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

Plastiques — polyéthylène (PE) — Détermination de la teneur en co-monomères par spectroscopie RMN du carbone 13

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Foreword

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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

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.

1 Scope

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

— 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 a mass fraction of 50 %.

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*

3 Terms, definitions, symbols and abbreviated terms

3.1 Terms and definitions

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

ISO and IEC maintain terminology 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/

3.1.1
insensitive nuclei enhanced by polarization transfer
INEPT
^{13}C NMR method in which magnetisation is transferred from sensitive nuclei to directly linked insensitive nuclei enhanced by polarisation transfer

Note 1 to entry: See Reference [4].

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
^{1}H	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”[4]. NMR pulse program to excite the ^{13}C nuclei directly. Method B excites the proton initially by the “Refocused INEPT with proton decoupling”[5][6]. NMR Pulse program to enhance the signal sensitivity of ^{13}C nuclei. The principles of two different NMR spectrometer pulse programs are shown in Annex H.

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

Test 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 representative and has not been damaged or changed during transport or storage.

8 Method A — Inverse gated decoupling method

8.1 Sample preparation

8.1.1 Weigh approximately 30 mg of the test sample, put them into a diameter 5 mm sample tube (6.3) or weigh approximately 120 mg of the test sample, put them into a diameter 10 mm sample tube (6.3).

NOTE In some cases, larger sample mass is preferred to get a satisfying result. Any sample mass larger than the minimum requirement of 8.1.1 can be chosen, 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). Solution concentration can be modified according to the instrument magnetic field strength, on condition that the minimum signal to noise ratio should meet 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 can be 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	$\geq 5 \times T_{1,\,\text{max}}$ (^{13}C nuclei)
Flip angle [b]	degree	90
Pulse width [c]	s	$< 4 \times \text{SW (Hz)}^{-1}$
Sweep width	Hz/MHz	100
Offset resonance frequency of ^{13}C nuclei	Hz/MHz	30
Window function (exponential)	Hz	2
Zero-filling	—	Equal to the time domain data size
LOQ [d]	—	SNR (branch CH-carbon peak): ≥ 20:1 and SNR (isolated methylene carbon peak) : ≥ 4000:1
LOD [d]	—	SNR (branch CH-carbon peak): ≥ 3:1 and SNR (isolated methylene carbon peak) : ≥ 4000:1

[a] For most samples, 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° 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] 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 Hz/MHz to 70 Hz/MHz. The signal to noise ratio of isolated methylene carbons is defined as the signal intensity for the region of 29 Hz/MHz to 31 Hz/MHz peaks divided by the peak to peak noise for the region from 50 Hz/MHz to 70 Hz/MHz.

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

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[8][9].

NOTE Automatic spectra phase and baseline correction program which built-in acquisition software can be used to get a satisfying result.

8.2.5 Calibrate the maximum intensity peak (isolated methylene carbons) to 30 Hz/MHz.

8.3 Calculation

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

8.3.2 The results are substituted into the formulae in Annex B. The sum of peak integral is substituted into the corresponding formula in B.1 [i.e. Formulae (B.1) to (B.5)] to calculate the mole percent 1-olefins. For calculation examples of method A, see Annex C.

8.3.3 Use Formula (B.11) 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.

9.1.3 See 8.1.3.

9.2 Procedure

9.2.1 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, b]	s	$\geq 5\times T_{1,\,max}$ (^{1}H nuclei)
Polarization transfer time [b]	s	2×10^{-3}
Refocus time [b, c]	s	$2{,}15\times10^{-3}$
Pulse width [d]	s	$< 4 \times$ SW (Hz)$^{-1}$
Sweep width	Hz/ MHz	100
Offset resonance frequency of ^{13}C nuclei	Hz/ MHz	30

NOTE 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 samples, 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] See pulse program diagram in Annex H for more details.

[c] Some commercial NMR console do not bear the function of editing the polarization transfer time and refocus time directly at parameter setting interface, in this case, tests with some deviation on the polarization transfer time at a price of slightly lower SNR give equally satisfactory results.

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

[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 Hz/MHz to 70 Hz/MHz . The signal to noise ratio of isolated methylene carbons is defined as the signal intensity for the region of 29 Hz/MHz to 31 Hz/MHz peaks divided by the peak to peak noise for the region from 50 Hz/MHz to 70 Hz/MHz.

