DRAFT INTERNATIONAL STANDARD
ISO/DIS 4504

ISO/TC **61**/SC **9**

Secretariat: **KATS**

Voting begins on:
2022-09-13

Voting terminates on:
2022-12-06

Plastics — Polyethylene (PE) — Determination of co-monomer content by solution state ^{13}C-NMR spectrometry

ICS: 83.080.20

This document is circulated as received from the committee secretariat.

Reference number
ISO/DIS 4504:2022(E)

© ISO 2022

COPYRIGHT PROTECTED DOCUMENT

Contents

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC *61*, *Plastics*, Subcommittee SC 9, *Thermoplastic materials*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Plastics — Polyethylene (PE) — Determination of co-monomer content by solution state ^{13}C-NMR spectrometry

WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the user's responsibility to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1   Scope

This document specifies two methods for the determination of the of co-monomer content of polyethylene products by solution state ^{13}C-NMR spectrometry (nuclear magnetic resonance spectroscopy):

— Method A: inverse gated decoupling method;

— Method B: insensitive nuclei enhanced by polarization transfer method.

This document is applicable to copolymers of ethylene having a content of other 1-olefinic monomers of less than 50 % (m/m) according to ISO 17855-1.

This document is not applicable to ethylene homopolymers or copolymers in which ethylene is polymerized with two or more type 1-olefin comonomers.

2   Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 472, *Plastics — Vocabulary*

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1043-1, *Plastics — Symbols and abbreviated terms — Part 1: Basic polymers and their special characteristics*

ISO 17855-1, *Plastics — Polyethylene (PE) moulding and extrusion materials — Part 1: Designation system and basis for specifications*

3   Terms, definitions, symbols and abbreviated terms

For the purposes of this document, the terms and definitions given in ISO 472 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1   Terms and definitions

3.1.1
INEPT
insensitive nuclei enhanced by polarization transfer.
a type of NMR technique which is insensitive nuclei enhanced by polarization transfer.

3.1.2
refocused INEPT
INEPT pulse program with a pair of refocus delay and π inversion pulse in both sensitive and insensitive nuclei resonance channels.

3.2   Symbols

T_1 Longitudinal relaxation time

$T_{1, max}$ longest T_1 of atom nuclei

^{13}C Carbon 13.

^1H Hydrogen 1.

T_p polarization transfer time.

T_R refocusing time.

3.3   Abbreviated terms

NMR   nuclear magnetic resonance.

^{13}C-NMR   Carbon 13 Nuclear Magnetic Resonance.

PFT-NMR   pulse Fourier transform nuclear magnetic resonance spectrometer.

LOQ   Limit of quantitation.

LOD   Limit of detection.

SNR   signal-to-noise ratio.

SW   sweep width.

4   Principle

4.1   Polyethylene samples are dissolved in the deuterated solvent and put in the magnetic field. Radio pulses are applied to excite the nuclei, and a set of resonance signals are generated from nuclei with different chemical circumstances. With proper excitation pulse or pulses combination, the intensities of a resonance signal are proportional to the molar fractions of nuclei with identical or similar chemical circumstances. A linear relationship is established between the carbon molar content of different chemical shifts and the comonomer content. In this document, two methods with different NMR pulse programs are established to acquire ^{13}C NMR spectra. Method A utilizes the "single pulse with inverse gated proton decoupling". NMR pulse program to excite the ^{13}C nuclei directly. Method B excites the proton initially by the "Refocused INEPT with proton decoupling" NMR Pulse program to enhance the signal sensitivity of ^{13}C nuclei.

5   Reagents and materials

5.1   Deuterated reagents, deuterated *ortho*-dichlorobenzene, or *para*-dichlorobenzene (*o*-DCB-*d*4 or *p*-DCB-*d*4), or 1,1,2,2-tetrachloroethane-d*2* (TCE-d*2*), analytical grade.

