Designation: D6866 – 22

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

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

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

[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.

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

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

3.3.7 *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.

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

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

3.3.10 *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] 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.

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 CO_2 uptake within artificial environments is beyond the present scope of this standard.

4.2 Method B utilizes AMS along with Isotope Ratio Mass Spectrometry (IRMS) techniques to quantify the biobased content of a given product. Instrumental error can be within 0.1-0.5 % (1 relative standard deviation (RSD)), but controlled studies identify an inter-laboratory total uncertainty up to ±3 % (absolute). This error is exclusive of indeterminate sources of error in the origin of the biobased content (see Section 22 on precision and bias).

4.3 Method C uses LSC techniques to quantify the biobased content of a product using sample carbon that has been converted to benzene. This test method determines the biobased content of a sample with a maximum total error of ±3 % (absolute), as does Method B.

4.4 The test methods described here directly discriminate between product carbon resulting from contemporary carbon input and that derived from fossil-based input. A measurement of a product's $^{14}C/^{12}C$ or $^{14}C/^{13}C$ content is determined relative to a carbon based modern reference material accepted by the radiocarbon dating community such as NIST Standard Reference Material (SRM) 4990C, (referred to as OXII or HOxII). It is compositionally related directly to the original oxalic acid radiocarbon standard SRM 4990B (referred to as OXI or HOxI), and is denoted in terms of f_M, that is, the sample's fraction of modern carbon. (See Terminology, Section 3.)

4.5 Reference standards, available to all laboratories practicing these test methods, must be used properly in order that traceability to the primary carbon isotope standards are established, and that stated uncertainties are valid. The primary standards are SRM 4990C (oxalic acid) for ^{14}C and RM 8544 (NBS 19 calcite) for ^{13}C. These materials are available for distribution in North America from the National Institute of Standards and Technology (NIST), and outside North America from the International Atomic Energy Agency (IAEA), Vienna, Austria.

4.6 Acceptable SI unit deviations (tolerance) for the practice of these test methods is ±5 % from the stated instructions unless otherwise noted.

5. Safety

5.1 The specific safety and regulatory requirements associated with radioactivity, sample preparation, and instrument operation are not addressed in these test methods. It is the responsibility of the user of these test methods to establish appropriate safety and health practices. It is also incumbent on the user to conform to all the federal and state regulatory requirements, especially those that relate to the use of open radioactive source, in the performance of these test methods. Although ^{14}C is one of the safest isotopes to work with, State and Federal regulations must be followed in the performance of these test methods.

5.2 The use of glass and metal, in particular with closed systems containing oxygen that are subjected to 700°C temperatures pose their own safety concerns and care should be taken to protect the operators from implosion/explosion of the glass tube. Safety Data Sheets should always be followed with special concern for eye, respiratory, and skin protection. Radioactive ^{14}C compounds should be handled and disposed of in accordance with State and Federal regulations.

NOTE 2—Prior to D6866 - 11, this standard contained a Method A, which utilized LSC and CO_2 absorption into a cocktail vial. Error was cited as ±15 % absolute due to technical challenges and low radiocarbon counts. Empirical evidence now indicates error may be ±20 % or higher in routine use. This method was removed in this revision due to the inapplicability of this low precision method to biobased analysis.

NOTE 3—Prior to D6866-16, this standard contained a CARBONATE OPTION A (CARBONATE SUBTRACTION) procedure, to exclude inorganic carbonate from the biobased result. Empirical evidence now indicates error may be unreasonably high in routine use, especially in products with very low in organic carbon and very high in inorganic carbonate. This method was removed in this revision due to potential low precision results which are not observed in CARBONATE OPTION B (ACID RESIDUE COMBUSTION).

5.3 In Method C, benzene is generated from the sample carbon. Benzene is highly toxic and is an EPA-listed carcinogen. It must be handled accordingly, using all appropriate eye, skin, and respiratory protection. Samples must be handled and disposed of in accordance with State and Federal regulations. Other hazardous chemicals are also used, and must be handled appropriately (see Safety Data Sheets for proper handling procedures).

METHOD B: AMS

6. Apparatus and Reagents

6.1 *AMS and IRMS Apparatus:*

6.1.1 A vacuum manifold system with capabilities for air and non-condensable gas evacuation, sample introduction, water distillation, cryogenic gas transfer, and temperature and pressure monitoring. The following equipment is required:

6.1.2 Manifold tubing that is composed of clean stainless steel and/or glass.

6.1.3 Vacuum pump(s) capable of achieving a vacuum of 101 Pa or less within the vacuum region.

6.1.4 Calibrated pressure transducers with coupled or integrated signal response controllers.

6.1.5 A calibrated sample collection volume with associated temperature readout.

6.1.6 Clean quartz tubing for sample combustion and subsequent gas transfer, quantification and storage.

6.1.7 A hydrogen/oxygen torch or other heating device and/or gas for sealing quartz tubing.

7. AMS and IRMS Reagents

7.1 A stoichiometric excess of oxygen for sample combustion; introduced into sample tube as either a pure gas or as solid copper (II) oxide.

7.2 A stoichiometric excess of silver, nominally 30 mg, introduced into sample tube for the removal of halogenated species.

7.3 A −76°C slurry mixture of dry ice (frozen CO_2) and alcohol distillation and removal of sample water.

7.4 Liquid nitrogen.

8. Sample Preparation

8.1 Method B is a commonly used procedure to quantitatively combust the carbon fraction within product matrices of varying degrees of complexity. The procedure described here for Method B is recommended based on its affordability and extensive worldwide use. Nevertheless, laboratories with alternative instrumentation such as continuous flow interfaces and associated CO_2 trapping capabilities are equally suitable provided that the recovery of CO_2 is quantitative, 100 ± 5 %.

8.2 Based on the stoichiometry of the product material, sufficient sample mass shall be weighed such that 1-10 mg of carbon is quantitatively recovered as CO_2. Weighed sample material shall be contained within a pre-cleaned quartz sample container, furnace-baked at 900°C for ≥2 h, and torch sealed at one end. Typically 2 mm OD/1 mm ID quartz tubing is sufficient, however any tubing configuration needed to accommodate large sample volumes is acceptable.

8.3 The weighed sample shall then be transferred into an appropriately sized quartz tube, typically 6 mm OD/4 mm ID.

8.4 The sample, thus configured shall then be adapted to a vacuum manifold for evacuation of ambient air to a pressure 101 Pa or less.

8.5 If the material is known to be volatile or contains volatile components, the sample material within the tube shall be frozen with liquid nitrogen to –196°C prior to evacuation. The evacuated tube shall be torch sealed then combusted in a temperature controlled furnace at 900°C for 2 to 4 h.

8.6 After combustion, the quartz sample tube shall be scored to facilitate a clean break within a flexible hose portion of a "tube cracker" assembly adapted to the manifold. One example configuration of a tube cracker is shown in Fig. X1.2. The materials are composed of stainless steel. Compression fittings with appropriate welds are used to assemble the individual parts. This and alternative assemblies are given in the References section (**18**, **19**, **20**, **21**).

8.7 With the manifold closed to the vacuum pump, the quartz tubing is cracked, the sample CO_2 is liberated and immediately cryogenically (with liquid nitrogen) transferred to a sample collection bulb attached to a separate port on the manifold.

8.8 The contents of the sample collection bulb shall be distilled to remove residual water using a dry ice/alcohol slurry maintained at approximately −76°C. Simultaneously the sample CO_2 gas is released and immediately condensed in a calibrated volume.

8.9 The calibrated volume is then closed and the CO_2 shall equilibrate to room temperature.

8.10 Recovery shall be determined using the ideal gas law relationship.

8.11 The sample shall be transferred to a borosilicate break seal tube for storage and delivery to an AMS facility for analysis of $^{14}C/^{12}C$ and $^{13}C/^{12}$ C isotopic ratios.