Table 2 *(continued)*

Parameters	Unit	Value
Offset resonance frequency of ^{1}H nuclei	Hz/MHz	1,2
Window function (exponential)	Hz	2
Zero-filling	—	Equal to the time domain data size
LOQ [e]	—	SNR (branch CH-carbon peak): ≥ 20:1 and SNR (isolated methylene carbon peak): ≥ 4000:1
LOD [e]	—	SNR (branch CH-carbon peak): ≥ 3:1 and SNR (isolated methylene carbon peak): ≥ 4000:1

NOTE 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 samples, 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] See pulse program diagram in Annex H for more details.

[c] Some commercial NMR console do not bear the function of editing the polarization transfer time and refocus time directly at parameter setting interface, in this case, tests with some deviation on the polarization transfer time at a price of slightly lower SNR give equally satisfactory results.

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

[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 Hz/MHz to 70 Hz/MHz . The signal to noise ratio of isolated methylene carbons is defined as the signal intensity for the region of 29 Hz/MHz to 31 Hz/MHz peaks divided by the peak to peak noise for the region from 50 Hz/MHz to 70 Hz/MHz.

9.2.2 See 8.2.2.

9.2.3 Calibrate the 90° pulse width of ^{1}H nuclei before measurement[7].

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 Sum of peak integral is substituted into the corresponding formula in B.2 [Formula (B.6) to (B.10) 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 Express the result 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 polyethylene samples. The results are summarized in Annex G.

The purpose of consistency test is to compare whether the results obtained by different methods are consistent. To verify whether the results of the two methods are consistent, results of the intra lab Student t-test and inter lab Student t-test are shown in Annex I.

12 Test report

The test report shall include the following information:

a) a reference to this document, i.e. ISO 4504:2023;

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 document, 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.

Annex A
(normative)

Spectral integration method and integration limits outlines

Use regions given in Table A.1 to find the peaks in the specific regions. Calculate the integrations of these peaks.

Table A.1 — Integration limits for ethylene copolymers

Co-monomer	Area	Region Hz/MHz
Propene	A_p	47,5~44,5
	B_p	39,8~36,8
	C_p	35,5~32,5
	D_p+E_p	32,5~25,8
	F_p	25,8~23,8
	G_p	22,5~18,5
	H_p	Peak at 21,6
1-butene	A_B	41,5~38,5
	A'_B	Peak at 39,4
	B_B	37,8~36,8
	C_B	36,0~33,2
	D_B+E_B	33,2~25,5
	F_B	25,2~24,0
1-hexene	A_H	41,5~40,5
	B_H	40,5~39,5
	C_H	39,5~37,0
	D_H	Peak at 35,8
	E_H	35,2~33,2
	F_H+G_H	33,2~25,5
	G_H	28,5~26,5
	H_H	24,9~24,1
1-octene	A_O	41,5~40,5
	B_O	40,5~39,5
	C_O	39,5~37,0
	D_O	Peak at 35,8
	E_O	35,4~33,2
	$F_O+G_O+H_O$	33,2~25,5
	H_O	28,5~26,5
	I_O	25,0~24,0
	J_O	24,0~22,0

NOTE Calibrate the maximum intensity peak (Isolated methylene carbons) to 30,0 Hz/MHz prior to integrate the spectra.

Table A.1 *(continued)*

Co-monomer	Area	Region Hz/MHz
4-methyl-1-pentene	A_M	46,5~43,5
	B_M	43,0~41,8
	C_M	41,8~40,5
	D_M	37,5~35,8
	E_M	35,8~34,2
	F_M	Peak at 33,7
	G_M	33,2~28,0
	H_M	28,0~26,6
	I_M	26,6~25,2
	J_M	Peak at 24,1
NOTE Calibrate the maximum intensity peak (Isolated methylene carbons) to 30,0 Hz/MHz prior to integrate the spectra.		

Annex B
(normative)

Summary of formulae

B.1 Method A — Formulae for calculating mole fraction composition

B.1.1 Mole fraction of propene in the ethylene-propene-1 copolymer *P*

$$P=\frac{6A_P+B_P+2C_P-2H_P}{4A_P+B_P+4C_P+2(D_P+E_P)+2F_P-2H_P} \tag{B.1}$$

where A_P, B_P, C_P, D_P, E_P, F_P, H_P are the integration areas acquired from Table A.1.

