of the age of objects.

6.2 Principle

The amount of bio-based carbon in the bio-based product is proportional to this ^{14}C content.

Complete combustion (see Annex B) is carried out in a way to comply with the requirements of the subsequent measurement of the ^{14}C content and shall provide the quantitative recovery of all carbon present in the sample as CO_2 in order to yield valid results.

This measurement shall be carried out according to one of the two following methods:

- Method A: Liquid scintillation-counter method (LSC): indirect determination of the isotope abundance of ^{14}C, through its emission of beta-particle (interaction with scintillation molecules), specified in Annex C, or

- Method B: Accelerator mass spectrometry (AMS): direct determination of the isotope abundance of ^{14}C, specified in Annex E.

Possibly, this measurement can also be carried out according to Method C: Beta-ionization (BI): indirect determination of the isotope abundance of ^{14}C, through its emission of beta-particle (Geiger-Müller type detector), described in Annex D.

6.3 Sampling

In Annex A sampling methods for products that are mentioned in the scope are given.

For any sampling procedure, the samples shall be representative of the material or product and the quantity or mass of sample shall be accurately established.

6.4 Procedure for the conversion of the carbon present in the sample to a suitable sample for ^{14}C determination

The conversion of the carbon present in the sample to a suitable sample for the determination of the ^{14}C content shall be carried out according to Annex B.

6.5 Measurements

The measurement of the ^{14}C content of the sample shall be performed according to one of the methods as described in Annexes C, D or E.

When collected samples are sent to specialized laboratories, the samples shall be stored in a way that no CO_2 from air can enter the absorption solution. A check on the in leak of CO_2 from air shall be performed by preparing laboratory blanks during the sampling stage.

For the determination of the 0 % biomass content the combustion of a coal standard may be used.

For validation of the 100 % biomass content, oxalic acid standard reference material, NIST SRM 4990b or NIST SRM 4990c or Sucrose (NIST SRM 8542) may be used. Mixing reference material NIST 4990 with a known amount of fossil combustion aid improves its combustion behaviour, as oxalic acid is difficult to combust due to its low calorific value. For routine checks, a fresh wood sample calibrated against the standard reference material is sufficient.

7 Calculation of the bio-based carbon content

7.1 General

The calculation of the bio-based carbon content includes the following steps:

a) the determination of the total carbon content of the sample, x^{TC}, expressed as a percentage of the total dry mass;

b) the calculation of the bio-based carbon content by mass, x_{B}, using the ^{14}C content value, determined by calculation from one of the test methods specified in 7.3, and applying the correction factors detailed in 7.2, and

c) the calculation of the bio-based carbon content as a fraction of the total carbon content, $x_{\mathrm{B}}^{\mathrm{TC}}$ (see 7.3.2).

7.2 Reference value for 100 % bio-based carbon

Before the above-ground hydrogen bomb testing (started around 1955 and terminated in 1962) the atmospheric ^{14}C level had been constant to within a few percent, for the past millennium. Hence, a sample grown during this time has a well-defined “modern” activity, and the fossil contribution could be determined in a straightforward way. However, ^{14}C created during the weapons testing increased the atmospheric ^{14}C level to up to 200 pMC in 1962, with a decline to 102 pMC in 2015. The ^{14}C activity of a sample grown since year 1962 is elevated according to the average ^{14}C level over the growing interval. In addition, the large emission of fossil C during the last decades contributes to the decrease of the atmospheric $^{14}C/^{12}C$ ratio.

In ASTM D 6866-16 [4] the 100 % bio-based C value of 101.5 pMC (for year 2016) is used. This value shall be the base of calculations. Other values are only acceptable if evidence can be given on the pMC value of the biogenic part of the material. From the 102 pMC value the correction factor of 0,98 (1/1,02) is derived. It is considered that such correction factor is now stable during a period of a few years.

For the calculation of the bio-based carbon content, a ^{14}C content of 100/0,98 pMC or 13,56/0,98 dpm per gram C is considered as a 100 % bio-based carbon content for biomass that is grown in year 2015.

NOTE 1 This correction factor of 0,98 is in accordance with the value that is given in ASTM D 6866–16 [4].

The fraction of biomass content by dry mass shall be calculated using the biomass carbon in the bio-based product as for other organic carbon materials. Table 2 lists typical values for such common materials.

NOTE 2 The reference value is based on the measurements of CO_2 in air in a rural area in the Netherlands (Lutjewad, Groningen), performed by CIO (Centre for Isotope Research, university Groningen). New reference values for 2016 and later will be available on the CIO internet site (http://www.rug.nl/research/isotope-research/klanten/14cbio-values-standards).

Table 2 — Typical values for biomass fractions

Material [a]	x^{TC} %	**REF** pMC
Wood (coniferous and deciduous)	48	112
Bark	52	110
Paper	47	112
Fresh biomass (from year 2015)	48	102
Silk	49	105
Wool	51	105

[a] These values are given on "dry basis".

7.3 Calculation method

7.3.1 Calculation of the bio-based carbon content by dry mass x_{B}

7.3.1.1 ^{14}C content determined by Method A (LSC) or Method C (BI)

Calculate the bio-based carbon content by dry mass, x_{B}, expressed as a percentage, using Formula (1):

$$x_{\mathrm{B}} = \frac{^{14}C_{activity}}{13,56 \times \frac{REF}{100} \times m} \times 100 \tag{1}$$

where

$^{14}\mathrm{C}_{\mathrm{activity}}$ is the ^{14}C activity, expressed in dpm, of the sample obtained by calculation when using Method A or Method C (see Annex C or E);

REF is the reference value, expressed in pMC, of 100 % bio-based carbon of the biomass from which the sample is constituted;

m is the mass, expressed in grams, of the sample.