9. Analysis, Interpretation, and Reporting

9.1 $^{14}C/^{12}C$ and $^{13}C/^{12}C$ isotopic ratios are measured using AMS. The isotopic ratios of $^{14}C/^{12}C$ or $^{13}C/^{12}C$ are determined relative to a standard traceable to the NIST SRM 4990C (oxalic acid) modern reference standard. The calculated "fraction of modern" (f_M) represents the amount of ^{14}C in the product or material relative to the modern standard. This is most commonly referred to as percent modern carbon (pMC), the percent equivalent to f_M (for example, f_M 1 = 100 pMC).

9.2 All pMC values obtained from the radiocarbon analyses must be corrected for isotopic fractionation using stable isotope data (**25**). Correction shall be made using $^{13}C/^{12}C$ values determined directly within the AMS where possible. In the absence of this capability (and citable absence of fractionation within the AMS) correction shall be made using the delta 13C ($\delta^{13}C$) measured by IRMS, CRDS (cavity ring down spectroscopy) or other equivalent technology that can provide precision to ±0.3 per mil. Reference standard must be traceable to Vienna Pee Dee Belemite (VPDB) using NIST SRM 8539, 8540, 8541, 8542 or equivalent.

9.3 Zero pMC represents the entire lack of measurable ^{14}C atoms in a material above background signals thus indicating a fossil (for example, petroleum based) carbon source. One hundred pMC indicates an entirely modern carbon source. A pMC value between 0 and 100 indicates a proportion of carbon derived from fossil vs. modern source.

9.4 The pMC can be greater than 100 % due to the continuing, but diminishing effects from injection of ^{14}C into the atmosphere with atmospheric nuclear testing programs (see 22.5). Because all sample ^{14}C activities are referenced to the pre-bomb NIST traceable standard, all pMC values must be adjusted by atmospheric correction factor (REF) to obtain the true biobased content of the sample. The correction factor is based on the excess ^{14}C activity in the atmosphere at the time of testing. A REF value of 102 pMC was determined for 2015 based on the measurements of CO_2 in air in a rural area in the Netherlands (Lutjewad, Groningen). The first version of this standard (ASTM D6866-04) in 2004 referenced a value of

107.5 pMC and the ASTM D6866-10 version (2010) cited 105 pMC. These data points equate to a decline of 0.5 pMC per year. Therefore, on January 2 of each year, the values in Table 1 are used as REF through 2019, reflecting the same 0.5 pMC decrease per year. The REF (pMC) values for 2020 through 2022 were determined to be 100.0 based on continued measurements at The Netherlands (Lutjewad, Groningen) through 2020, which is reflective of a slowing in the dilution of excess ^{14}C in the atmosphere. References for reporting carbon isotopic ratio data are given in Refs. **(15, 26)** for ^{14}C and ^{13}C, respectively.

9.5 Calculation of % biobased carbon content is made by dividing pMC by REF and multiplying the result by 100. (for example, [102 (pMC) / 102 (REF)] × 100 = 100 % biobased carbon. Results are reported as % biobased carbon content or % biogenic carbon content rounded to the nearest 1 unit with an applied error of 3 % absolute (see 4.2).

9.6 See 22.7 for calculating and reporting results for materials which calculate to greater than 100 % biobased carbon content.

9.7 As stated in 4.1, this testing standard is applicable to materials whose carbon source was directly in equilibrium with CO_2 in the atmosphere at the time of cessation of respiration or metabolism. See 22.11 for calculating and reporting results for materials from marine and aquatic environments.

METHOD C: Liquid Scintillation Counting

10. Detailed Requirements

NOTE 4—Acceptable tolerance levels of ±5 % are standard to this method unless otherwise stated.

10.1 Low level LSCs with active shielding that can produce consistent background counts of less than 5 dpm.

10.2 Anti-coincidence systems such as two and three PMTs (multidetector systems).

10.3 Coincidence circuits.

10.4 Software and hardware that include thresholds and statistics, pulse rise and shape discrimination, and three-dimensional spectrum analysis.

10.5 Use of external and internal standards must be used in LSC operation.

10.6 Optimized counting regions to provide very low background counts while maintaining counting efficiency greater than 60 % of samples 0.7 to 1.5 g in clean, 3-mL, 7-mL or 20-mL low potassium glass counting vials. Alternatively, clean PTFE or quartz counting vials may be used in this method.

10.7 No single LSC is specified for this method. However, minimum counting efficiency and control of background interference is specified. Like all analytical instruments, LSCs require study as to their specific components and counting optimization.

10.8 Standardization of sample preparation is required.

10.9 Standardization and optimization of clean sample vials, which must be made of either PTFE, quartz, or low-potassium glass with PTFE tops. Sample vials may be either 3-mL, 7-mL or 20-mL in volume. Plastic vials must not be used for this method.

10.10 Counting efficiency and background optimization should be performed using a suitable reference standard (for example, NIST SRM-4990B or SRM-4990C oxalic acid) using the same reagents and counting parameters as the samples.

10.11 Counting efficiency (E) shall be determined by dividing the measured cpm by the known dpm, and multiplying this by 100 to obtain the counting efficiency as a percentage. For example, for the Oxalic Acid I standard, E = (cpm/g Oxalic Acid/ 14.27 dpm/g) × 100, where E = counting efficiency in %, cpm/g Oxalic Acid is the net activity per gram measured for the oxalic acid after subtracting background, and 14.27 dpm/g is the absolute value of the NIST "OxI" reference standard. (SRM 4990B). The NIST "OxII" standard (SRM 4990C) has a slightly different ^{14}C activity level. ANU sucrose (NIST SRM 8542) can be used as a suitable standard in place of oxalic acid.

10.12 Counting interference concerns that must be addressed as part of specific instrument calibration and normalization include luminance, chemical or color quench, static electricity, random noise, temperature, and humidity variability **(27)**.

10.13 Alternate regions of interest parameters may be used based upon testing of 20, or more, 6-h counts of the same reference (STDCT) standard that record the raw data and spectrum for keV regions of interest 4 through 96. Optimal counting conditions should be established by maximizing the Figure of Merit (E^2/bkg) values to obtain the highest count efficiency and the lowest background and other interference. Counting efficiency of less than 60 % is unacceptable and can be improved by LSC instrument optimization and sample/reagent compatibility or shielding improvements.

10.14 Samples will be equilibrated with reference standards under identical conditions of time and temperature.

10.15 Samples will be counted for a minimum of 10 h with region of interest (ROI) channels including ROI energy levels of 0-155 keV such that E^2/B is 1,000 or higher in 20 to 120-min subsets with raw data saved to disk for later statistical analysis and documentation of stable counting conditions.

10.16 Before commercial testing, laboratories that intend to implement this method must participate in an inter-laboratory comparison study to assess between laboratory reproducibility.

11. Apparatus and Reagents

11.1 *Benzene Synthesis Apparatus:*

TABLE 1 Percent Modern Carbon (pMC) Reference

Year	REF (pMC)
2015	102.0
2016	101.5
2017	101.0
2018	100.5
2019	100.0
2020	100.0
2021	100.0
2022	100.0

11.1.1 A benzene synthesis unit will be required to convert sample carbon to benzene. These units are commercially available, but can also be homemade if desired. Examples of benzene synthesis units are discussed in (**28**) and (**29**).

11.2 *LSC Apparatus:*

11.2.1 LSC as described in Section 10.

11.2.2 Clean low potassium scintillation vials with a volume of 3-mL, 7-mL, or 20-mL.

11.3 *LSC and Benzene Synthesis Reagents:*

11.3.1 High purity oxygen used for converting sample carbon to CO_2. Alternatively, technical grade oxygen can be used if scrubbed with a suitable material such as Ascarite.

11.3.2 High purity nitrogen used to combine with the oxygen when combusting highly volatile samples. Alternatively, technical grade nitrogen can be used if scrubbed with a suitable material such as Ascarite.