B.1.2 Mole fraction of butene in the ethylene-butene-1 copolymer *B*

$$B=\frac{4A_B+A'_B+4B_B+2C_B}{4A_B-A'_B+2B_B+2C_B+4(D_B+E_B)+4F_B} \tag{B.2}$$

where A_B, A'_B, C_B, D_B, E_B, F_B are the integration areas acquired from Table A.1.

B.1.3 Mole fraction of hexene in the ethylene-hexene-1 copolymer *H*

$$H=\frac{3A_H+2B_H+3C_H+3D_H+E_H}{3(F_H+G_H)-3A_H-5B_H+6C_H+6D_H+2E_H-3G_H-3H_H} \tag{B.3}$$

where A_H, B_H, C_H, D_H, E_H, F_H, G_H, H_H are the integration areas acquired from Table A.1.

B.1.4 Mole fraction of octene in the ethylene-octene-1 copolymer *O*

$$O=\frac{3A_O+2B_O+3C_O+3D_O+E_O}{3(F_O+G_O+H_O)-3A_O-5B_O+6C_O+6D_O+2E_O-3H_O-3I_O-3J_O} \tag{B.4}$$

where A_O, B_O, C_O, D_O, E_O, F_O, G_O, H_O, I_O, J_O are the integration areas acquired from Table A.1.

B.1.5 Mole fraction of 4-methylpentene-1 in the ethylene-4-methylpentene-1 copolymer *MP*

$$M=\frac{3A_M+2B_M+C_M+D_M+E_M+1{,}5F_M}{7{,}5A_M-B_M+2{,}5C_M+2{,}5D_M+2{,}5E_M+0{,}75F_M+3(G_M+H_M+I_M)-3H_M-3I_M-3J_M} \tag{B.5}$$

where A_M, B_M, C_M, D_M, E_M, F_M, G_M, H_M, I_M, J_M are the integration areas acquired from Table A.1.

B.2 Method B — Formulae for calculating mole fraction composition

B.2.1 Mole fraction of propene in the ethylene-propene-1 copolymer *P*

$$P=\frac{7{,}5A_P+1{,}5B_P+4C_P-3H_P}{6A_P+1{,}5B_P+8C_P+3(D_P+E_P)+3F_P} \tag{B.6}$$

where A_P, B_P, C_P, D_P, E_P, F_P, H_P are the integration areas acquired from Table A.1.

B.2.2 Mole fraction of butene in the ethylene-butene-1 copolymer *B*

$$B=\frac{8A_B+1{,}5A'_B+8B_B+3C_B}{8A_B-1{,}5A'_B+4B_B+3C_B+6(D_B+E_B)+6F_B} \quad (B.7)$$

where A_B, A'_B, C_B, D_B, E_B, F_B are the integration areas acquired from Table A.1.

B.2.3 Mole fraction of hexene in the ethylene-hexene-1 copolymer *H*

$$H=\frac{3A_H+2B_H+4C_H+4D_H+E_H}{3(F_H+G_H)-3A_H-5B_H+8C_H+8D_H+2E_H-3G_H-3H_H} \quad (B.8)$$

where A_H, B_H, C_H, D_H, E_H, F_H, G_H, H_H are the integration areas acquired from Table A.1.

B.2.4 Mole fraction of octene in the ethylene-octene-1 copolymer *O*

$$O=\frac{3A_O+2B_O+4C_O+4D_O+E_O}{3(F_O+G_O+H_O)-3A_O-5B_O+8C_O+8D_O+2E_O-H_O-J_O-3I_O} \quad (B.9)$$

where A_O, B_O, C_O, D_O, E_O, F_O, G_O, H_O, I_O, J_O are the integration areas acquired from Table A.1.

B.2.5 Mole fraction of 4-methylpentene-1 in the ethylene-4-methylpentene-1 copolymer *MP*

$$M=\frac{4{,}5A_M+3B_M+2D_M+1{,}5E_M+2F_M}{11{,}25A_M-1{,}5B_M+3{,}75C_M+5D_M+3{,}75E_M-4F_M+4{,}5(G_M+H_M+I_M)-4{,}5H_M-4{,}5I_M-4{,}5J_M}$$

(B.10)

where A_M, B_M, C_M, D_M, E_M, F_M, G_M, H_M, I_M, J_M are the integration areas acquired from Table A.1.

