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Standard test method for determining the biobased content of liquid petroleum products using radiocarbon analysis by accelerator mass spectrometry

液体石油产品中含放射性碳的生物基含量测定 加速器质谱法

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Warning: The use of this document may involve certain hazardous materials, operations, equipment; however, it does not address all safety concerns. Therefore, users shall establish appropriate safety precautions and determine the applicability of relevant regulatory restrictions before using this document.

1 Scope

This document specifies a method for determining the biobased content of liquid petroleum products by radiocarbon analysis using accelerator mass spectrometry.

This document applies to organic liquid petroleum products containing carbon-based components that produce carbon dioxide (CO_2) gas when burned in the presence of oxygen.

Caution: This document is intended for use in laboratories that are not exposed to artificial ^{14}C. Artificial ^{14}C is commonly used in biomedical research in accelerator mass spectrometry (AMS) laboratories, where biobased materials can be present at concentrations exceeding 1000 or 100% and 100000 times greater than 1% biobased material. Artificial ^{14}C can be ubiquitous on laboratory door handles, pens, desks, other surfaces, potentially contaminating samples and producing falsely high biobased content results. Isolation has been shown to be the only effective method to prevent contamination. Laboratories exposed to artificial ^{14}C require a completely independent chemistry laboratory and rigorous testing and validation procedures. Acceptable conditions include the following:

a) Disclosure to clients that the laboratory whose samples are being tested also handles ^{14}C;

b) The chemistry laboratories handling ^{14}C and testing biobased carbon samples are located in different buildings;

c) Separate testing personnel and no access to each other's buildings;

d) No shared common areas such as lunchrooms and offices;

e) No sharing of supplies or chemicals;

f) Quasi-simultaneous quality assurance measurements are performed on the detectors to ensure that the detectors themselves are not contaminated.

2 Normative references

The contents of the following documents, through normative references, constitute essential provisions of this document. For dated references, only the edition corresponding to that date applies to this document. For undated references, the latest edition (including all amendments) applies to this document.

GB/T 4756 Method for manual sampling of petroleum liquids

NB/SH/T 0656 Determination of carbon, hydrogen and nitrogen in petroleum products and lubricants - Elemental analyzer method

3 Terms and definitions

The following terms and definitions apply to this document.

3.1

Radiocarbon ^{14}C

A radioactive isotope of carbon, namely carbon-14 (^{14}C); the nucleus of carbon-14 consists of 6 protons and 8 neutrons.

Note: ^{14}C is produced by cosmic rays striking nitrogen atoms in the air. Its half-life is approximately 5730 years ± 40 years. On earth, 99% of carbon exists as ^{12}C, approximately 1% as ^{13}C, only one part per trillion (0.0000000001%) is ^{14}C, presenting in the atmosphere.

3.2

Half-life

The time required for half of the nuclei of a radioactive element to decay. The half-life of ^{14}C is approximately 5730 ± 40 years.

3.3

Fossil carbon

Carbon which is essentially free of radioactive ^{14}C, because its age is much greater than the half-life of ^{14}C.

3.4

Modern carbon

Organic carbon content

The mass percentage of organic carbon in a sample relative to the total mass of the sample.

3.11

Biobased carbon content on mass basis

The percentage of mass of biobased carbon in a sample to the total mass of the sample.

3.12

Accelerator mass spectrometry (AMS)

An ultrasensitive technique used to measure naturally occurring radionuclides. In AMS, atoms are ionized and accelerated to high energies; separated based on momentum, charge, mass; counted individually in a Faraday collector or solid-state or gas detector. This high-energy separation is very effective in filtering out isobaric interferences, allowing AMS to accurately measure the abundance ratio of $^{14}C/^{12}C$ to the order of 10^{-15}. At this level, the uncertainty is based on the statistics of a Poisson distribution.

4 Method overview

Carbon-based components in a specimen are burned to CO_2 in a high-temperature oxygen environment. The CO_2 is then purified, dehydrated, collected, reduced to graphite. The $^{14}C/^{12}C$ ratio in graphite is measured using accelerator mass spectrometry (AMS) and compared to international radiocarbon reference materials, to obtain the percentage modern carbon (pMC) or fraction modern carbon (f_M). The pMC is divided by the atmospheric correction factor (REF) used at the time of specimen measurement, to determine the specimen's biobased carbon content.

5 Application of the method

5.1 This document provides a method for accurately determining the biobased carbon content of liquid petroleum products derived from living organisms. Carbon in living organisms (such as crops or plants growing in nature) exchanges in equilibrium with atmospheric CO_2 until respiration or metabolism ceases. When applying this test method, special consideration shall be given to samples from artificial environments; samples that have absorbed CO_2 from artificial environments are not within the scope of this method.