11.3.3 Cupric oxide wire for conversion of CO to CO_2 when combusting highly volatile samples with oxygen/nitrogen blends.

11.3.4 Reagent grade powdered lithium or lithium rod (each packed in argon) for converting CO_2 to lithium carbide (Li_2C_2).

11.3.5 Reagent grade potassium chromate (in sulfuric acid) or phosphoric acid for purifying acetylene gas.

11.3.6 Suitable catalyst material such as a Si_2O_3/Al_2O_3 substrate activated with either chromium (as Cr_2O_3) or vanadium (as V_2O_5) for converting acetylene gas to benzene (**30**).

11.3.7 Scintillation cocktail.

11.3.8 De-ionized or distilled water for hydrolysis of Li_2C_2 to acetylene gas.

12. Sample Preparation and Analysis

12.1 Tolerance of ±5 % is to be assumed unless otherwise stated.

12.2 Standard procedures are to be employed for the conversion of original sample material to benzene using the liquid scintillation dating technique (**28**).

12.3 Based on the stoichiometry of the product material, sufficient sample mass shall be weighed such that quantitative recovery of the carbon would theoretically yield 1.00-4.00 g of carbon for conversion to benzene.

12.4 The carbon within each sample shall first be combusted to CO_2 by placing the sample in a closed system which is purged or evacuated of air.

12.5 The system is then purged several times with pure nitrogen. After verifying the integrity of the closed system, the sample is bathed in 100 % oxygen (non-volatile samples) or a mixture of nitrogen and oxygen (volatile samples) and ignited. Samples ignited using a nitrogen/oxygen mix must pass through a cupric oxide furnace at 850°C to avoid carbon loss to CO. The generated sample CO_2 is collected using liquid nitrogen cold traps. If desired, the CO_2 can be passed through a series of chemical traps to remove various contaminants prior to cryogenic collection of the CO_2 (**28**).

12.6 As an alternative combustion approach for volatile materials, the samples can be combusted in a bomb that is pressurized with oxygen to 300-400 psi. The CO_2 generated in the bomb is subsequently released to a dry ice trap for moisture removal, followed by a liquid nitrogen cold trap for CO_2 collection.

12.7 The collected CO_2 is reacted with a stoichiometric excess (3:1 lithium:carbon ratio) of molten lithium which has been preheated to 700°C. Li_2C_2 is produced by slowly bleeding the CO_2 onto the molten lithium in a stainless steel vessel (or equivalent) while under a vacuum of ≤135 mPa.

12.8 The Li_2C_2 is heated to about 900°C and placed under vacuum for 15-30 minutes to remove any unreacted gases and to complete the Li_2C_2 synthesis reactions (**15**).

12.9 The Li_2C_2 is cooled to room temperature and gently hydrolyzed with distilled or de-ionized water to generate acetylene gas (C_2H_2) by applying the water in a drop-wise fashion to the carbide. The evolved acetylene is dried by passing it through dry ice traps, and the dried acetylene is subsequently collected in liquid nitrogen traps.

12.10 The acetylene gas is purified by passing it through a phosphoric acid or potassium chromate (in sulfuric acid) trap to remove trace impurities, and by using dry ice traps to remove water.

12.11 The C_2H_2 gas is catalyzed to benzene (C_6H_6) by bleeding the acetylene onto a chromium catalyst which has been preheated to ≥90°C, or onto a vanadium catalyst (the later activates at ambient temperature). In the former case, the reaction is cooled with a water jacket to avoid decomposition from excessive heat generated during the exothermic reaction.

12.12 The benzene is thermally evolved from the catalyst at 70-110°C and then collected under vacuum at roughly –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 temperatures.

12.13 The ^{14}C content shall be determined in an LSC with optimization of the instrument as described in Section 10. Either single vial counting or "chain" counting is acceptable.

12.14 Radiocarbon activity in the sample is to be determined by "benzene cocktail" analysis, consisting of a scintillator plus sample benzene, in constant volume and proportion. A recommended scintillator is butyl-PBD or PPO/POPOP dissolved in toluene or equivalent (**27**) and (**11**). Alternatively, some scintillators (including butyl-PBD) can be added to the benzene as a solid.

12.15 Standard methods consist of counting a cocktail containing sample benzene plus a scintillation solution. For example, a cocktail might contain 4-mL sample benzene plus 0.5-mL scintillation solution. In this example, if 4-mL of sample benzene is not available, reagent grade (99.999 % pure) thiophene-free benzene can be added to bring the sample volume to 4-mL. Larger or smaller volumes may be utilized depending upon the configuration of the specific laboratory's counting protocols.

12.16 LSCs are to be monitored for background and stability with traceable documentation.

12.17 Should anomalies appear during sample counting, the benzene is to be re-measured in another counter to verify the activity, or the sample must be completely re-analyzed.

12.18 Traceable quench detection should be performed on each sample to ensure benzene purity. In the event the sample is substantially quenched, the data should be discarded and the sample should be re-analyzed.

12.19 Measurements are to be made on an interval basis (usually 50 or 100 minutes) to allow statistical analysis of the measurement.

12.20 Prior to removing the sample from the counter, stability is to be verified and the data scrutinized for anomalies. If the distribution does not closely follow Gaussian statistics, the sample should be transferred and counted in another counter for verification, or the sample should be completely re-analyzed.

12.21 Counting should be performed as needed to obtain an accuracy of 2 % or better.

12.22 Calculation of the data should be performed only after cross-checking all transcribed numbers, synthesis records, cocktail preparation, counting data, and counting analysis.

12.23 Any unused sample material shall be maintained at the laboratory for potential re-analysis for a minimum of 180 days. The sample will then be disposed of in accordance with state and federal regulations.

12.24 Because of problems in storing benzene over extended periods of time, it may be necessary to re-distill (to remove scintillant) and re-weigh the benzene if re-analysis is desired at a later date. Alternatively, a fresh portion of the biobased product can be processed to obtain a fresh benzene sample.

NOTE 5—The benzene derived from the sample carbon is toxic and is a known carcinogen. Special handling and disposal procedures will be required.

13. Interpretation and Reporting

13.1 The counts shall be compared, directly or through secondary standards, to the primary NIST ^{14}C oxalic acid SRM 4990C (or other suitable standard traceable to SRM 4990C), with stated uncertainties. Significantly lower ^{14}C counts than the standard indicate the presence of ^{14}C-depleted carbon source. The lack of any measurable ^{14}C counts above the background signal in a material indicates a fossil (for example, petroleum based) carbon source. A sample that has the same ^{14}C activity level (after correction for the post-1950 bomb injection of ^{14} C into the atmosphere) as the oxalic acid standard is 100 % biobased and signifies an entirely modern carbon source. The inherent assumption is that all of the organic components within the analyzed material are either fossil or present day in origin. See Section 22 on precision and bias.

13.2 The relative number of counts between the modern reference and the sample is term "fraction of modern" (f_M). This is most commonly referred to as percent modern carbon (pMC), the percent equivalent to f_M (for example, f_M = 100 pMC). All pMC values obtained from the radiocarbon analyses must be corrected for isotopic fractionation (**25**) after performing stable carbon isotope analyses. Correction shall be made using the $\delta^{13}C$ measured by IRMS, CRDS or other equivalent technology that can provide precision to ±3 per mil. IRMS Reference standard must be traceable to Vienna Pee Dee Belemite (VPDB) using NIST SRM 8539, 8540, 8541, 8542, or equivalent. The $\delta^{13}C$ must be measured on combustion CO_2 or benzene.

