DD CEN/TS 16137:2011

BSI Standards Publication

Plastics — Determination of bio-based carbon content

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National foreword

This Draft for Development is the UK implementation of CEN/TS 16137:2011.

This publication is not to be regarded as a British Standard.

It is being issued in the Draft for Development series of publications and is of a provisional nature. It should be applied on this provisional basis, so that information and experience of its practical application can be obtained.

Comments arising from the use of this Draft for Development are requested so that UK experience can be reported to the international organization responsible for its conversion to an international standard. A review of this publication will be initiated not later than 3 years after its publication by the international organization so that a decision can be taken on its status. Notification of the start of the review period will be made in an announcement in the appropriate issue of *Update Standards.*

According to the replies received by the end of the review period, the responsible BSI Committee will decide whether to support the conversion into an international Standard, to extend the life of the Technical Specification or to withdraw it. Comments should be sent to the Secretary of the responsible BSI Technical Committee at British Standards House, 389 Chiswick High Road, London W4 4AL.

The UK participation in its preparation was entrusted to Technical Committee PRI/-/1, UK co-ordination for international work on plastics.

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

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

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Compliance with a British Standard cannot confer immunity from legal obligations.

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Plastics - Determination of bio-based carbon content

Plastiques - Détermination de la teneur en carbone biosourcé

Kunststoffe - Bestimmung des biobasierten Kohlenstoffgehalts

This Technical Specification (CEN/TS) was approved by CEN on 20 December 2010 for provisional application.

The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

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Foreword

This document (CEN/TS 16137:2011) has been prepared by Technical Committee CEN/TC 249 “Plastics”, the secretariat of which is held by NBN.

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Introduction

This Technical Specification specifies the calculation method for the determination of bio-based carbon content in monomers, polymers, plastics materials and products using the ^{14}C method.

This calculation method using the ^{14}C method is based on the well established analytical test methods used for the determination of the age of objects containing carbon.

This Technical Specification provides the reference test methods for laboratories, producers, suppliers and purchasers of bio-based polymer materials and products. It can be also useful for authorities and inspection organizations.

NOTE 1 This Technical Specification is based on EN 15440 [4] prepared by CEN/TC 343, Solid recovered fuels.

NOTE 2 The analytical test methods specified in this Technical Specification are compatible with those described in ASTM D6866 - 10 [9].

1 Scope

This Technical Specification specifies a calculation method for the determination of the bio-based carbon content in monomers, polymers and plastic materials and products, based on the ^{14}C content measurement.

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

— Method A: Proportional scintillation-counter method (PSM);

— Method B: Beta-ionisation (BI);

— Method C: Accelerator mass spectrometry (AMS).

The bio-based carbon content is expressed by a fraction of sample mass, as a fraction of the total carbon content or as a fraction of the total organic carbon content.

This calculation method is applicable to any polymers containing organic carbon, including biocomposites.

NOTE This Technical Specification does not provide the methodology for the calculation of the biomass content of a sample.

2 Normative references

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

CEN/TR 15932:2010, *Plastics — Recommendation for terminology and characterisation of biopolymers and bioplastics*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in CEN/TR 15932:2010 and the following apply.

3.1
bio-based carbon content
amount of carbon in a sample that is of recent origin, as evidenced by its ^{14}C isotope content

3.2
biomass content
mass fraction of bio-based material in a sample

3.3
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

3.4
organic carbon
carbon from organic material

3.5
isotope abundance
fraction of atoms of a particular isotope of an element

3.6
percentage modern carbon
pmC
percent modern carbon relative to the N.I.S.T. [1)] oxalic acid radiocarbon standard reference material SRM 4990B

NOTE In 1950, the internationally accepted radiocarbon dating reference value is 95 % of this activity of this NBS oxalic acid SRM 4990b. In 2010, the value of 100 % bio-based carbon is set at 105 pmC.

