INTERNATIONAL STANDARD

ISO 13833

First edition
2013-04-01

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

Émissions de sources fixes — Détermination du rapport du dioxyde de carbone de la biomasse (biogénique) et des dérivés fossiles — Échantillonnage et détermination du radiocarbone

Reference number
ISO 13833:2013(E)

COPYRIGHT PROTECTED DOCUMENT

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

ISO 13833 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

Introduction

Reliable data for biogenic carbon dioxide (CO_2) emissions are needed for carbon emission trading and in order to provide more accurate inventories.

When combusting mixtures of fuels from fossil and biogenic origin, it is often difficult to determine the exact ratio of biogenic and fossil CO_2 in the total CO_2 that is emitted through the stack gas, because the biogenic and fossil composition of the combusted fuels is not always known or cannot be determined with sufficient accuracy. This is the case when solid recovered fuels (SRF) are used.

The contribution of solid, liquid, and gaseous biofuels to energy production is likely to increase. A reliable and robust method for the determination of the ratio of fossil and biogenic CO_2 in the total emitted CO_2 of stack gas will enhance the implementation of these products, as reliable data for carbon emission trading can be generated with this approach.

Different methods exist to determine the ratio of fossil and biogenic CO_2 in stack gas. The radiocarbon (^{14}C isotope) method has been applied since the 1950s in a variety of sample types, like food, fuels, polymers, and atmospheric and combustion CO_2 to determine the ratio of biogenic and fossil carbon (Reference [18]). Biogenic and fossil carbon can be distinguished based on the measured amount of the ^{14}C isotope in the sample. Another, relatively new applied method is the “balance method”, which combines standard data on the chemical composition of biogenic and fossil organic matter with routinely measured operating data of the plant (Reference [10]). Similar methods using stoichiometric methods, for example, can also be used.

This International Standard gives sampling and analysis methods for the determination of the ratio of biomass and fossil fuel-derived CO_2 in the total emitted CO_2 from exhaust gases of stationary sources, based on the radiocarbon (^{14}C isotope) method. Sample strategies for integrated sampling for periods from 1 h up to 1 month are given. Radiocarbon determination procedures include accelerated mass spectrometry (AMS), beta-ionization (BI), and liquid scintillation (LS) measurement procedures for the determination of the radiocarbon content.

The International Organization for Standardization (ISO) draws attention to the fact that it is claimed that compliance with this document may involve the use of patents concerning the use of the radiocarbon isotope as biogenic marker: a) *Method for determining the relationship of renewable to non-renewable sources of energy*; b) *Method for determining the fossil fuel content in a fuel stream, as well as a an incineration furnace*.

ISO takes no position concerning the evidence, validity and scope of these patent rights.

The holders of these patent rights have assured ISO that they are willing to negotiate licences under reasonable and non-discriminatory terms and conditions with applicants throughout the world. In this respect, statements of the holders of these patent rights are registered with ISO. Information may be obtained from:

a) European Cement Research Academy (ECRA)

Tannenstrasse 2, D-40476, DÜSSELDORF. Tel.: +49 211 23 98 38 0; E-mail: info@ecra-online.org

b) Energy Research Centre of the Netherlands

Westerduinweg 3, PO Box 1, NL-1755 ZG PETTEN. Tel.: +31 224 56 4475; E-mail: denuijl@ecn.nl

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

ISO (www.iso.org/patents) maintains on-line databases of patents relevant to its documents. Users are encouraged to consult the databases for the most up to date information concerning patents.

INTERNATIONAL STANDARD **ISO 13833:2013(E)**

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

1 Scope

This International Standard specifies sampling methods and analysis methods for the determination of the ratio of biomass- and fossil-derived carbon dioxide (CO_2) in the CO_2 from exhaust gases of stationary sources, based on the radiocarbon (^{14}C isotope) method. The lower limit of application is a biogenic to total CO_2 fraction of 0,02. The working range is a biogenic to total CO_2 fraction of 0,02 to 1,0.

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.

ISO 7934, *Stationary source emissions — Determination of the mass concentration of sulfur dioxide — Hydrogen peroxide/barium perchlorate/Thorin method*

ISO 10396, *Stationary source emissions — Sampling for the automated determination of gas emission concentrations for permanently-installed monitoring systems*

ISO 15713, *Stationary source emissions — Sampling and determination of gaseous fluoride content*

3 Terms and definitions

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

3.1
biogenic
produced in natural processes by living organisms but not fossilized or derived from fossil resources

3.2
biomass
material of biological origin excluding material embedded in geological formation or transformed to fossil

3.3
isotope abundance
fraction of atoms of a particular isotope of an element

3.4
organic carbon
amount of carbon bound in an organic material

3.5
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, SRM 4990c1)

Note 1 to entry: In 2009, the value of 100 % bio-based carbon was set at 105 pmC.

---

1) SRM 4990c is the trade name of a product supplied by the US National Institute of Standards and Technology.

3.6
proportional sampling
flow proportional sampling
technique for obtaining a sample from flowing stack gas in which the wet or dry sample flow rate is directly proportional to the mass flow rate, volume flow rate or velocity in the stack

3.7
radiocarbon
radioactive isotope of the element carbon, ^{14}C, having 8 neutrons, 6 protons, and 6 electrons

Note 1 to entry: Of the total carbon on Earth, 1×10^{-10} % mass fraction is ^{14}C. It decays exponentially with a half-life of 5 730 years and as such it is not measurable in fossil materials derived from petroleum, coal, natural gas or any other source older than about 50 000 years.

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

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

3.10
test portion
quantity of material drawn from the test sample (or from the laboratory sample if both are the same) and on which the test or observation is actually carried out

3.11
beta-particle
electron or positron which has been emitted by an atomic nucleus or neutron in a nuclear transformation
[ISO 921:1997,[1] definition 81]

4 Symbols and abbreviated terms

4.1 Symbols

A	disintegrations per second
b	default ^{14}C content (in pmC) of 100 % biomass, produced and harvested in 2011
E	counting rate
C_V	coefficient of variation
$E(R_0)$	counting rate of blank
$E(R_{n,\mathrm{LLD}})$	lower limit of detection
i	increment number
$k_{1-\alpha} + k_{1-\beta}$	coverage factor (typical value: 1,645)
m	measured ^{14}C content of the sample
$m_{\mathrm{CO_2}}$	mass of CO_2

This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

M_{CO_2}	44,01 kg/kmole
n	number of increments
r	biogenic CO_2 to total CO_2 ratio derived from the measured pmC value
t	operating time
t_b	counting time of sample
t_0	counting time of blank
V	total amount of stack gas emitted
V_{CO_2}	volume of CO_2
$\dot{V}_i$	actual stack gas flow at moment i
V_m	22,41 m^3/kmol (at 273 K and 1 013 hPa)
β^-	beta-particle (electron emitted during radioactive decay)
φ_{CO_2}	average concentration of CO_2
$\varphi_{CO_2,i}$	actual concentration of CO_2
η	counting efficiency of the apparatus ($0 < \eta < 1$)

4.2 Abbreviations

AMS	accelerator mass spectrometer; accelerator mass spectrometry
BI	beta-ionization measurement, gas proportional counter, proportional gas counter
cpm	counts per minute
cps	counts per second
dpm	disintegrations per minute
dps	disintegrations per second, equivalent to becquerel
GM	Geiger–Müller
LLD	lower limit of detection
LSC	liquid scintillation counter; liquid scintillation counting
pmC	percentage modern carbon
SRF	solid recovered fuel

5 Principle

5.1 General

The measurement of the presence of the ^{14}C isotope in flue gas or stack gas enables the determination of the biogenic and fossil fractions of the CO_2 that is emitted. The determination of the biogenic CO_2 fraction in flue gas or stack gas consists of:

- representative sampling of CO_2;
- measurement of the sampled ^{14}C;
- calculation of the biogenic CO_2 fraction in the stack gas emitted during the sampling period.

Procedures for collection of whole gas samples and absorption of CO_2 in liquid and solid alkaline media are given. Three ^{14}C determination procedures that can be used are described. The biogenic fraction is determined using the measured ^{14}C value. From the calculated biogenic CO_2 fraction, the emitted amount of biogenic and fossil CO_2 can be calculated. Examples are given.

5.2 Principles of sampling

5.2.1 General

Sampling of CO_2 in stack gas is in principle not different from sampling of other acid gaseous substances like sulfur dioxide (SO_2) or hydrogen chloride (HCl). The CO_2 present in a representative stack gas sample is absorbed in an alkaline medium or transferred to a gas bag or lecture bottle and after sampling the collected CO_2 is prepared for ^{14}C analysis.

Standard equipment as used for other gaseous components may be utilized. As CO_2 is present in relatively high concentrations compared to other acidic gaseous substances, the capacity of the absorption media used requires consideration, an excess of alkaline media shall be used to ensure complete absorption during the sampling period.

Sampling shall be carried out in accordance with applicable standards.

NOTE Sampling and sampling strategies for continuous and intermittent measurements of stationary source emissions are specified, for example, in ISO 10396 and EN 15259.[4] Unlike other species where a concentration is determined, for biogenic CO_2 a ratio of biogenic CO_2 to the total is determined. Many uncertainties that occur if a concentration is actually measured can be excluded if an amount of a component with exactly the same chemical behaviour as the various CO_2 isotopes is determined instead. Some uncertainties specific for spectroscopic measurement can, however, affect the preferred CO_2 analyser for flow proportional sampling.

5.2.2 Grab gas samples

If applicable, use accepted procedures for the collection of gas in gas bags, canisters or gas bottles.

Only gas bags impenetrable to CO_2 shall be used. Most aluminium-lined gas bags are suitable.

5.2.3 Absorption samples

When liquid or solid absorbers are used, the CO_2 is collected in a medium containing alkaline reagents. For sampling with liquids, alkaline solutions of, for example, 2 mol/l to 4 mol/l potassium hydroxide (KOH) or equivalent (sodium hydroxide, NaOH) are suitable. For solid CO_2 absorbers, commercial products are suitable.

After collection of the samples, close the absorbers and ensure that they are gastight, in order to prevent the ingress of atmospheric CO_2.

