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Standard Guide for Sampling and Reporting of Results for Determination of Percent Biobased Content of Materials via Carbon Isotope Analysis[1]

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INTRODUCTION

The biobased content of a material and the resources consumed in creation of the material, both energy and raw materials are defined in Guide D6852. These resources are expressed as carbon equivalent. Percent Biobased Carbon Content represents new or recently fixed carbon, opposed to fossil carbon fixed millions of years ago. Test Methods D6866 presents two methods for experimentally determining the percentage of recently fixed carbon in a sample by means of its radioisotope content, allowing direct determination of its biobased content. The following guide represents a companion document to Test Methods D6866 and defines the sampling and sample handling procedures for the radioisotope methods for determination of biobased content.

There are a great variety of biobased materials that may be tested using one of the radioisotope methods, with a wide range of physical characteristics and special sampling problems.

It is not the intent of this guide to provide specific sample collection and handling instructions for a specific material. Rather, the guide presents general outlines to be followed in sampling procedures and encourages the use of existing material-specific sampling procedures validated by extensive use in industry. The emphasis in the guide is to provide thorough and transparent reporting that allows subsequent evaluation of the validity of the claims regards biobased content.

1. Scope

1.1 This guide provides a framework for collecting and handling samples for determination of biobased content of materials by means of the carbon isotope method described in Test Methods D6866. Tests for sampling adequacy based on the standard statistical tools are provided. In addition, reporting of the results, including sampling techniques and handling procedures and chain-of-custody issues are discussed.

1.2 This guide is concerned with collecting representative samples within a given material or a lot, not with lot-to-lot variations such as considered in quality control schemes.

1.3 Biobased materials often represent sampling problems specific to a given material, such as heterogeneity, and so forth, which require employment of material-specific sampling methods. The use of specialized sampling methods already accepted and validated by industries that manufacture and/or use the biomaterial is encouraged. However, all sampling techniques, especially non-standard techniques developed for specific materials must be reported in sufficient detail to allow critical assessment of the techniques used.

1.4 Carbon isotope analysis involves thermal processing in presence of oxidants. Compatibility of any given material with Test Methods D6866 must be assessed. Special attention must be given to materials with potential for explosion hazards, such as peroxides, nitrated compounds, azides, and so forth. Examples of peroxide-forming compounds are ethers, some ketones and a number of other compounds.

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

1.6 *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 requirements prior to use.*

NOTE 1—There is no known ISO equivalent to this standard.

[1] This guide is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.96 on Environmentally Degradable Plastics and Biobased Products.

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2. Referenced Documents

2.1 *ASTM Standards:*[2]

D6852 Guide for Determination of Biobased Content, Resources Consumption, and Environmental Profile of Materials and Products (Withdrawn 2011)[3]

D6866 Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis

E105 Practice for Probability Sampling of Materials

E122 Practice for Calculating Sample Size to Estimate, With Specified Precision, the Average for a Characteristic of a Lot or Process

2.2 *Other Reference:*

Cramer, H., "Elements of Probability Theory," Wiley & Sons, NY, 1961

3. Terminology

3.1 *Definitions:*

3.1.1 *representative sample*—a sample or subunit of material that shows a composition, within statistical limits, that is the same as would be detected if the whole material would be analyzed as a sample.

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

3.1.3 *biobased carbon*—carbon in a sample that is of recent origin, as evidenced by its ^{14}C isotope content.

3.1.3.1 *Discussion*—^{14}C decays with a half-life of about 5700 years and thus fossil carbon, whose age since fixation is measured in millions of years, does not contain any ^{14}C.

3.1.4 $\mu(0)$—true biobased content of lot.

3.1.5 $\mu(n)$—lot average biobased content based on analysis of n samples from the lot.

3.1.6 $E = I\mu(0) - \mu(n)I$, *abs*—maximum tolerable error for the sample average, or maximum acceptable difference between average of samples and true average of the lot, $\mu(0)$

3.1.6.1 *Discussion*—The $I\_\_\_\_I$ are supposed to designate absolute value.

3.1.7 $n(k)$—number of samples that must be tested to provide assurance that the average of these samples lies within E of the true average with a probability defined by k.

3.1.8 k—factor defining the degree of accuracy desired in estimation of the lot average from the average of n samples.

3.1.9 $[sigma](0)$—estimated or experimentally determined standard deviation of the analytical procedure.

3.1.10 *S.D.*—standard deviation (abbreviation used in text).

