Designation: D7459 – 08 (Reapproved 2016)

Standard Practice for
Collection of Integrated Samples for the Speciation of Biomass (Biogenic) and Fossil-Derived Carbon Dioxide Emitted from Stationary Emissions Sources[1]

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 (ε) 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 Test Methods 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:*[2]

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

2.2 *Federal Standards:*[3]

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_2, n*—CO_2 recently removed from the atmosphere by plants, then returned to the atmosphere by combustion or biogenic decay.

3.2.1.1 *Discussion*—Biomass CO_2 emitted from combustion devices is often referred to as "carbon-neutral CO_2."

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^{-12} 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_2, n*—CO_2 introduced into the atmosphere through the combustion or thermal dissociation of fossil materials.

3.2.3.1 *Discussion*—Fossil-derived CO_2 is void of radiocarbon and consists entirely of the "stable carbon" isotopes

---

[1] 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.

Current edition approved March 1, 2016. Published March 2016. Originally approved in 2008. Last previous edition approved in 2008 as D7459 – 08. DOI: 10.1520/D7459-08R16.

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

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

carbon-13 (having 7 neutrons, 6 protons, and 6 electrons) making up 1.2 % natural abundance carbon on earth and 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_2 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 Test Methods 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_2 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_2 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_2" emitted from combustion devices represents a net-zero carbon contribution to the atmosphere (that is, plants remove CO_2 from the atmosphere and subsequent combustion returns it), it does not contribute additional CO_2 to the atmosphere. The measurement of biomass (biogenic) CO_2 allows regulators and stationary source owners/operators to determine the ratio of fossil-derived CO_2 and biomass CO_2 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_2 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_2 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 U.S. 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_2. The condenser may be omitted if the moisture concentrations are too low for condensation, for example, after dilution CEMS.

NOTE 4—CO_2 is slightly soluble in water; its effect is estimated to be less than about 0.2 %. Acid gases (for example, SO_2, HCl) reduce the solubility of CO_2 to a negligible level. In addition, since the method involves ratios of biomass to fossil derived CO_2, any solubility (if any) of CO_2 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^3 of CO_2 (sample container capacity (L) $\times$ $\%CO_2 \times 10 \geq 2\ cm^3$) 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^3 of pure CO_2.

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.

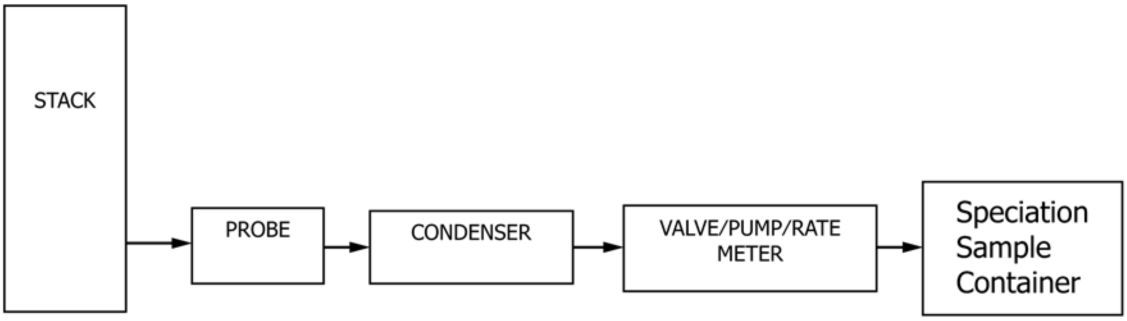

FIG. 1 Sampling Train Configuration Using a Probe

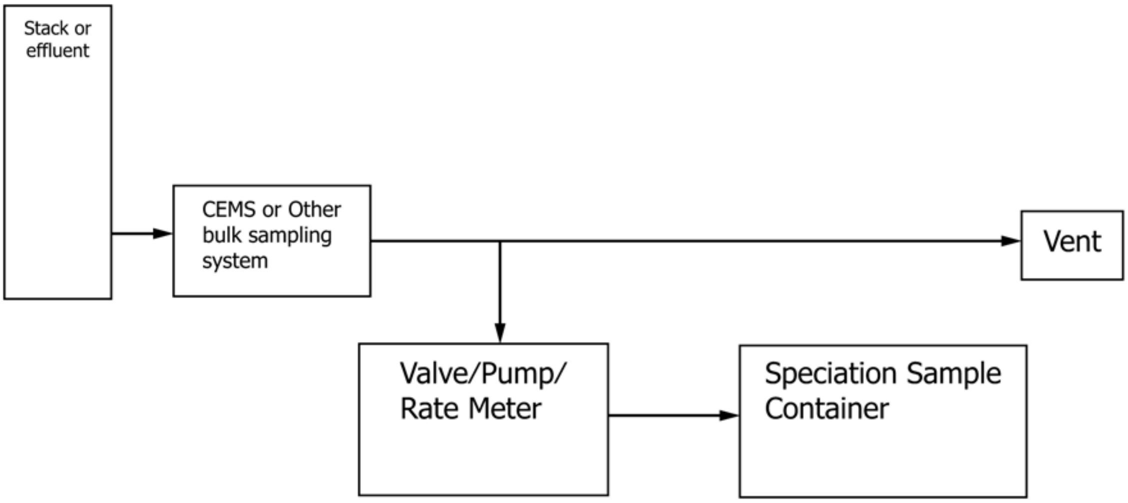

FIG. 2 Sampling Train Configuration After CEMS

7.2 When using the Fig. 1 configuration, locate the tip of the sampling probe within or centrally located over the centroidal area of the duct or stack cross-section or at least 1 meter in from the duct or stack wall. When using the Fig. 2 configuration, it is preferable to sample after the CO_2 monitor's intake. Ensure that the attachment of the CO_2 sampling equipment does not interfere with the normal operation of the existing equipment by adding significant restriction or back pressure, or affecting the analyzer flow rate(s).