NOTE The pMC value of NIST SRM 4990 is set at 100, being equivalent to a ^{14}C activity of 13,56 dpm/g C.

7.3.1.2 ^{14}C content determined by Method B (AMS)

Calculate the bio-based carbon content by dry mass, x_{B}, expressed as a percentage, using Formula (2):

$$x_{\mathrm{B}} = x^{\mathrm{TC}} \frac{\frac{pMC(s)}{100}}{\frac{REF}{100}} = x^{\mathrm{TC}} \frac{pMC(s)}{REF} \tag{2}$$

where

x^{TC} is the total carbon content, expressed as a percentage, of the total dry mass of the sample;

pMC(s) is the measured value, expressed in pMC, of the sample;

REF is the reference value, expressed in pMC, of 100 % bio-based carbon of the biomass from which the sample is constituted.

7.3.2 Calculation of the bio-based carbon content $x^{\mathrm{TC}}_{\mathrm{B}}$ as a fraction of TC

Calculate the bio-based carbon content as a fraction of the total carbon content, $x_{\mathrm{B}}^{\mathrm{TC}}$, expressed as a percentage, using Formula (3):

$$x_{\mathrm{B}}^{\mathrm{TC}} = \frac{x_{\mathrm{B}}}{x^{\mathrm{TC}}} \times 100 \tag{3}$$

where

x_{B} is the bio-based carbon content by dry mass, expressed as a percentage;

x^{TC} is the total carbon content, expressed as a percentage, of the sample.

7.3.3 Examples

EXAMPLE 1 Measurement according to Method A

Sample made from pure wood (REF = 112 pMC, x^{TC} = 48,0 %)

Dry mass of sample: m = 1,010 g

^{14}C activity = 7,34 dpm

$$x_{\mathrm{B}} = \frac{7,34}{13,56 \times {}^{112}\!/_{100} \times 1,01} \times 100 = 47,8\%$$

$$x_{\mathrm{B}}^{\mathrm{TC}} = \frac{47,8}{48,0} \times 100 = 99,6\%$$

EXAMPLE 2 Measurement according to Method B

Sample made from xxx (REF = 112 pMC, x^{TC} = 52,0 %)

NaOH solution: 1 M

pMC(s) (Measured ^{14}C value) = 61,7 pMC

$$x_{\mathrm{B}} = 52 \frac{{}^{61,7}\!/_{100}}{{}^{112}\!/_{100}} = 28,6\%$$

$$x_{\mathrm{B}}^{\mathrm{TC}} = \frac{28,6}{52,0} \times 100 = 55,0\%$$

EXAMPLE 3 Calculation of bio-based carbon content as a fraction of TC

Pure bio-based polymer material

Sample made from PLA material: (x^{TC} = 50,0 %; x_{B} = 50 %)

$$x_B^{TC} = \frac{50,0}{50,0} \times 100 = 100\%$$

7.3.4 Examples of calculations x^{TC}_B

Table 3 gives examples of calculations of x_B^{TC} for different materials.

Table 3 — Examples

Material	Biomass content %	x^{TC} %	x_B %	x_B^{TC} %
Wood	100	48	48	100
Polymer containing 50 % of PE from fossil source and 50 % of bio-based PE	50	90	45	50
Polymer containing 40 % of calcium carbonate from fossil source, 30 % of PE from fossil source and 30 % of bio-based PLA	30	47	15	32

8 Performance characteristics

See Annex F.

9 Test report

The test report shall contain at least the following information:

a) a reference to this document (EN 16640:2017);

b) all information necessary for complete identification of the bio-based material or product tested, including the origin of the biomass from which the material or product is constituted;

c) identification of the laboratory performing the test;

d) sample preparation;

e) storage conditions;

f) test method used for the determination of the ^{14}C content (Method A, B or C, see Annex C, D or E);

g) results of the test including the basis on which they are expressed and application of the isotope correction, including a precision statement;

h) method for the conversion of the carbon (see Annex B);

i) ^{14}C activity, expressed in dpm, of the sample or ^{14}C value, expressed in pMC;

j) total carbon content, x^{TC}, expressed as a percentage, of the sample;

k) bio-based carbon content by dry mass, x_B, expressed as a percentage, of the sample;

l) bio-based carbon content by total carbon content, $x_{\mathrm{B}}^{\mathrm{TC}}$,expressed as a percentage, of the sample;

m) any additional information, including details of any deviations from the test methods and any operations not specified in this document which could have had an influence on the results;

n) date of receipt of laboratory sample and dates of the test (beginning and end).

Annex A
(informative)

Procedures for sampling of products

A.1 General

If available, product-sampling procedures for the determination of the total carbon content shall be used. If no such standard is available, a list of most suitable standards is given in Table A.1 as guidance.

In the case of solid products, the sampling procedures mentioned in Table A.1 shall be used. If the procedure for solid product sampling is not available, then EN 15442 [8] or EN 15443 [9] shall be used.

