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Standard Test Methods for Determining the Biobased Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis[1]

This standard is issued under the fixed designation D 6866; 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 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.

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 Currently, there are no ISO test methods that are equivalent to the test methods outlined in this standard.

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

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 883 Terminology Relating to Plastics

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 D 883 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 *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 by 10^6 dpm / uCi (**13**,**16**).[3]

3.3.2 *dps*—disintegrations per second (rather than minute as above) (**13**,**16**).

3.3.3 *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) Bq (**13**,**16**).

3.3.4 *specific activity (SA)*—refers to the quantity of radioactivity per mass unit of product, that is, dpmh % (**13**,**16**).

3.3.5 *automated efficiency control (AEC)*—a method used by scintillation counters to compensate for the effect of quenching on the sample spectrum (**13**).

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

3.3.7 *accelerator mass spectrometry (AMS)*—an ultrasensitive technique 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 abundance to a level of 1 in 10^{15}. At these levels, uncertainties are based on counting statistics through the Poisson distribution (**7**,**8**).

3.3.8 *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 (**1**,**3**,**6**,**7**,**13-18**).

3.3.9 *coincidence circuit*—a portion of the electronic analysis system of a Liquid Scintillation Counter which acts to reject

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

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

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

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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 (**6,13,16**).

3.3.10 *coincidence threshold*—the minimum decay energy required for a Liquid Scintillation Counter to detect a radioactive event. The ability to set that threshold is a requirement of any LSC used in these test methods (**13,16**).

3.3.11 *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 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 the f_M ratio had decreased to ca. 1.2 (**7,8**).

3.3.12 *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 (**3,6,16**).

3.3.13 *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 (**13,16,26**).

3.3.14 *cocktail*—the solution in which samples are placed for measurement in a LSC. Solvents and Scintillators (chemicals that absorbs decay energy transferred from the solvent and emits light (photons) proportional in intensity to the decay energy) (**3,6,13,16**).

3.3.15 *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 (**7,13,16**).

3.3.16 *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 (**13,16,17,31**).

3.3.17 *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 (**13,16**).

3.3.18 *external standard*—a radioactive source placed adjacent to the liquid sample in to produce scintillations in the sample for the purpose of monitoring the sample's level of quenching. Required with Method (A) (**13,16**).

3.3.19 *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 (**13,16,19**).

3.3.20 *fluorescence*—the emission of light resulting from the absorption of incident radiation and persisting only as long as the stimulation radiation is continued (**13,16,24**).

3.3.21 *fossil carbon*—carbon that contains essentially no radiocarbon because its age is very much greater than the 5730 year half-life of ^{14}C (**7,8**).

3.3.22 *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 5730 years (**7,13,24**).

3.3.23 *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 (**13,16**).

3.3.24 *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, the activity of the Internal Standard, and the Internal Standard must be of certified activity (**13,16**).

3.3.25 *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 (**8**), the fraction of modern carbon is multiplied by 0.93 (as of the year 2004).

3.3.26 *noise pulse*—a spurious signal arising from the electronics and electrical supply of the instrument (**13,16,20,28**).

3.3.27 *phase contact*—the degree of contact between two phases of heterogeneous samples. In liquid scintillation counting, better phase contact usually means higher counting efficiency (**13,16**).

3.3.28 *photomultiplier tube (PMT, pmt)*—the device in the LSC that counts the photons of light simultaneously at two separate detectors (**28,31**).

3.3.29 *pulse*—the electrical signal resulting when photons are detected by the Photomultiplier tubes (**13,16,17,31**).

3.3.30 *pulse height analyzer (PHA)*—an electronic circuit which sorts and records pulses according to height or voltage (**13,16,17,31**).

3.3.31 *pulse index*—the number of afterpulses following a detected coincidence pulse (used in three dimensional or pulse height discrimination) to compensate for the background of a liquid scintillation counter performing (**13,17,28,31**).

3.3.32 *quenching*—any material that interferes with the accurate conversion of decay energy to photons captured by the PMT of the LSC (**1,3,6,13,14,16,19**).

3.3.33 *region*—regions of interest, also called window and/or channel in regard to liquid scintillation counters. Refers to an energy level or subset specific to a particular isotope (**3,13,17,20,28**).

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3.3.34 *scintillation reagent*—chemicals that absorbs decay energy transferred from the solvent and emits light (photons) proportional in intensity to the decay energy (**3**,**13**,**28**).