5.2 This method can directly distinguish between carbon derived from biomass and carbon derived from fossil fuels, for example, distinguishing between biofuel ethanol derived from biomass such as corn and sorghum and coal-based ethanol derived from fossil fuels such as coal. This document can be used to quantify the biofuel content in fossil fuels, for example, by measuring the amount of biofuel ethanol added to ethanol gasoline and the amount of biobased additives added to aviation fuel. This document can provide testing methods for the promotion and implementation of products containing biofuels, such as ethanol gasoline.

5.3 This document does not consider the sample's inherent properties, function, geographic origin, or environmental influences.

5.4 All laboratories implementing this document shall properly use international standard reference materials, to ensure the traceability of carbon isotope determinations and the validity of the stated uncertainties. The primary international standard reference materials for ^{14}C are NIST SRM 4990B (designated as OXI, HOxI, Oxalic acid I) or NIST SRM 4990C (designated as OXII, HOxII, Oxalic acid II). The f_M value for NIST SRM 4990B is 1.0398; the f_M value for NIST SRM 4990C is 1.3407.

5.5 The $^{14}C/^{12}C$ isotope ratio of the sample is measured, using accelerator mass spectrometry (AMS). The $^{14}C/^{12}C$ isotope ratio of the sample is compared to the $^{13}C/^{12}C$ isotope ratio of an international standard radiocarbon reference material (NIST SRM 4990B or NIST SRM 4990C), then corrected using the ratio of the stable isotopes $^{13}C/^{12}C$. This yields the percentage modern carbon (pMC) or the fraction modern carbon (f_M) of the sample.

5.6 The pMC value measured by accelerator mass spectrometry (AMS) shall be corrected using the ratio of the stable isotopes $^{13}C/^{12}C$. Whenever possible, the $^{13}C/^{12}C$ value measured within the AMS should be used for correction. If the instrument cannot measure the $^{13}C/^{12}C$ value, calibration shall be performed using $\delta^{13}C$ measured by IRMS (stable isotope mass spectrometry), CRDS (cavity ring-down spectroscopy isotope carbon analyzer), or other equivalent techniques that provide a measurement accuracy within ±0.3‰. For $\delta^{13}C$ measurements, standard materials shall be NIST SRM 8539, NIST SRM 8540, NIST SRM 8541, NIST SRM 8542, or other equivalent materials traceable to Vienna Pee Dee Belemite (VPDB).

5.7 The accelerator mass spectrometer used in this document has a measurement error of 0.1% ~ 0.5% (1 RSD) and a relative standard deviation of 0.1 pMC ~ 0.4 pMC. However, comparative experiments have found that the total uncertainty of biobased carbon content measured by different laboratories can reach ±3% (absolute value). This error does not include uncertain sources of error due to biological sources.

5.8 Unless otherwise specified, the error in this method for determining the percentage of modern carbon in international standard reference materials shall not exceed ±5% of the certified value.

6 Safety considerations

6.1 This document does not address specific safety and regulatory requirements related to radioactivity, sample preparation, instrument operation. Users of this document are responsible for establishing appropriate safety and health practices. When implementing this document, users shall also comply with relevant Chinese regulations, particularly those related to the use of open radioactive sources. Although ^{14}C is one of the safest isotopes, relevant Chinese regulations shall be followed when implementing the methods in this document.

6.2 Glass and metal used must withstand temperatures exceeding 900 °C in a closed oxygen-containing system; failure to do so may pose a safety hazard. Operators shall avoid implosion/explosion of glass tubes. Laboratory safety precautions shall always be observed, with particular attention to eye, respiratory, skin protection.

7 Instrumentation

7.1 Accelerator mass spectrometer: Determine the ratio of $^{14}C/^{12}C$ in a sample with an instrumental measurement error of 0.1% ~ 0.5% (1RSD). Details regarding instrument operation shall be obtained from the instrument manufacturer.

7.2 Vacuum manifold system: A device that combusts samples into CO_2 and purifies and collects the resulting gas. It has gas lines for exhausting air and non-condensable gases; functions for introducing samples, distilling water, transferring cryogenic gases, monitoring temperature and pressure. This device is used to quantitatively combust carbon-based components in samples of varying complexity. This document recommends the device shown in Figure A.1 in Appendix A. However, other devices with continuous flow interfaces and CO_2 capture capabilities are also suitable, provided that a CO_2 recovery rate of 100% ± 5% can be achieved. This apparatus requires the following components, with appropriate weld fittings used to assemble the components:

a) Fragile seal tube, see Figure A.2 in Appendix A;

b) Flexible fracture tube, see Figure A.2 in Appendix A;

c) A vacuum pump capable of achieving a vacuum of 101 Pa or less;

d) A pressure sensor with a coupled or integrated signal-responsive controller;

e) A CO_2 calibration chamber with a volume scale and temperature readout, see Figure A.2 in Appendix A;

f) Clean quartz tubing for sample combustion and gas transfer, dosing, storage;

g) A hydrogen/oxygen torch or other heating device and/or a gas torch for sealing the quartz tubing.