Table A.1. — Sampling procedures

Products	Sampling methods
Solid products	
Plastics, polymers	ISO 10210 [10]
Fuels	EN 14780 [11], EN 14778 [12], EN 15442 [13], EN 15443 [14] ISO 13909 [15], ISO/NP 18135 [16], ISO 18283 [17], ISO 20904 [19], ASTM D7026–13 [20],
Ceramics, glass, concrete, cement, construction materials / waste	ASTM C172/C172M-10 [21], ASTM C224–78 [22], ASTM C322–09 [23], ASTM C1704/C1704M-09A [24], ASTM D3665–12 [25]
Rubber	ISO 1795 [26], ASTM D1485–07 [27] (2011), ASTM D6085–97 [28] (2011)
Paper	EN ISO 186 [29], EN 27213 [30], ASTM D2915–10 [31]
Liquid products	
Solvents	ASTM D 268–01 [33] (2012), ASTM D802–02 [34] (2013), ASTM D3437–11 [35]
Fuels	ASTM D4057–12 [36], EN ISO 3170 [37], ASTM D4177–95 [38], EN ISO 3171 [39], ASTM D1265–11 [40], EN ISO 4257 [41], ISO 8943 [42], ASTM D233–12 [43],
Gaseous products	EN ISO 13833 [2] ISO 10715 [44] ASTM D7459–08 [45]
Other suitable procedures	EN ISO 15528 [46], ASTM D460–91 [47], ASTM D6866–12 [4], ASTM D7455–08 [48], ASTM D7718–11 [49], ASTM E300–03 [50] EPA 340/1–91–010 [51] ISO 5555:2001 [58]

Annex B
(normative)

Procedure for the conversion of the carbon present in the sample to a suitable sample for ^{14}C determination

B.1 General

In this annex, all steps are described to prepare samples for ^{14}C determinations. In this way, a laboratory that is not equipped for ^{14}C analysis can prepare their samples for distribution to laboratories that are equipped for ^{14}C analysis.

For the determination of the ^{14}C content, the carbon that is present in the sample has to be converted to CO_2.

The conversion is done by combustion in oxygen. If necessary, a combustion aid can be used to ensure complete oxidation of the carbon to CO_2.

For a number of liquid samples, no conversion to CO_2 is needed and direct measurement of the ^{14}C content can be performed using LSC.

B.2 Sample preparation

For sample preparation procedures the following standards can be used:

Table B.1— Sample preparations

Products	Sample preparation methods
Solid products	ISO 1928 [52], EN ISO 21068-2 [53], EN 15400, EN 15440 [1], CEN/TS 16137 [3], ASTM D6866 [4]
Liquid products	ASTM D6866 [4], ASTM D7455 [55], ASTM D5291 [56]
Gaseous products	EN ISO 13833 [2], ASTM D6866 [4]

B.3 Preparation for ^{14}C measurement

B.3.1 General

The ^{14}C content of a bio-based product is determined on the CO_2 produced by the sample combustion. For the conversion of the sample to CO_2, used for the determination of the ^{14}C content, the following three methods are allowed:

- combustion in a calorimetric bomb;
- combustion in a tube furnace;
- combustion in a laboratory scale combustion apparatus.

For gaseous samples, combustion in a calorimetric bomb is not applicable.

Conversion of gaseous hydrocarbons to CO_2 can be done at temperatures from 600 °C, using a suitable catalyst and absorption of the CO_2 in a NaOH solution as described in B.3.2.

In case of combustion, it depends on the method to be used for the determination of ^{14}C content, how the formed CO_2 is collected and prepared for the measurement.

When Method B (Annex E) is used, there are three options:

a) direct collection of the formed CO_2 in a gas-bag;

b) absorption of CO_2 in a 4 M NaOH solution;

c) absorption in a for this purpose developed solid absorber, usually NaOH or KOH fixed on a silica carrier.

As Method B (Annex E) requires only a few milligrams of carbon containing matter, sample material containing CO_2 amounts of a few milligrams may be used.

In case of Method C (Annex D), a direct collection of CO_2 in a gasbag, lecture bottle or NaOH solution is allowed as well, provided the total amount of carbon present in the sample is at least 2 grams.

In case of Method A (Annex C), three options are possible after combustion:

d) direct absorption of the formed CO_2 in a carbamate solution;

e) absorption of the CO_2 in a 2 M NaOH solution and transfer of CO_2 in NaOH to a carbamate solution;

f) direct conversion of CO_2 to benzene.

B.3.2 Reagents and materials

— Carbamate solution;

— scintillation medium;

— glass bottles (standard glass sample bottles with plastic screw caps that are resistant to 4 M NaOH);

— 4 M NaOH absorption liquid.

For the preparation of a carbonate free absorption liquid, preparation using freshly opened NaOH pellet containers is sufficient. Dissolve the NaOH pellets in a small amount of water (the heat produced during the dissolution process will enhance the dissolution process). Small amounts of precipitation are an indication of the presence of Na_2CO_3. By decanting the clear phase the almost carbonate free solution is diluted to the desired volume. As the dissolution of NaOH is an exothermic process extra care shall be taken as boiling of the concentrated solution during dilution can occur.

B.4 Combustion of the sample

B.4.1 Combustion of the sample in a calorimetric bomb

For the combustion of the sample in a calorimetric bomb, any suitable test method such as EN ISO 1716, ISO 1928 or EN 15400 shall be used.

After the complete combustion in the oxygen bomb the combustion gases are collected in a gas bag.

For products that are difficult to combust, use a combustion aid to obtain complete combustion. Examples of combustion aids are polyethylene combustion bags, benzoic acid and glucose. Take care not to exceed the maximum amount of organic material allowable for the oxygen bomb that is used. Determine the amount of ^{14}C present in the combustion aid and correct for the contribution of the use of the combustion aid. (^{14}C content and total carbon content).