5.2   Relaxation reagents, chromium (III) acetylacetonate, analytical grade.

6   Apparatus

6.1   PFT-NMR spectrometer, with a minimum magnet field strength of 7,05 Tesla (equivalent proton resonance frequency at 300 MHz, or ^{13}C nuclei resonance frequency at 75 MHz), capable of being maintained at 120 °C ± 1 °C.

6.2   Analytical balance, accurate to 1 mg.

6.3   Sample tube, capped NMR tube with 5 mm or 10 mm outer diameter.

6.4   Adjustable pipette, 5 ml capacity, meet the requirement of Class A defined in ISO 648.

6.5   Supplementary heating equipment, capable of uniformly heating the samples to 130 °C ± 1 °C. It can ensure that the sample tube is kept in a vertical position during the heating process.

7   Preparation and preservation of test samples

The samples can be obtained from materials in the form of powders, pellets, or moulded parts. To ensure the required accuracy of sample mass, large samples should be cut into smaller pieces. It is important that the laboratory receive a sample which is truly representative and has not been damaged or changed during transport or storage.

iTeh STANDARD PREVIEW

8   Method A – Inverse gated decoupling method

(standards.iteh.ai)

8.1   Sample preparation

8.1.1   Weigh nearest 30 mg of the test sample into a 5 mm sample tube ([6.3](#)) or nearest 120 mg of the test sample into a 10 mm sample tube ([6.3](#)).

Note   In some cases, larger sample mass is preferred to get a satisfying result. User of this method can choose any sample mass larger than the minimum requirement of [8.1.1](#) as long as the sample is able to be dissolved at 120 °C to 130 °C.

8.1.2   Add 0,4 ml to 0,6 ml of deuterated reagent ([5.1](#)) using adjustable pipette ([6.4](#)) to 5 mm sample tube ([6.3](#)), or 1,6 ml to 2,0 ml of deuterated reagent ([5.1](#)) using adjustable pipette ([6.4](#)) to 10 mm sample tube ([6.3](#)).

Note   Solution concentration can be modified according to the instrument magnetic field strength, on condition that the minimum signal-to-noise meets requirement of [Table 1](#).

8.1.3   Uniformly heat the sample part in the tube on a supplementary heating device at 120 °C to 130 °C until the whole sample is well dissolved in deuterated reagent, appropriate mechanical stirring is helpful for better dissolution of the sample in the deuterated reagent. Keep the sample tube in a vertical position during the heating step.

Note   Any method for uniformly dissolution is acceptable.

8.2 Procedure

8.2.1 Turn on the PFT-NMR Spectrometer (6.1) and warm up to readiness. Set up the PFT-NMR Spectrometer and detection instrument parameters. The instrument recommended parameters of method A are listed in Table 1.

Table 1 — Instrument parameters of method A

Parameters	Unit	Value
Pulse program	—	single pulse with inverse gated proton decoupling
Decoupling mode	—	composite pulse decoupling
Measurement temperature	°C	120 °C ± 1 °C
Relaxation delay [a]	s	$\geq 5 \times T_{1,\,max}$ (^{13}C nuclei)
Flip angle [b]	degree	90
Pulse width [c]	s	$< 4 \times SW\ (Hz)^{-1}$
Sweep width	ppm [d]	100
Offset resonance frequency of ^{13}C nuclei	ppm [d]	30
Window function (exponential)	Hz	2
Zero-filling	—	Equal to the time domain data size
LOQ [e]	—	SNR (branch CH-carbon peak): $\geq 20{:}1$ and SNR (isolated methylene carbon peak) : $\geq 4000{:}1$
LOD [e]	—	SNR (branch CH-carbon peak): $\geq 3{:}1$ and SNR (isolated methylene carbon peak) : $\geq 4000{:}1$

[a]   For most cases, 10 s is enough for method A to get a quantitative result. T_1 of ^{13}C nuclei can be determined for each sample. Precise T_1 of different carbon types in polyethylene copolymer are listed in Annex E by inversion recovery method.