7.3 CO_2 reduction system to graphite: An apparatus for reducing CO_2 to graphite. The reduction process must prevent contamination with CO_2 from the air and loss of CO_2 from the sample. This process shall be performed in an enclosed space.

7.4 Temperature-controlled furnace: Capable of reaching 950 °C.

7.5 Analytical balance: Sensitivity 0.00001 g.

8 Reagents and materials

8.1 Dehydrating agent: A slurry mixture of dry ice (frozen solid CO_2) and ethanol at -76 °C, or other material capable of separating water from CO_2 in the CO_2 collector.

8.2 International standard reference material for radiocarbon: NIST SRM 4990B or NIST SRM 4990C.

8.3 Note: Available from the National Institute of Standards and Technology (NIST) in the United States and also from the Atomic Energy Agency (IAEA) in Vienna, Austria.

8.4 Oxygen source: High-purity oxygen, $\geq$ 99.999% purity, or solid copper oxide (CuO).

8.5 Silver: For halide removal.

8.6 Liquid nitrogen.

8.7 Iron, cobalt, or other catalyst for the reduction of CO_2 to graphite.

8.8 Hydrogen: Purity $\geq$ 99.9%.

9 Sampling

Representative samples shall be collected in accordance with the provisions of GB/T 4756.

10 Preparation of graphitized specimens

10.1 The specimen preparation procedures described in this document utilize a commonly used method for quantitatively combusting carbon components in specimen matrices of varying complexity. While this preparation procedure is recommended, other equipment with continuous flow interfaces and CO_2 capture capabilities is also suitable, provided that a CO_2 recovery rate of 100% ± 5% can be achieved.

10.2 Weigh a sufficient amount of specimen. Calculations indicate that the carbon content of the CO_2 recovered after sample combustion shall be 1 mg ~ 10 mg. Place the weighed specimen in a pre-cleaned quartz tube that has been baked at 900 °C for at least 2 h and sealed at one end. A quartz tube with an outer diameter of 2 mm and an inner diameter of 1 mm is typically used. Any quartz tube size that can accommodate a sufficient specimen is acceptable.

10.3 Then transfer the weighed quartz tube containing the test specimen to another quartz tube of appropriate size, typically 6 mm outer diameter and 4 mm inner diameter.

10.4 Then connect the above quartz tubes to the vacuum manifold and evacuate to 101 Pa or less.

10.5 If the test specimen is volatile or contains volatile components, first freeze the test specimen in the quartz tube to -196 °C with liquid nitrogen before evacuating the tube. After evacuating the tube, seal the quartz tube containing the test sample and then burn the test specimen in the sealed quartz tube in a 900 °C temperature-controlled furnace for 2 ~ 4 hours, to convert it to CO_2.

10.6 After combustion, score the quartz tube containing the CO_2 to create a breakable seal that will break cleanly within the flexible break tube in the vacuum manifold system (see Appendix A, Figure A.2).

10.7 The breakable sealed tube containing CO_2 is broken within the flexible break tube in the vacuum manifold system, releasing the CO_2 into a CO_2 collector, which is connected to the vacuum manifold (see Appendix A, Figure A.2), where it is rapidly frozen by cryogenic liquid nitrogen.

10.8 A desiccant is used to distill and separate the water and CO_2 in the CO_2 collector. The water is condensed in the sample collector, whilst the CO_2 sublimates into a gas and is transferred to a CO_2 calibration chamber at another port on the vacuum manifold (see Appendix A, Figure A.2) for condensation.

10.9 After all the CO_2 has been transferred, close the CO_2 calibration chamber and allow the CO_2 to equilibrate to room temperature.

10.10 Use the ideal gas law to calculate the CO_2 recovery rate.

10.11 Release the CO_2 from the CO_2 calibration chamber into the graphitization system to reduce the CO_2 to graphite.

10.12 The process of converting CO_2 gas to graphite requires the use of an iron or cobalt catalyst and the reduction is carried out according to formulas (1) and (2):

$$CO_2+H_2 \longrightarrow H_2O+CO \quad \cdots\cdots (1)$$

$$CO+H_2 \longrightarrow H_2O+C \quad \cdots\cdots (2)$$

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