Determination of the carbonate content in the solution that is collected after combustion can be used to determine the yield of conversion. The carbonate content shall be equivalent to the amount of total carbon present in the combusted sample (including combustion aid)

When Method A is used, the CO_2 shall be collected in a 4 M NaOH solution prior to the conversion to benzene or collected in a cooled mixture of carbamate solution and a suitable scintillation liquid.

For the collection of CO_2 in 4 M NaOH solution use a 250 ml washing bottle filled with 200 ml 4 M NaOH solution, apply a flow flow of 50 ml/min

For the collection of CO_2 in a carbamate solution the gas sample bag is connected to a pump with a connection line into a 20 ml glass vial, filled with a mixture of 10 ml of the carbamate sorption liquid and 10 ml of the scintillation cocktail, placed in an ice bath, to remove the heat of the exothermic carbamate formation reaction. The pumping speed is low, typically 50 $ml \cdot min^{-1}$ to 60 $ml \cdot min^{-1}$. The transfer of the gas from the bag takes about 2 h to 3 h. After the sample has been collected, it is ready to be counted on a liquid scintillation counter. Blank samples shall also be counted at the same time to allow that small day-to-day variations in the background can be accounted for.

Measurements shall be done as soon as possible after collection, at the latest within one week after sampling. There are strong indications that the NO_x formed during the combustion reacts with the absorption mixture resulting in yet unexplained errors after a few days of storage. If the one week limit cannot be realized, collection of the CO_2 in a 4 M NaOH solution is a good alternative.

When Method B or Method C is used, the carbon dioxide shall be collected in a 4 M NaOH solution or on a suitable solid absorber.

For Method B, alternatively ca. 2 ml of the CO_2 gas can be taken from the bag using a glass syringe and the gas can be transferred to the AMS target preparations system. As the bomb volume is released to atmospheric pressure, there will be a residual amount left over in the bomb that is directly related to the pressure in the bomb after the combustion.

NOTE With a residual pressure of 2,5 MPa, 4 % of the combustion gas will be left after release to atmospheric pressure.

To overcome this artefact:

a) perform the calibration and the analysis taking account of this residual amount by using the pressure correction factor;

b) use the vacuum pump to remove the residue;

c) flush the bomb with Argon and collect the CO_2 in the rinsing gases as well.

B.4.2 Combustion of the sample in a tube furnace or a combustion apparatus

The tube furnace or the combustion apparatus shall be able to combust the bio-based product, with a complete conversion of the carbon present to CO_2. For the determination of the ^{14}C content by Method A the CO_2 shall be collected using a suitable impinger filled with a cooled mixture of carbamate and a suitable scintillation liquid, a scintillation medium already containing a CO_2 absorber or a 4 M NaOH solution (see B.3.2, second paragraph). For the determination of the ^{14}C content by Method C or Method B the CO_2 shall be collected using a suitable impinger filled with a 4 M NaOH solution. As a result of the absorption of the CO_2 a large volume reduction of the gas volume will be observed after trapping. Therefore, the gas pump is to be positioned in front of the impinger and the gas pump used shall be gas tight.

As an alternative, the CO_2 can be trapped by means of a cryogenic trap. In that case the cryogenic trap shall consist of a water trap (dry ice in ethanol or acetone) followed by a cryogenic trap. Care shall be taken to avoid formation of liquid oxygen, which can be achieved by heating the trap slightly above the boiling point of oxygen, using liquid argon or performing the separation at diminished pressure. As an alternative, when Method C is being used, CO_2 shall be collected by mixing homogenized bio-based product with cupric oxide (CuO) in a sealed, evacuated quartz or Vycor glass tube. Water vapour (up to 3 Pa) can be added to the tube prior to introduction of the CO_2 to help remove sulfur compounds. The tube is heated to 900 °C for 3 h to 5 h. The CO_2 is collected by breaking the tube using a tube-cracker connected to an evacuated glass collection line.

B.4.3 Direct LSC measurement on the product

For liquid clear products direct measurement on the bio-based product with the LSC technique is possible. This option is only allowed if equivalence with the methods with conversion to CO_2 can be demonstrated. This will in general be the case if no quenching is observed, or if correction for quenching is performed using standard addition technique using the same, ^{14}C labelled, bio-based product with known ^{14}C activity.

The dissolution method may not be appropriate to some bio-based products, for instance when fillers are present.

For direct LSC measurements DIN 51637 [56] is recommended.

B.5 Standardization of LSC and BI measurement results

A liquid scintillation counter measures β-decay counts of ^{14}C (in counts per minute, cpm) indirectly by measuring the interaction signals of the β particles with scintillation molecules (emission of photons – light- proportional to the decay energy). For this measurement, sample CO_2 is either absorbed in a suitable absorbing solution to which also a scintillation reagent is added ('CO_2-cocktail') or the CO_2 has been converted to benzene and is then mixed with liquid (scintillation) reagents to a 'benzene-cocktail'. The 'benzene cocktail' method is more precise than the 'CO_2-cocktail' method.

The same standardization as used for AMS and proportional gas counters shall be used for LSC measurement results:

$$
\begin{aligned}
{}^{14}C_{sampleC}(pMC) &= {}^{14}a_N^s \cdot 100\% = \frac{{}^{14}A_N^s}{{}^{14}A_{RN}^0} \cdot 100\% = \\
&\frac{({}^{14}A_{sample} - {}^{14}A_{bg\,sample}) \cdot \eta_{meas} \cdot \left[\dfrac{1 + {}^{13}\delta_N}{1 + {}^{13}\delta_{sample}}\right]^2}{{}^{14}A_{RN}^0} \cdot 100\%
\end{aligned}
\tag{B.1}
$$

In the case that no primary or secondary reference standard has been measured, the measuring efficiency is not cancelled out and shall be determined using an internal standard. It is also necessary in that case to determine the activity of the sample in dpm/gC (disintegrations per minute) instead of cpm/gC. ${}^{14}A_{RN}^0$ = 13,56 ± 0,07 dpm/gC = 0,226 ± 0,001 Bq/gC.