4. Significance and Use

4.1 The carbon isotope analysis is designed to be an adjunct to other information in determination of biobased content, specifically the manufacturer's records. It is also a means of verifying the authenticity of a disputed lot of material which may be manufactured by different means, from different raw materials. FTIR or other chemical analysis means will identify the molecule as being ethanol, but not give indication of the source (that is, fossil carbon versus modern carbon). The carbon isotopes will give both indication of source and the presence of a mixture of sources.

4.2 Representative sampling and handling methods are clearly a prerequisite to obtaining accurate results from the radiocarbon composition determination and any other quantitative analytical method.

4.3 This guide provides for accurate and complete reporting of the sample collection, handling, chain of custody, sample preparation and treatment that allows any independent party to assess the validity of the reported biobased content of the material.

5. Sample Collection

5.1 This guide is designed for materials that can be classified either as solids or liquids.

5.2 If there is a standard sampling technique for the material to be tested that is widely accepted by the industry, such a procedure may be used and the details of sampling recorded, as called for under Reporting.

5.3 The primary requirements for any sampling strategy are that *(a)* the sample be representative of the material to be tested and that *(b)* the quantity or weight of sample be accurately established.

5.4 Test Methods D6866 presents two methods for determining % biobased content: *(1)* LSC or Liquid Scintillation Counting of sample carbon that has been converted to benzene, with presently established maximum error of 3 % absolute, and *(2)* AMS or Accelerated Mass Spectrometry, with maximum error of about 1 to 3 %. LSC requires a sample that contains 1.0 to 4.0 g of carbon. AMS requires a sample that contains 1-10 mg of carbon.

5.5 Samples should be taken from the most homogenous subunit of an object or material. If there are suspected gradual trends in the sample, the material should be subdivided to a set of smaller units or sub lots that can be considered essentially homogenous, except for possible small-scale graininess in some materials (that is, particle board). These sub lots are then treated as independent units or lots. In cases of extreme heterogeneity, portions of the object should be sub-sampled, combined and analyzed in the same proportion they exist within the object. In the case where this is still not practical, portions should be combusted separately to CO_2 in the same proportions they exist within the object, and the CO_2 (or sub-sample thereof) be used as the homogenous representation of the biobased carbon in the product.

5.6 The sampling should be performed in accordance with the probability sampling methods described in Practice E105. The lot should be divided into sample size elements. These elements should be assigned numbers and the samples (elements) collected using random numbers, as described in Practice E105.

[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 last approved version of this historical standard is referenced on www.astm.org.

5.7 If there is a good technical reason to believe that the material is truly homogenous, such reasons must be fully and thoroughly recorded as described under Reporting. The randomized sample selection may then be bypassed.

5.8 An example of such a homogenous material may be a polymer consisting of alternating units (A-B)-n, where the alternating structure is dictated by the chemical reaction and where one of the units, either A or B, contains biobased carbon.

5.9 Representative sampling requires that either the material be homogenous on scale of sampling, or the initial sample taken is large enough to encompass inhomogeneities in a representative way, as described above.

5.10 The estimate of the % biobased content of the material is the average of several independently analyzed samples. The number of samples to be included in the average depends on the desired accuracy, as described in 6.2.

6. Determination of Number of Samples Required

6.1 The determination of the required number of samples described in 6.2 assumes that *(a)* the variability of results arises primarily from a single source and *(b)* that the error is randomly distributed.

6.2 The number of independent samples to be analyzed depends on *(a)* the maximum acceptable error E in estimation of the biobased content, *(b)* the desired degree of certainty regarding the correctness of the answer, and *(c)* the standard deviation [sigma](0) of the analysis procedure.

6.3 The procedure for estimating the number of samples needed is given in Practice E122. Assuming that the analytical error is randomly distributed, the number of samples needed for a desired E is given by:

$$n(k) = (k \times \sigma(0)/E)^2 \quad (1)$$

where:

k = factor defining the probability of the deviation of the average of n samples exceeding E; that is, the degree of certainty of correctness of the estimate. Some k-values and the corresponding levels of uncertainty are presented in Practice E122,
k = 1.64 for 10 % chance of the error exceeding E,
k = 2 for 5.5 % chance of the error exceeding E, and
k = 3 for 0.3 % chance (practical certainty).

6.3.1 These numbers are derived from the properties of the random distribution curve.

NOTE 2—Following examples use hypothetical values for [sigma](0). They do not represent the values for the two analytical methods described in Test Methods D6866, for which the [sigma](0) are not yet available.

6.4 *Example I*

[sigma](0) is 5 %.

The expected biobased content is 50 %.

It is desired to establish with 90 % certainty that the biobased content is greater than 45 %.