3.3.35 *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 (**3**.**13**,**16**,**28**).

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

3.3.37 *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 (**13**,**16**,**17**).

3.3.38 *true beta event*—an actual count which represents atomic decay rather than spurious interference (**9**,**10**).

3.3.39 *flexible tube cracker*—the apparatus in which the sample tube (Break Seal Tube) is placed (**4**,**5**,**9**,**10**).

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

4. Significance and Use

4.1 Presidential (Executive) Orders 13101, 13123, 13134, Public Laws (106-224, 107.117), AG ACT 2003 and other Legislative Actions all require 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.

4.2 Method A utilizes Liquid Scintillation Counting (LSC) radiocarbon (^{14}C) techniques to quantify the biobased content of a given product with maximum total error of 15 % count, which is associated with sample preparation and actual counting. This test method is based on LSC analysis of CO_2 cocktails after collecting the CO_2 in a suitable absorbing solution.

4.3 Method B utilizes Accelerator Mass Spectrometry (AMS) and Isotope Ratio Mass Spectrometry (IRMS) techniques to quantify the biobased content of a given product with possible uncertainties of 1 to 2 % and 0.1 to 0.5 %, respectively. Sample preparation methods are identical to Method A, 9.2–9.5. Method B diverges after 9.5 and rather than LSC analysis the sample CO_2 remains within the vacuum manifold and is distilled, quantified in a calibrated volume, transferred to a quartz tube, torch sealed. Details are given in 12.7-12.10. The stored CO_2 is then delivered to an AMS facility for final processing and analysis.

4.4 Method C uses LSC techniques to quantify the biobased content of a product. However, whereas Method A uses LSC analysis of CO_2 cocktails, Method C uses LSC analysis of 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).

4.5 Although Methods A and C are less sensitive than that of using AMS/IRMS, they have two distinct advantages: *(1)* lower costs per evaluation, and *(2)* much higher instrument availability worldwide. Benzene synthesis is the preferred method to be used when sample size is not an issue. Indeed, LSC is the most widely used measurement for ^{14}C determination. Method B will be used primarily in extraordinary situations such as when the authenticities of the LSC radiocarbon results are in dispute, when sample size is greatly restricted or costly per mass of sample, or when the carbon content of the sample is less than 10 % by weight.

4.6 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 $^{14}C/^{12}C$ content is determined relative to the modern carbon-based oxalic acid radiocarbon Standard Reference Material (SRM) 4990c, (referred to as HOxII). It is compositionally related directly to the original oxalic acid radiocarbon standard SRM 4990b (referred to as HOxI), and is denoted in terms of f_M, that is, the sample's fraction of modern carbon. (See Terminology, Section 3.)

4.7 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.

4.8 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. Strong bases used for CO_2 absorption, including Carbosorb E+ which is also flammable, are particularly hazardous and instructions in *Material Safety Data Sheets* should be followed with special concern for eye protection. Radioactive ^{14}C compounds should be handled and disposed of in accordance with State and Federal Regulations.

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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 Material Safety Data Sheets for proper handling procedures).

METHOD A

6. Detailed Requirements

NOTE 1—Acceptable tolerance levels of ±5 % are standard to this method unless otherwise stated.

6.1 Low Level Liquid Scintillation analyzers with active shielding.

6.2 Anticoincidence systems such as 2 and 3 Photomultiplier Tubes (Multidetector systems).

6.3 Coincidence circuits.

6.4 Software that includes thresholds, and statistics; Pulse rise and shape discrimination, and three Dimensional Spectrum Analysis.

6.5 Use of External and Internal Standards.

6.6 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, 20-mL Low Potassium glass count vials.

6.7 No single Liquid Scintillation Counter is specified for this method. However, minimum counting efficiency and control of background interference is specified. Like all analytical instruments, LS counters require study as to their specific components and counting optimization.

6.8 Standardization of sample preparation is required.

6.9 External and internal standards must be used in LSC operation.

6.10 Standardization and optimization of 20-mL sample vials, which must be of clean, low potassium glass with PTFE insert tops. Inspect scintillation vials for contaminants such as dirt, oils, or residues. Do not use the vials if they do not appear to be clean.

NOTE 2—Plastic vials should not be used for this method.

6.11 Optimization of Scintillation Cocktail, CO_2 trap reagents, and additives such as emulsifiers, surfactants, alcohols, and sample material is required.