13.3 The pMC can be greater than 100 % because of the continuing but diminishing effects of the 1950s nuclear testing programs, which resulted in a considerable enrichment of ^{14}C in the atmosphere (see 22.5). The decrease in ^{14}C from the bomb testing programs has been nonlinear in the past, but has been linear since at least 2004 to present. Although it continues to decrease by a small amount each year, the current ^{14}C activity in the atmosphere has not reached the 1950 level of 13.56 dpm per gram carbon that is defined as 100 pMC. Because all sample ^{14}C activities are referenced to a "pre-bomb" standard, and because nearly all new biobased products are produced in a post-bomb environment, all pMC values (after correction for isotopic fractionation) must be adjusted by atmospheric correction factor (REF) obtain the true biobased content of the sample. The correction factor is based on the excess ^{14}C activity in the atmosphere at the time of testing. A REF value of 102 pMC was determined for 2015 based on the measurements of CO_2 in air in a rural area in the Netherlands (Lutjewad, Groningen). The first version of this standard (ASTM D6866-04) in 2004 referenced a value of 107.5 pMC and the ASTM D6866-10 version (2010) cited 105 pMC. These data points equate to a decline of 0.5 pMC per year. Therefore, on January 2 of each year, the values in Table 2 are used as REF through 2019, reflecting the same 0.5 pMC decrease per year. The REF (pMC) values for 2020 through 2022 were determined to be 100.0 based on continued measurements at The Netherlands (Lutjewad, Groningen) through 2020, which is reflective of a slowing in the dilution of excess ^{14}C in the atmosphere. References for reporting carbon isotopic ratio data are given in Refs. (**15, 26**) for ^{14}C and ^{13}C, respectively.

13.4 Calculation of % biobased carbon content is made by dividing pMC by REF and multiplying the result by 100. For example, using the REF for 2015, [102 (pMC) / 102 (REF)] × 100 = 100 % biobased carbon. Results are reported as % biobased carbon content or % biogenic carbon content rounded to the nearest 1 unit with an applied error of 3 % absolute (see 4.2).

13.5 See Section 22 on precision and bias for calculating and reporting results for materials which calculate to greater than 100 % biobased.

TABLE 2 Percent Modern Carbon (pMC) Reference

Year	REF (pMC)
2015	102.0
2016	101.5
2017	101.0
2018	100.5
2019	100.0
2020	100.0
2021	100.0
2022	100.0

13.6 As stated in 4.1, this testing standard is applicable to materials whose carbon source was directly in equilibrium with CO_2 in the atmosphere at the time of cessation of respiration or metabolism. See 22.11 for calculating and reporting results for materials from marine and aquatic environments.

SPECIAL PROCEDURES FOR CARBONATE-BEARING PRODUCTS

14. Background

14.1 Some biobased products contain substantial amounts of inorganic carbonates. When using the sample preparation procedures stipulated in Methods B and C, some or all of the carbon associated with the inorganic carbonates could be included in the analysis. However, according to the USDA BioPreferred Program's use of "biobased carbon content," the biobased carbon content determination must be based only on the organic carbon content. As such, the carbon associated with inorganic carbonates is excluded from the "biobased carbon content" determination for any given product, regardless of whether those carbonates contain ^{14}C. Therefore, special procedures must be used to analyze biobased products that contain detectable (using procedures described in 15.1) levels of inorganic carbonates. The procedures described herein are applicable to solid materials.

15. Sample Analysis and Reporting

15.1 If it is not known whether or not a biobased product contains inorganic carbonates, the product must be checked for the presence of carbonates before any biobased carbon content determinations are performed. The presence of carbonates can be adequately detected in powdered samples using 10 % HCl and seeing if the sample effervesces. Even low (for example, 1 %) concentrations of carbonates can be readily detected by applying 2-3 mL of 10 % HCl onto at least one gram of the powdered sample to see if the acidified sample effervesces (indicating the presence of carbonates). However, a limitation to this approach is that it assumes that the carbon content of the sample is reasonably high. If the carbon content of a sample is low (for example, 10 % or less), then even very small concentrations of inorganic carbonate in the sample could constitute a significant fraction of the total carbon, yet the carbonate may not be detectable using the acidification procedure. This could incur significant analytical errors if suitable corrections are not made for the inorganic carbon. This approach also assumes that the carbonate particles are not coated with a material that is not quickly dissolved in the dilute acid. Judgment calls are often required by the analyst in such cases. If there is some question as to whether or not a product contains significant levels of inorganic carbonate, the product manufacturer should be contacted to address this issue.

15.2 *Acid Residue Combustion (ARC)* is used to eliminate the inorganic carbonate fraction in a biobased product. This involves making a single measurement on the soluble and insoluble organics remaining within an acidic solution following acid digestion of the product. It is recommended only for laboratories having qualified expertise in acid/base chemistry and wet combustion.

ACID RESIDUE COMBUSTION (ARC)

15.3 In this method, the product is digested in phosphoric acid (H_3PO_4) and the residue solution is combusted. Organic carbon bearing species within the solution are oxidized to CO_2 suitable for biobased content determination. Note that due to the complicated nature of combusting an acid solution, small quantities are recommended applicable to analysis by way of Method B.

15.4 In the case of solid material, surface area is increased as necessary via grinding, pulverizing or crushing prior to dispersion in the acid. This is especially important in the case of bioplastics or other materials which may encapsulate carbonate grains. It is important to produce sub-millimeter or sub-micron particle sizes to ensure maximum exposure to carbonate surfaces. The powder is then poured into a glass vessel suitable for evacuation of all air, to –30 psi (standard rotary vacuum pump range). H_3PO_4 is added to the vessel (in the absence of air) and observation is made for the presence or absence of effervescence. If effervescence is observed, the material is identified to contain inorganic carbon. In the case of aqueous solution, H_3PO_4 is added directly to the solution under observation for effervescence.

NOTE 6—It is useful to know the pH of the solution prior adding the acid. It is understood caution, best laboratory practice and safety is used in adding the acid. High pH solutions can get very hot and react strongly. If effervescence is observed, carbonate is indicated.

NOTE 7—Some materials may "boil" with the addition of the acid. If it can be determined the effervescence is not related to the generation of CO_2, it is reasonable to assume the material does not contain carbonate and the product can be analyzed as such. If such a determination cannot be made, it is reasonable to assume the material does contain carbonate and combustion of the residual solution is warranted.

15.5 Next, the acid product solution is combusted. In some cases, it may be necessary to repeat the above steps to produce an appropriate size sample for combustion. If for example, the glass vessel used for the test was quartz or Vycor, the combustion system can be designed to incorporate it in such a way that the original solution can be combusted directly without transfer. In any case, the solution to be used is subjected to an active flow of oxygen (100 % or N_2 diluted dependent upon the flammability or volatility of the solution) and heated. Evolved CO_2 is collected in a liquid nitrogen trap for subsequent analysis by Method B. The most volatile/least pyrolizable components will evolve first. The system should be designed with a furnace at >800°C packed with quartz wool or turnings downstream from the sample to combust vaporized organic compounds. Upon removal of volatile components, it is common to see solids precipitate, burn or pyrolize as the heating continues. In the final steps of combustion, heat should be applied to the vessel containing the remnants of the product (minerals, ash, or highly pyrolizable organic compounds) to temperatures such that no organic constituents (usually black) may remain uncombusted.

NOTE 8—It is common for the caustic nature of the combusted solution to damage the heated glass and components beyond repair. As such, it is often necessary to replace the system with new glass components after each sample.

15.6 The biobased carbon content value obtained from this acid residue combustion procedure is expected to be accurate

to within ±3 % (absolute) since it involves just a single analysis step rather than the two-step procedure described for the carbonate subtraction approach.

ANALYSIS OF GASEOUS EMISSIONS AND BULK MATERIALS CONTAINING RENEWABLE CARBON

16. Background

16.1 The initial step in determining the biobased carbon content of any solid or liquid sample is to convert the sample carbon to gaseous CO_2 (any CO resulting from incomplete combustion during this step is also oxidized to CO_2). Therefore, the overall analytical methods described in this standard are also applicable to determining the biobased carbon content of gases where the carbon is already in gaseous form. This includes gaseous emissions from electric utility boilers, waste incinerators, and syngas plants. To avoid confusion in terminology, results obtained for gaseous emissions should be reported as "biogenic carbon content" or "biogenic CO_2 content," not "biobased carbon content" because inorganic carbon cannot be eliminated from the final result.