5.3 ^{14}C measurement techniques

The ^{14}C content of the collected samples can be determined using:

- — accelerator mass spectrometry (AMS);
- — beta-ionization (BI) measurement (gas proportional counter);
- — the liquid scintillation counting technique (LSC).

All sampling methods mentioned in 5.2 are suitable for the collection of CO_2.

Depending on the ^{14}C analysis technique different amounts of sampled CO_2 are required. For AMS measurements the minimum volume of CO_2 is 4 ml. For BI measurements, 2 l to 10 l CO_2 are required. For LSC measurements, the required amount of CO_2 depends on the way the sample is prepared for measurement, but at least a few grams are necessary.

6 Reagent, materials and equipment

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and distilled or demineralized water or water of equivalent purity containing negligible amounts of carbonate, i.e. at concentrations that do not contribute significantly to the determinations.

6.1 Reagent. A setup consisting of:

- — glass bottle (standard glass sample bottle with plastic screw cap resistant to the alkaline medium used);
- — alkaline absorption medium;
- — solid absorber suitable for the collection of CO_2.[2)]

Mixing of water and NaOH or KOH should be done under the addition of inert gas, in order to reduce absorption of CO_2 from ambient air and exhalation.

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

6.2 Materials and equipment. The components in the sampling device are listed in the following.

- — Stack gas flow measurement device (typically based on S-type, P-type or L-type Pitot tube) according to ISO 10780.[2]

NOTE 1 Under “steady-state” conditions, the stack gas flow can be calculated from the fuel consumption. If this is done, no instrumentation for stack gas flow determination is needed.

- — Standard equipment for sampling stack gas for main component analysis.

NOTE 2 If a conditioning system for gas analysis is already present, this needs to be taken into consideration in the sampling plan and part of the conditioned gas used, e.g. using a T-piece somewhere in the sampling line. In these standard gas conditioning devices, usually a typical gas flow of 60 l/h to 100 l/h is available after conditioning,

- — Mass flow controller, externally adjustable. An external adjustable mass flow controller is needed only for proportional sampling as it is necessary to use the signal obtained from the measurement of the total flow in the duct to adjust the sampling flow linearly proportionally to it. Use mass flow

---

2) Ascarite II is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

controllers in the range of e.g. 0,1 ml/min ... 1 ml/min or 10 ml/min ... 100 ml/min, tuned for stack gas composition.

- Sample containers.
  - Gas sampling: use air tight vessels, compatible with the system design, which includes flexible bags, evacuated canisters, lecture gas bottles.
  - Liquid sampling: use accepted gas wash bottles (e.g. 250 ml glass wash bottles).
  - Solid sampling: use air tight container (e.g. glass tube, length by diameter: 200 mm × 18 mm, with standard fitting).
- Gas analysis system for CO_2 and O_2 measurement.

Perform any CO_2, CO, or O_2 measurements required according to ISO 12039.[3]

Before measurement, the homogeneity of the stack gas shall be tested. Perform homogeneity testing in accordance with ISO 10396. Use the CO_2 concentration as measurand. If homogeneity testing is successful, sampling can be done on a single point.

Comprehensive measurement planning shall be performed before sampling, taking into consideration the specific measurement task.

If stack gas pre-sample and analysis equipment is already present, part of this gas sampling stream can be used to collect the sample. If that is not the case, a probe suitable for gas sampling, equipped with an in-stack or out of stack filter for removal of particulate matter shall be used, and provisions shall be made for excess water removal. To ensure representative sampling and to ensure the equivalence between the measured total CO_2 concentration and the CO_2 sampled for the ^{14}C analysis, accepted standards for the measurement of bulk components in stack gas, namely ISO 10396 or EN 15259,[4] shall be used.

There are several methods for intermediate storage of the collected CO_2. The simplest solution is the use of a gasbag. If long storage periods are expected, the use of aluminium-lined gas bags is preferred to prevent the ingress of CO_2 from ambient air. Proper blank procedures shall ensure that suitable gas bags were used.

When more CO_2 has to be collected, a gas cylinder can be used for storage. Standard canisters can be used for this purpose. Provisions shall be made for controlled intake of stack gas independent of pressure build-up during the sampling process.

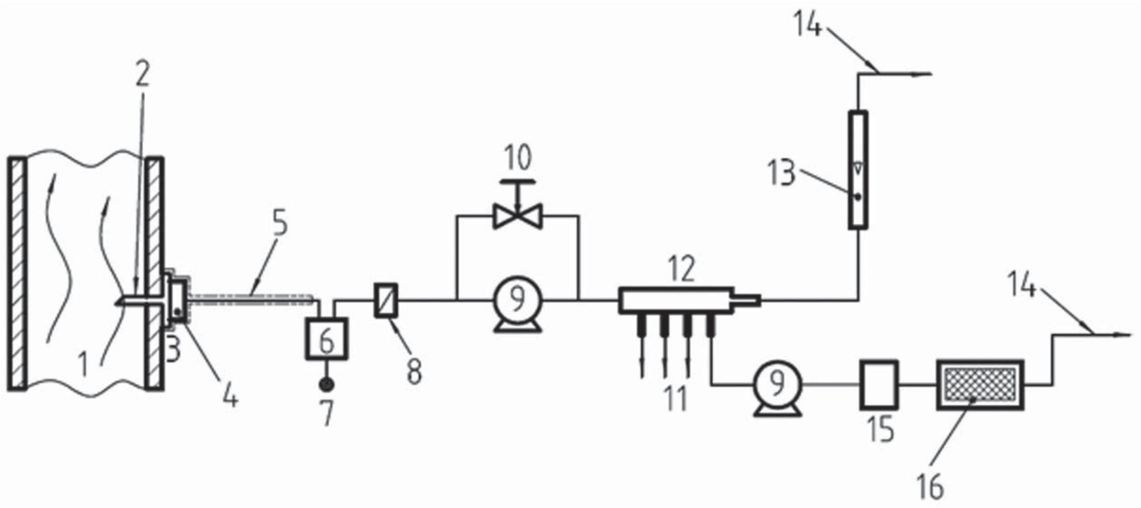
As CO_2 in stack gas can be trapped with 100 % efficiency using alkaline media, collection of the emitted CO_2 can be done using a wash bottle filled with alkaline solution or a suitable solid alkaline scrubber, as long as excess absorption capacity is present and the sample flow does not exceed the flow that is typical for the type of scrubber used.

Typical values for liquid sampling are: 250 ml wash bottle filled with 200 ml 2 mol/l KOH solution, sampling flow 1 ml/min to 50 ml/min, corresponding to sampling periods in the range of 1 day (50 ml/min) to 1 month (1 ml/min) for flue gas with ~10 % volume fraction CO_2.

Typical values for solid sampling are: glass tube (200 × 18 mm) packed with 40 g Ascarite II®2) absorbent (~8 mesh to ~20 mesh), sampling flow 1 ml/min to 50 ml/min, corresponding to sampling periods in the range of 1 day (50 ml/min) to 1 month (1 ml/min) for flue gas with ~10 % volume fraction CO_2.

If standard gas analysis probes and pre-sample systems are present, part of the conditioned gas can be used for CO_2 sampling. The standard gas analysis can be combined with simultaneous sampling of CO_2 as long as this sampling does not affect the standard gas analysis (consider the required sample flow and the risk of leakage).

If the required measurements concern a steady-state situation, a sampling setup as shown in Figure 1 or equivalent may be used.



Key

1	flue gas	9	sampling pump
2	probe	10	bypass valve
3	heater	11	to analyser(s)
4	primary filter	12	manifold
5	heated sample line	13	flow meter (optional)
6	dehumidifier unit	14	exhaust
7	water discharge	15	mass flow controller
8	secondary filter	16	CO_2 absorber (LS)

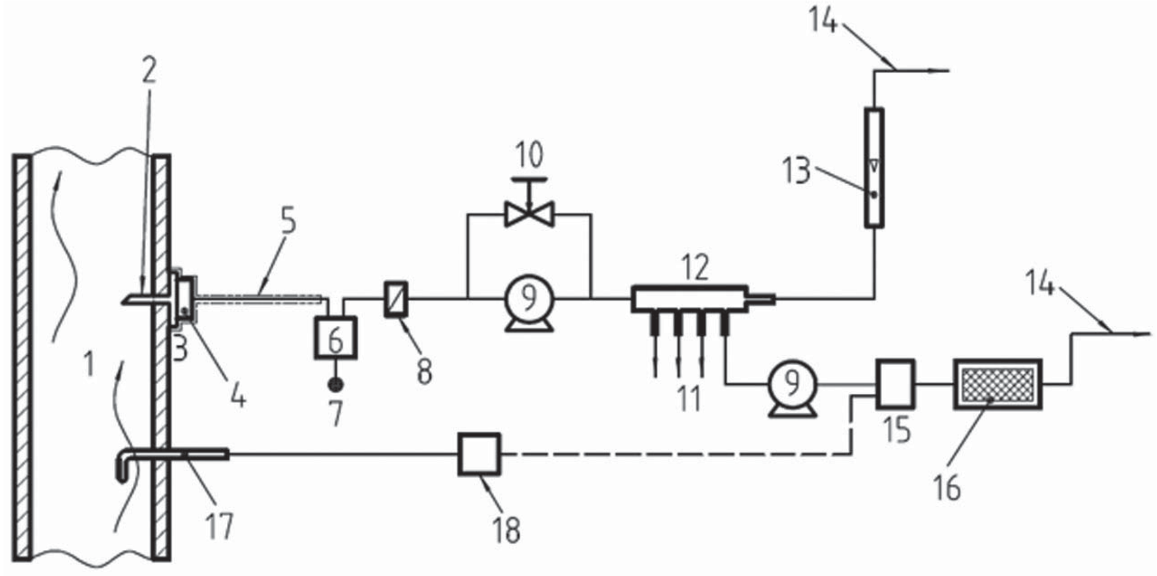
Figure 1 — Example of sampling train for steady-state measurements

If the stack gas flow rate of the installation is expected to be fluctuating, then an assessment of that influence will have to be made and if a significant contribution from fluctuation is foreseen, a sampling setup as shown in Figure 2 or equivalent may be used. Guidelines of how to prepare a sampling plan are available (see EN 15259[4]).

In practice, overall changes in stack gas flow rates not exceeding a coefficient of variation ($2C_V$) of 55 % can be considered as a condition for constant sampling, assuming continuous operation in the sampling period.