B.6 Standardization of AMS measurement results

The AMS system measures the carbon isotopes ^{12}C, ^{13}C and ^{14}C of a carbon sample in the same sample run. A batch of samples shall also contain reference material samples. The measured ^{14}C amount (=^{14}C isotope concentration) in a sample is calculated relative to the measured (average) ^{14}C amount of the reference material samples in the same batch. If the reference material is the primary reference standard Oxalic Acid II (HOx-II, SRM 4990c), which is commonly used for this purpose, the standardized ^{14}C amount in the sample, ${}^{14}C_{sampleC}$ (= ${}^{14}a_N^S \cdot 100\%$ = pMC), shall be calculated as following:

$$ {}^{14}C_{sampleC}(pMC) = \frac{({}^{14}A_{sample} - {}^{14}A_{bg\,sample})\cdot \eta_{meas} \cdot \left[\frac{1+{}^{13}\delta_N}{1+{}^{13}\delta_{sample}}\right]^2}{0,7459\cdot({}^{14}A_{OX2} - {}^{14}A_{bg_{OX2}})\cdot \eta_{meas} \cdot \left[\frac{1+{}^{13}\delta_N}{1+{}^{13}\delta_{OX2}}\right]} \cdot 100\% \tag{B.2} $$

B.7 Symbols and abbreviations

${}^{14}C_{sampleC}$	measured ^{14}C value (in pMC) of the investigated CO_2 sample
${}^{14}a_N^S$	standardized and normalized ^{14}C amount of the measured sample; ${}^{14}a_N^S \cdot 100\% = pMC$
${}^{14}A_N^S$	normalized ^{14}C signal (isotope concentration or activity) of the measured sample
${}^{14}A_{RN}^0$	standardized and normalized ^{14}C amount of the primary reference standard, Oxalic acid (HOx-II, SRM 4990c).
${}^{14}A_{sample}$	measured ^{14}C signal (isotope concentration or activity) of the sample
${}^{14}A_{bg\,sample}$	measured ^{14}C signal (isotope concentration or activity) of the background sample/blank sample, measured in the same batch as the sample and represents the background ^{14}C signal of the measured samples
${}^{14}A_{OX2}$	measured (average) ^{14}C signal (isotope concentration or activity) of Oxalic acid reference standard samples (HOx-II, SRM 4990c), measured in the same batch as the unknown samples
${}^{14}A_{bg\,OX2}$	measured (average) ^{14}C signal (isotope concentration or activity) of background samples, which represent the background signal of the measured Oxalic Acid reference standard (HOx-II, SRM 4990c), measured in the same batch as the Oxalic Acid samples
η_{meas}	measuring efficiency of the used measurement technique
${}^{13}\delta_N$	standardized value for isotope fractionation. ${}^{13}\delta_N$ = - 0,025 (relative to VPDB)
${}^{13}\delta_{sample}$	measured isotope fractionation value of the sample. It is obtained by measuring the $^{13}C/^{12}C$ ratio of the sample, relative to the measured $^{13}C/^{12}C$ ratio of a reference standard with known isotope fractionation value related to VPDB
${}^{13}\delta_{OX2}$	standardized isotope fractionation value of the Oxalic Acid reference standard (HOx-II, SRM 4990c). ${}^{13}\delta_{OX2}$ = - 0,0176 (relative to VPDB).

Annex C
(normative)

Method A - Liquid scintillation-counter method (LSC)

C.1 General

This annex describes the method for the determination of the ^{14}C content by LSC in carbonate solutions or carbamate solutions obtained from the combustion of bio-based product samples in a calorimetric bomb, a tube furnace or a laboratory scale combustion device as described in Annex B.

C.2 Principle

LSC (Liquid scintillation counter method) determines the isotope abundance of ^{14}C indirectly, through its emission of beta particles due to the radioactive decay of the ^{14}C isotope. The beta particles are observed through their interaction with scintillation molecules. The CO_2 formed by the combustion of a bio-based product is trapped in an alkaline or carbamate solution. The CO_2 present in the alkaline solution is converted to benzene; the carbamate solution can directly be measured. The formed benzene or carbamate solution is mixed with the organic solution containing the scintillation molecules and the ^{14}C activity of this mixture is measured in a liquid scintillation counter.

C.3 Reagents and materials

- oxalic acid primary standard (e.g. SRM 4990c);
- HCl solution (5 M);
- scintillation liquid;
- carbamate solution;
- ^{14}C substance for standard addition purposes;
- coal standard;
- reagent grade powdered lithim or lithium rod (each packed in Argon);
- reagent grade potassium chromate (in sulfuric or phosphoric acid);
- suitable catalyst (based on Cr_2O_3 or V_2O_5).

C.4 Apparatus

The low natural levels of radiocarbon in the earth's atmosphere (about 10^{-12} %) require extra precautions for accurate measurement of ^{14}C. Care shall be taken to eliminate the influence of cosmic and environmental background radiation, other radioisotopes being present, electronic noise and instability, and other factors. These background factors limit the accuracy, precision, and range of the radiocarbon method as finite ages can only be calculated where sample activity is at least three standard deviations above background activity [41]. Any liquid scintillation counter used shall meet these specifications.