3.7
laboratory sample
sub-quantity of a sample suitable for laboratory tests

3.8
sample
quantity of material, representative of a larger quantity for which the property is to be determined

3.9
sample preparation
actions taken to obtain representative analyses samples or test portions from the original sample

3.10
β particle
electron emitted during radioactive decay

3.11
total carbon
TC
quantity of carbon present in a sample in the form of organic, inorganic and elemental carbon

[EN 13137:2001]

3.12
total organic carbon
TOC
quantity carbon that is converted into carbon dioxide by combustion and which is not liberated as carbon dioxide by acid treatment

[EN 13137:2001]

4 Symbols and abbreviations

4.1 Symbols

C symbol for element carbon

^{14}C carbon isotope with an atomic mass of 14

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

x^{TOC} total organic carbon content, expressed as a percentage of the mass of the sample

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

1) National Institute of Standards and Technology - Gaithersburg, Maryland, USA.

x_B^{TC} bio-based carbon content by total carbon content, expressed as a percentage of the total carbon content

x_B^{TOC} bio-based carbon content by total organic carbon content, expressed as a percentage of the total organic carbon content

pmC(s) measured value, expressed in pmC, according to AMS method, of the sample

REF reference value, expressed in pmC, of 100 % bio-based carbon depending on the origin of organic carbon

m mass of a sample expressed in grams

4.2 Abbreviations

AMS accelerator mass spectroscopy

BI beta-ionisation

Bq Bequerel (desintegrations per second)

cpm counts per minute

CV coefficient of variation

dpm disintegrations per minute

GM Geiger-Müller

LLD lower limit of detection

LSC liquid scintillation-counter or liquid scintillation-counting

MOP 3-methoxy 1-propyl amine

PE polyethylene

PLA poly(lactic acid)

pmC percentage of modern carbon

PSM proportional scintillation-counter method

TC total carbon

TOC total organic carbon

5 Principle

The ^{14}C present in chemicals 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 chemicals 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 polymers which allows the calculation of the bio-based carbon fraction.

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

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

— Method B: Beta-ionisation (BI), or

— Method C: Accelerator mass spectrometry (AMS).

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

Table 1 — Advantages and disadvantages of the methods

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

6 Sampling

If there is a standard sampling procedure for the material or product to be evaluated that is widely accepted by the different parties, such a procedure may be used and the details of sampling recorded.

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.

7 Determination of the ^{14}C content

7.1 General

A general sample preparation and three test methods for the determination of the ^{14}C content are described in this Technical Specification. 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.

7.2 Principle

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

Complete combustion (see Annex A) 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 three following methods:

— Method A: Proportional scintillation-counter method (PSM): indirect determination of the isotope abundance of ^{14}C, through its emission of β particles (interaction with scintillation molecules), specified in Annex B;

— Method B: Beta-ionisation (BI): indirect determination of the isotope abundance of ^{14}C, through its emission of β particles (Geiger-Müller type detector), specified in Annex C, or

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

7.3 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 the Annex A.

7.4 Measurements

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

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 blank's during the sampling stage.

For the determination of the 0 % biomass content the combustion of a coal standard (e.g. BCR 181) may be used.

For the 100 % biomass content the N.I.S.T. oxalic acid standard reference material (SRM 4990b) may be used. Mixing this reference material 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 wood standard reference material calibrated against the oxalic acid is sufficient.

8 Calculation of the bio-based carbon content

8.1 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 mass or the determination of the total organic carbon content of the sample, x^{TOC}, expressed as a percentage of the total 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 Clause 7, and applying the correction factors detailed in 8.2 (see 8.3.1).

c) the calculation of the bio-based carbon content as a fraction of the total carbon content, x_B^{TC} (see 8.3.2) or as a fraction of the total organic carbon content, x_B^{TOC} (see 8.3.3).

8.2 Correction factors

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 105 pmC in 2010. 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 D6866 - 10 [9] the 100 % bio-based C value of 105 pmC (for year 2010) is used. This value shall be the base of calculations. Other values are only acceptable if they are based on experimental evidence. From the 105 pmC value the correction factor of 0,95 (1/1,05) 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 100/0,95 pmC or 13,56/0,95 dpm per gram C is considered as a 100 % bio-based carbon content for biomass that is grown in year 2009.

NOTE This correction value of 0,95 is in accordance with the value that is given in ASTM D6866 - 10 [9].

