Designation: D6866 – 16

Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis[1]

This standard is issued under the fixed designation D6866; 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 standard is a test method that teaches how to experimentally measure biobased carbon content of solids, liquids, and gaseous samples using radiocarbon analysis. These test methods do not address environmental impact, product performance and functionality, determination of geographical origin, or assignment of required amounts of biobased carbon necessary for compliance with federal laws.

1.2 These test methods are applicable to any product containing carbon-based components that can be combusted in the presence of oxygen to produce carbon dioxide (CO_2) gas. The overall analytical method is also applicable to gaseous samples, including flue gases from electrical utility boilers and waste incinerators.

1.3 These test methods make no attempt to teach the basic principles of the instrumentation used although minimum requirements for instrument selection are referenced in the References section. However, the preparation of samples for the above test methods is described. No details of instrument operation are included here. These are best obtained from the manufacturer of the specific instrument in use.

1.4 *Limitation*—This standard is applicable to laboratories working without exposure to artificial carbon-14 (^{14}C). Artificial ^{14}C is routinely used in biomedical studies by both liquid scintillation counter (LSC) and accelerator mass spectrometry (AMS) laboratories and can exist within the laboratory at levels 1,000 times or more than 100 % biobased materials and 100,000 times more than 1% biobased materials. Once in the laboratory, artificial ^{14}C can become undetectably ubiquitous on door knobs, pens, desk tops, and other surfaces but which may randomly contaminate an unknown sample producing inaccurately high biobased results. Despite vigorous attempts to clean up contaminating artificial ^{14}C from a laboratory, isolation has proven to be the only successful method of avoidance. Completely separate chemical laboratories and extreme measures for detection validation are required from laboratories exposed to artificial ^{14}C. Accepted requirements are:

(1) disclosure to clients that the laboratory(s) working with their products and materials also works with artificial ^{14}C

(2) chemical laboratories in separate buildings for the handling of artificial ^{14}C and biobased samples

(3) separate personnel who do not enter the buildings of the other

(4) no sharing of common areas such as lunch rooms and offices

(5) no sharing of supplies or chemicals between the two

(6) quasi-simultaneous quality assurance measurements within the detector validating the absence of contamination within the detector itself. **(1, 2, and 3)**[2]

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.*

NOTE 1—ISO 16620-2 is equivalent to this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D883 Terminology Relating to Plastics

2.2 *Other Standards:*[4]

CEN/TS 16640:2014 Biobased Products—Determination of the biobased carbon content of products using the radiocarbon method

CEN/TS 16137:2011 Plastics—Determination of biobased carbon content

ISO 16620-2:2015 Plastics—Biobased content—Part 2: Determination of biobased carbon content

[1] These test methods are under the jurisdiction of ASTM Committee D20 on Plastics and are the direct responsibility of Subcommittee D20.96 on Environmentally Degradable Plastics and Biobased Products.

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[2] The boldface numbers in parentheses refer to a list of references at the end of this standard.

[3] 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.

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

***A Summary of Changes section appears at the end of this standard**

EN 15440:2011 Solid recovered fuels—Methods for the determination of biomass content

ISO 13833:2013 Stationary source emissions—Determination of the ratio of biomass (biogenic) and fossil-derived carbon dioxide—Radiocarbon sampling and determination

3. Terminology

3.1 The definitions of terms used in these test methods are referenced in order that the practitioner may require further information regarding the practice of the art of isotope analysis and to facilitate performance of these test methods.

3.2 Terminology D883 should be referenced for terminology relating to plastics. Although an attempt to list terms in a logical manner (alphabetically) will be made as some terms require definition of other terms to make sense.

3.3 *Definitions:*

3.3.1 *AMS facility*—a facility performing Accelerator Mass Spectrometry.

3.3.2 *accelerator mass spectrometry (AMS)*—an ultra-sensitive technique that can be used for measuring naturally occurring radio nuclides, in which sample atoms are ionized, accelerated to high energies, separated on basis of momentum, charge, and mass, and individually counted in Faraday collectors. This high energy separation is extremely effective in filtering out isobaric interferences, such that AMS may be used to measure accurately the $^{14}C / ^{12}C$ abundance to a level of 1 in 10^{15}. At these levels, uncertainties are based on counting statistics through the Poisson distribution **(4,5)**.

3.3.3 *automated efficiency control (AEC)*—a method used by scintillation counters to compensate for the effect of quenching on the sample spectrum **(6)**.

3.3.4 *background radiation*—the radiation in the natural environment; including cosmic radiation and radionuclides present in the local environment, for example, materials of construction, metals, glass, concrete **(7,8,9,4,6-14)**.