Use the readings from the flow rate indicator (e.g. pressure differential, steam rate, fuel rate) to calculate the mean (μ) and standard deviation (s).

NOTE The 55 % ($2C_v$) specification is in accordance with ASTM 7459.[7]



Key

1	flue gas
2	probe
3	heater
4	primary filter
5	heated sample line
6	dehumidifier unit
7	water discharge
8	secondary filter
9	sampling pump
10	bypass valve
11	to analyser(s)
12	manifold
13	flow meter (optional)
14	exhaust
15	mass flow controller
16	CO_2 absorber (LS)
17	velocity measurement
18	flow rate meter

Figure 2 — Example of sampling train for proportional sampling

If proportional sampling is required, the flow rate of the mass flow controller shall be proportional to the measured flue gas velocity, volume flow or mass flow.

In the sampling plan, an assessment of the minimum number of increments (sampling rate) needed for effective proportional sampling shall be made.

6.3 Minimum requirements for sampling equipment

In order to be able to obtain the performance characteristics as given in this International Standard, the following requirements shall be met:

- external adjustable mass flow controller: accuracy at least 5 % of reading;
- solid adsorber: containing more than 90 % mass fraction NaOH;
- liquid adsorber: concentration more than 1 mol/l NaOH;
- capacity left after sampling: more than 25 % of the total capacity of the adsorber.

NOTE Instead of NaOH, other strong bases like KOH can be used.

6.4 Interferents

Consider the possible interferents listed in the following.

— Several acidic substances (e.g NO_x, SO_x, HCl, RCOOH) may be present in the flue gas and may be captured by alkaline samplers. Care shall be taken to avoid potential interference from such substances; see description of the particular analysis methods (in Annex B and C).

— CO concentrations well above 0,1 % volume fraction in the stack gas (e.g. pyrolysis plants), might contribute to the measured pmC value in CO_2.

— Take into account the presence of CO_2 in the combustion air (0,04 % volume fraction if ambient air is used as combustion air) when the biogenic CO_2 fraction is <0,1 (see EN 15259[4]). The ^{14}C value (in pmC) of the ambient air depends on the location of the sampling site and on the time of sampling (specific year and time of year).

7 Analysis

The methods for the determination of the carbon dioxide content derived from biomass specified in this International Standard are based on the determination of the ^{14}C content.

The measurement of the ^{14}C content of the sample shall be done according to one of the methods in Annexes A, B or C. The performance characteristics of the three techniques are different, the typical analytical error (expressed as standard deviation) for AMS and proportional gas counting is 0,1 pmC to 0,5 pmC, the typical analytical error for LSC with benzene synthesis is 0,3 pmC to 2 pmC and the typical analytical error for LSC with CO_2 absorption is 20 pmC, which can be improved to 2 pmC to 4 pmC under strict laboratory controlled conditions and using high-precision LSC instrumentation.

The results of the measurements shall be expressed as the percentage modern carbon (pmC).

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

8 Calculation of the results

Calculate the ratio of biogenic CO_2 in the total CO_2 of a sample from the measured ^{14}C content and a reference ^{14}C value for 100 % biogenic CO_2 using Formula (1):

$$r = \frac{m}{b} \tag{1}$$

where

r is the biogenic CO_2 to total CO_2 ratio derived from the measured pmC value;

m is the measured ^{14}C content of the sample (in pmC) (as determined according to Annex A, B or C);

b is the default ^{14}C content (in pmC) of 100 % biomass, produced and harvested in 2011.

NOTE 1 In 2011, a consensus outdoor air CO_2 value of 104 was used by radiocarbon laboratories. Therefore the pmC value for 100 % biomass, grown and harvested in 2011 is set at 104 pmC. An annual decrease of 0,3 % can be taken into account.

NOTE 2 For municipal waste or other mixed fuel streams, typical regional values are reported in studies on local reference pmC values. These values can be used as local reference value if generally accepted evidence is provided.

NOTE 3 See Annex E for detailed information about the definition of pmC and discussion on the used reference value.

EXAMPLE A ^{14}C value of 40 pmC is measured in the CO_2 sample. Then the percentage biogenic CO_2 in the CO_2 sample is (40/104) × 100 = 38 % and the fossil CO_2 fraction is 100 % − 38 % = 62 %

The total amount of biogenic CO_2 emitted in the sampling period can be derived from the measured total CO_2 concentration, the total stack gas amount emitted and the calculated biogenic CO_2 fraction.

For steady-state sampling conditions, use Formula (2)

$$V_{\mathrm{CO_2}} = \frac{\varphi_{\mathrm{CO_2}}}{100} Vr \tag{2}$$

where

$V_{\mathrm{CO_2}}$ is the total amount of biogenic CO_2 emitted in m^3;

$\varphi_{\mathrm{CO_2}}$ is the average concentration of CO_2 expressed as a % volume fraction;

V is the total amount of stack gas emitted in m^3;

r is the biogenic CO_2 to total CO_2 ratio derived from the measured pmC value.

If no CO_2 measurements are available, the total amount of emitted CO_2 can be derived from the amount of fuel that was combusted during the sampling period taking in account the carbon content of that fuel.

For proportional sampling conditions use Formula (3).

$$V_{\mathrm{CO_2}} = \left[\left(\sum_{i}^{n} \varphi_{\mathrm{CO_2},i} \dot{V}_i \right) \Big/ 100 \times n \right] \times \frac{r}{100} \times t \tag{3}$$

where

$V_{\mathrm{CO_2}}$ is the total amount of biogenic CO_2 emitted in m^3;

$\varphi_{\mathrm{CO_2},i}$ is the actual CO_2 concentration at moment i expressed as a % volume fraction;

$\dot{V}_i$ is the actual stack gas flow at moment i in m^3/h;

r is the calculated biogenic CO_2 fraction of the sample CO_2 expressed as a %;

n is the number of increments;

i is the increment number;

t is the operating time in hours.

Calculate m_{CO_2} from V_{CO_2} using Formula (4):

$$m_{CO_2} = \frac{V_{CO_2}}{1\,000} \times \frac{M_{CO_2}}{V_m} \tag{4}$$

where

m_{CO_2}	is the mass of CO_2 in tonnes;
V_{CO_2}	is the volume of CO_2 in m^3;
M_{CO_2}	is the molar mass of CO_2, i.e. 44,01 kg/kmol;
V_m	is the molar volume of a gas at 273 K and 1 013 hPa, i.e. 22,41 m^3/kmol.

Water can be removed before collection in the bag or container using a condensation unit, in which case consider the necessity of corrections to Formulae (1) to (4) for concentration changes resulting from this water removal.

9 Quality assurance and quality control procedures

The collection of the carbonate from the stack gas is in principle in line with the collection of other gases like HF, SO_2, and NH_3 using wash bottles, therefore the quality assurance and control procedures specified in ISO 7934 and ISO 15713 shall be used.

When liquid or solid CO_2 absorbers are used, blank samples shall be measured to confirm the absence of ingress of CO_2 from ambient air.

For proportional sampling, the total amount of CO_2 collected shall be verified by standard chemical analysis (e.g. titration) of a test portion.

The values obtained can be compared with values calculated from the fuel composition (if available).

Performance characteristics are given in Annex D.

10 Test report

The test report shall be in accordance with international or national regulations. If not specified otherwise, the test report shall include at least the following information:

a) reference to this International Standard (ISO 13833:2013);

b) description of the purpose of tests;

c) principle of gas sampling;

d) information about the sampling and conditioning line;

e) identification of the analysis technique used;

f) description of plant and process;

g) identification the sampling plane;

h) actions taken to achieve representative samples;

i) description of the location of the sampling point(s) in the sampling plane;

j) description of the operating conditions of the plant process;

k) changes in the plant operations during sampling;

l) sampling date, time and duration;

m) time averaging on relevant periods;

n) measurement uncertainty;

o) any deviations from this International Standard.

Annex A
(normative)

Procedure for ^{14}C determination by accelerator mass spectrometry

A.1 General

This annex specifies the procedure for the determination of the ^{14}C content by accelerator mass spectrometry (AMS) in the CO_2 and exhaust gas samples collected at stationary sources.

A.2 Principle

The AMS method determines the presence of the ^{14}C isotope directly. The atoms in the sample are converted into a beam of ions. The ions formed 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 but also to specifically form only C^{n+} ions ($n = 1 \ldots 4$) that are allowed into the spectrometer, excluding all other ionic species. This greatly enhances sensitivity without compromising selectivity. In most AMS systems, the ^{14}C is currently determined from graphite (carbon) sample targets. To obtain graphite sample targets, it is necessary to convert the CO_2 in each sample into graphite before analysing.

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

A.3 Reagents and materials

Use only reagents of recognized analytical grade.

A.3.1 Catalyst (iron, copper).

A.3.2 Reducing reagents, hydrogen or Zn powder.

A.3.3 Oxalic acid primary standard, e.g. SRM 4990c.1)

A.3.4 Acid solution, extra pure; containing no carbon.

A.3.5 Liquid nitrogen.

A.4 Apparatus

Usual laboratory equipment and in particular the following.

A.4.1 Sample preparation equipment.

A.4.2 Liquid nitrogen trap.

A.4.3 Accelerator mass spectrometer.

A.5 Procedure

A.5.1 Transfer the carbonate solution to the extraction bottle.

A.5.2 Attach the acid solution dosing device.

A.5.3 Evacuate the bottle and dosing device (degassing, removal of dissolved N_2 and O_2 from air).

A.5.4 Add acid solution to the carbonate solution.

A.5.5 Remove water vapour by using a trap filled with acetone and dry ice.

A.5.6 Collect the CO_2 formed in a trap that is submersed in liquid N_2 (A.4.2).

A.5.7 Transfer the CO_2 to the graphitizing rig system.

A.5.8 When the samples are collected in gas bags, follow the same procedure, but start at A.5.5. Alternatively, gas samples might be analysed with an AMS (A.4.3) with a direct gas inlet and a gas-capable ion source.