6.12 Optimization of reagents shall include sample to reagent volume, scintillator to CO_2 trap reagent and additive volumes and compatibility of all reagents.

6.13 Quench curves and counting efficiency and background optimization should be performed using a reference standard based on comparison to NIST oxalic acid reference standards and the same reagents and counting parameters as the samples.

6.14 Counting efficiency of the sample shall be determined by adding to a vial a known activity of the same radionuclide and computing the increase of the sample cpm.

6.15 The internal standard technique for computing counting efficiency should be calculated by the equation:

$$E = \frac{(cpmb - cmpa)}{D} \quad (1)$$

where:

E = counting efficiency,
$cpma$ = standard counts of (STDCT) sample without added known activity,
$cpmb$ = counts of (STDCT) sample plus added known activity, and
D = dpm of the internal standard.

Other counting interference concerns that must be addressed as part of specific instrument calibration and normalization include luminance, static electricity, random noise, temperature and humidity variability.

6.16 Alternate regions of interest parameters may be used based upon testing of twenty, 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 energy windows counting should be determined by comparison of E^2/bkg values to obtain the highest count efficiency and the lowest background and other interference. Counting efficiency of less that 60 % is unacceptable and can be improved by LSC instrument optimization and sample/reagent compatibility or shielding improvements.

6.17 All samples will be allowed to equilibrate for a minimum of 8 h prior to counting and will be inspected for phase separation after the period of equilibration and prior to counting.

6.18 Samples will be counted for a minimum of 20 h with region of interest integrals (RIO) channels including RIO energy levels of 10 to 82 in 120 min subsets with complete spectra saved to disk as well as raw data for later statistical analysis and inclusion with final report.

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

7. Apparatus and Reagents

NOTE 3—Certain commercial equipment, instruments or materials are identified to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the ASTM or by NIST, nor does it imply that the materials or equipment are necessarily the best available for the purpose. A great deal of effort has been expended to optimize reagents. Suggestions are provided for ease of practice of the method.

7.1 A key to the ease of application of Method (A) is the selection of cocktail components. The interaction and compatibility of these chemicals can produce one of the greatest sources of interference with the method. One possible combination for Method (A) = 12 mL of Ultima Gold Scintillation Reagent + 6 mL of Carbosorb CO_2 trapping reagent (that contains the trapped CO_2 resulting from combustion of the sample) + 2 mL of high quality (spectrometer grade) methanol. Although other combinations are allowed, the combination used must produce an efficiency of greater than 75 % using the Reference Standard from NIST. Otherwise the combination should not be used. Commercial oxidizers are available, and can be adapted to produce a carbon dioxide sample for carbon dating. Such a commercial oxidizer may be used to prepare the

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samples for LSC analysis in Method (A) if the adaptations can produce a sample with the following minimum requirements:

7.1.1 Temperature of oxidation and oxidation time are sufficient to produce carbon recovery as CO_2 in CO_2 trap reagent at a minimum of 98 %.

7.1.2 LSC Count Efficiency of the sample is greater than 60 %.

7.2 *LSC Apparatus*:

7.2.1 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.

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

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

7.2.4 Three-way valve adapted to the manifold at one valve to vacuum, another to cryogenic liquid Nitrogen, and the other valve position closed to all but the sample.

7.2.5 A second three-way valve adapted to the manifold at one valve to cryogenic liquid Nitrogen, to a valve connected to a reservoir of liquid CO_2 trap reagent, and the other valve position closed to all but the sample.

7.2.6 A sample bulb adapted to the manifold.

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

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

7.2.9 Flexible Tube Cracker.

7.2.10 Break Seal Tube.

7.2.11 Liquid Scintillation Analyzer as described in Section 6.

7.2.12 Clean scintillation vials, 20-mL volume, with PTFE-lined screw caps.

7.2.13 Long thin pipettes for transfer of the sample from the sample bulb to the scintillation vial.

7.3 *LSC Reagents*:

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

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

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

7.3.4 Liquid nitrogen.

7.3.5 Scintillation reagent.

7.3.6 CO_2 trapping reagent.

7.3.7 Methanol, spectrometry grade.

8. Sample Preparation and Analysis

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

8.2 Based on the stoichiometry of the product material, sufficient sample mass shall be weighed such that 0.500 to 1.000 g of carbon are quantitatively recovered as CO_2. 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 101.3 Pa or less. 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 400°C for 2 to 4 h. Otherwise the material will be torch sealed at one end and furnace-baked at 900°C for ≥2 h.