3.3.5 *biobased*—containing organic carbon of renewable origin like agricultural, plant, animal, fungi, microorganisms, marine, or forestry materials living in a natural environment in equilibrium with the atmosphere.

3.3.6 *biobased carbon content*—the amount of biobased carbon in the material or product as a percent of the total organic carbon (TOC) in the product.

3.3.7 *biobased carbon content on mass basis*—amount of biobased carbon in the material or product as a percent of the total mass of product.

3.3.8 *biogenic*—containing carbon (organic and inorganic) of renewable origin like agricultural, plant, animal, fungi, microorganisms, macroorganisms, marine, or forestry materials.

3.3.9 *biogenic carbon content*—the amount of biobased carbon in the material or product as a percent of the total carbon (TC) in the product.

3.3.10 *biogenic carbon content on mass basis*—amount of biogenic carbon in the material or product as a percent of the total mass of product.

3.3.11 *break seal tube*—the sample tube within which the sample, copper oxide, and silver wire is placed.

3.3.12 *coincidence circuit*—a portion of the electronic analysis system of an LSC which acts to reject pulses which are not received from the two Photomultiplier Tubes (that count the photons) within a given period of time and are necessary to rule out background interference and required for any LSC used in these test methods **(9, 6, 12)**.

3.3.13 *coincidence threshold*—the minimum decay energy required for an LSC to detect a radioactive event. The ability to set that threshold is a requirement of any LSC used in these test methods **(6, 12)**.

3.3.14 *contemporary carbon*—a direct indication of the relative contributions of fossil carbon and "living" biospheric carbon can be expressed as the fraction (or percentage) of contemporary carbon, symbol f_C. This is derived from "fraction of modern" (f_M) through the use of the observed input function for atmospheric ^{14}C over recent decades, representing the combined effects of fossil dilution of ^{14}C (minor) and nuclear testing enhancement (major). The relation between f_C and f_M is necessarily a function of time. By 1985, when the particulate sampling discussed in the cited reference was performed, the f_M ratio had decreased to approximately 1.2 **(4, 5)**.

3.3.15 *chemical quenching*—a reduction in the scintillation intensity (a significant interference with these test methods) seen by the Photomultiplier Tubes (PMT, pmt) due to the materials present in the scintillation solution that interfere with the processes leading to the production of light. The result is fewer photons counted and a lower efficiency **(8, 9, 12)**.

3.3.16 *chi-square test*—a statistical tool used in radioactive counting in order to compare the observed variations in repeat counts of a radioactive sample with the variation predicted by statistical theory. This determines whether two different distributions of photon measurements originate from the same photonic events. LSC instruments used in this measurement should include this capability **(6, 12, 15)**.

3.3.17 *cocktail*—the solution in which samples are placed for measurement in an LSC. Solvents and Scintillators—chemicals that absorb decay energy transferred from the solvent and emits light (photons) proportional in intensity to the deposited energy **(8, 9, 6, 12)**.

3.3.18 *decay (radioactive)*—the spontaneous transformation of one nuclide into a different nuclide or into a different energy state of the same nuclide. The process results in a decrease, with time, of the number of original radioactive atoms in a sample, according to the half-life of the radionuclide **(4, 6, 12)**.

3.3.19 *discriminator*—an electronic circuit which distinguishes signal pulses according to their pulse height or energy; used to exclude extraneous radiation, background radiation, and extraneous noise from the desired signal **(6, 12, 13, 16)**.

3.3.20 *dpm*—disintegrations per minute. This is the quantity of radioactivity. The measure dpm is derived from cpm or counts per minute (dpm = cpm − bkgd / counting efficiency). There are 2.2×10^6 dpm / μCi **(6, 12)**.

3.3.21 *dps*—disintegrations per second (rather than minute as above) (**6, 12**).

3.3.22 *efficiency*—the ratio of measured observations or counts compared to the number of decay events which occurred during the measurement time; expressed as a percentage (**6, 12**).

3.3.23 *external standard*—a radioactive source placed adjacent to the liquid sample to produce scintillations in the sample for the purpose of monitoring the sample's level of quenching (**6, 12**).

3.3.24 *figure of merit*—a term applied to a numerical value used to characterize the performance of a system. In liquid scintillation counting, specific formulas have been derived for quantitatively comparing certain aspects of instrument and cocktail performance and the term is frequently used to compare efficiency and background measures (**6, 12, 17**).

3.3.25 *flexible tube cracker*—the apparatus in which the sample tube (Break Seal Tube) is placed (**18, 19, 20, 21**).