NOTE 7—When using EPA Method 3 in conjunction with EPA Method 5 sampling apparatus, an integrated multipoint sample taken at each sampling point is acceptable.

7.3 If the flow indicator is a pitot tube, insert the sensing portion of the pitot in an interference-free location next to the probe, for example, attaching the pitot to the probe with the sensor tip extending at least 5.1 cm beyond the tip of the probe.

7.4 Record the sample location, time and date of the commencement of collection and the operator's name on the container. During the sampling period, record the date and time, the sample flow rate (including temperature and pressure), and readings from the flow rate indicator at least at the following frequencies.

7.4.1 ≥6 hours sampling time — every hour

7.4.2 3, 4, or 5 hours sampling time — every 30 minutes

7.4.3 2 hours sampling time — every 20 minutes

7.4.4 1 hour sampling time — every 10 minutes

7.5 Sample at a constant rate within ±10 % of the initial reading. Record the % deviation from initial reading at each recording of sampling rate.

7.6 Using the readings from the flow rate indicator (for example, pressure differential, steam rate, fuel rate), calculate the mean (μ) and standard deviation (σ). If 2 σ/μ x 100 (or two times the relative standard deviation or 2RSD) ≤55 %, the condition for constant rate sampling has been met; if not, then sampling must be conducted proportionally in accordance with 7.6.1 through 7.6.3.

NOTE 8—The ≤55 % (2RSD) specification was developed based on electric utility coal-fired units where the $\%CO_2$ variation was ≤40 % (2RSD). Under steady state conditions, the velocity or $\%CO_2$ variations from municipal solid waste or agricultural waste combustors are not expected to reach these levels, that is, 55 % for velocity or 40 % for $\%CO_2$.

7.6.1 Record the initial sampling flow and pitot tube pressure differential (or other stack flow monitoring devices or flow rate indicator), and calculate the ratio.

7.6.2 Maintain this ratio throughout the sampling period to within ±10 % of the initial ratio.

7.6.3 Calculate the % deviation from the initial ratio as follows:

$$\%Deviation\,(each\ sampling\ period) = \left(\frac{Sampling\ Period\ Ratio}{Initial\ Ratio} - 1\right) \times 100 \tag{1}$$

7.7 At the end of the sampling period, securely close the sample container and remove it from the apparatus.

7.8 Prepare the sample for shipment to the analytical laboratory by one of the following procedures:

NOTE 9—The final sample must contain at least 2 cm^3 CO_2. In some cases, several sub-sample containers may be required for analysis. Several sub-samples may be proportionately combined into a single sample container for analysis. The source may wish to retain several back-up samples.

7.8.1 Ship the sample container as is.

7.8.2 Transfer a sub-sample into a smaller container or proportionately combine multiple sub-samples.

7.9 Document sample custody to ensure sample and data integrity in accordance with Guide D4840.

8. Quality Assurance and Quality Control

8.1 *Constant Sampling Rate Check*—Calculate the percent deviation from the initial sampling rate. No value shall exceed ±10 %. If this limit is exceeded, invalidate the sample.

8.2 *Stack Flow Rate Variation*—Calculate the average stack flow rate indicator and 2RSD (twice the standard deviation relative to the average). The 2RSD must be less than 30 %.

8.3 *Leak Checks*—Conduct a leak check of the container as follows:

NOTE 10—Since the analysis is based on a ratio of $^{14}C/^{12}C$, leaking containers would not invalidate the sample. However, large leaks might pose a problem by diluting the samples to the point where there is insufficient CO_2 to analyze; therefore containers indicating leaks should not be used.

8.3.1 Perform the leak check before (mandatory) the test. Fill the container with gas, connect a water manometer, and pressurize the container to 5 to 10 cm H_20. Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak.

8.3.2 An alternative leak check method for flexible bags is to pressurize the bag to 5 to 10 cm H_20 and allow to stand overnight. A deflated bag indicates a leak.

8.3.3 Do not use any container that indicates a leak.

8.4 *Rate Meter Check*—The rate meter needs no calibration. Ensure that it is clean and free flowing.

9. Report

9.1 Include the following information in the Field Sampling Report:

9.1.1 Source Identification and Description

9.1.2 Tester Information

9.1.3 Sampling Point Description (Outlet of CEMS, Sample Probe, or Other)

9.1.4 Sampling Data (Include pertinent data to substantiate results.)

9.1.4.1 Sample Identification

9.1.4.2 Dates, Start Time, End Time, Initial Sampling Rate

9.1.4.3 Maximum Deviation of Sampling Rate from Initial

9.1.4.4 Average Flow Rate (or Proportional Equivalent) and 2 Relative Standard Deviation (2RSD)

9.1.4.5 Sub-Sample Volume and Number of Sub-Samples Being Shipped

9.1.4.6 Approximate Stack CO_2 Concentration (Dry Basis)

9.1.5 QA/QC Data (From Most Recent Test)

9.1.5.1 Leak Check

9.1.5.2 Rate Meter Check: Cleanliness and Free Flowing (Non-sticking)

10. Keywords

10.1 biomass; biomass (biogenic) CO_2; carbon dioxide; emissions; fossil CO_2; integrated; proportional; sampling; speciation