



Designation: D7459 – 08

# Standard Practice for Collection of Integrated Samples for the Speciation of Biomass (Biogenic) and Fossil-Derived Carbon Dioxide Emitted from Stationary Emissions Sources<sup>1</sup>

This standard is issued under the fixed designation D7459; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This practice defines specific procedures for the collection of gas samples from stationary emission sources for subsequent laboratory determination of the ratio of biomass (biogenic) carbon to total carbon (fossil derived carbon plus biomass or biogenic carbon) in accordance with [D6866](#).

1.2 This practice applies to stationary sources that burn municipal solid waste or a combination of fossil fuel (for example, coal, oil, natural gas) and biomass fuel (for example, wood, wood waste, paper, agricultural waste, biogas) in boilers, combustion turbines, incinerators, kilns, internal combustion engines and other combustion devices.

1.3 This practice applies to the collection of integrated samples over periods from 1 hour to 24 hours, or longer.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

[D1356](#) Terminology Relating to Sampling and Analysis of Atmospheres

[D4840](#) Guide for Sample Chain-of-Custody Procedures

[D6866](#) Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee [D22](#) on Air Quality and is the direct responsibility of Subcommittee [D22.03](#) on Ambient Atmospheres and Source Emissions.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

2.2 *Federal Standards:*<sup>3</sup>

40 CFR 60 Appendix B, Performance Specification

40 CFR 60 Appendix A, Reference Method

Uncertainties In Non-Proportional Sampling, Part 75 Policy And Communication Efforts, EPA Contract No. EP-W-07-064, Work Assignment No. 0-8, Task No. 6 (February 15, 2008 – Draft)

## 3. Terminology

3.1 *Definitions*—For additional definitions of terms used in this practice, refer to Terminology [D1356](#) and Test Methods [D6866](#).

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *biomass (biogenic) CO<sub>2</sub>, n*—CO<sub>2</sub> recently removed from the atmosphere by plants, then returned to the atmosphere by combustion or biogenic decay.

3.2.1.1 *Discussion*—Biomass CO<sub>2</sub> emitted from combustion devices is often referred to as “carbon-neutral CO<sub>2</sub>.”

3.2.1.2 *Discussion*—Biomass carbon contains the isotope radiocarbon (carbon-14) in measurable quantities. Radiocarbon is a radioactive isotope of the element carbon, carbon-14, having 8 neutrons, 6 protons, and 6 electrons making up 1 × 10<sup>-12</sup> natural abundance of carbon on earth. It decays exponentially with a half-life of about 5700 years and as such is not measurable in fossil materials derived from petroleum, coal, natural gas or any other source more than about 50,000 years old.

3.2.2 *constant rate sampling, n*—sampling conducted at a fixed sampling rate.

3.2.3 *Fossil CO<sub>2</sub>, n*—CO<sub>2</sub> introduced into the atmosphere through the combustion or thermal dissociation of fossil materials.

3.2.3.1 *Discussion*—Fossil-derived CO<sub>2</sub> is void of radiocarbon and consists entirely of the “stable carbon” isotopes carbon-13 (having 7 neutrons, 6 protons, and 6 electrons) making up 1.2 % natural abundance carbon on earth and

<sup>3</sup> Available from Standardization Documents Order Desk, DODSSP, Bldg. 4, Section D, 700 Robbins Ave., Philadelphia, PA 19111-5098, <http://www.dodssp.daps.mil>.

carbon-12 (having 6 neutrons, 6 protons, and 6 electrons) and making up 98.8 % natural abundance carbon on earth.

3.2.4 *proportional sampling, n*—sampling conducted such that the ratio of the sampling rate to stack gas velocity or volumetric flow rate is constant.

3.2.5 *speciation, n*—identification of the biomass and fossil-derived CO<sub>2</sub> components within bulk air effluents.

3.2.6 *sub-sampling, n*—the process of taking a representative smaller amount of sample volume from a large bulk sample volume.

## 4. Summary of Practice

4.1 Representative gas samples are collected at a constant rate from stationary emission sources into portable containers for shipment to off-site analytical facilities performing D6866 analysis.

NOTE 1—The complexity of the analytical method requires analysis to be performed off-site.

4.2 If the variability of stack gas velocity or CO<sub>2</sub> concentration, or both, is beyond specified limits, proportional rate sampling may need to be used. See Section 8.

NOTE 2—The majority of combustion sources are such that their operational conditions do not vary significantly and, hence, constant rate sampling would provide representative samples. However, there are some sources, for example, peaking units, whose effluent flow rate (velocity) and CO<sub>2</sub> concentrations vary considerably. In such cases, it is necessary to sample proportionally. Guidelines are given on when proportional sampling is necessary.

