
**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*

iTeh STANDARD PREVIEW
(standards.iteh.ai)
Full standard available on
<https://standards.iteh.ai/catalog/standards/sist/791421b8b-35e1-442a-991e-20e7af555860/iso-13833-2013>



iTeh STANDARD PREVIEW
(standards.iteh.ai)
Full standard:
<https://standards.iteh.ai/catalog/standards/sist/79142b8b-35e1-442a-991e-20e7af555860/iso-13833-2013>



COPYRIGHT PROTECTED DOCUMENT

© ISO 2013

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

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

	Page
Foreword.....	iv
Introduction.....	v
1 Scope.....	1
2 Normative references.....	1
3 Terms and definitions.....	1
4 Symbols and abbreviated terms.....	2
4.1 Symbols.....	2
4.2 Abbreviations.....	3
5 Principle.....	4
5.1 General.....	4
5.2 Principles of sampling.....	4
5.3 ¹⁴ C measurement techniques.....	5
6 Reagent, materials and equipment.....	5
7 Analysis.....	9
8 Calculation of the results.....	9
9 Quality assurance and quality control procedures.....	11
10 Test report.....	11
Annex A (normative) Procedure for ¹⁴C determination by accelerator mass spectrometry.....	13
Annex B (normative) Procedure for ¹⁴C determination by liquid scintillation counter method.....	16
Annex C (normative) Procedures for ¹⁴C determination by beta-ionization.....	21
Annex D (informative) Performance characteristics ¹⁴C methods.....	24
Annex E (informative) Definitions and equations of the ¹⁴C-based method.....	28
Bibliography.....	36

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*.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

Full standard:
<https://standards.iteh.ai/catalog/standards/sist/79142b8b-35e1-442a-991e-20e7af555860/iso-13833-2013>

Introduction

Reliable data for biogenic carbon dioxide (CO₂) 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 CO₂ in the total CO₂ 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 CO₂ in the total emitted CO₂ 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 CO₂ in stack gas. The radiocarbon (¹⁴C isotope) method has been applied since the 1950s in a variety of sample types, like food, fuels, polymers, and atmospheric and combustion CO₂ 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 ¹⁴C 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 CO₂ in the total emitted CO₂ from exhaust gases of stationary sources, based on the radiocarbon (¹⁴C 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 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.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

Full standard:
<https://standards.iteh.ai/catalog/standards/sist/79142b8b-35e1-442a-991e-20e7af555860/iso-13833-2013>

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 (CO₂) in the CO₂ from exhaust gases of stationary sources, based on the radiocarbon (¹⁴C isotope) method. The lower limit of application is a biogenic to total CO₂ fraction of 0,02. The working range is a biogenic to total CO₂ 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 ¹⁴C isotope in a sample, calculated relative to the standardized and normalized ¹⁴C 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
$E(R_{n,LLD})$	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_{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
$\varphi_{\text{CO}_2,i}$	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 CO₂ and O₂ measurement.

Perform any CO₂, CO, or O₂ 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 CO₂ 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 CO₂ concentration and the CO₂ sampled for the ¹⁴C 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 CO₂. 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 CO₂ from ambient air. Proper blank procedures shall ensure that suitable gas bags were used.

When more CO₂ 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 CO₂ in stack gas can be trapped with 100 % efficiency using alkaline media, collection of the emitted CO₂ 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 CO₂.

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 CO₂.

If standard gas analysis probes and pre-sample systems are present, part of the conditioned gas can be used for CO₂ sampling. The standard gas analysis can be combined with simultaneous sampling of CO₂ 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.