16.2 The analytical methods for determining biobased content are also directly applicable to the determination of renewable carbon content of solid fuels combusted in waste-to-energy plants and municipal incinerators. In this case, the source of the carbon is very often the same as described above for gaseous emission, but with the solid fuel itself being the material submitted for analysis. Additionally, applicability of the result is related to total CO_2 emissions, including both organic and inorganic sourced carbon. Therefore, the overall analytical methods described in this standard are applicable to determining the renewable content of solid fuels where the renewable carbon relative to the total carbon (versus total organic carbon) is the value of interest. As such, all analytical methods are the same, with the exclusion of consideration of inorganic carbon contribution. Therefore, to avoid confusion in terminology, results obtained for any material containing inorganic carbonates should be reported as "biogenic carbon content," not "biobased carbon content" since inorganic carbon is included in the final result. Examples of such materials are solid fuels, municipal solid waste (MSW) and precipitated calcium carbonate (PCC).

17. Sample Analysis and Reporting

17.1 Gas sampling issues are not addressed in these test methods. However, once a gas sample is collected, it can be processed in accordance with the post-combustion procedures already stipulated in this method.

17.2 The age of the biomass used in industrial processes will affect the accuracy of the biobased carbon content measurement and there will likely be cases where the age of the biomass is not accurately known. The results are anticipated to be accurate to within 5 % biobased carbon content if the renewable carbon components are within ten years of present day and if the samples are analyzed by AMS. The accuracy of the measurement will increase as the age of the renewable carbon components diminishes.

18. Percent Biobased Carbon Content of Complex Assemblies

18.1 A complex assembly is a product for which an accurate representation of % biobased carbon content cannot be obtained from a SINGLE radiocarbon measurement. Examples; bicycle seat, loose leaf binder, computer bag, tennis shoe, umbrella, arm chair, automobile, and liquids comprised of volatile petrochemicals, biobased chemicals, and sodium bicarbonate.

18.2 Factors most commonly forcing a product into the category of complex assembly are size and the presence of inorganic carbonate. Size is a factor since radiocarbon methodology is mass limited to a maximum of about 25 grams per analysis. Inorganic carbonate presents challenges with recovery of TOC from products containing VOCs since the VOCs are lost during the removal of the carbonate.

18.3 Three options are provided to obtain accurate % biobased carbon content from complex assemblies: Complex Biobased Option A, Complex Biobased Option B, and Complex Biobased Option C.

Complex Biobased Option A:

18.4 Sub-sample each organic constituent in a proportion representative of its content within the assembly. Combine them in a measurable quantity so that a single ASTM D6866 analysis is representative of the assembly.

Complex Biobased Option B:

18.5 In some cases it is not possible to completely remove all inorganic carbon while recovering all TOC. Examples are oil based paints containing nanoparticle carbonates. The oil encapsulates the particles such that acid reaction is attenuated or non-existent. The same challenge exists with certain plastics. Also, in the case of some chemicals containing biobased VOCs and inorganic carbonate, the VOCs are lost during the acid attack.

18.6 In the case of the oil based paint, best accuracy is derived from analysis prior to addition of the carbonate filler. In the case of plastic, best accuracy is derived from analysis of the resin. In any case, the plastic should be ground to a very fine powder to expose surface area.

18.7 In the case of solutions containing VOCs and inorganic carbonate, two analyses should be performed. One analysis on TC (including the inorganic carbonate and the VOCs) and one analysis on the ARC (with loss of VOCs and removal of inorganic carbonate). The higher value of the two results is to be reported as the % biobased carbon content or the % biogenic carbon content, accordingly.

Complex Biobased Option C:

18.8 Measure the % biobased carbon content of each organic constituent, then using the known % organic carbon content and proportion of each constituent within the assembly, formulate the % biobased carbon content for the assembly.

18.9 For an assembly containing "n" organic components, this can be achieved using Eq 1.

$$\% \text{ Biobased Carbon Content of Product} = \sum_{i=1}^{n} M_i * BCC_i * OCC / \sum_{i=1}^{n} M_i * OCC_i \quad (1)$$

where:

M_i = mass of the nth component present in the assembly,
BCC_i = % biobased carbon content of the nth component, and
OCC_i = % organic carbon content of the nth component.

19. Percent Biobased Carbon Content on a Mass Basis

19.1 Knowing the total % biobased carbon content of a product and the % total organic carbon (TOC) of the product, the percentage of biobased carbon content on a mass basis (weight) of the product can be determined by Eq 2

$$\% \text{ Biobased Carbon Content (mass basis)} = [\% \text{ total organic carbon}/100 \times (\% \text{ biobased carbon content}/100)] \times 100 \quad (2)$$

20. Percent Biogenic Carbon Content of Complex Assemblies

20.1 The distinction between "biobased" and "biogenic" (as defined in Section 3) is such that "biobased" relates only to total organic carbon while "biogenic" relates to total carbon.

20.2 A complex assembly is a product for which an accurate representation of % biogenic carbon content cannot be obtained from a SINGLE radiocarbon measurement. Examples: bicycle seat, loose leaf binder, computer bag, tennis shoe, umbrella, arm chair, automobile, and liquids comprised of volatile petrochemicals, biobased chemicals, and sodium bicarbonate.

20.3 Because the removal of inorganic carbon is not required, size is usually the only factor that qualifies a biogenic carbon material as complex since radiocarbon methodology is mass limited to a maximum of about 25 grams per analysis. As with complex biobased material, three options are provided to obtain accurate % biogenic carbon content from complex assemblies.

Complex Biogenic Option A:

20.4 Sub-sample each constituent in a proportion representative of its content within the assembly. Combine them in a measurable quantity so that a single ASTM D6866 analysis is representative of the assembly.

Complex Biogenic Option B:

20.5 In the case of low carbon solutions containing volatile organic compounds (VOCs), two analyses should be performed: one analysis on the entire product and one analysis on the product after evaporation of the VOCs. The higher value of the two results is to be reported as the % biogenic carbon content.

Complex Biogenic Option C:

20.6 Measure the % biogenic carbon content of each constituent, then using the known % carbon content and proportion of each constituent within the assembly, formulate the % biogenic carbon content for the assembly.

20.7 For an assembly containing carbon containing components, this can be achieved using Eq 3.

$$\text{Biogenic Carbon Content of Product} = \sum_{i=1}^{n} M_i * BgCC_i * CC / \sum_{i=1}^{n} M_i * CC_i \quad (3)$$

where:

M_i = mass of the nth component present in the assembly,
$BgCC_i$ = biogenic content of the nth component, and
CC_i = carbon content of the nth component.

21. Percent Biogenic Carbon Content on a Mass Basis

21.1 Similar to determining % biobased carbon content on a mass basis, knowing the total % biogenic content of a product and the % total carbon (TC) of the product, the percentage of biogenic carbon content on a mass basis (weight) of the product can be determined by Eq 4.

$$\% \text{ Biogenic Carbon Content (mass basis)} = [\% \text{ total carbon}/100 \times (\% \text{ biogenic carbon content}/100)] \times 100 \quad (4)$$

22. Precision and Bias

22.1 The precision and bias of Methods B and C from any reporting laboratory will be deemed acceptable if it can be shown that the data are traceable to the primary standards and within the uncertainties stated in 4.2 and 4.3.