Gaseous samples can be either introduced into the system by release from a quartz tube or after they have been trapped in liquid nitrogen followed by subsequent heating. Then convert (A.3.2) the gas to graphite using an iron or copper catalyst (A.3.1) according to the equations:

$$CO_2 + H_2 \rightleftharpoons H_2O + CO \tag{A.1}$$

$$CO + H_2 \rightleftharpoons H_2O + C \tag{A.2}$$

NOTE Alternatively, a Zn-based reduction process can be used, provided that its accuracy and precision are controlled by reference measurements.

A.5.9 Ensure a complete reduction to graphite to avoid fractionation (e.g. water removal, controlling the reaction pressures).

A.5.10 Press the graphite into a target and mount it on a wheel before it is loaded into the AMS (A.4.3). 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 beam of C^- ions. Targets are kept 10 mm away from each other to avoid cross-contamination and moved 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.

A.5.11 In the tandem accelerator the C^- ions are accelerated to the terminal, then changed to multiply-charged ions in the gas stripper. These positive ions are accelerated to higher velocities to allow for accurate separation in the high-energy mass spectrometer.

A.5.12 Measure the ^{12}C and ^{13}C in the Faraday cups (typical current, 250 nA).

A.5.13 Purify the ^{14}C ions by an electromagnetic mass analyser and detect the ions by either a gas-filled or a solid state detector. The detector may need separation from the accelerator vacuum by a thin foil.

A.6 Calculation of the results

The isotopic ratios of $^{14}C/^{12}C$ or $^{14}C/^{13}C$ and $^{13}C/^{12}C$ are determined relative to the appropriate primary reference material (see Annex E). All pmC values obtained from the radiocarbon analysis measurements shall be corrected for isotopic fractionation using stable isotope data ($^{13}\delta$-values, based on measured $^{13}C/^{12}C$ ratios).

Calculate the ^{14}C amount of each sample in pmC, according to the standardization procedure for the AMS measurement described in E.4.2.2.

Annex B
(normative)

Procedure for ^{14}C determination by liquid scintillation counter method

B.1 General

This annex specifies the procedure for ^{14}C determination by LSC in CO_2 and exhaust gas samples collected from a stationary source.

B.2 Principle

LSC 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 a scintillator.

There are two methods that can be used for the preparation of the collected CO_2 for activity measurement.

- The CO_2 extracted from the flue gas is converted to benzene. This benzene is mixed with an organic solution containing a scintillator.
- The CO_2 extracted from the flue gas is trapped in an amine solution thus forming carbamates. This solution is mixed with the organic solution containing the scintillation reagent.

The ^{14}C activity of the mixture is measured in a liquid scintillation counter in Bq. This measured activity of the sample is calculated relative to the known ^{14}C activity of a standard reference material to obtain standardized and normalized ^{14}C content (in pmC) for each sample.

B.3 Reagents and materials

Use only reagents of recognized analytical grade and distilled or demineralized water or water of equivalent purity

B.3.1 General

B.3.1.1 Oxalic acid primary standard, e.g. SRM 4990c.1)

B.3.1.2 HCl solution, 5 mol/l, or **H_2SO_4 solution**, 4 mol/l.

B.3.1.3 Dry ice.

B.3.1.4 Scintillation cocktail.

B.3.1.5 Amine-based trapping solution, e.g. 3-methoxypropylamine in ethanolamine or Carbo-Sorb E®3).

B.3.1.6 ^{14}C-labelled spike solutions for standard addition purposes.

---

3) Carbo-Sorb E is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

B.3.2 Benzene method

B.3.2.1 Metallic lithium.

B.3.2.2 Concentrated phosphoric acid.

B.3.2.3 Chromium or **vanadium catalyst**.

B.3.2.4 Liquid nitrogen.

B.4 Apparatus

The extremely low levels of radiocarbon even in biomass (in the Earth's atmosphere about 1×10^{-10} % mass fraction) requires 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.

Therefore, quality of liquid scintillation counting equipment, and the proper operation of it, is crucial to be able to meet the desired specifications.

B.5 Procedure

B.5.1 General

The best performance characteristics are obtained when conversion of the collected CO_2 to benzene and direct counting of the benzene in a suitable scintillation cocktail (B.3.1.4), e.g. as specified in ASTM D6866,[6] is applied.

Direct measurement of carbonate can also be used. Then CO_2 is absorbed in a suitable trapping solution and mixed with the scintillation solution. As limited amounts of carbon can be trapped, this option is only feasible with samples with relative high biogenic C-content.

Procedures are specified for the benzene conversion method in B.5.2 and for direct absorption methods in B.5.3.

B.5.2 Benzene conversion

The collected CO_2 is reacted with a stoichometric excess (3:1 lithium:carbon ratio) of molten lithium (B.3.2.1) which has been preheated to 700 °C.

Li_2C_2 is produced by slowly bleeding the CO_2 on to the molten lithium in a stainless steel vessel (or equivalent) while under a vacuum of <135 mPa.

The Li_2C_2 is heated to about 900 °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 vessel.

The evolved acetylene is dried by passing it through dry ice (B.3.1.3) traps, and the dried acetylene is subsequently collected in liquid nitrogen (B.3.2.4) traps.

The acetylene is purified by passing it through a phosphoric acid (B.3.2.2) 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 on to a chromium catalyst (B.3.2.4) which has been preheated to 90 °C or above, applying a water jacket cooler to avoid decomposition from excessive heat generated during the exothermic reaction.

NOTE 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 test portion shall be taken extra for ^{13}C analysis.

B.5.3 Direct absorption

B.5.3.1 General

If the desired performance characteristics can be met, the direct absorption technique can be used.

An absorption flask is loaded with a known volume of CO_2 absorbent (B.3.1.5). The absorbing capacity of Carbo-Sorb E[3] of about $4,8 \times 10^{-3}$ mol/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 directly obtained from the gas bag or gas bottle, or collected after acidification (B.3.1.2) of the liquid or solid CO_2 absorber.

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.

In the case where CO_2 is liberated from a carbonate absorption liquid and thus is present without other gases, the absorption flask may be the vial itself. In this case a lot of liquid handling steps (and the possibility of introducing errors) can be omitted.

If absorbing CO_2 directly into the vial, a loss due to incomplete absorption cannot be avoided though, especially in the late stage of the process. This can be handled by weighing the vial and its absorbent filling [e.g Carbo-sorb E[3]] before and after absorption (with proper correction for minor amounts adhering to used utensils etc).

The amount of water vapour carried over and absorbed can be minimized as well as quantified by keeping the CO_2 producing vessel cooled and at a well defined temperature, in which case the liberated gas can be assumed to consist of CO_2 and H_2O only, the latter with a partial pressure determined by temperature and liquid composition only.

The release of CO_2 from the alkaline liquid absorber solution has to be done under closely controlled pH conditions in the range of 7 to 5,5. From the chemistry of any nitrite ion that might be absorbed in the solution, NO/NO_2 is thereby only released as HNO_2 from the absorber solution to a very limited extent.

The use of an internal standard will determine and correct for quenching, the net effect being a slight loss in precision.

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

NOTE The absorbent, containing a primary amine, forms carbamates after reaction with two parts carbon dioxide. These carbamates are significantly more stable at pH values below 7 than carbonates; however, when long counting times are required, some carbamates might decompose under acidic conditions resulting in loss of carbon dioxide. These problems can be avoided using absorbent and scintillation liquid mixtures that are more compatible.

B.5.3.2 LSC measurement

Then the vial containing the mixture is placed in the LSC and measured. Typical counting times are 6 h to 24 h. Conversion of instrumental output to activity is done according B.1

$$A = \frac{E}{\eta} \qquad \text{(B.1)}$$

where

A is the disintegrations per second [Bq];

E is the counting rate in counts per second;

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

NOTE Counts per second is usually abbreviated as cps.

The activity of a sample is compared with the activity of a reference material. The number of ^{14}C registrations [equal to the 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 suitable ^{14}C labelled components shall be used. When the sampled CO_2 was absorbed in the primary amine solution, carbonate-based spike solutions (B.3.1.6) shall be used.

Measurement shall be performed together with a measurement of a blank sample.

B.5.3.3 Blank correction

The blank value shall be obtained using a CO_2 solution using carbonate obtained from fossil origin, with a total carbonate amount in the concentration range of the collected sample.

This blank sample shall be 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).

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 can be calculated from the counting time of the sample and the background counting rate assuming the same counting times for background and sample.

$$E(R_{n,\mathrm{LLD}})=(k_{1-\alpha}+k_{1-\beta})\sqrt{E\left(R_0\right)\left(\frac{1}{t_0}+\frac{1}{t_\mathrm{b}}\right)} \tag{B.2}$$

where

$E(R_{n,\mathrm{LLD}})$	is the lower limit of detection;
$k_{1-\alpha}+k_{1-\beta}$	constitutes the coverage factor (typical value: 1,645);
$E(R_0)$	is the counting rate of blank;
t_0	is the counting time of blank;
t_b	is the counting time of sample.

B.6 Calculation of the results

The background count rate of the counter is subtracted from the sample count rate to give the 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 4990c[1)] (B.3.1.1).

Calculate the ^{14}C amount of each sample in pmC, according to the standardization procedure for the LSC measurement described in E.4.2.2.

The pmC values obtained require correction for isotopic fractionation using ^{13}C/^{12}C ratios using Formula (E.7).

If a constant (but maybe regional) δ^{13}C shift can be assumed for the biogenic part of the carbon this value can be used. If no information about the δ^{13}C shift is available, the data from measured ^{13}C analysis shall be used.

NOTE Reference [21] suggests using the general assumption that the δ^{13}C shift equals −25 ‰, as this is “the postulated mean value of terrestrial wood”.

Annex C
(normative)

Procedures for ^{14}C determination by beta-ionization

C.1 General

This annex describes the procedure for the determination of the ^{14}C determination by BI in the CO_2 and exhaust gas samples collected at the stationary source.

C.2 Principle

The BI method determines the isotopic abundance of ^{14}C indirectly. This method employs the emission of beta-particles by ^{14}C due to the radioactive decay of the ^{14}C isotope. It detects beta-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-Müller (GM) counter works, the difference being the mechanism of 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 CO_2 extracted from the stack gas is purified to be suitable as a counting gas in a proportional gas counter, e.g. by removal of electronegative impurities, e.g. oxygen, SO_2, water vapour, and radon. The purity of the gas is critical (e.g. O_2 levels need to 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 β^- particle produced by ^{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 quench the multiplication of electrons, leading to some decay events being undetected. The number of counts per minute, the activity of the sample, is detected with the proportional gas counters. This measured activity of the sample is calculated relative to the measured activity of a reference material with standardized ^{14}C amount, to obtain standardized and normalized ^{14}C content (in pmC) for each sample.