B.3 Conversion from mole fraction alkene-1 to branches per 1 000 carbons

$$N_{br}=\frac{1\,000X}{2E+nX} \quad (B.11)$$

where

N_{br} is the number of branches per 1 000 carbon atoms;

X is the mole percentage of co-monomer;

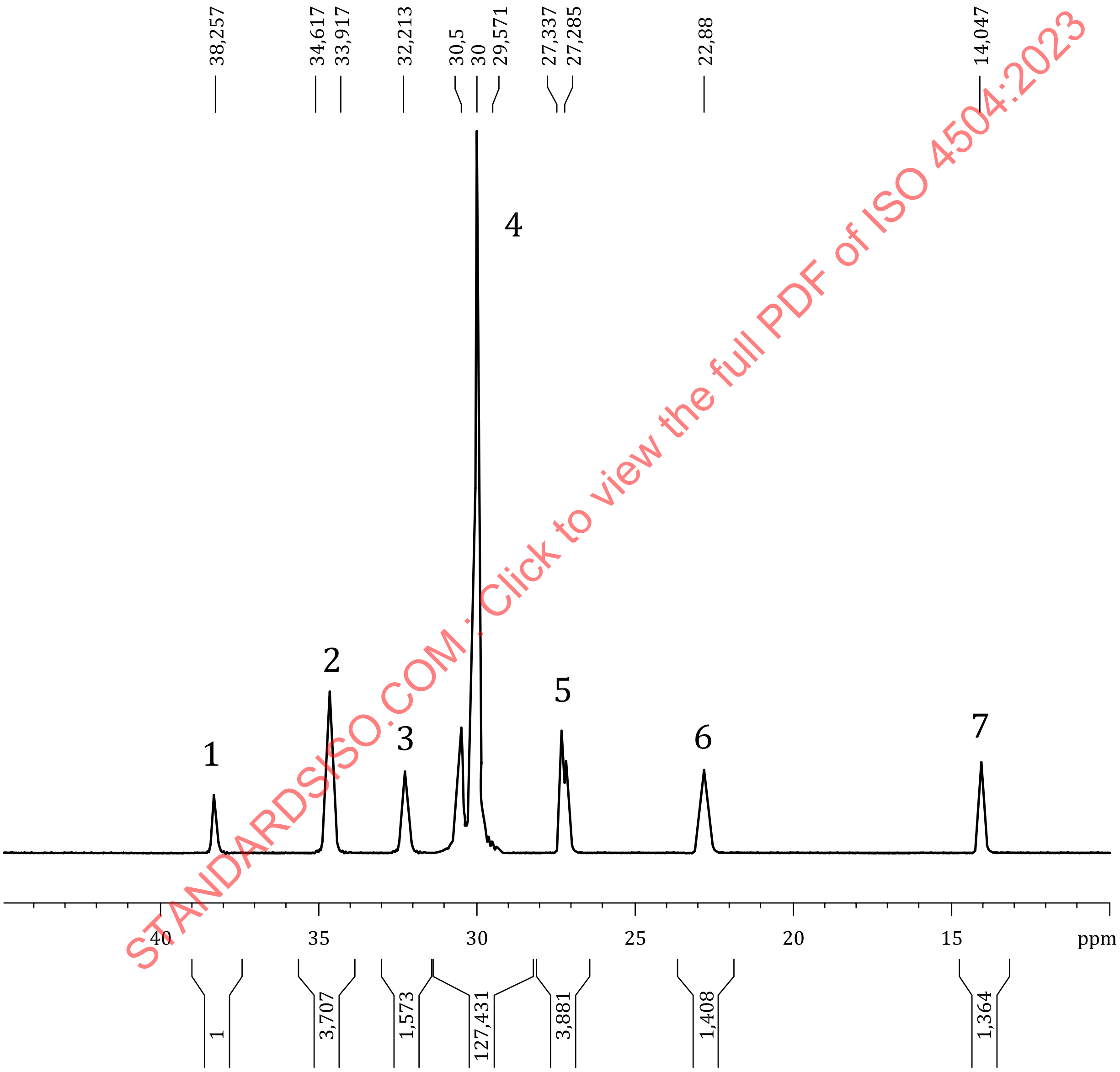
E is the mole percentage of ethylene;

n is the number of carbons in the co-monomer.