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

Table 2 — Typical values [a] for biomass fractions

Material	x^{TC} %	REF pmC
Wood (coniferous and deciduous)	48	114
Bark	52	111
Paper	47	114
Fresh biomass (from year 2010)	48	104
Silk	49	107
Wool	51	107
[a] These values are given on “dry basis”.		

8.3 Calculation method

8.3.1 Calculation of the bio-based carbon content by mass x_B

8.3.1.1 ^{14}C content determined by Method A (PSM) or Method B (BI)

Calculate the bio-based carbon content by mass, x_B, expressed as a percentage, using Equation (1):

$$x_B = \frac{^{14}C_{activity}}{13{,}56 \times \frac{REF}{100} \times m} \times 100 \quad (1)$$

where

$^{14}C_{activity}$ is the ^{14}C activity, expressed in dpm, of the sample obtained by calculation when using Method A (see Annex B);

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.

8.3.1.2 ^{14}C content determined by Method C (AMS)

Calculate the bio-based carbon content by mass, x_B, expressed as a percentage, using Equation (2):

$$x_B = x^{TC} \frac{\frac{pmC(s)}{100}}{\frac{REF}{100}} = x^{TC} \frac{pmC(s)}{REF} \quad (2)$$

where

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

8.3.2 Calculation of the bio-based carbon content x_B^{TC} as a fraction of TC

Calculate the bio-based carbon content as a fraction of the total carbon content, x_B^{TC}, expressed as a percentage, using Equation (3):

$$x_B^{TC} = \frac{x_B}{x^{TC}} \times 100 \quad (3)$$

where

x_B is the bio-based carbon content by mass, expressed as a percentage;

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

8.3.3 Calculation of the bio-based carbon content x_B^{TOC} as a fraction of TOC

Calculate the bio-based carbon content as a fraction of the total organic carbon content, x_B^{TOC}, expressed as a percentage, using Equation (4):

$$x_B^{TOC} = \frac{x_B}{x^{TOC}} \times 100 \quad (4)$$

where

x_B is the bio-based carbon content by mass, expressed as a percentage;

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

8.3.4 Examples

EXAMPLE 1 Measurement according to Method A

Sample made from pure wood (REF = 114 pmC, x^{TC} = 48,0 %)

Mass of sample: m = 1,050 g

^{14}C activity = 7,75 dpm

$$x_B = \frac{7,75}{13,56 \times {114}/{100} \times 1,05} \times 100 = 47,8\%$$

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

EXAMPLE 2 Measurement according to Method C

Sample made from bark (REF = 111 pmC, x^{TC} = 52,0 %)

NaOH solution: 1 M

^{14}C value = 61,7 pmC

$$x_B = 52 \frac{{61,7}/{100}}{{111}/{100}} = 28,9\%$$

$$x_B^{TC} = \frac{28,9}{52,0} \times 100 = 55,6\%$$

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 %)

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

EXAMPLE 4 Calculation of bio-based carbon content as a fraction of TOC

Mixed bio-based polymer material

Sample made from PE material containing a mixture of fossil PE and PE produced from biogenic syngas:

x^{TOC} = 86,0 %; x_B = 24,0 %

$$x_B^{TOC} = \frac{24,0}{86,0} \times 100 = 27,9\%$$

8.3.5 Examples of calculations of x_B^{TC} and x_B^{TOC}

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

Table 3 — Examples

Material	Biomass content %	x^{TC} %	x^{TOC} %	x_B %	x_B^{TC} %	x_B^{TOC} %
Wood	100	48	48	48	100	100
Polymer containing 50 % of PE from fossil source and 50 % of bio-based PE	50	90	90	45	50	50
Polymer containing 40 % of calcium carbonate from fossil source, 30 % of PE from fossil source and 30 % of bio-based PLA	30	46,8	42	15	32	36

9 Test report

The test report shall contain at least the following information:

a) a reference to this document (CEN/TS 16137:2011);

b) all information necessary for complete identification of the bio-based polymer 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);

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 A.4);

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

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

m) bio-based carbon content by total carbon content, x_B^{TC} ,expressed as a percentage, of the sample;

n) bio-based carbon content by total organic carbon content, x_B^{TOC} ,expressed as a percentage, of the sample;

o) 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;

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

Annex A
(normative)

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

A.1 General

The ^{14}C content of a bio-based polymer is determined on 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.