C.5 Procedure

C.5.1 General

The best LSC performance characteristics are obtained applying conversion of the collected CO_2 to benzene and direct counting of the benzene in a suitable scintillation cocktail, as for instance described in ASTM D 6866. For material with a high bio-based carbon content (>10 %) direct absorption of the CO_2 in a carbamate solution can be applied.

C.5.2 Benzene conversion

The collected CO_2 is reacted with a stoichiometric excess (3:1 lithium: carbon ratio) of molten lithium which has been preheated to 700 °C. Li_2C_2 is produced by slowly bleeding the CO_2 onto the molten lithium in a stainless steel vessel (or equivalent) while under a vacuum of < 135 mPa. The Li_2C_2 is heated to at least 640 °C and placed under vacuum for 15 min to 30 min to remove any unreacted gases and to complete the Li_2C_2 synthesis reaction. The Li_2C_2 is cooled to room temperature and gently hydrolysed with distilled or de-ionized water to generate acetylene gas (C_2H_2) by applying the water in a drop-wise fashion to the cartridge. Passing it through dry ice traps dries the evolved acetylene, and the dried acetylene is subsequently collected in liquid nitrogen traps. The acetylene is purified by passing it through a phosphoric acid or potassium chromate (in sulphuric acid) trap to remove trace impurities, and by using dry ice traps to remove water. The C_2H_2 gas is catalysed to benzene (C_6H_6) by bleeding the acetylene onto a chromium catalyst which has been preheated to ≥ 90 °C applying a water jacket cooler to avoid decomposition from excessive heat generated during the exothermic reaction. As an alternative, a vanadium catalyst at ambient temperature can be used. The benzene is thermally evolved from the catalyst at 70 °C to 110 °C and then collected under vacuum at −78°C. The benzene is then frozen until it is counted. Radon can be removed by pumping on the benzene while it is at dry ice temperature. Mix the benzene and scintillation liquid in constant volume and proportion, if necessary the benzene can be diluted with benzene from fossil origin (99,999 % pure, thiophene-free).

If ^{13}C isotope analysis is required, a representative subsample shall be taken extra for ^{13}C analysis.

C.5.3 Direct absorption of the CO_2 in a carbamate solution

An absorption flask is loaded with a known volume of CO_2 absorbent, e.g. with Carbosorb. The absorbing capacity of Carbosorb of about $4{,}8 \cdot 10^{-3}$ M/ml shall be taken into account; no more than 80 % of this capacity shall be used. The flask shall be cooled in ice during the absorption process. After absorption of the CO_2, the absorbent is transferred to the measuring vial. An equal volume of the scintillation medium is added and the mixture is homogenized.

The CO_2 may also be absorbed in a scintillation medium already containing a CO_2 absorber, which shall be measured in the LSC without further handling.

Then the vial containing the mixture is placed in the LSC and measured. Typical counting times are 6 h to 24 h.

C.5.4 Measurement

The activity of a sample is compared with the activity of a reference material. The number of ^{14}C registrations (Beta counts of ^{14}C decay) in radiometric detectors (LSC) is related to the number of registrations of the reference sample under the same conditions.

Standard addition techniques shall be used to check for the occurrence of chemical or optical quenching for each sampling or sample type. For that purpose ^{14}C labelled components shall be used.

For clear liquids direct LSC counting can by applied, e.g. as described in DIN 51637 [40]; mix 10 ml. of sample with 10 ml of suitable scintillation cocktail and count after 12 h settling time. For each product a quench curve shall be established before measurements can be done.

As ^{13}C isotope analysis is required, a representative subsample shall be taken extra for ^{13}C analysis.

C.5.5 Blank correction

Measurement shall be performed together with a measurement of the “blank” sample, which is a scintillation vial filled with counting liquid that is counted for at least the same period of time as the actual sample. The result obtained is the background level for the whole system (apparatus and reagent) given in cpm or dpm. After this the actual sample is counted, which also gives a counting result in cpm or dpm.

The statistical error of counting, background and standard is a result of the decay counting, (Poisson) process; hence the precision of the result depends on the number of counts observed, where the relative error is inversely proportional to the square-root of the number of counts. The total error is then the combination of the analytical errors and the errors of the standard and background determination.

C.6 Calculation of the results

From the sample count rate the background count rate of the counter is subtracted (net count rate). The ^{14}C activity (dpm/g C) is obtained by normalizing the net count rate to the count rate of the reference standard (oxalic acid SRM).

Standardization of the AMS results shall be done as described in B.6.

Annex D
(informative)

Method C - Beta-ionization (BI)

D.1 General

This informative annex describes the procedure for the determination of the ^{14}C content by BI in basic carbonate solutions obtained from the combustion of bio-based product samples in a calorimetric bomb, a tube furnace or a laboratory scale combustion device as described in Annex B.

D.2 Principle

The beta ionization method determines the isotope abundance of ^{14}C indirectly. This method uses the emission of beta-particle by ^{14}C due to the radioactive decay of the ^{14}C isotope, like LSC. It detects beta-particle by means of discharge current pulses between high-voltage electrodes in a proportional gas counter. Those pulses are initiated by the beta particles. The detection principle resembles the way a Geiger-Mueller (GM) counter works, the difference being details of the electron avalanche in the counter. To use this method, the sample has to be in the form of CO_2 or converted to CO_2. The carbonate as obtained from the combustion of a bio-based product is converted to CO_2 by acidifying the NaOH solution with HCl. CO_2 is purified to be suitable as a counting gas in a gas proportional counter, e.g. by removal of electron-negative impurities, such as oxygen, SO_2 or water vapour through activated charcoal. This step also removes radon. The purity of the gas is critical (for example, O_2 shall be kept well below a few microlitres per litre).