## 5. Significance and Use

5.1 Greenhouse gases are reported to be a major contributor to global warming. Since “biomass CO<sub>2</sub>” emitted from combustion devices represents a net-zero carbon contribution to the atmosphere (that is, plants remove CO<sub>2</sub> from the atmosphere and subsequent combustion returns it), it does not contribute additional CO<sub>2</sub> to the atmosphere. The measurement of biomass (biogenic) CO<sub>2</sub> allows regulators and stationary source owners/operators to determine the ratio of fossil-derived CO<sub>2</sub> and biomass CO<sub>2</sub> in developing control strategies and to meet federal, state, local and regional greenhouse gas reporting requirements.

5.2 The distinction of the two types of CO<sub>2</sub> has financial, control and regulatory implications.

## 6. Apparatus

6.1 *Probe*—Tubing of sufficient length, equipped with an in-stack or out-stack filter to remove particulate matter. The probe may be made of any material that is inert to CO<sub>2</sub> and resistant to temperature at sampling conditions, for example, stainless steel, borosilicate glass, quartz, or polytetrafluoroethylene. The filter may be a plug of glass wool. Samples may also be taken at the exhaust of any extractive continuous emission monitoring system (CEMS) used for monitoring pollutant or diluent concentrations, including both full extractive and dilution sampling systems.

NOTE 3—Samples may be collected using EPA Method 3 in conjunction with applicable US EPA reference test methods requiring Method 5 sampling apparatus.

6.2 *Condenser*—Air-cooled, water-cooled, or other condenser to remove excess moisture that would interfere with the operation of the pump and flow meter. The condenser must not remove any CO<sub>2</sub>. The condenser may be omitted if the moisture concentrations are too low for condensation, for example, after dilution CEMS.

NOTE 4—CO<sub>2</sub> is slightly soluble in water; its effect is estimated to be less than about 0.2 %. Acid gases (for example, SO<sub>2</sub>, HCl) reduce the solubility of CO<sub>2</sub> to a negligible level. In addition, since the method involves ratios of biomass to fossil derived CO<sub>2</sub>, any solubility (if any) of CO<sub>2</sub> in water does not affect the results.

6.3 *Valve*—Needle valve, or equivalent, to adjust sampling flow rate. The valve may be omitted if a pump that samples at a constant rate is used.

6.4 *Pump*—Leak-free diaphragm-type pump, or equivalent, to transport sample gas to the flexible bag. It may be necessary to install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

6.5 *Rate Meter*—Rotameter, or equivalent rate meter, capable of measuring sample flow rate to within ±2.0 % of the selected flow rate.

6.6 *Sample Container*—Air tight vessel that is compatible with the system design, which includes flexible bags, evacuated canisters such as Summa canisters, vacutainer, Tedlar bag, or syringes.

6.6.1 The capacity of the sample container must be large enough to contain at least 2 cm<sup>3</sup> of CO<sub>2</sub> (sample container capacity (L) × %CO<sub>2</sub> × 10 ≥ 2 cm<sup>3</sup>) at the end of the sampling period.

6.6.2 If sub-samples are used for shipment to the laboratory, then determine the size of the sub-sample container such that it will contain at least 2 cm<sup>3</sup> of pure CO<sub>2</sub>.

6.7 *Flow Rate Indicator*—Indicator that is proportional to stack gas velocity or volumetric flow rate. The following are acceptable indicators: Type S pitot tube (velocity pressure, as measured by manometer, transducer, etc.); ultrasonic, scintillation, thermal or other continuous flow devices; steam rates, boiler feed water, power generation (MW), process loads, fuel rates, or other proportional effluent flow equivalents.

NOTE 5—In most combustion sources, moisture can be assumed to be constant; however, if moisture varies by more than ±10 % moisture (absolute) from the average, record hourly moisture content values to determine the effect on the constant sample rate. Constant sampling rate is based on the moisture content at stack conditions, while the actual sampling rate is determined on a dry basis.

NOTE 6—If a pitot tube is used, the determination of gas density is not needed. The square root of the velocity pressure should be used in the calculations.

6.8 *Quality Assurance/Quality Control Equipment*—As indicated in Section 8.

## 7. Procedure

7.1 Set up the sampling train as shown in Fig. 1 or Fig. 2.

7.2 When using the Fig. 1 configuration, locate the tip of the sampling probe within or centrally located over the centroidal