A fourth method, based on the dissolution of the bio-based polymer and a direct measurement, may be used only when it is technically achievable.

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 C is used, there are two options:

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

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

As Method C 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 B, 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, three options are possible after combustion:

c) direct adsorption of the formed CO_2 in a carbamate solution (a suitable CO_2 absorption solution containing an amine, e.g. 1 M 3-methoxy 1-propyl amine in methanol, or a commercial available solution);

d) adsorption of the CO_2 in a 2 M NaOH solution and transfer of CO_2 in NaOH to a carbamate solution;

e) direct conversion of CO_2 to benzene.

A.2 Reagents and materials

— Carbamate solution;

— scintillation medium;

— glass bottle (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.

A.3 Combustion of the sample in a calorimetric bomb

A.3.1 Procedure

For the combustion of the sample in a calorimetric bomb, any suitable test method such as EN ISO 1716 [6], ISO 1928 [7] or EN 15400 [3] may be used.

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

When Method A is used, the CO_2 shall be collected in a cooled mixture of carbamate solution and a suitable scintillation liquid.

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

For Method C, 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 artifact:

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.

A.3.2 Adsorption of the gas sample

The gas sample bag is connected to a small 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 medium, placed in an ice bath, to remove the heat of the exothermic carbamate formation reaction. The pumping speed is low, typically 50 ml·min^{-1} to 60 ml·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 should also be counted at the same time to allow that small day-to-day variations in the background can be accounted for.

NOTE Measurements should 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.

A.4 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 polymer, 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 note above). 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 may be collected by mixing homogenized biopolymer 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 sulphur 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.

A.5 Dissolution and LSC direct measurement on the polymer

Only in some cases direct measurement on the biopolymer with the LSC technique is possible. This option is only allowed if equivalence with the methods with conversion to CO_2 may 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 polymer with known ^{14}C activity.

NOTE The dissolution method may not be appropriate to some biopolymers, for instance when fillers are present.

Annex B
(normative)

Method A - Proportional scintillation-counter method (PSM)

B.1 General

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

B.2 Principle

PSM (also called Liquid Scintillation Counter method, LSC) determines the isotope abundance of ^{14}C indirectly, through its emission of β particles due to the radioactive decay of the ^{14}C isotope. The β particles are observed through their interaction with scintillation molecules. The CO_2 formed by the combustion of a bio-based polymer is trapped in a carbamate solution. This solution is mixed with the organic solution containing the scintillation molecules and the ^{14}C activity of this mixture is measured in a proportional (liquid) scintillation counter.

B.3 Reagents and materials

— Oxalic acid primary standard (e.g. SRM 4990b);

— HCl solution (5 M);

— scintillation liquid;

— carbamate solution;

— ^{14}C substance for standard addition purposes.

B.4 Apparatus

The extremely low natural levels of radiocarbon in the earth's atmosphere (about 10^{-12} %) require extra precautions for accurate measurement of ^{14}C. Care should 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 dating method as finite ages can only be calculated where sample activity is at least 3 standard deviations above background activity [13]. Any liquid scintillation counter used shall meet these specifications.

B.5 Procedure

An absorption flask is loaded with a known volume of CO_2 absorbent, e.g. with a suitable CO_2 absorption solution containing an amine, e.g. 1 M 3-methoxy 1-propyl amine in methanol, or a commercial available solution. The absorbing capacity of a suitable CO_2 absorption solution containing an amine, e.g. 1 M 3-methoxy 1-propyl amine in methanol, or a commercial available solution 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. The sample gas is acquired from a flue gas duct or from a gas bag. In either case, the

sample has to be dried and the CO_2 concentration of the dried sample has to be known (either by a flue gas monitor or by ultimate analysis of the solid sample that was used to generate the CO_2). If acquired directly from a flue gas duct, the sample volume has to be measured with a gas meter and corrected for the volume of CO_2 absorbed by the MOP (3-methoxy 1-propyl amine, the active component in a suitable CO_2 absorption solution containing an amine, e.g. 1 M 3-methoxy 1-propyl amine in methanol, or a commercial available solution). 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.