C.3 Reagents and apparatus

Use only reagents of recognized analytical grade and distilled or demineralized water or water of equivalent purity.

C.3.1 Reagents and materials

C.3.1.1 Acid solution, e.g. HCl, 5 mol/l or H_2SO_4**,** 2,5 mol/l.

C.3.1.2 Alkaline solution, e.g. KOH or NaOH, 2 mol/l to 4 mol/l.

C.3.1.3 Dry ice.

C.3.1.4 Organic solvent, acetone or ethanol.

C.3.1.5 Liquid nitrogen.

C.3.1.6 Oxalic acid primary standard, e.g. SRM 4990c.[1)]

C.3.2 Equipment

C.3.2.1 System for the conversion of carbonate trapped in an alkaline solution to CO_2.

C.3.2.2 CO_2 purification system, e.g. using activated charcoal.

C.3.2.3 System to obtain a fixed amount of sample, e.g. by adjusting the CO_2 pressure in a fixed volume and known gas temperature.

C.3.2.4 System to prepare standard and background samples.

C.3.2.5 Low-level counting system using a gas proportional counter.

The instruments used for the BI measurements are custom-made high-tech devices developed at several radiocarbon institutes. No commercial systems are available at the time of publication of this International Standard. For radiocarbon to be detectable, minimize background counts. Gas (in this case purified CO_2 derived from the combustion gases) is loaded and counted in a copper counting tube (ultrapure copper) and the desired low background is obtained applying heavy shielding with old lead and anti-coincidence 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.

C.4 Procedure

C.4.1 For gas samples start at C.4.6.

C.4.2 Transfer the carbonate solution to extraction bottle.

C.4.3 Attach the acid solution dosing device.

C.4.4 Evacuate the bottle and dosing device (degassing, removal of dissolved N_2 and O_2 from air).

C.4.5 Add acid solution to the carbonate solution.

C.4.6 Remove water using a trap filled with acetone or alcohol and dry ice.

C.4.7 Collect the formed CO_2 in a stainless steel trap that is submersed in liquid N_2. The amount of CO_2 that is required for the proportional gas counter measurement depends on the size of the gas counter tube (and on the pressure needed in the tube). In general, 2 l to 10 l CO_2 is required.

C.4.8 Purify the CO_2.

C.4.9 A small sample shall be taken at this stage for analysis of the $^{13}\delta$-value of the sample with an isotope ratio mass spectrometer (IRMS).

C.4.10 The CO_2 volume shall be calculated measuring temperature and pressure and the known volume of the trapping system.

C.4.11 Transfer the CO_2 to the proportional gas counter (volume of CO_2 needed to fill the gas counter is counter specific; in general in the range 2 l to 10 l).

C.4.12 Count for several days until the desired precision is obtained. For samples with a high biogenic carbon content two days of counting will be sufficient, for samples with a high fossil carbon contents four days will be required

C.4.13 Calculate the activity of the sample (in cpm) using the sample count rate and the blank count rate.

C.4.14 The statistical counting error of 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.

C.4.15 The total error is then the combination of the analytical errors and the errors of the standard and background determination. The latter errors are usually small compared to the sampling errors. With counting times of a few days, a typical overall (absolute) precision of 0,3 % to 0,4 % can be obtained. The estimated precision shall be reported in addition to the value declared.

C.4.16 When using activated charcoal for the purification of CO_2, the cartridge should be preheated for ~1 h in order to remove traces of radon (build-up of decay product of uranium traces present in the activated charcoal). For other cleaning techniques, a waiting time of 2 days is sufficient to avoid any radon contribution.

C.5 Calculation of the results

The count rate of CO_2 measured in a blank sample is subtracted from the sample count rate resulting in the net count rate (in dpm). The ^{14}C activity (pmC) is obtained by normalizing the net count rate to the count rate of the measured reference standard [oxalic acid SRM 4990c1) or materials that are traceable to this reference standard]. Calculate the ^{14}C amount of each sample in pmC, according to the standardization procedure for the BI measurement described in E.4.2.2. If no correction for isotope fractionation is applied in the calculation of the ^{14}C amount, this should be mentioned in the test report.

Annex D
(informative)

Performance characteristics ^{14}C methods

D.1 Performance characteristics ^{14}C methods

In Tables D.1 to D.8, a summary of available information on this subject is presented. These data are obtained from studies that have been performed using equivalent sampling and analysis techniques.

Table D.1 — Performance data validation study ^{14}C measurement methods

Study	Reference	No. measurements	Biogenic to total CO_2 ratio	Coefficient of variation
		n	r	C_V, %
Sample x, AMS lab	[20]	224	0,506	0,6
Sample y, AMS lab	[20]	79	0,531	0,4
Sample y, LSC lab	[17]	7	1,00	4,0
Sample z, LSC lab	[18]	4	0,579	4,3

Table D.2 — Performance data validation study laboratory scale combustion devices (Reference [23])

Study	No. measurements	Biogenic to total CO_2 ratio	Coefficient of variation
	n	r	C_V, %
Sample x, AMS	79	0,531	0,4
Sample x, BI	5	0,560	1,8
Sample y, LSC direct	16	0,482	4,7

Table D.3 — Performance data validation study power plant, the Netherlands (Reference [19])

Study	No. measurements	Biogenic to total CO_2 ratio	Coefficient of variation
	n	r	C_V, %
Sample 27-8	4	0,051	2,4

Table D.4 — Performance data validation study incineration plant, the Netherlands (Reference [19]))

Study	No. measurements	Biogenic to total CO_2 ratio	Coefficient of variation
	n	r	C_V, %
Sample 28-8	8	0,479	2,4
Sample 29-8	4	0,501	1,7

Table D.5 — Performance data validation study incineration plant, Denmark (Reference [26])

Study	Percentage modern carbon	Coefficient of variation
	pmC	C_V, %
Field samples high	62	3,2
Field samples low	26	6,0

Table D.6 — Performance data validation study incineration plant, Belgium (Reference [25])

Study	No. measurements	Measured biogenic to total CO_2 ratio	Calculated biogenic to total CO_2 ratio
	n	r_{measured}, % mass fraction	$r_{\text{calculated}}$, % mass fraction
Sample 1, AMS	1	0,538	0,55
Sample 2, AMS	1	0,506	0,46
Sample 3, AMS	1	0,526	0,51

Table D.7 — Performance data validation study cement plants, Germany (Reference [27])

Parameter	**Biogenic CO_2 to total CO_2 ratio derived from the measured pmC value**	
	Stack measurement; absorption in 4 mol/l NaOH solution; duration 30 min; 45 Nl, r_{measured}	Input mass balance; ^{14}C-determination in all input materials, $r_{\text{calculated}}$
LSC		
Cement plant 1 3 samples 3 days	10,3 8,1 7,8	8,3 9,2 9,1
Average, %	8,7	8,9
Standard deviation	1,1	0,4
Coefficient of variation, C_V, %	12,8	4,5
Beta-ionization		
Cement plant 2 3 samples 3 days	21,3 19,3 18,3	20,9 20,8 19,8
Average, %	19,6	20,5
Standard deviation	1,2	0,5
Coefficient of variation, C_V, %	6,4	2,4
AMS		
Cement plant 3 3 samples 1 day	12,0 13,0 13,0	12,5
Average, %	12,7	12,5
Standard deviation	0,5	—
Coefficient of variation, C_V, %	3,7	—
LSC		
Cement plant 3 3 samples 1 day	11 8 15	12,5 12,5 12,5
Average, %	11,3	12,5
Standard deviation	2,9	—
Coefficient of variation, C_V, %	25,3	—

Table D.8 — Performance data validation study municipal solid waste plant, Italy (Reference [9])

Method	**Biogenic biomass content**	**Biogenic biomass content**
	w_{bio}, % mass fraction	e_{bio}, % energy fraction
Mass-energy balance	53	35
^{14}C, radiocarbon (LSC)	49	32
Manual sorting	67	50

Table D.9 — Performance data validation study from three waste incinerators, Switzerland
(Reference [15][16])

Study	No. measurements	Measured biogenic to total CO_2 ratio	Coefficient of variation	Calculated biogenic to total CO_2 ratio	Coefficient of variation
	n	$r_{measured}$, % mass fraction	C_V, %	$r_{calculated}$, % mass fraction	C_V, %
Plant A, AMS	6	0,527	2,2[a]	0,519	2,2 [a]
Plant B, AMS	6	0,521	7,2[a]	0,518	2,5 [a]
Plant C, AMS	6	0,512	6,2[a]	0,497	3,3 [a]

[a] Standard uncertainty of mean value calculated from six 3 d to 4 d sampling periods.

D.2 Summary of performance characteristics

Based on the information available, the following consensus values for the expanded uncertainty of measurement of the method are given.

Range	U
r = 0,02 − 1	10
r = 0,1 − 1	5

where

r is the biogenic CO_2 to total CO_2 ratio derived from the measured pmC value;

U is the relative expanded uncertainty of measurement (using a coverage factor of 2).

When high fluctuations in the stack flow are present, the quality of the measurements depends mainly on the contribution of the error in the measurement of the flow in the stack.

When the ^{14}C analysis is done by AMS or BI, the contribution to the analytical error of these ^{14}C results usually has a minor contribution to the total error, in the case of LSC analysis, this contribution can be more significant, especially at low r values (<0,2).

Annex E
(informative)

Definitions and equations of the ^{14}C-based method

E.1 Introduction

This annex describes definitions and equations of the ^{14}C based method to determine the biogenic CO_2 fraction of stack gas CO_2. The aim of this annex is to give users of this International Standard background knowledge about this specific ^{14}C application and to ensure standardization of the calculated results when using different ^{14}C measurement techniques.

E.2 Symbols, abbreviations and definitions

Used symbols, abbreviations and definitions others than those already described in Clauses 3 and 4.