Annex C
(informative)

Calculation example of method A

Sample calculation example for an ethylene-octene-1 copolymer of method A is shown in Figure C.1. The calculation results are shown in Table C.1.



Key

1 to 7 notation of the spectral peaks

Figure C.1 — Example of NMR spectra of the ethylene-octene-1 sample of method A

Table C.1 — Integral value for the example sample of ethylene-octene-1 copolymers in Figure C.1

Area	Peak	Chemical shift Hz/MHz	Peak integral	Sum of integral in the area
A_O	—	—	0	0
B_O	—	—	0	0
C_O	1	38,257	1,000	1,000
D_O	—	—	0	0
E_O	2	34,617	3,707	3,707
$F_O+G_O+H_O$	3	32,213	1,573	132,885
	4	30,000	127,431	
	5	27,337 to 27,285	3,881	
H_O	5	27,337 to 27,285	3,881	3,881
I_O	—	—	0	0
J_O	6	14,047	1,408	1,408

a) **Mole fraction of octene in the ethylene-octene-1 copolymer *O***

$$O=\frac{3A_O+2B_O+4C_O+4D_O+E_O}{3(F_O+G_O+H_O)-3A_O-5B_O+8C_O+8D_O+2E_O-H_O-J_O-3I_O} \tag{C.1}$$

$$O=\frac{4\times1{,}000+3{,}707}{3\times132{,}885+8+2\times3{,}707-3{,}881-1{,}408}=1{,}9\ \mathrm{mmol}/\mathrm{mol} \tag{C.2}$$

b) **Branches per 1 000 carbons**

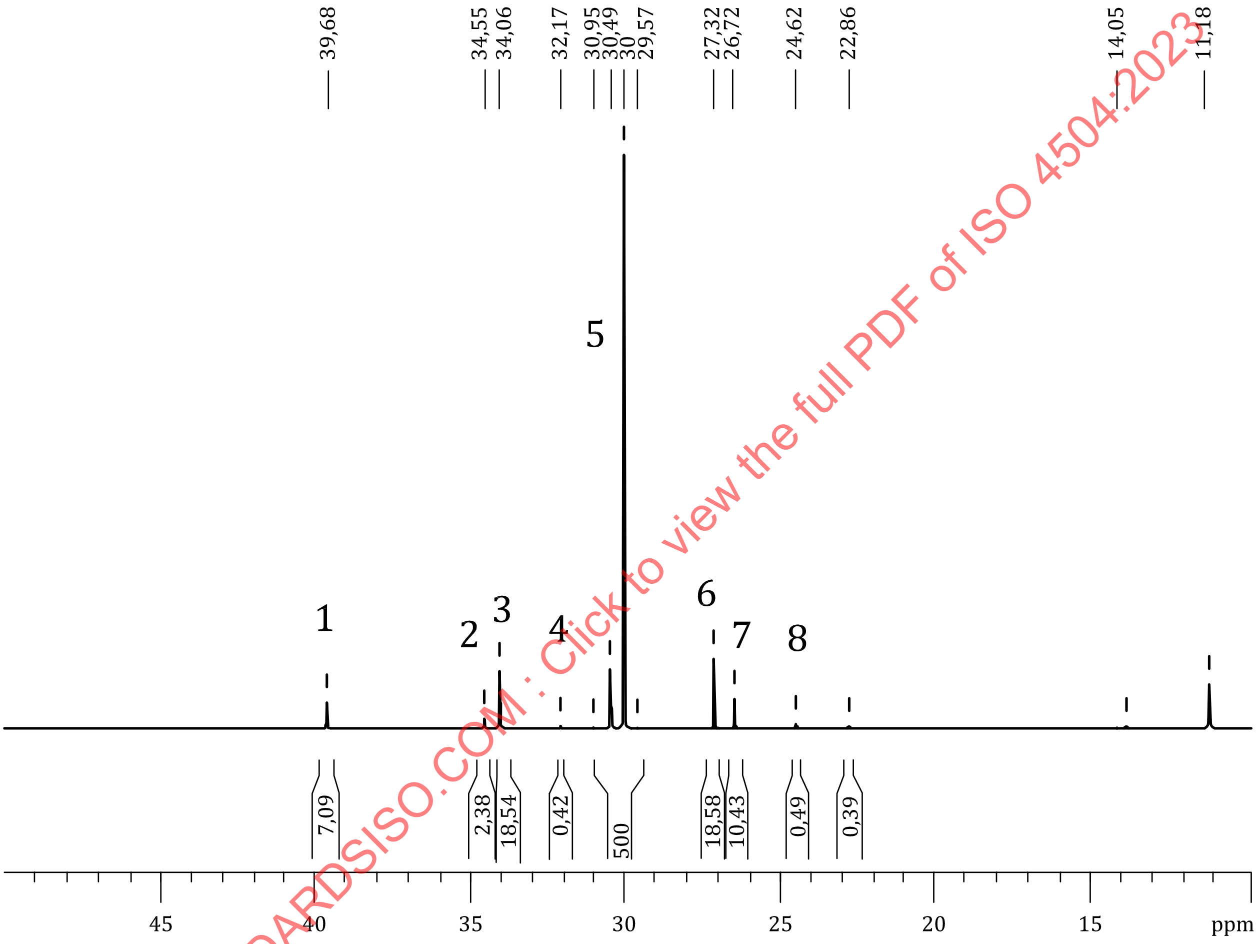
$$N_{br}=\frac{1\ 000X}{2E+nX}=\frac{1\ 000\times1{,}9}{2\times98{,}1+8\times1{,}9}=8{,}99 \tag{C.3}$$