The sample is counted for several days in a low-level counting system to reach the number of counts desired for statistical precision.

The CO_2 is held under pressure in the central tube (typically at 0,2 MPa to 0,3 MPa) and a high voltage is introduced between the central wire and the counter wall. An ionizing event, such as a beta particle produced by a ^{14}C decay, creates an ionization trail and an avalanche of electrons. This avalanche is measured as an electrical pulse. Any impurities in the gas will quench the multiplication of electrons, leading to some decay events being undetected.

D.3 Reagents and materials

- HCl solution (5 M);
- NaOH solution (4 M);
- dry ice;
- acetone or ethanol;
- liquid N_2;
- oxalic acid primary standard (SRM 4990c);
- coal standard;
- activated charcoal.

D.4 Apparatus

- System for the conversion of carbonate trapped in a 4 M NaOH solution to CO_2;
- CO_2 purification system, e.g. using activated charcoal;
- system to obtain a fixed amount of sample, e.g. by adjusting the CO_2 pressure in a fixed volume and known gas temperature;
- system to prepare standard and background samples;
- low-level counting system using a gas proportional counter.

The instruments used for the BI measurements are homemade high tech devices developed at several radiocarbon institutes. No commercial systems are available at the time of writing this European Standard. For radiocarbon to be detectable, background counts shall be minimized. Gas (in this case purified CO_2 derived from the combustion gases) is loaded and counted in a copper counting tube (ultra-pure copper) and the desired low background is obtained applying heavy shielding with old lead and anticoincidence filtering of cosmic radiation. Usually BI devices are located below ground level in cellars in order to obtain extra protection against cosmic radiation. Typical counting times are several days for low-level measurements.

D.5 Procedure

a) Transfer the carbonate solution to extraction bottle.

b) Attach the HCl dosing device.

c) Evacuate the bottle and dosing device (degassing, removal of dissolved N_2 and O_2 from air).

d) Add HCl to the carbonate solution.

e) Water vapour is removed using a trap filled with acetone and dry ice.

f) The formed CO_2 is collected in a stainless steel trap that is submersed in liquid N_2.

g) The CO_2 shall be cleaned, e.g. using activated carbon at 0° C.

h) A small sample shall be taken for ^{13}C determination at this stage (optional).

i) The CO_2 volume shall be calculated measuring temperature and pressure and the known volume of the trapping system.

j) Transfer the CO_2 to the proportional counter (amounts up to 4 gram of CO_2).

k) Count for several days until precision as desired is obtained.

l) Calculate the modern carbon value using the sample count rate and the blank count rate.

The statistical error of counting the sample, background and standard is a result of the decay counting, following the statistical Poisson distribution. Hence, the precision of the result depends on the number of counts observed, where the relative error is inversely proportional to the square-root of the number of counts.

The total error is then the combination of the analytical errors and the errors of the standard and background determination. The latter errors usually are small compared to the sampling errors. With counting times of a few days a typical overall precision of 0,3 % to 0,4 % shall be obtained. The estimated precision shall be reported in addition to the value declared.

When using active carbon for clean up, the active carbon cartridge shall be preheated ± 1 h in order to remove traces of Radon (build-up of decay product of Uranium traces present in the active coal). For other cleaning techniques, a waiting time of 2 d is sufficient to get rid of the Radon contribution.

D.6 Calculation of the results

From the sample count rate the count rate of the NaOH blank solution is subtracted resulting in the net count rate. The ^{14}C activity (pMC) is obtained by normalizing the net count rate to the count rate of the reference standard (Oxalic acid SRM 4990c or materials that are traceable to this reference standard).

As correction for isotopic fractionation has to be performed, the $^{13}C/^{12}C$ isotopic ratio has to be determined as well. Standardization of the BI results shall be done as described in B.6.

Annex E
(normative)

Method B - Accelerator Mass Spectrometry (AMS)

E.1 General

This annex describes the procedure for the determination of the ^{14}C determination by AMS in the carbonate solutions obtained from the combustion of bio-based product samples in a calorimetric bomb, a tube furnace or a laboratory scale combustion device as described in Annex B.

E.2 Principle

The accelerator mass spectrometry (AMS) method determines the presence of ^{14}C directly. The atoms in the sample are converted into a beam of ions. The formed ions are accelerated in an electric field, deflected in a magnetic field and 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 them but also to specifically form only C^{n+} ions (n = 1,,,4) that are allowed into the spectrometer, excluding all other ionic species. This greatly enhances sensitivity without compromising selectivity. As the ^{14}C is determined in graphite (carbon), all the carbon in the samples has to be converted into graphite before analysing.

With AMS, the modern fraction in the carbon, present in the sample, is determined. The total carbon content is not determined with this technique and shall be determined separately.

E.3 Reagents and materials

- Oxalic acid primary standard (e.g. SRM 4990c);
- coal standard;
- iron or cobalt catalyst;
- hydrogen;
- HCl solution (5 M);
- dry ice;
- acetone or ethanol;
- liquid N_2.

E.4 Apparatus

- Sample preparation equipment;
- liquid nitrogen freezing station;
- accelerator mass spectrometer (AMS).