${}^{14}C_{\text{sampleC}}$	measured ^{14}C value (in pmC) of the investigated CO_2 sample
${}^{14}C_{\text{bioC}}$	^{14}C value (in pmC) of the biogenic carbon part of the CO_2 sample
${}^{14}C_{\text{fossilC}}$	^{14}C value (in pmC) of the fossil carbon part of the CO_2 sample, equal to 0 pmC
${}^{14}C_{\text{otherC}}$	^{14}C value (in pmC) of the carbon part of the CO_2 sample, not from fossil or biogenic carbon origin (like CO_2 from combustion air)
f_{bioC}	biogenic CO_2 fraction of the CO_2 sample
f_{fossilC}	fossil CO_2 fraction of the CO_2 sample
f_{otherC}	CO_2 fraction of the CO_2 sample from other CO_2 sources than biogenic and fossil (fuel-derived) CO_2
${}^{14}a_{\text{N}}^{\text{S}}$	standardized and normalized ^{14}C amount of the measured sample, ${}^{14}a_{\text{N}}^{\text{S}} \times 100\,\% = \text{pmC}$
${}^{14}A_{\text{N}}^{\text{S}}$	normalized ^{14}C signal (isotope concentration or activity) of the measured sample
${}^{14}A_{\text{RN}}^{0}$	standardized and normalized ^{14}C amount of the primary reference standard, oxalic acid [HOx-II, SRM 4990c[1]]
${}^{14}A_{\text{sample}}$	measured ^{14}C signal (isotope concentration or activity) of the sample
${}^{14}A_{\text{bg sample}}$	measured ^{14}C signal (isotope concentration or activity) of the background sample or blank sample, measured in the same batch as the sample and represents the background ^{14}C signal of the measured samples
${}^{14}A_{\text{OX2}}$	measured (average) ^{14}C signal (isotope concentration or activity) of oxalic acid reference standard samples [HOx-II, SRM 4990c[1]], measured in the same batch as the unknown samples

$^{14}A_{\mathrm{bg_{OX2}}}$	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 4990c1)], measured in the same batch as the oxalic acid samples
η_{meas}	is the measuring efficiency of the measurement technique used
$^{13}\delta_{\mathrm{N}}$	standardized value for isotope fractionation, $^{13}\delta_{\mathrm{N}}$ = −0,025 (relative to VPDB calibration standard NBS 19 calcite, RM8544)
$^{13}\delta_{\mathrm{sample}}$	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 calibration standard, NBS 19 calcite, RM8544
$^{13}\delta_{\mathrm{OX2}}$	standardized isotope fractionation value of the oxalic acid reference standard [HOx-II, SRM 4990c1)]. $^{13}\delta_{\mathrm{OX2}}$ = −0,017 6 relative to VPDB calibration standard, NBS 19 calcite, RM8544
λ	decay rate of ^{14}C (in year) — ^{14}C has a half-life of 5 730 years
t_{m}	time of measurement (in year; e.g. 2010-08-15 is 2010,612 year)
t_{s}	time of harvest (dead) (in year; e.g. 2010-08-15 is 2010,612 year) of the biogenic carbon in the sample
t_0	reference year in the calculation of the standardized and normalized ^{14}C amount of a sample, t_0 = 1950 year

E.3 Principle of the method: How to determine the biogenic and fossil CO_2 ratio of stack gas samples

The main feature of the method is the use of ^{14}C to determine the biogenic and fossil CO_2 ratio of stack gas CO_2. The basic principle of the ^{14}C method: Fossil fuel CO_2 emissions do not contain the radioactive isotope ^{14}C anymore (due to the age of the fossil fuels and the ^{14}C half-life of 5730 year: all ^{14}C atoms have decayed), while the biogenic CO_2 emissions (from biomass carbon; age <200 years) contain a certain amount of ^{14}C. The less ^{14}C we measure in a CO_2 sample compared to the ^{14}C amount of biogenic CO_2, the lower the biogenic CO_2 fraction in the particular sample and the higher the fossil CO_2 fraction. This relation is used to calculate the biogenic and fossil CO_2 ratio.

$$^{14}C_{\mathrm{sampleC}} = {}^{14}C_{\mathrm{bioC}} f_{\mathrm{bioC}} + {}^{14}C_{\mathrm{fossilC}} f_{\mathrm{fossilC}} + {}^{14}C_{\mathrm{otherC}} f_{\mathrm{otherC}} \qquad \text{(E.1)}$$

Formula (E.1) shows that the measured ^{14}C value of a CO_2 sample, $^{14}C_{\mathrm{sampleC}}$, is determined by both the ^{14}C values and the carbon ratio of the biogenic CO_2 (bioC), and fossil CO_2 (fossilC) in the sample and also by the CO_2 from other sources (otherC) than those from biofuels or fossil fuels, like (combustion) air, or contamination sources (during sampling) (Reference [19])

Since, ${}^{14}C_{\text{fossilC}} = 0$

$$ {}^{14}C_{\text{sampleC}} = {}^{14}C_{\text{bioC}} f_{\text{bioC}} + {}^{14}C_{\text{otherC}} f_{\text{otherC}} \tag{E.2}$$

From Formula (E.2) we can derive an equation to calculate the biogenic CO_2 fraction, f_{bioC}, of the CO_2 from the stack gas sample:

$$ f_{\text{bioC}} = \frac{{}^{14}C_{\text{sampleC}} - \left({}^{14}C_{\text{otherC}} f_{\text{otherC}} \right)}{{}^{14}C_{\text{bioC}}} \tag{E.3}$$

Only if the sample does not contain CO_2 from sources other than biogenic and/or fossil carbon, the equation simplifies to:

$$ f_{\text{bioC}} = \frac{{}^{14}C_{\text{sampleC}}}{{}^{14}C_{\text{bioC}}} \tag{E.4}$$

The fossil CO_2 fraction of the sample can be calculated from the biogenic CO_2 fraction as following:

$$ f_{\text{fossilC}} = 1 - f_{\text{bioC}} \tag{E.5}$$

NOTE In Clause 8, instead of “biogenic CO_2 fraction” the description “ratio of biogenic CO_2 to total CO_2” is used for which r is used as the symbol instead of f_{bioC}. Formula (1) can be compared with Formulae (E.3) and (E.4). The quantity “measured ^{14}C content” is defined as ${}^{14}C_{\text{sampleC}} - ({}^{14}C_{\text{otherC}} f_{\text{otherC}})$ in (E.3) and as ${}^{14}C_{\text{sampleC}}$ in (E.4). The reference ^{14}C content is described as ${}^{14}C_{\text{bioC}}$ in (E.3) and (E.4) (defined in this International Standard to be 105 % for 2009).

E.4 Determination of standardized ^{14}C values for the calculation of the biogenic and fossil CO_2 ratio of CO_2 samples

E.4.1 General

^{14}C amounts in samples can currently be determined using three measurement instruments: an accelerator mass spectrometer (AMS); a proportional gas counter (employing the BI technique in this International Standard); and a liquid scintillation counter (LSC). To calculate the biogenic CO_2 fraction of a sample according to Formula (E.3), all separate ^{14}C values (${}^{14}C_{\text{sampleC}}$, ${}^{14}C_{\text{bioC}}$, and ${}^{14}C_{\text{otherC}}$) should be calculated according to the same standardization procedures. This is necessary in order to obtain identical results for samples that have the same biogenic CO_2 fraction, irrespective of when, where, and how (measurement instrument and technique) these samples are measured. See Reference [21].

E.4.2 Standardization of ^{14}C results for the three different measurement instruments

E.4.2.1 General

In using ^{14}C to determine the biogenic CO_2 fraction of samples, the standardization procedure of the ^{14}C amount measured in samples should contain:

a) a correction for the ^{14}C amount from background and contamination sources introduced during pretreatment and analysis of the sample, determined with a “background sample” or “blank sample”;

b) a correction for the measuring efficiency;

c) a calculation to standardize the measured ^{14}C amount to the ^{14}C amount per gram of carbon (relevant for proportional gas counter and LSC);

d) a correction for isotope fractionation with normalization to a standardized ^{13}C-isotope fractionation value;

e) a correction for decay between day of measurement and day of harvest (of the biomass material);

f) a calculation to calculate the measured and corrected ^{14}C amount of the sample as a percentage (or fraction) of a defined and internationally standardized ^{14}C amount in a reference standard material valid for the year 1950:

$$^{14}C_{\text{sampleC}}\,(\text{pmC}) = {}^{14}a_{\text{N}}^{\text{S}} \times 100\,\% = \frac{^{14}A_{\text{N}}^{\text{S}}}{^{14}A_{\text{RN}}^{0}} \times 100\,\% =$$

$$\frac{\left({}^{14}A_{\text{sample}} - {}^{14}A_{\text{bg}}\right)\eta_{\text{meas}}\left[\left(1+{}^{13}\delta_{\text{N}}\right)\Big/\left(1+{}^{13}\delta_{\text{sample}}\right)\right]^{2} \exp\left[\lambda\left(t_{\text{m}}-t_{\text{s}}\right)\right]}{^{14}A_{\text{RN}}^{0}} \times 100\,\% \qquad \text{(E.6)}$$

Most of the symbols used in Formula (E.6) are similar to those defined in Reference [17].

In Formula (E.6), the amount of ^{14}C measured in a particular carbon sample, $^{14}A_{\text{sample}}$, is first corrected for background signals and carbon contamination sources, $^{14}C_{\text{bg}}$, (from sample pretreatment and analysis) and for the measuring efficiency. The measured ^{14}C activity (proportional gas counter and LSC) should be calculated per gram of carbon.

The measured ^{14}C amount should be corrected for isotope fractionation based on the ^{13}C/^{12}C measurement of graphite (AMS, during same measurement run as ^{14}C) or sample CO_2 (measured separately with IRMS for LSC and BI), to a normalized value with factor: $[(1 + {}^{13}\delta_{\text{N}})/(1 + {}^{13}\delta_{\text{sample}})]^2$, and with $^{13}\delta_{\text{N}} = -0{,}002\,5$ (relative to the VPDB standard, NBS 19 calcite, RM8544).

$$^{13}\delta_{\text{sample}} = \frac{\left({}^{13}C\,/\,{}^{12}C\right)_{\text{sample}}}{\left({}^{13}C\,/\,{}^{12}C\right)_{\text{ref}}}\left(1 - {}^{13}\delta_{\text{ref}}\right) - 1 \qquad \text{(E.7)}$$

where

$(^{13}C/^{12}C)_{\text{sample}}$	is the measured ^{13}C/^{12}C ratio of the sample;
$(^{13}C/^{12}C)_{\text{ref}}$	is the (average) ^{13}C/^{12}C ratio of reference material measured;
$^{13}\delta_{\text{ref}}$	is the standardized value of the reference material (relative to the VPDB standard, NBS 19 calcite, RM8544).