8.5 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 the photo in the Appendixes to these test methods. The materials are composed of stainless steel. Compression fittings with appropriate welds are used to assemble the individual parts. This and alternative assemblies are also identified in the References section of these test methods (**4,5,9,10**).

8.6 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 also attached to a separate port on the manifold.

8.7 A three-way valve (or electronic equivalent) attached to the sample bulb will be open to allow the CO_2 to enter the sample bulb. It will be then turned to allow the addition of 6 mL of CO_2 trapping reagent. The three-way valve is then closed and the sample is allowed to remain undisturbed for a minimum of 1 h. The sample should then be further processed within 3 h.

8.8 After 1 to 3 h, the sample bulb is removed from the manifold. The trapping reagent is then transferred to a 20 mL glass Scintillation vial.

8.9 To the sample vial is added 2 mL of methanol and 12 mL of compatible scintillation reagent.

8.10 A PTFE-lined cap is screwed tight on the vial and the vial is inverted 10 times.

8.11 All samples will then be allowed to equilibrate for a minimum of 8 h prior to counting and will be inspected for phase separation after the period of equilibration and prior to counting. Samples may be counted at any time after the 8 h as long as phase separation has not taken place.

8.12 The ^{14}C content shall be determined in a Liquid Scintillation Counter with optimization of the instrument as described in the References section.

8.13 Samples will be maintained for recounting within the laboratory for a minimum of 180 days.

8.14 The sample will then be disposed of in accordance with State and Federal Regulations.

9. Interpretation

9.1 The counts shall be compared, directly or through secondary standards, to the ^{14}C oxalic acid SRM 4990c, with stated uncertainties. Significantly lower ^{14}C counts indicate the presence of ^{14}C-depleted carbon. Zero percent ^{14}C, when compared to the standard, signifies the entire lack of ^{14}C atoms in a material thus indicating a fossil (for example, petroleum

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based) carbon source. One hundred percent ^{14}C, after correction for the post-1950 bomb injection of ^{14}C into the atmosphere, likewise signifies an entirely modern carbon source. The percent modern carbon can be slightly greater than 100 % due to the continuing, but diminishing, effects of the 1950s nuclear testing programs. Because all sample ^{14}C activities are referenced to a "pre-bomb" standard, all percent modern carbon values must be multiplied by 0.93 to correct for the bomb carbon and to subsequently obtain the true biobased content of the sample.

METHOD B

10. Apparatus and Reagents

10.1 *AMS and IRMS Apparatus*:

10.1.1 A vacuum manifold system for 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:

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

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

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

10.1.5 A calibrated sample collection volume with associated temperature readout.

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

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

11. AMS and IRMS Reagents

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

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

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

11.4 Liquid nitrogen.

12. Sample Preparation

12.1 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 %.

12.2 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.

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

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

12.5 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.

12.6 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 the photo below. 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 (**4**,**5**,**9**,**10**).

12.7 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.

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

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

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

12.11 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.

13. Analysis, Interpretation, and Report

13.1 $^{14}C/^{12}C$ and $^{13}C/^{12}C$ isotopic ratios are counted (^{14}C) and measured $^{13}C/^{12}C$ using accelerator mass spectrometry. The isotopic ratios of $^{14}C/^{12}C$ and $^{13}C/^{12}C$ are determined relative to the appropriate primary reference material, that is, SRM 4990c and RM 8544, for ^{14}C and ^{13}C, respectively. Zero percent ^{14}C represents the entire lack of ^{14}C atoms in a material thus indicating a fossil (for example, petroleum based) carbon source. One hundred percent ^{14}C, after correction for the post-1950 bomb injection of ^{14}C into the atmosphere, likewise indicates an entirely modern carbon source. The percent modern carbon can be slightly greater than 100 % due to the continuing, but diminishing, effects of the 1950s nuclear testing programs. Because all sample ^{14}C activities are referenced to a "pre-bomb" standard, all percent modern carbon values must be multiplied by 0.93 to correct for the bomb carbon and to subsequently obtain the true biobased content of the sample. References for reporting carbon isotopic ratio data are given in Refs (**26**,**2**) for ^{14}C and ^{13}C, respectively.

13.2 All percent modern carbon (pMC) values obtained from the radiocarbon analyses must be corrected for isotopic fractionation (**27**) using stable isotope data ($^{13}C/^{12}C$ ratios)

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