Thus:

$E = 50 - 45 = 5$

$k = 1.64$

$n = (1.64 \times 5/5)^2 = 2.69 = \sim 3$

6.4.1 That means that the average of 3 samples must be at least 50 % to state with 90 % assurance that the sample biobased content is 45 % or greater. If the average of the samples is less than 50 %, then the effective E is less and the number of samples must be increased until the criteria specified by the above formula are met.

6.5 *Example II*

Let [sigma](0) = 5 %.

E = 2 %.

It is desired to state with 95 % assurance that the true mean does not lie outside of E from the measured average.

Hence:

k = 2 (rounded off; true uncertainty is 5.5 %)

n(95 %) = $(2 \times 5/2)^2 = 25$

6.5.1 The above illustrates the rapid increase in number of samples required as the E decreases and/or need for assurance increases. Obviously, it would be worthwhile to seek an instrument with smaller [sigma](0). The effects of decreased variability are shown in example below.

6.6 *Example III*

Let:

E = 1 %

k = 2 %

[sigma](0) = 2 %

n(95 %) = $(2 \times 1/1)^2 = 4$ samples

6.6.1 Thus, the required number of samples is decreased from 25 to 4, or roughly by a factor of 6.

6.7 It is recommended that at least three samples be taken, even if the theoretical accuracy does not require that many, to verify that the underlying assumptions about the material and sampling are valid. For example, a spread of 10 units between two samples in Example III would be highly suspicious. Such a spread would be possible, but not probable. In this case additional sampling would be appropriate.

6.8 If E is greater than 2 × [sigma](0), one can assume uncertainty in the answer is not a problem. Thus the number of samples would be controlled by 3.14.

7. Sample Preparation

7.1 Sample preparation is discussed in Test Methods D6866, Section 8 for LSC and Section 12 for AMS.

7.2 Size reduction of the particles of initial sample is often required so that a final, smaller sample can be obtained that is still representative of the initial sample. This is especially true for the AMS method due to the smaller sample size.

7.3 The recommended procedure for the size reduction of pliable materials (for example, many plastics) is cryogenic grinding. The grinding should be done with liquid N_2 cooling. Liquid or dry CO_2 should be avoided to prevent contamination of sample with extraneous carbon.

7.4 The final particle size should be 250 µm or less.

7.5 Powdered or granular materials must be well mixed due to possible segregation of particles by density.

7.6 Transfer of sample after weighing should be avoided, if at all possible. The ultimate destination of the sample is the

combustion tube, where the carbon is converted to CO_2. If at all possible, the tube should be tared and the weight of the sample obtained as difference from the tare weight and final weight of the tube.

8. Special Considerations for Liquids

8.1 All liquids should be either single phase or relatively stable emulsions (such as latex paints) which can be stirred and sampled without significant settling of the particles in the interim. Any turbidity should be removed by centrifuging and the clear liquid and the sediment examined separately. In case of viscous liquids or materials with volatile components the transfer problems make accurate weighing of the sample much more difficult. Effort should be made to obtain the sample weight in the combustion tube, rather than transferring a previously weighed sample to the oxidation tube.

9. Chain of Custody

9.1 Any sample of a material that is being used for authentication of biobased content should be accompanied by a chain of custody sheet. Each individual handling the sample should mark his/her possession time and transfer to the next person. All mailings of the samples should be done in containers with initialed seal, to be broken by the recipient and so noted in the custody sheet.

10. Report

10.1 It is essential that the reporting include all phases of the sample acquisition and handling. This guide provides much flexibility in the specific procedures used, provided the procedure is fully and clearly documented.

10.2 The report must include the following:

10.2.1 Description of material: morphology, other salient features of the material,

10.2.2 Basis for choice of the subunit or lot to be tested,

10.2.3 Rationale for choice of sampling plan, including reason for not using a random sampling plan,

10.2.4 Method of sample collection,

10.2.5 Drying and storing operations,

10.2.6 Size reduction methods,

10.2.7 Final sample weighing,

10.2.8 Equipment used to perform radioisotope measurements: type, location, established [sigma](0),

10.2.9 Analytical results for each sample (as “percent modern carbon (pMC) with one relative standard deviation),

10.2.10 Reason for discarding a sample, if applicable,

10.2.11 Chain of custody sheet, and

10.2.12 Version of ASTM D6866 represented.

11. Precision and Bias

11.1 The precision and bias of the radioisotope methods are discussed in Test Methods D6866.

11.2 The weighing accuracy is to be 1 mg for both the LSC and the AMS methods.

11.3 Provided that proper procedures are followed, sampling should contribute minimally to the ultimate error in estimation of biobased content.

12. Keywords

12.1 biobased; radioisotope authentication; sampling