The normalized ^{14}C amount, $^{14}A_{\text{N}}$, should be corrected for decay between the time of harvest (dead), t_{s}, and the time of measurement t_{m}, with the decay rate

$$\lambda = \frac{\ln 2}{5\,730\ \text{years}} = \frac{1}{8\,267}\ \text{year}^{-1}$$

giving $^{14}A_{\text{N}}^{\text{S}}$.

To obtain $^{14}a_{\text{N}}^{\text{S}}$, $^{14}A_{\text{N}}^{\text{S}}$ is calculated relative to $^{14}A_{\text{RN}}^{0}$, which is a standardized and normalized ^{14}C amount of primary reference standard oxalic acid [HOx-II, SRM 4990c$^{1)}$] that is valid for the year 1950 (t_0) only.

Reference [22] has defined the percentage of $^{14}a_{\text{N}}^{\text{S}}$ as percent modern, pM. In some literature, $^{14}a_{\text{N}}^{\text{S}}$ is sometimes mentioned as fraction modern (carbon). Reference [17] recommends abandoning the use of the abbreviation pM, because it is already used in water chemistry and oceanography for picomole per litre. In the literature, the abbreviations pMC, pmC and pmc are also used, which define “percentage modern carbon”. The use of the abbreviation “pmC” seems to have the least similarity with picomole per litre (pM). The abbreviation “pmC” is therefore recommended for use for the biogenic fraction determination application.

By definition, the relative ^{14}C amount expressed as pmC in a sample is given by $^{14}a_{\mathrm{N}}^{\mathrm{S}} \times 100\ \%$. In addition, the specific results should be normalized for isotope fractionation and should be corrected for decay.

E.4.2.2 Standardization of AMS measurement results

The AMS system measures the isotopes ^{12}C, ^{13}C and ^{14}C of a carbon sample in the same run. A batch of samples should 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$^{1)}$], which is commonly used for this purpose, the standardized ^{14}C amount in the sample, $^{14}C_{\mathrm{sampleC}} = {}^{14}a_{\mathrm{N}}^{\mathrm{S}} \times 100\ \% = \mathrm{pmC}$, should be calculated using Formula (E.8):

$$^{14}C_{\mathrm{sampleC}}(\mathrm{pmC}) = \frac{\left({}^{14}A_{\mathrm{sample}} - {}^{14}A_{\mathrm{bg\,sample}}\right)\eta_{\mathrm{meas}}\left(\dfrac{1+{}^{13}\delta_{\mathrm{N}}}{1+{}^{13}\delta_{\mathrm{sample}}}\right)^{2}\exp\left[\lambda\left(t_{\mathrm{m}}-t_{\mathrm{s}}\right)\right]}{0{,}745\,9\times\left({}^{14}A_{\mathrm{OX2}} - {}^{14}A_{\mathrm{bg_{OX2}}}\right)\eta_{\mathrm{meas}}\left(\dfrac{1+{}^{13}\delta_{\mathrm{N}}}{1+{}^{13}\delta_{\mathrm{OX2}}}\right)^{2}\exp\left[\lambda\left(t_{\mathrm{m}}-t_{0}\right)\right]} \times 100\ \% \qquad \text{(E.8)}$$

See Reference [17] for explanation of the factor 0,745 9 used to obtain a standardized value for $^{14}A_{\mathrm{RN}}^{0}$. Since the sample pretreatment of the reference material and the sample can be different, $^{14}A_{\mathrm{bg}}$ can be different for both materials as well.

Since the measuring efficiencies of the reference standard and the sample are equal, this correction factor is cancelled out.

$$^{14}C_{\mathrm{sampleC}}(\mathrm{pmC}) = \frac{\left({}^{14}A_{\mathrm{sample}} - {}^{14}A_{\mathrm{bg\,sample}}\right)\left(\dfrac{1+{}^{13}\delta_{\mathrm{N}}}{1+{}^{13}\delta_{\mathrm{sample}}}\right)^{2}\exp\left[\lambda\left(t_{\mathrm{m}}-t_{\mathrm{s}}\right)\right]}{0{,}745\,9\times\left({}^{14}A_{\mathrm{OX2}} - {}^{14}A_{\mathrm{bg_{OX2}}}\right)\left(\dfrac{1+{}^{13}\delta_{\mathrm{N}}}{1+{}^{13}\delta_{\mathrm{OX2}}}\right)^{2}\exp\left[\lambda\left(t_{\mathrm{m}}-t_{0}\right)\right]} \times 100\ \% \qquad \text{(E.9)}$$

In Formula (E.9), $^{13}\delta_{\mathrm{sample}}$ is determined from the ^{13}C/^{12}C ratio measured with the AMS in the same sample run in which the ^{14}C/^{12}C ratio or ^{14}C/^{13}C ratio is measured.

In this way (using the AMS measurement results), normalization is possible for isotope fractionation that has occurred during the growth of the carbon when it was part of a living organism, during the sampling and sample pretreatment (including graphitization), and during the AMS measurement (which can vary considerably between individual sample measurements).

E.4.2.3 Standardization of liquid scintillation counter measurement results

An LSC measures beta-decay counts of ^{14}C (in counts per minute) indirectly by measuring the interaction signals of the beta-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 is converted to benzene and mixed with liquid (scintillation) reagents in 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 should be used for LSC measurement results:

$$ {}^{14}C_{\text{sampleC}}(\text{pmC}) = {}^{14}a_{\text{N}}^{\text{S}} \times 100\,\% = \frac{{}^{14}A_{\text{N}}^{\text{S}}}{{}^{14}A_{\text{RN}}^{0}} \times 100\,\% = \frac{\left({}^{14}A_{\text{sample}} - {}^{14}A_{\text{bg}}\right)\eta_{\text{meas}}\left[\left(1+{}^{13}\delta_{\text{N}}\right)\Big/\left(1+{}^{13}\delta_{\text{sample}}\right)\right]^{2} \exp\left[\lambda\left(t_{\text{m}}-t_{\text{s}}\right)\right]}{{}^{14}A_{\text{RN}}^{0}} \times 100\,\% \qquad \text{(E.10)} $$

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

LSC measurements have been described (as in ASTM D6866[6]) in which both internal and external reference standards are used. Internal standards are used to determine the counting efficiency (in cpm/dpm; see ASTM D6866.[6] External reference standards can be used to determine overall measuring efficiencies. Based on literature as well as this International Standard, it is, however, not always clear when the different internal and external reference standards should be measured or whether it is part of a standardized procedure. Therefore, the exact standardization procedure for LSC measurements is not yet clear. Input from experts in the LSC measuring field is required for standardization of the measuring efficiency correction factor.

According to ASTM D6866,[6] no correction for isotope fractionation is required for this “CO_2-cocktail”-LSC method. This is, according to Reference [18], due to the fact that the precision of the measurement method is so low (up to a factor 30 lower compared to the AMS method and a factor 5 lower compared to the “benzene-cocktail”-LSC method due to variations in the sample preparation and the actual counting), that a systematic error in the measured activity due to ignoring the isotope fractionation correction is negligible.

For the “benzene-cocktail-LSC” method and for the “CO_2-cocktail-LSC” method with relatively high accuracy, isotope fractionation correction should be applied. The value of ${}^{13}\delta_{\text{sample}}$ can be measured with an IRMS and should be calculated according to Formula (E.7).

If the isotope fractionation correction (= normalization) is left out of the standardization procedure, it results in an additional uncertainty in the final result (that is in the calculated biogenic CO_2 fraction). See also Reference[18] about the expected deviations in the biogenic CO_2 fraction if correction for isotope fractionation that has occurred while the carbon was part of a living organism, is left out of the standardization procedure. If carbon from ‘biogas’ is part of the sample investigated and the biogenic CO_2 fraction is relatively high, the deviations can even be higher than those published in Reference [18], due to the sometimes relatively low ${}^{13}\delta_{\text{sample}}$ values of biogas.

E.4.2.4 Standardization of proportional gas counter measurement results

A proportional gas counter measures the decay counts of ${}^{14}C$ (in counts per minute, cpm) in CO_2 samples. Comparable to the AMS measurement, the measured ${}^{14}C$ amount (the “activity” = ${}^{14}C$ decay counts per minute; calculated per gram C) in a sample should be corrected for background activity and it should be compared with the measured (average) ${}^{14}C$ activity of a reference sample, according to Formula (E.8) or (E.9). The measurement efficiency correction factor is cancelled out in these equations. The reference sample can be the primary standard oxalic acid HOx-II, SRM 4990c,1) or a secondary reference standard with a known activity ratio to the primary standard, and it should be measured with the same proportional gas counter as the sample.

To correct for isotope fractionation, ${}^{13}\delta_{\text{sample}}$ can be measured with an IRMS and calculated according to Formula (E.7). Because ${}^{13}C$ and ${}^{14}C$ are not measured by the same method and in the same run, it is not possible to correct the ${}^{14}C$ amount for isotope fractionation that might have occurred during the measurement. Since this factor is (in general) very small compared to the correction factor for isotope fractionation that has occurred in the carbon material when it was part of a living organism or during sampling and sample pretreatment, it can be neglected.

E.5 Calculation of the biogenic carbon fraction

E.5.1 General

$$f_{\text{bioC}} = \frac{{}^{14}C_{\text{sampleC}} - \left({}^{14}C_{\text{otherC}} f_{\text{otherC}}\right)}{{}^{14}C_{\text{bioC}}} \tag{E.11}$$

To calculate the biogenic carbon fraction of a sample, f_{bioC}, all ^{14}C values used should be pmC values, i.e. ${}^{14}a_{\text{N}}^{\text{S}} \times 100\,\%$, calculated according to the standardization procedure as described in E.3.