[b]   The set flip angle of 90 degrees can satisfy method A to obtain quantitative results. In the case of high magnetic field NMR system, the flip angle range can be set from 30° to 90°.

[c]   The sweep width for method A is set based on the 100 MHz nuclear magnetic field strength of ^{13}C.

[d]   For the explanation of ppm, see bibliography.

[e]   The limit of quantification and limit of detection depends on the signal-to-noise ratio of the acquired spectrum. The chemical shift region of branch CH-carbon of different co-monomers have been listed in Annex F. The signal to noise ratio of branch CH-carbon is defined as the signal intensity for the region which given in Annex F divided by the peak to peak noise for the region from 50 to 70 ppm. The signal to noise ratio of isolated methylene carbons is defined as the signal intensity for the region of 29 to 31 ppm peaks divided by the peak to peak noise for the region from 50 to 70 ppm.

8.2.2 Transfer the sample tube to the NMR spectrometer and equilibrate 10 to 30 minutes.

8.2.3 Calibrate the 90° pulse width of ^{13}C nuclei before measurement.

8.2.4 Acquire the spectra. Execute phase and baseline correction requirement according to the spectrometer operation manual.

Note   Automatic spectra phase and baseline correction program which built-in acquisition software can be used to get a satisfying result. see bibliography 6 to 7 for more details.

8.2.5 Calibrate the maximum intensity peak (isolated methylene carbons) to 30 ppm.

8.3 Calculation

8.3.1 Use the obtained NMR spectrum to measure and sum the area between the appropriate integration limits listed in Annex A.

8.3.2 The sum of peak integral is substituted into the corresponding formula in Annex B.1 to calculate the mole percent 1-olefins. For calculation examples of method A, see Annex C.

8.3.3 Use the formula in Annex B.3 to convert the result from the mole percentage of 1-olefin to the number of branches per 1 000 carbons (br / 1 000 C).

9 Method B –-Insensitive nuclei enhanced by polarization transfer method

9.1 Sample preparation

9.1.1 See 8.1.1.

9.1.2 See 8.1.2.

Note   Solution concentration can be modified according to the instrument magnetic field strength, on condition that the minimum signal-to-noise meets requirement of Table 2.

9.1.3 See 8.1.3.

9.2 Procedure

9.2.1 The instrument recommended parameters of method B are listed in Table 2. For other content, see 8.2.1.

Table 2 — Instrument parameters of method B

Parameters	Unit	Value
Pulse program	—	refocus INEPT with proton decoupling
Decoupling mode	—	composite pulse decoupling
Measurement temperature	°C	120 °C ± 1 °C
Relaxation delay [a]	s	$\geq 5 \times$ T$_{1, max}$ (^{1}H nuclei)
Refocus time	s	$2{,}15 \times 10^{-3}$
Pulse width [b]	s	$< 4 \times$ SW (Hz)$^{-1}$
Sweep width	ppm [c]	100
Offset resonance frequency of ^{13}C nuclei	ppm [c]	30
Offset resonance frequency of ^{1}H nuclei	ppm [c]	1,2
Window function (exponential)	Hz	2
Zero-filling	—	Equal to the time domain data size

NOTE 1 Additional relaxation reagents (chromium (III) acetylacetonate) can be used for sample preparation. The ^{1}H nuclei T$_1$ value of copolymer can be 3 to 5 times reduced by adding 0,35 mg of additional relaxation agent to 5 mm sample tube, or 1,4 mg of additional relaxation agent to 10 mm tube, in procedure 9.1.2.

[a]   For most cases, 5 s of relaxation delay is enough by adding relaxation reagent to get a quantitative result. Precise T$_1$ value of different ^{1}H nuclei can be determined for each sample. T$_1$ of different ^{1}H nuclei types in polyethylene copolymer are listed in Annex E by inversion recovery method.