22.2 The application of this test method is built on the same concepts as radiocarbon dating used by archaeologists. A radiocarbon signature is obtained by Method B or Method C relating to modern references. If the signature is today, the product or material is 100 % biobased/biogenic carbon, indicating the product's carbon content was derived entirely from recently living materials and no petrochemical or other fossil carbon is present in the product. If the signature is zero, the product is 0 % biobased/biogenic and indicates that only petrochemical or other fossil carbon compounds carbon are present in the product. If the signature is between zero and today, the product is a mixture of recent and fossil carbon. The analytical term for this signature is pMC. This will typically have a 1 RSD of 0.1-0.4 pMC (Method B) and 0.7-1.5 pMC (Method C). This value is converted to the % biobased carbon

TABLE 3 Illustration for Eq 1

Constituents	Grams Present (M_i)	% Biobased Carbon Content (BCC_i)	% Organic Carbon Content (OCC_i)	Grams Biobased Carbon	Grams Organic Carbon	Total % Biobased Carbon Content
Organic A	25	0	67	0	16.75	
Organic B	45	100	36	16.20	16.20	47
Organic C	17	40	52	3.54	8.84	(47.24)
Total:				19.74	41.79	

TABLE 4 Illustration for Eq 2

Constituents	Grams Present (M_i)	% Biobased Carbon Content (BCC_i)	% Organic Carbon Content (OCC_i)	Grams Biobased Carbon	Grams Organic Carbon	Total % Biobased Carbon Content (mass basis)
Organic A	25	0	67	0	16.75	
Organic B	45	100	36	16.20	16.20	22.69
Organic C	17	40	52	3.54	8.84	
Total:	87			19.74	41.79	

% Biobased Carbon Content = (19.74 / 41.79) × 100 = 47.24
% Total Organic Carbon (TOC) = (41.79 / 87) × 100 = 48.04
Total % Biobased Carbon Content (mass basis) = [(47.24 / 100) × (48.04 / 100)] × 100 = 22.69 %

TABLE 5 Illustration for Eq 3

Constituents	Grams Present (M_i)	% Biogenic Carbon Content ($BgCC_i$)	% Carbon Content (CC_i)	Grams Biogenic Carbon	Grams Carbon	Total % Biogenic Carbon Content
Organic A	25	0	67	0	16.75	
Organic B	45	100	36	16.20	16.20	
Organic C	17	40	52	3.54	8.84	48.17
Inorganic D	3	0	12	0	0.36	
Inorganic E	10	95	12	1.14	1.2	
Total:				20.88	43.35	

Total % Biogenic Carbon Content = (20.88 / 43.35) × 100 = 48.17

TABLE 6 Illustration for Eq 4

Constituents	Grams Present (M_i)	% Biogenic Carbon Content ($BgCC_i$)	% Carbon Content (CC_i)	Grams Biogenic Carbon	Grams Carbon	Total % Biogenic Carbon (mass basis)
Organic A	25	0	67	0	16.75	
Organic B	45	100	36	16.20	16.20	
Organic C	17	40	52	3.54	8.84	20.88
Inorganic D	3	0	12	0	0.36	
Inorganic E	10	95	12	1.14	1.20	
Total:	100			20.88	43.35	

% Biogenic Carbon Content = (20.88 / 43.35) × 100 = 48.17
% Total Carbon (TC) = (43.35 / 100) × 100 = 43.35
Total % Biogenic Carbon Content (mass basis) = [(48.17 / 100) × (43.35 / 100)] × 100 = 20.88

content or % biogenic carbon content using an atmospheric correction factor (REF) applicable to the amount of excess radiocarbon in the atmosphere generated with thermonuclear weapons testing termed bomb carbon. The excess ^{14}C peaked at about 193 pMC in 1965 after the signing of a global treaty banning atmospheric nuclear weapons testing and has gradually declined with uptake in the biosphere. As of this version in 2016 (D6866-16) the excess was approximately 2 pMC (see 9.1), indicating a modern plant value should measure 102 pMC. Therefore, 102 pMC indicates 100 % biobased carbon content and the equivalent 100 % biobased carbon content is derived by dividing 102 pMC by REF and multiplying by 100: (102/102) × 100 = 100 % biobased carbon. Similarly so, if a product or material's signature measures 102 pMC, its biobased carbon content is 100 %.

22.3 Indeterminate error exists in the absolute value of the present day atmospheric correction factor (REF). This will translate directly to the accuracy of the % biobased carbon content calculation. There may be latitude/local variations relating to meteorological patterns. Local geographic depletions of up to 5 % in extreme cases have been documented due to industrial pollution. Materials from marine environments may be depleted by 2 % or more due to old carbon equilibrium in marine waters. And bomb carbon from past living components such as forestry products can be dramatic. These indeterminate errors cannot be accurately quantified for a given product or material based solely on the pMC value. However, accuracy of the correction factor (REF) can be qualitatively assessed based on the magnitude of the product's pMC value and factual knowledge of the source components for the analyzed product or material.

22.4 This test method version is therefore most applicable to products and materials containing short-lived renewable carbon which recently ceased to be within an active respiratory or metabolic system in equilibrium with pMC CO_2 in the air. Example sources are corn stover, switch grass, sugar cane bagasse, coconut husks, flowers, bushes, branches, leaves, twigs, stems, algae, animal fat, and collagen. Such materials, either by themselves or when mixed with petrochemicals will yield the highest accuracy in % biobased carbon content results. As materials increasingly deviate from this criteria, accuracy correspondingly will decrease.

BOMB CARBON EFFECT

22.5 Atmospheric thermonuclear weapons testing was extensive between 1952 and 1963. During this time period the $^{14}CO_2$ content in the air increased by 90 %. This means that a plant living in 1965 would measure about 190 pMC. Since the

signing of the testing ban in 1963 this signature declined to about 140 pMC by 1975, 120 pMC by 1985, and 101.5 pMC by 2016. The consequence of this effect to error in biobased content analysis today relates to when the biobased material used in the product was last actively part of a respiring/metabolizing system. It is predominant in products made from forestry products. The rings within trees each represent the previous growth season within which the previous year's $^{14}CO_2$ signature was recorded. The center most ring of a tree living today but planted in 1965 would be about 190 pMC whereas the outermost ring/bark would be 101.5 pMC. If this tree is harvested and used in manufacturing a biobased product, the % biobased carbon content of the product will be dependent on where the carbon came from within the tree.

22.6 Bomb carbon is readily identified in a product when the product's pMC value is greater than the prescribed correction factor (REF). A high value can be predicted based on the origin of the manufacturing components. High values are typically observed in paper, cardboard, forestry products, and forestry-derived chemicals. An exact correction factor REF is not possible based strictly on the measured pMC value of the product.

INSTRUCTIONS FOR CALCULATING AND REPORTING RESULTS GREATER THAN 100 % BIOBASED CARBON CONTENT

22.7 BOMB CARBON—OPTION 1: sample pMC = 1 to 5 above REF

Assign a final result of 100 % biobased carbon content.

Example: 106 sample pMC – 101.5 pMC REF = 4.5 pMC; final result = 100 %

22.8 BOMB CARBON—OPTION 2: sample pMC = 6 to 22 pMC above REF

% biobased carbon content = pMC × (REF/112)

If the result is greater than REF report as 100 % biobased carbon content:

Example 1: sample pMC = 120 pMC, REF = 101.5 pMC

% biobased carbon content = 120 × (101.5/112) = 108.8 pMC; 108.8 pMC > REF (101.5 pMC); result = 100 %

Example 2: sample pMC = 109 pMC, REF = 101.5 pMC

% biobased carbon content = 109 × (101.5/112) = 99 %

22.9 BOMB CARBON—OPTION 3: sample pMC > 22 pMC above REF

For pMC values greater than 22 pMC above REF, calculate using REF/138.

If the result is greater than REF report as 100 % biobased carbon content:

Example 1: sample pMC = 145 pMC, REF = 101.5 pMC

% biobased carbon content = 145 × (101.5/138) = 107 pMC; 107 pMC > REF (101.5 pMC); result = 100 %

Example 2: sample pMC = 131 pMC, REF = 101.5 pMC

% biobased carbon content = 131 × (101.5/138) = 96 %

22.10 The correction of REF using 112 pMC in BOMB CARBON—OPTION 2 is based on an average pMC value for a tree that lived 0-30 years ago. The correction of REF using 138 pMC in BOMB CARBON—OPTION 3 is based on an average pMC value for a tree that lived 30-60 years ago.