E.5.2 How to determine $^{14}C_{\text{otherC}}$ and f_{otherC}

For application to stack gas CO_2 samples, ^{14}C from sources other than biomass needs to be corrected for in the calculation. Both the ^{14}C value and the fraction of CO_2 in the total sampled CO_2 should be determined for each alternative carbon source.

In Reference [19], a correction has been described for sampled atmospheric air CO_2 and for CO_2 contamination of the liquid CO_2-absorber used. Correction for atmospheric air CO_2 is only necessary if the biogenic CO_2 fraction of the sample is <10 %.

It is sometimes not possible to measure the ^{14}C value of other carbon sources or it might be difficult to determine the fraction. Only if the fraction of these sources in the total CO_2 of the sample is relatively high, does the estimated ^{14}C value and its variation used significantly influence the calculated biogenic CO_2 fraction. This factor should, however, never be ignored without prior investigation.

E.5.3 Definition of $^{14}C_{\text{bioC}}$

In this International Standard, a fixed (annual) value is used for $^{14}C_{\text{bioC}}$ [the reference ^{14}C content in Formula (1)]. The value chosen is based on recent atmospheric $^{14}CO_2$ measurements at background measurement stations in remote areas. Biomass takes up CO_2 from the atmosphere by photosynthesis. The ^{14}C value of biomass carbon measured shows the average ^{14}C amount in the atmosphere of the location where the biomass was growing and for the period in which the biomass part investigated has taken up CO_2. Different processes determine the ^{14}C value (in pmC) of the atmosphere and cause temporal and spatial variations in its value. ^{14}C is produced in the atmosphere (reaction between ^{14}N and neutrons) at a relatively constant rate by cosmic radiation. Because of the decay of ^{14}C, the ^{14}C amount in the atmosphere stays relatively stable. Production of ^{14}C in the atmosphere is influenced by anthropogenic factors, e.g. above ground nuclear bomb tests (~1955–1980) and nuclear power plant emissions. Above ground nuclear bomb tests caused an increase of the relative ^{14}C amount in the atmosphere by a factor of 2 in the 1960s. Since the ban on above ground tests, the ^{14}C value in the atmosphere has decreased (see Figure E.1), mainly due to carbon exchange of the atmosphere with the oceans and biosphere. Nowadays, the decrease is to a large extent influenced by fossil fuel CO_2 emissions Reference [13].

The ^{14}C value that is measured in biomass carbon is therefore determined by when, for how long, and where the biomass has grown. Since the biomass that is combusted in energy and industrial plants has very variable origin, a large variation can be expected in the (average) ^{14}C values of the CO_2 from these combusted materials (example for waste in References [16][11]). If taken into account in the calculation of the biogenic CO_2 fraction, the uncertainty in $^{14}C_{\text{bioC}}$ of the combusted biogenic carbon adds considerably to the total uncertainty of the calculated biogenic CO_2 fraction (see the results in References [15][19]).

Reference [16] reports an extensive year-long field study (2010–2011) at five incinerators on the share of biogenic and fossil CO_2 emission from waste incineration in Switzerland. For this project, a reference value (^{14}C content of pure biogenic waste) of 111,3 pmC ± 3,8 pmC (1*s*, normal distribution) was employed for 2010. This level will decrease to 109,2 pmC ± 3,8 pmC in 2015 due to continuous dilution of carbon dioxide with fossil CO_2 in the atmosphere. The reference values are published in Reference [15] and are calculated from the ratio of characteristic biogenic waste fractions and their respective ^{14}C content (personal communication J. Mohn dated 2011-11-18).

Based on the ^{14}C values measured in the summer of 2011 at measurement site Lutjewad (NL), a pmC value of 104 % for biomass grown and harvested in the period of 2010–2012 is obtained (oral communication with S. Palstra dated 2011-11-07).

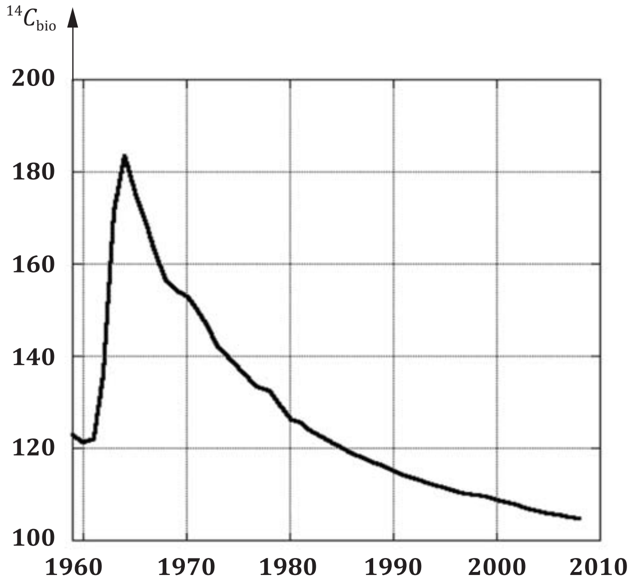


Figure E.1 — Decrease in $^{14}C_{\text{bio}}$ value in atmospheric air CO_2 (in pmC), measured at high Alpine stations Vermunt (Austria) and Jungfraujoch (Switzerland) (see Reference [14]; for data 2004–2008: personal communication S. Palstra with I. Levin)

Bibliography

[1] ISO 921:1997, *Nuclear energy — Vocabulary*

[2] ISO 10780, *Stationary source emissions — Measurement of velocity and volume flowrate of gas streams in ducts*

[3] ISO 12039, *Stationary source emissions — Determination of carbon monoxide, carbon dioxide and oxygen — Performance characteristics and calibration of automated measuring systems*

[4] EN 15259, *Air quality — Measurement of stationary source emissions — Requirements for measurement sections and sites and for the measurement objective, plan and report*

[5] EN 15440, *Solid recovered fuels — Methods for the determination of biomass content*

[6] ASTM D6866, *Standard test methods for determining the biobased content of solid, liquid, and gaseous samples using radiocarbon analysis*

[7] ASTM D7459, *Standard practice for collection of integrated samples for the speciation of biomass (biogenic) and fossil-derived carbon dioxide emitted from stationary emissions sources*

[8] Ciceri G., Achilli M., Calcagnile L., Toscano G., Corinaldesi F. Comparison of different methodologies for the determination of the biogenic carbon content in a sample of solid recovered fuels, 3rd International Conference on Sustainable Energy and Environmental Protection, Dublin, 2009-08-12/15

[9] Ciceri G., Cipriano D., Roberto G., Scacchi C., Bianchilli B., Catanzani G. Quantification of biomass content in municipal solid waste and solid recovered fuels by means of the measuring of C at the plant emission, 3rd International Conference on Sustainable Energy and Environmental Protection, Dublin, 2009-08-12/15

[10] Fellner J., Cencic O., Rechberger H. A new method to determine the ratio of electricity production from fossil and biogenic sources in waste-to-energy plants. *Environ. Sci. Technol.* 2007, **41** pp. 2579–2586

[11] Fellner J., & Rechberger H. Abundance of ^{14}C in biomass fractions of wastes and solid recovered fuels. *Waste Manag.* 2009, **29** pp. 1495–1503

[12] Calcagnile L., Quarta G., D'Elia G., Ciceri G., Martinotti V. Radiocarbon AMS determination of the biogenic component in CO_2 emitted from waste incineration. *Nucl. Instrum. Meth. B*. 2011, **269** pp. 3158–3162

[13] Levin I., Naegler T., Kromer B., Diehl M., Francey R.J., Gomez-Pelaez A.J. et al. Observations and modelling of the global distribution and long-term trend on atmospheric $^{14}CO_2$. *Tellus*. 2010, **62B** pp. 26–46

[14] Levin I., & Kromer B. The tropospheric $^{14}CO_2$ level in mid-latitudes of the northern hemisphere (1959–2003). *Radiocarbon*. 2004, **46** pp. 1261–1272

[15] Mohn J., Szidat S., Fellner J., Rechberger H., Quartier R., Buchmann B. et al. Determination of biogenic and fossil CO_2 emitted by waste incineration based on $^{14}CO_2$ and mass balances. *Bioresour. Technol.* 2008, **99** pp. 6471–6479

[16] Mohn J., Szidat S., Zeyer K., Emmenegger L. Fossil and biogenic CO_2 from waste incineration based on a yearlong radiocarbon study. *Waste Manag.* 2012, **32** pp. 1516–1520

[17] Mook W.G., & van der Plicht J. Reporting ^{14}C activities and concentrations. *Radiocarbon*. 1999, **41** pp. 227–239

[18] Norton G.A., & Devlin S.L. Determining the modern carbon content of biobased products using radiocarbon analysis. *Bioresour. Technol.* 2006, **97** pp. 2084–2090

[19] Palstra S.W.L., & Meijer H.A.J. Carbon-14 based determination of the biogenic fraction of industrial CO_2 emissions — Application and validation. *Bioresour. Technol.* 2010, **101** pp. 3702–3710

[20] Performance of AMS analysis of a biomass reference material, quality chart data

[21] Polach H.A.Four decades of LS counting and spectrometry. In: *Radiocarbon after four decades. An interdisciplinary perspective*, (Taylor R.E., Long A., Kra R.eds.). Springer, New York, NY, 1992

[22] Stuiver M., & Polach H.A. Discussion: Reporting of ^{14}C data. *Radiocarbon*. 1977, **19** pp. 355–363

[23] Flamme S., Hams S. Bestimmung des biogenen Kohlenstoffs — Methodenvergleich [Determination of biogenic carbon — Method comparison], DepoTech, Leoben, 2008-11-12

[24] Biogenic carbon determination in flue gas of a German cement kiln, ECRA, VDZ, Leoben University, ECN

[25]. Validation study on waste incinerators Belgium, ECN. TU Vienna. In press.

[26]. Validation study municipal waste incinerators Denmark. Force. In press.

[27] VDZ, ed. Messung von biogenen CO_2-Emissionen in Drehofenabgasen [Measurement of biogenic CO2 emissions in rotary kiln exhaust gases]. In: *Tätigkeitsbericht* [Progress report] 2009–2012, p. 41. Düsseldorf: Verlag Bau & Technik, 2012

ICS 13.040.40

Price based on 37 pages