E.5 Procedure

In practice every AMS lab perform their measurements using their own optimized measurement procedures. An example of a procedure is given in this Clause. Comparable procedures can be used as long as the AMS results are obtained using the same reference standard (SRM 4990c).

a) Transfer the carbonate solution to the extraction bottle.

b) Attach the HCl dosing device.

c) Evacuate the bottle and dosing device (degassing, removal of dissolved N_2 and O_2 from air).

d) Add HCl to the carbonate solution.

e) Remove water vapour by using a trap filled with acetone and dry ice.

f) Collect the formed CO_2 in a trap that is submersed in liquid N_2.

g) Take a small sample for ^{13}C determination at this stage.

h) Transfer the CO_2 to the graphitizing rig system.

Gaseous sample shall be either introduced in the system released from a quartz tube or after they are trapped in liquid nitrogen followed by subsequent heating. Then convert the gas to graphite using an iron catalyst according to the formulae:

$$CO_2 + H_2 \leftrightarrow H_2O + CO$$

$$CO + H_2 \leftrightarrow H_2O + C$$

i) Remove the water produced by this reaction to ensure a complete reduction to graphite. This is particularly important to avoid fractionation.

j) Press the graphite into a target and mount it on a wheel before it is loaded into the accelerator mass spectrometer. In the ion source a high current beam of caesium ions (Cs^+) is focused on the target. This liberates negatively charged target atoms, producing a 36 keV beam of C- ions. Keep the targets 10 mm away from each other to avoid cross-contamination and move them during sputtering to avoid cratering, which causes fractionation. A lens into a recombinator then focuses the negative ion beam. Here a series of magnets remove non-carbon ions from the beam and separate the three carbon isotopes (^{12}C, ^{13}C and ^{14}C). The chopper wheel then physically blocks most of the ^{12}C, allowing a much-reduced beam of carbon ions to be recombined for simultaneous injection into the accelerator.

k) In the tandem accelerator the C- ions are accelerated to the terminal (at +2,5 MeV) then changed to C^{3+} ions by collision with Ar atoms in the gas stripper. These positive ions are accelerated to 10 MeV. A charge state of 3+ is chosen because the mass/charge ratio of $^{14}C^{3+}$ is truly unique, allowing its accurate separation in the high-energy mass spectrometer.

l) Measure the ^{12}C and ^{13}C in the Faraday cups (typical current, 250 nA).

m) Purify the $^{14}C^{3+}$ ions by an electrostatic deflector and a 90° magnet. Measure them in an isobutene-filled ionization chamber, isolated from the accelerator vacuum by a thin metal foil. Typically, a sample is counted for one hour.

E.6 Calculation of the results

The isotopic ratios of $^{14}C/^{12}C$ and $^{13}C/^{12}C$ are determined relative to the appropriate primary reference material. All percentage modern carbon (pMC) values obtained from the radiocarbon analyses measurements shall be corrected for isotopic fractionation using stable isotope data ($^{13}C/^{12}C$ ratios) obtained on CO_2 derived from combustion of the sample. Do not determine $^{13}C/^{12}C$ ratios on the raw product material itself, since that approach can lead to erroneous results in some cases. Standardization of the AMS results shall be done as described in B.6.

Annex F
(informative)

Performance characteristics

The round robin assessment was initiated in the frameworks of European KBBPPS and Open-Bio projects (www.biobasedeconomy.eu). The aim of the study was to investigate the performance characteristics of the method that was described in CEN/TS 16640 for the bio-based carbon content determination.

The assessment involved 11 independent laboratories to whom in total 132 samples were delivered (11 equivalent sets of samples, 12 samples each set). The round robin was carried out by laboratories in Germany, France, Poland, the Netherlands, New Zealand, the United Kingdom and the USA. Accordingly to the aim of the study, each participating laboratory was asked to follow the method proposed in CEN/TS 16640 and to determine the total carbon content and subsequently the bio-based carbon content of different types of materials or products. The selection of samples for the assessment was done to cover different and challenging materials. The set of samples that were sent to each laboratory involved: water soluble matt paint with volatile component about 34 %; non-volatile emulsions used as components of sun lotion and in cosmetics; a panel made from wheat straw that can be used for building purposes; bio-diesel; bio-gas; surfactant granules that are used in cosmetics; multilayer packaging film; silk paint; binder that is used in paints; wooden particle board ground to 0.5mm. All results were reported on dry basis.

For the description of sample type see Table F.1

The performance data according to ISO 5725-2 [57] are presented in Table F.2.

Table F.1 — description of sample types

Sample	Matrix
1	Water based paint
2	Sun lotion component
3	Sun lotion component
4	Wheat straw panel
5	Biodiesel
6	Bio gas
7	Emulsion granules (in sample 8)
8	Cosmetic emulsion
9	Multi-layer package film
10	Bio-based paint
11	Water binder
12	Particle board, wood based

Table F.2 — Performance data for 14C methods

Sample	n	l	o	x	s_R	CV_R
			%	% m/m	% m/m	%
1	10	8	20	10,2	1,8	17,7
2	10	9	10	14,4	1,5	10,6
3	10	9	10	96,7	0,8	0,9
4	10	9	10	94,0	1,4	1,5
5	10	9	10	97,3	2,3	2,3
6	4	3	25	96,0	1,7	1,8
7	10	10	0	98,0	1,0	1,1
8	10	9	10	95,0	1,4	1,5
9	11	10	9,1	12,2	1,2	10,1
10	10	9	10	73,2	2,0	2,7
11	10	9	10	94,1	1,8	1,9
12	11	11	0	99,3	0,8	0,8

n	is the number of laboratories
l	is the number of outlier free individual analytical values
o	is the percentage of outlying values
x	is the overall means
s_R	is the reproducibility standard deviation
CV_R	is the coefficient of the variation of the reproducibility

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