BIOBASED MATERIALS OF MARINE AND AQUATIC ORIGIN: RESERVOIR EFFECT

22.11 Materials of marine origin will be depleted in ^{14}C relative to the atmosphere. This depletion is due to excess limestone carbonate in ocean waters and is termed reservoir effect. A globally modeled average for this depletion is about 3-6 pMC. Additionally, local effects are well known, especially in areas of upwelling. Generally speaking, these can add another 3-4 pMC to the dilution (6-10 pMC total). These values are most accurately related to food chains which incorporate dissolved inorganic carbon (DIC) into the tissue and tests of the individuals.

22.12 Reservoir correction is not known to apply to photosynthesizing marine organisms such as seaweed, kelp, and phytoplankton. Reservoir effects from materials of freshwater origins such as lakes streams, rivers and springs will be variable depending on what bedrock the water is exposed to and what aerobic or anaerobic biogenic activity may be on-going within the system. Aquatic plants growing in waters fed by natural hot springs are cited to be as much as 50 % depleted.

22.13 Indeterminate error will increase as deviation from REF inherent to the source location of marine and aquatic biobased materials. There is no exact measure to quantify this effect from the % biobased or % biogenic carbon content result. Approximations must be made.

22.14 Complex systems of terrestrial derived and aquatic derived biobased components are to be expected. Indeterminate error cannot be quantified in these cases. Calculation and reporting of results should be per AQUATIC OPTION 3 as listed below to best account for variation in REF due to multiple REF values associated with the biobased components.

INSTRUCTIONS FOR CALCULATING AND REPORTING % BIOBASED CARBON CONTENT FOR MATERIALS OF AQUATIC ORIGIN

22.15 No correction to REF is required for natural marine organics such as seaweed, kelp, phytoplankton, or other organisms which photosynthesize.

22.16 AQUATIC OPTION 1: % biobased carbon content = pMC / (REF/105)

REF is corrected by 105 pMC for the modeled global average of depletion in marine sea waters.

If the result is greater than REF report as 100% biobased carbon content:

Example 1: sample pMC = 101 pMC, REF = 101.5 pMC

% biobased carbon content = 101 / (101.5/105) = 104 pMC; 104 pMC > REF (101.5 pMC); result = 100 %

Example 2: sample pMC = 95 pMC, REF = 101.5 pMC

% biobased carbon content = 95 / (101.5/105) = 98 %

22.17 AQUATIC OPTION 2: % biobased carbon content = pMC / (REF/108)

REF is corrected by 108 pMC to account for additional local depletion.

If the result is greater than REF, report as 100 % biobased carbon content.

Example 1: sample pMC = 98 pMC, REF = 101.5 pMC

% biobased carbon content = 98 / (101.5/108) = 104 pMC; 104 pMC > REF (101.5 pMC); result = 100 %

Example 2: sample pMC = 93 pMC, REF = 101.5 pMC

% biobased carbon content = 93 / (101.5/108) = 99 %

22.18 AQUATIC OPTION 3: % biobased carbon content = pMC / (REF/X)

REF is corrected by X pMC based on empirical data supporting unique correction for the biobased material.

22.19 The above examples apply equally to % biogenic carbon content results. In consideration of all sources of total error, % biobased carbon content and % biogenic carbon content are rounded to the nearest 1 and assigned an error of 3 % absolute as the final result.

FINAL REPORTING OF RESULTS

22.20 Final reports shall include the following:

(A) Name of testing laboratory,

(B) Date of testing,

(C) Standard name and version,

(D) REF value used,

(E) % biobased carbon content or % biogenic carbon content, ±3 % absolute,

(F) Designation of results as:

(a) % biobased carbon content,

(b) % biogenic carbon content,

(c) % biobased carbon content on a mass basis,

(d) % biogenic carbon content on a mass basis.

(G) Percent modern carbon, ±1 sigma RSD,

(H) BOMB CARBON OPTION with justification, if applicable,

(I) AQUATIC OPTION with justification, if applicable,

(J) Validation criteria supporting validity of the results (quality assurance report, blanks, etc.),

(K) All participating laboratories, including supporting validation data from each laboratory,

(L) Disclosure if any participating laboratory works with artificial ^{14}C.

23. Keywords

23.1 accelerator mass spectrometry; biobased; biogenic; bomb carbon; ^{14}C (carbon-14); carbon dating; isotope ratio mass spectrometry; liquid scintillation counting; new carbon; old carbon; percent modern carbon

APPENDIX

(Nonmandatory Information)

X1. FIGURES

NOTE X1.1—Biobased initiatives are pursuant to Presidential (Executive) Orders 13101, 13123, 13134, 13693, Public Laws (106-224), AG ACT 2003, and other Legislative Actions all requiring Federal Agencies to develop procedures to identify, encourage and produce products derived from biobased, renewable, sustainable and low environmental impact resources so as to promote the Market Development Infrastructure necessary to induce greater use of such resources in commercial, non-food products. Section 1501 of the Energy Policy Act of 2005 (Public Law 109–58) and EPA 40 CFR Part 80 (Regulation of Fuels and Fuel Additives: Renewable Fuel Standard Requirements for 2006) require petroleum distributors to add renewable ethanol to domestically sold gasoline to promote the nation's growing renewable economy, with requirements to identify and trace origin. The US Agricultural Act of 2014 continues support of biobased product application through the Biobased Markets Program (also known as the BioPreferred Program).