[b]   The sweep width for method B is set based on the 100 MHz field strength of ^{13}C.

[c]   For the explanation of ppm, see bibliography.

[d]   The limit of quantification and limit of detection depends on the signal-to-noise ratio of the acquired spectrum. The chemical shift region of branch CH-carbon of different co-monomers have been listed in Annex F. The signal to noise ratio of branch CH-carbon is defined as the signal intensity for the region which given in Annex F divided by the peak to peak noise for the region from 50 to 70 ppm. The signal to noise ratio of isolated methylene carbons is defined as the signal intensity for the region of 29 to 31 ppm peaks divided by the peak to peak noise for the region from 50 to 70 ppm.

Table 2 *(continued)*

Parameters	Unit	Value
LOQ [d]	—	SNR (branch CH-carbon peak): $\geq$ 20:1 and
		SNR (isolated methylene carbon peak) : $\geq$ 4000:1
LOD [d]	—	SNR (branch CH-carbon peak): $\geq$ 3:1 and
		SNR (isolated methylene carbon peak) : $\geq$ 4000:1

NOTE 1 Additional relaxation reagents (chromium (III) acetylacetonate) can be used for sample preparation. The ^{1}H nuclei T_1 value of copolymer can be 3 to 5 times reduced by adding 0,35 mg of additional relaxation agent to 5 mm sample tube, or 1,4 mg of additional relaxation agent to 10 mm tube, in procedure 9.1.2.

[a]   For most cases, 5 s of relaxation delay is enough by adding relaxation reagent to get a quantitative result. Precise T_1 value of different ^{1}H nuclei can be determined for each sample. T_1 of different ^{1}H nuclei types in polyethylene copolymer are listed in Annex E by inversion recovery method.

[b]   The sweep width for method B is set based on the 100 MHz field strength of ^{13}C.

[c]   For the explanation of ppm, see bibliography.

[d]   The limit of quantification and limit of detection depends on the signal-to-noise ratio of the acquired spectrum. The chemical shift region of branch CH-carbon of different co-monomers have been listed in Annex F. The signal to noise ratio of branch CH-carbon is defined as the signal intensity for the region which given in Annex F divided by the peak to peak noise for the region from 50 to 70 ppm. The signal to noise ratio of isolated methylene carbons is defined as the signal intensity for the region of 29 to 31 ppm peaks divided by the peak to peak noise for the region from 50 to 70 ppm.

9.2.2   See 8.2.2.

9.2.3   Calibrate the 90° pulse width of ^{1}H nuclei before measurement [5].

9.2.4   See 8.2.4.

9.2.5   See 8.2.5.

9.3   Calculation

9.3.1   See 8.3.1.

9.3.2   The sum of peak integral is substituted into the corresponding formula in Annex B.2 to calculate the mole percent 1-olefins. For calculation examples of method B, see Annex D.

9.3.3   See 8.3.3.

10 Expression of results

10.1   The result is expressed as a calculation result of once measurement value.

10.2   The calculated result is the content of the second monomer in the sample, expressed as a percentage.

10.3   The result should be reported in one decimal.

11 Precision

Precision data have been determined by testing involving 7 laboratories and 4 different polyethlyene samples. The results are summarized in Annex G.

12 Test Report

The test report shall include the following information:

a) a reference to this document (ISO 4504:20XX);

b) full description of the sample and its origin;

c) the number of test portions used, and the mass of each;

d) the method used (method A or method B);

e) the details of any operation not included in this International Standard, together with details of any incidents which may have influenced the results, such as the NMR parameters if different from those specified;

f) the test result obtained, including the results of the individual determinations.

g) the date of the test.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO/FDIS 4504
https://standards.iteh.ai/catalog/standards/sist/f0c00635-a429-4a85-aef4-589054eac8c3/iso-
fdis-4504