where *n* for octene-1, n=8.

Annex D
(informative)

Calculation example of method B

Sample calculation example for an ethylene-hexene-1 copolymer of method A is shown in Figure D.1. The calculation results are shown in Table D.1.



Key

1 to 8 notation of the spectral peak

Figure D.1 — NMR spectra of a sample of the ethylene-butene-1 sample of method B

Table D.1 — Integral value for the sample of ethylene-butene-1 copolymer in Figure D.1

Area	Peak	Chemical shift Hz/MHz	Peak integral	Sum of integral in the area
A_B	1	39,68	7,09	7,09
A'_B	—	—	0	0
B_B	—	—	0	0
C_B	2	34,55	2,38	20,92
	3	34,06	18,54	
D_B+E_B	4	32,16	0,42	529,7
	5	29,56 to 30,48	500,00	
	6	27,32	18,85	
	7	26,32	10,43	
F_B	8	24,62	0,48	0,48

a) **Mole fraction of butene in the ethylene-butene-1 copolymer *B***

$$B=\frac{8A_B+1{,}5A'_B+8B_B+3C_B}{8A_B-1{,}5A'_B+4B_B+3C_B+6(D_B+E_B)+6F_B} \tag{D.1}$$

$$B=\frac{8\times7{,}09+3\times20{,}92}{8\times7{,}09+3\times20{,}92+6\times529{,}7+6\times0{,}48}=3{,}6\ \text{mmol}/\text{mol} \tag{D.2}$$

b) **Branches per 1 000 carbons**

$$N_{br}=\frac{1\ 000X}{2E+nX}=\frac{1\ 000\times3{,}6}{2\times96{,}4+4\times3{,}6}=17{,}4 \tag{D.3}$$

where *n* for butene-1, n=4.

Annex E
(informative)

Reference longitudinal relaxation time(T_1) values

E.1 General

In Table E.1 to Table E.10, the longitudinal relaxation times (T_1) of ^{13}C nuclei and ^{1}H nuclei of five PE samples with different 1-olefin co-monomer were measured by the inversion recovery method. All the samples were prepared according to 8.1 or 9.1 and analysed on a 400 MHz NMR Spectrometer.

E.2 Reference longitudinal relaxation time(T_1) values of ^{13}C nuclei

Table E.1 — Ethylene-1-propene copolymers

Chemical shift Hz/MHz	T_1 s
37,89	1,70
37,52	1,67
33,21	2,71
30,37	1,90
30,00	2,01
27,43	1,86
20,65	2,95
19,95	3,02

Table E.2 — Ethylene-1-butene copolymers

Chemical shift Hz/MHz	T_1 s
39,60	2,11
33,99	1,42
30,48	1,75
30,00	2,03
27,28	1,62
26,64	1,79

Table E.3 — Ethylene-1-hexene copolymers

Chemical shift Hz/MHz	T_1 s
38,07	1,42
34,4	0,99
34,08	1,23
30,00	2,19
27,26	1,53
23,38	4,18