NOTE When using an oxidizer, the combustion gas may be absorbed in a scintillation medium already containing a CO_2 absorber which can be measured in the PSM without further handling.

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

The activity of a sample is compared with the activity of a reference material. The number of ^{14}C registrations (β counts of ^{14}C decay) in radiometric detectors (PSM) 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.

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 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.

The detection limit of a counter is an important parameter, as it for a great part determines the sensitivity of the total analytical procedure. The sensitivity is normally expressed as “lower limit of detection” (LLD). This is the smallest amount of radioactivity that statistically differs from the background. The LLD is be calculated by means of Equation (A.1) from the counting time of the sample and the background counting rate assuming the same counting times for background and sample:

$$E\left(R_{n,LLD}\right) = \left(k_{1-\alpha} + k_{1-\beta}\right) \cdot \sqrt{E\left(R_0\right) \cdot \left(\frac{1}{t_0} + \frac{1}{t_b}\right)} \qquad \text{(A.1)}$$

where

$E(R_{n,LLD})$ is the lower limit of detection (LLD);

$k_{1-\alpha}$, $k_{1-\beta}$ is the confidence level (1,645);

$E(R_0)$ is the counting rate of blank (0,316 7 cps);

t_0 is the counting time of blank (16 000 s);

t_b is the counting time of sample (16 000 s).

The number of disintegrations per second is given by Equation (A.2):

$$dps = \frac{cps}{\eta} \qquad \text{(A.2)}$$

where

dps is the number of disintegrations per second, expressed in Bequerel (Bq);

cps is the counting rate of blank (0,316 7 cps);

η is the counting efficiency of the apparatus ($0 < \eta < 1$) (0,8).

B.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) is obtained by normalizing the net count rate to the count rate of the reference standard (oxalic acid SRM).

Annex C
(normative)

Method B - Beta-ionisation (BI)

C.1 General

This 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 polymer samples in a calorimetric bomb, a tube furnace or a laboratory scale combustion device as described in Annex A.

C.2 Principle

The beta ionisation method determines the isotope abundance of ^{14}C indirectly. This method uses the emission of β particles by ^{14}C due to the radioactive decay of the ^{14}C isotope, like PSM. It detects β particles 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 polymer 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 parts per million).

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 β-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.

C.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 4990b);

— activated charcoal.

C.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 home made high tech devices developed at several radiocarbon institutes. No commercial systems are available at the time of writing this Technical Specification. 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 the surface in cellars in order to obtain extra protection against cosmic radiation. Typical counting times are several days for low-level measurements.

C.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.

NOTE 1 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% can be obtained. The estimated precision shall be reported in addition to the value declared.

NOTE 2 When using active carbon for clean-up, the active carbon cartridge should 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 days is sufficient to get rid of the Radon contribution.

C.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 4990b or materials that are traceable to this reference standard).

If correction for isotopic fractionation has to be performed, then the $^{13}C/^{12}C$ isotopic ratio has to be determined as well. Isotopic fraction during the preparation of the sample can occur if only a part of the CO_2 from the combusted sample is treated.

It should always be mentioned if the $^{13}C/^{12}C$ isotopic ratio correction was applied to the reported results.

Annex D
(normative)

Method C - Accelerator Mass Spectrometry (AMS)

D.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 polymer samples in a calorimetric bomb, a tube furnace or a laboratory scale combustion device as described in Annex A.

D.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 is a form of mass spectrometry that 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 analyzing.

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.

D.3 Reagents and materials

— Oxalic acid primary standard (e.g. SRM 4990b);

— iron catalyst;

— hydrogen;

— HCl solution (5 M);

— dry ice;

— acetone or ethanol;

— liquid N_2.

D.4 Apparatus

— Sample preparation equipment;

— liquid nitrogen freezing station;

— accelerator mass spectrometer (AMS).

D.5 Procedure

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 can be either let 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 cesium 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. The negative ion beam is then focused by a lens into a recombinator. 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 beams in Faraday cups (typical currents 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.

D.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 percent 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.

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