3.3.26 *fluorescence*—the emission of light resulting from the absorption of incident radiation and persisting only as long as the stimulation radiation is continued (**6, 12, 22**).

3.3.27 *fossil carbon*—carbon that contains essentially no radiocarbon because its age is very much greater than the 5,730 year half-life of ^{14}C (**4, 5**).

3.3.28 *half-life*—the time in which one half the atoms of a particular radioactive substance disintegrate to another nuclear form. The half-life of ^{14}C is 5,730 years (**4, 6, 22**).

3.3.29 *intensity*—the amount of energy, the number of photons, or the numbers of particles of any radiation incident upon a unit area per unit time (**6, 12**).

3.3.30 *internal standard*—a known amount of radioactivity which is added to a sample in order to determine the counting efficiency of that sample. The radionuclide used must be the same as that in the sample to be measured, the cocktail should be the same as the sample, and the Internal Standard must be of certified activity (**6, 12**).

3.3.31 *modern carbon*—explicitly, 0.95 times the specific activity of SRM 4990B (the original oxalic acid radiocarbon standard), normalized to $\delta^{13}C = -19$ ‰ (Currie, et al., 1989). Functionally, the fraction of modern carbon equals 0.95 times the concentration of ^{14}C contemporaneous with 1950 wood (that is, pre-atmospheric nuclear testing). To correct for the post 1950 bomb ^{14}C injection into the atmosphere (**5**), the fraction of modern carbon is multiplied by a correction factor representative of the excess ^{14}C in the atmosphere at the time of measurements.

3.3.32 *noise pulse*—a spurious signal arising from the electronics and electrical supply of the instrument (**6, 12, 23, 24**).

3.3.33 *phase contact*—the degree of contact between two phases of heterogeneous samples. In liquid scintillation counting, better phase contact usually means higher counting efficiency (**6, 12**).

3.3.34 *photomultiplier tube (PMT, pmt)*—the device in the LSC that counts the photons of light simultaneously at two separate detectors (**24, 16**).

3.3.35 *pulse*—the electrical signal resulting when photons are detected by the PMTs (**6, 12, 13, 16**).

3.3.36 *pulse height analyzer (PHA)*—an electronic circuit which sorts and records pulses according to height or voltage (**6, 12, 13, 16**).

3.3.37 *pulse index*—the number of after-pulses following a detected coincidence pulse (used in three dimensional or pulse height discrimination) to compensate for the background of an LSC performing (**6, 13, 24, 16**).

3.3.38 *quenching*—any material that interferes with the accurate conversion of decay energy to photons captured by the PMT of the LSC (**7, 8, 9, 6, 10, 12, 17**).

3.3.39 *region*—regions of interest, also called window and/or channel in regard to LSC. Refers to an energy level or subset specific to a particular isotope (**8, 6, 13, 23, 24**).

3.3.40 *renewable*—being readily replaced and of non-fossil origin; specifically not of petroleum origin.

3.3.41 *scintillation*—the sum of all photons produced by a radioactive decay event. Counters used to measure this as described in these test methods are Liquid Scintillation Counters (LSC) (**6, 12**).

3.3.42 *scintillation reagent*—chemicals that absorbs decay energy transferred from the solvent and emits light (photons) proportional in intensity to the decay energy (**8, 6, 24**).

3.3.43 *solvent-in scintillation reagent*—chemical(s) which act as both a vehicle for dissolving the sample and scintillator and the location of the initial kinetic energy transfer from the decay products to the scintillator; that is, into excitation energy that can be converted by the scintillator into photons (**8, 6, 12, 24**).

3.3.44 *specific activity (SA)*—refers to the quantity of radioactivity per mass unit of product, that is, dpm per gram (**6, 12**).

3.3.45 *standard count conditions (STDCT)*—LSC conditions under which reference standards and samples are counted.

3.3.46 *three dimensional spectrum analysis*—the analysis of the pulse energy distribution in function of energy, counts per energy, and pulse index. It allows for auto-optimization of a liquid scintillation analyzer allowing maximum performance. Although different manufacturers of LSC instruments call Three Dimensional Analysis by different names, the actual function is a necessary part of these test methods (**6, 12, 13**).

3.3.47 *true beta event*—an actual count which represents atomic decay rather than spurious interference (**20, 21**).

4. Significance and Use

4.1 This testing method provides accurate biobased/biogenic carbon content results to materials whose carbon source was directly in equilibrium with CO_2 in the atmosphere at the time of cessation of respiration or metabolism, such as the harvesting of a crop or grass living its natural life in a field. Special considerations are needed to apply the testing method to materials originating from within artificial environments. Application of these testing methods to materials derived from