Table E.4 — Ethylene-1-octene copolymers

Chemical shift Hz/MHz	T_1 s
38,10	1,39
34,46	0,97
32,18	3,69
30,49	1,31
30,00	1,72
27,25	1,18
27,18	1,52
22,88	5,69

Table E.5 — Ethylene-4-methylpentene-1 copolymers

Chemical shift Hz/MHz	T_1 s
44,42	1,71
35,61	1,95
34,49	1,29
26,80	1,59
25,69	2,33
22,98	3,91

E.3 Reference longitudinal relaxation time(T_1) values of ^{1}H nuclei

Table E.6 — Ethylene-1-propene copolymers

Type	T_1 [a] s	T_1 [b] s
CH_2 and CH	0,42	1,65

[a] With relaxation reagent (chromium (III) acetylacetonate).

[b] Without relaxation reagent.

Table E.7 — Ethylene-1-butene copolymers

Type	T_1 [a] s	T_1 [b] s
CH_2 and CH	0,68	1,49

[a] With relaxation reagent (chromium (III) acetylacetonate).

[b] Without relaxation reagent.

Table E.8 — Ethylene-1-hexene copolymers

Type	T_1 [a] s	T_1 [b] s
CH_2 and CH	0,77	3,51

[a] With relaxation reagent (chromium (III) acetylacetonate)

[b] Without relaxation reagent

Table E.9 — Ethylene-1-octene copolymers

Type	T_1 [a] s	T_1 [b] s
CH_2 and CH	0,71	1,93

[a] With relaxation reagent (chromium (III) acetylacetonate)

[b] Without relaxation reagent

Table E.10 — Ethylene-4-methylpentene-1 copolymers

Type	T_1 [a] s	T_1 [b] s
CH_2 and CH	0,50	2,06

[a] With relaxation reagent (chromium (III) acetylacetonate)

[b] Without relaxation reagent

Annex F
(informative)

Chemical shift region of branch CH-carbon of different co-monomers

The chemical shift region of branch CH-carbon of different co-monomer types are listed in Table F.1.

Table F.1 — Branch CH-carbon limit of different co-monomers

Co-monomer	**Region** Hz/MHz
Propene	35,5 ~ 32,5
1-butene	41,5 ~ 38,5
1-hexene	39,5 ~ 37,0
1-octene	39,5 ~ 37,0
4-methyl-1-pentene	35,8 ~ 36,1

Annex G
(informative)

Summary of precision data

All the precision data have been calculated according to ISO 5725-2. Table G.1 and Table G.2 are a collection of original data. The results of precision data for co-monomer content are given in Table G.3 and Table G.4. In Table G.3 and Table G.4, No. is the serial number, sample is the sample name, m (%) is the molar fraction, S_r is the repeatability standard deviation, S_R is the reproducibility standard deviation, r (%) is the repeatability limit and R (%) is the reproducibility limit.

Table G.1 — Collection of original data for co-monomer content in samples of method A

Laboratory	PE-1 mmol/mol	PE-2 mmol/mol	PE-3 mmol/mol	PE-4 mmol/mol
1	3,4	1,7	3,7	8,5
	3,3	1,8	3,6	8,3
2	3,3	1,7	3,7	8,3
	3,3	1,7	3,7	8,1
3	3,3	1,8	3,6	8,4
	3,4	1,8	3,8	8,4
4	3,3	1,7	3,7	8,3
	3,3	1,7	3,9	8,5
5	3,4	1,7	3,8	8,2
	3,3	1,7	3,7	8,2
6	3,4	1,8	3,5	8,5
	3,4	1,7	3,6	8,3
7	3,5	—	4,0	8,6
	3,5	—	3,9	8,5

Table G.2 — Collection of original data for co-monomer content in samples of method B

Laboratory	PE-1 mmol/mol	PE-2 mmol/mol	PE-3 mmol/mol	PE-4 mmol/mol
1	3,3	1,8	3,6	8,6
	3,5	1,8	3,7	8,4
2	3,4	1,7	3,6	8,1
	3,5	1,6	3,6	8,2
3	3,4	1,7	3,9	8,5
	3,5	1,7	3,8	8,7
4	3,4	1,7	3,9	8,5
	3,4	1,7	3,8	8,6
5	3,4	1,7	3,8	8,6
	3,3	1,7	3,7	8,5