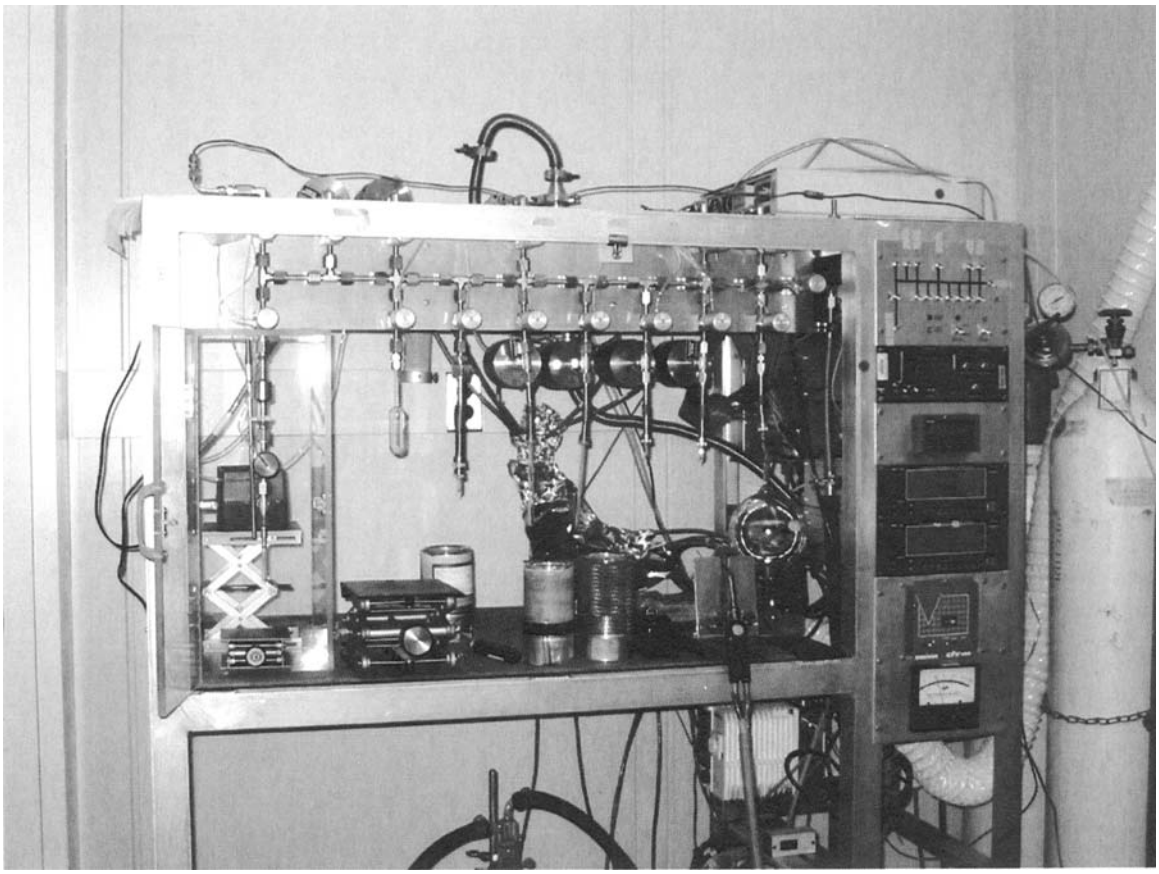

FIG. X1.1 Example of a Gas Transfer Manifold

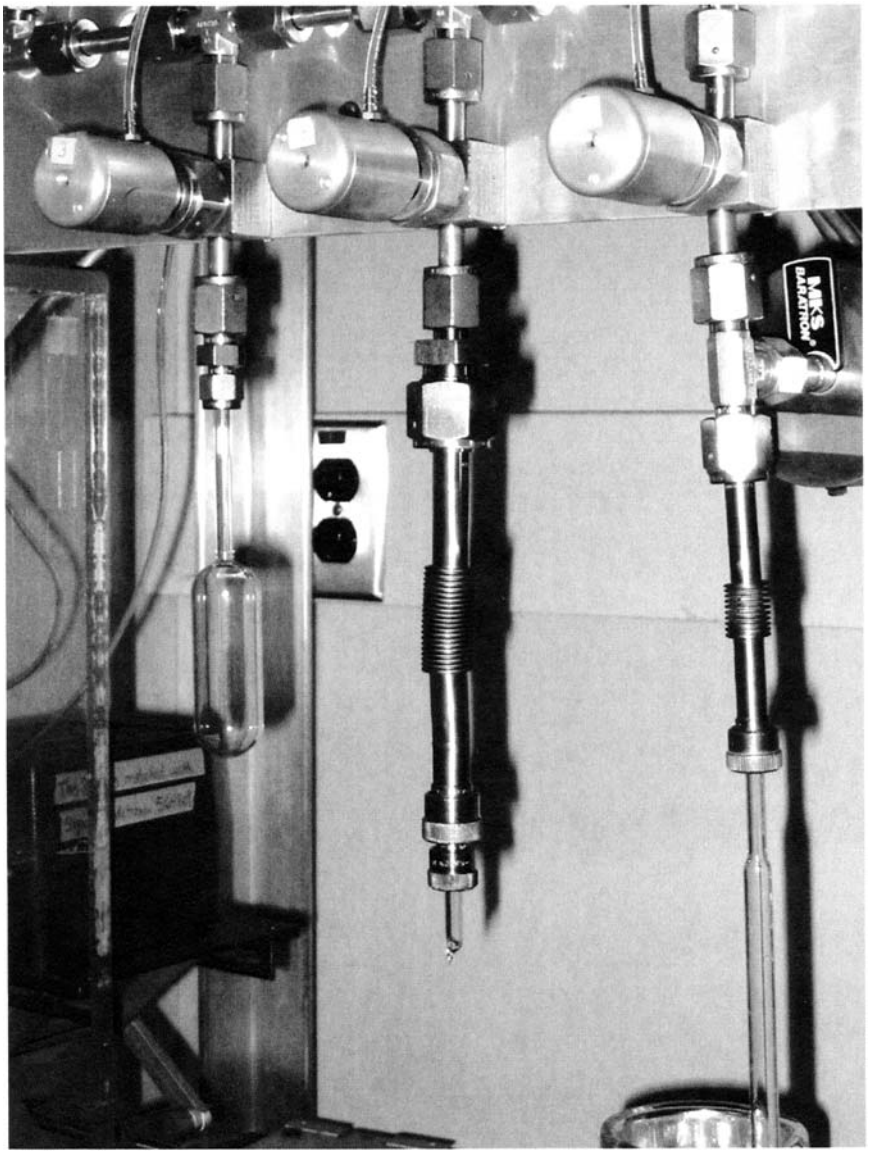

FIG. X1.2 Example of a Flexible Glass Tube Cracker

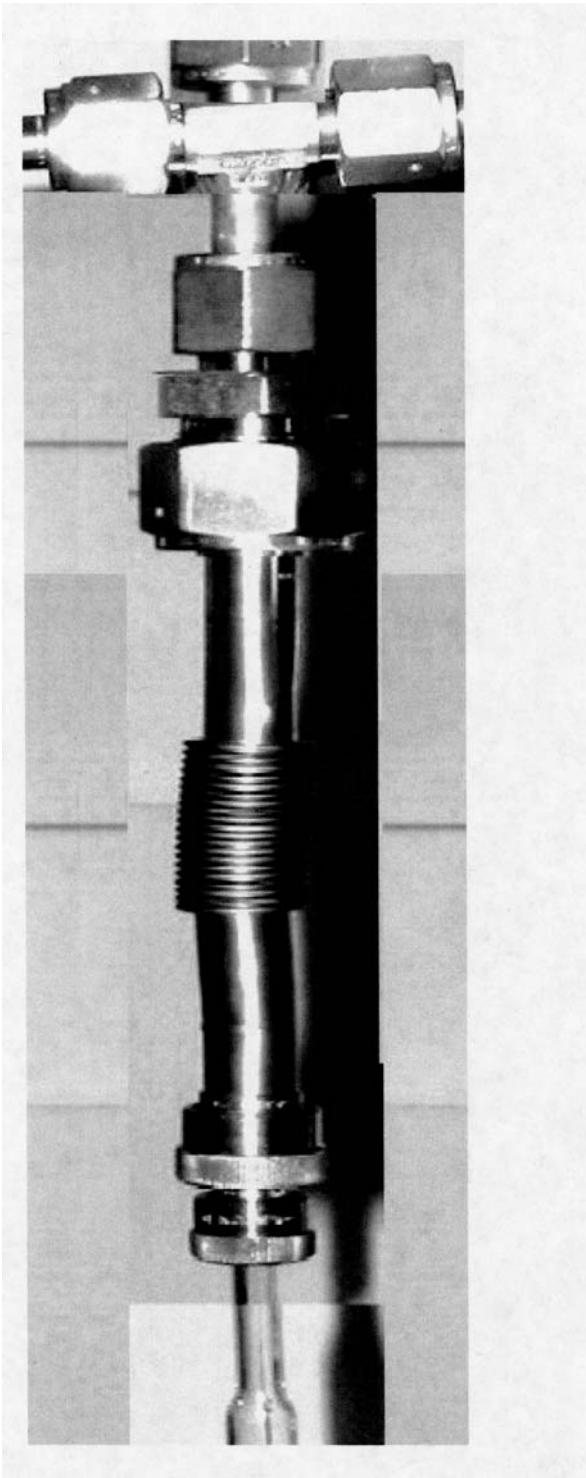

FIG. X1.3 Example of a Flexible Tube Cracker with Three-way Valve

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SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D6866 - 21) that may impact the use of this standard. (March 15, 2022)

(1) Revised 9.4, 13.3, and Tables 1 and 2.

Committee D20 has identified the location of selected changes to this standard since the last issue (D6866 - 20) that may impact the use of this standard. (January 15, 2021)

(1) Revised 9.4, 13.3, and Tables 1 and 2.