Designation: D8473 – 22

Standard Test Method for Determining the Biobased content of Liquid Hydrocarbon Fuels Using Liquid Scintillation Counting with Spiked Carbon-14[1]

This standard is issued under the fixed designation D8473; 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 test method covers quantitatively determining biocarbon content of liquid hydrocarbon fuels with a focus on those produced in a typical petroleum refinery using liquid scintillation counting (LSC). The method is designed to generate analogous results as Test Method D6866 Method C, for low quench samples, without the need of benzene synthesis. The purpose is to be able to use the produced data to report biocarbon content of refinery products to regulatory agencies and monitor refinery operation. The method does not address regulatory reporting or fuel performance.

1.2 The method is needed to support refinery operations when bio-feeds are co-processed with petroleum within a reactor with a focus on samples with 100 % biocarbon or less (not for ^{14}C labeled species). It allows refineries to report the biocarbon content of refinery products to regulatory agencies such as the Environmental Protection Agency (EPA) or California Air Resources Board (CARB) to comply with regulatory statutes such as The Renewable Fuel Standard (RFS) or Low Carbon Fuel Standard (LCFS).

1.3 This test method is applicable to any liquid fuel product, petroleum based (pure hydrocarbon), biobased (such as renewable diesel or those that can contain oxygenates such as ethanol), or blends, that contain 1 % to 100 % by mass biocarbon where an instrument background can be experimentally determined using a sample of similar matrix that contains no measurable carbon-14.

1.4 This test method makes no attempt to teach the basic principles of the instrumentation used although minimum requirements for instrument selection are referenced in Refs (**1-11**).[2] 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.

1.5 *Pre-Requisite Requirements For Method Execution*—This test method uses artificial carbon-14 (^{14}C) within the method. Great care shall be taken to prevent laboratory contamination of the elevated ^{14}C. Once in the laboratory, artificial ^{14}C can contaminate a variety of laboratory surfaces that can lead to artificially high sample biocarbon measurements. If vigorous cleaning attempts to remove the artificial ^{14}C from a laboratory are unsuccessful, instrumentation and sample preparation may have to be moved to a new laboratory away from the contamination or the laboratory may have to rely on outside third-party labs for analysis. Specific procedural steps have been incorporated into this method that minimize the risk of sample and lab contamination. Wipe tests and quality assurance samples can validate absence of contamination. In the event of contamination in the laboratory or instrument, vigorous cleaning protocols shall be implemented, and analysis cannot be resumed until the lab and instrument are free of contamination. Accepted requirements are:

1.5.1 Working with the elevated ^{14}C samples in a separate and defined area away from the instrument and the preparation of any non-spiked samples.

1.5.2 Using separate personnel to prepare the spiked samples and non-spiked samples.

1.5.3 Using separate laboratory spaces with separate HVAC systems for the handling of spiked and non-spiked samples. The use of separate fume hoods that have separate exhaust ventilation satisfies this requirement.

1.5.4 Weekly wipe tests of ^{14}C sample handling area(s) to detect lab contamination.

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

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the*

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0F on Absorption Spectroscopic Methods.

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

Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D5291 Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants

D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

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

2.2 *Other Standards:*

DIN 51637 Liquid Petroleum Products – Determination of the Bio-Based Hydrocarbon Content in Diesel Fuels and Middle Distillates Using Liquid Scintillation Method[4]

CSN EN 16640 Bio-based products - Bio-based carbon content - Determination of the Bio-Based Carbon Content using the Radiocarbon Method[5]

3. Terminology

3.1 The definitions of terms used in this test method are referenced in case the practitioner requires further information regarding the practice of the art of isotope analysis and to facilitate performance of these test methods.

3.2 *Definitions:*

3.2.1 *background radiation, n*—the radiation in the natural environment; this includes cosmic radiation and radionucleotides present in the local environment, for example, materials of construction, metals, glass, and concrete.

3.2.2 *background sample, n*—sample with no detectable ^{14}C (such as a carboniferous sample that should not contain any measurable ^{14}C because of its geologic age).

3.2.3 *biobased, adj*—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.

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

3.2.5 *biofeed, n*—a feedstock sourced from a plant or animal.

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

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

3.2.8 *carbon-14 (^{14}C), n*—naturally occurring radioactive isotope of carbon that contains six protons and eight neutrons with a true half-life of 5730 years.

3.2.9 *cocktail, n*—the solution in which samples are mixed for measurement in an LSC.

3.2.10 *coincidence circuit, n*—a portion of the electronic analysis system of an LSC which acts to reject pulses that are not received from the two or three 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 this test method.

3.2.11 *coincidence threshold, n*—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 this test method.

3.2.12 *coincidence time, n*—the time period used by the coincidence circuit that is used to determine if a detection event is counted or rejected.

3.2.13 *contemporary carbon, n*—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) using 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 (**10**, **11**).

3.2.14 *counting time, n*—the total time used by the liquid scintillation counter to count sample ^{14}C decays.

3.2.15 *counts per minute (cpm), n*—the average number of counts the liquid scintillation counter detections during analysis; is used to derive dpm.

3.2.16 *decay (radioactive), n*—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.

3.2.17 *delay time, n*—the time the instrument waits after method is started before it starts counting; allows user to delay the start of analysis to allow sample photoluminescence to stop before counting is initiated.

3.2.18 *discriminator, n*—an electronic circuit which distinguishes signal pulses according to their pulse height or energy;

[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 Deutsches Institut für Normung e.V. (DIN), Am DIN-Platz, Burggrafenstrasse 6, 10787 Berlin, Germany, http://www.din.de.

[5] Available from European Standards, Krimicka 134, 318 00 Pilsen, Czech Republic, VAT: CZ09567909, https://www.en-standard.eu/.