



# Standard Test Method for Methyl (Comonomer) Content in Polyethylene by Infrared Spectrophotometry<sup>1</sup>

This standard is issued under the fixed designation D6645; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the determination of methyl groups (that is, comonomer content) in polyethylenes by infrared spectrophotometry. The test method is applicable to copolymers of ethylene with 1-butene, 1-hexene, or 1-octene having densities above  $900 \text{ kg/m}^3$ . High-pressure low-density polyethylenes (LDPE) and terpolymers are excluded.

1.2 The values stated in SI units, based on [IEEE/ASTM SI-10](#), are to be regarded as the standard.

1.3 *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 limitations prior to use.*

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

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

D792 [Test Methods for Density and Specific Gravity \(Relative Density\) of Plastics by Displacement](#)

D1505 [Test Method for Density of Plastics by the Density-Gradient Technique](#)

D1898 [Practice for Sampling of Plastics](#) (Withdrawn 1998)<sup>3</sup>

[D2238 Test Methods for Absorbance of Polyethylene Due to Methyl Groups at  \$1378 \text{ cm}^{-1}\$](#)

D3124 [Test Method for Vinylidene Unsaturation in Polyethylene by Infrared Spectrophotometry](#)

D5576 [Practice for Determination of Structural Features in Polyolefins and Polyolefin Copolymers by Infrared Spectrophotometry \(FT-IR\)](#)

[E131 Terminology Relating to Molecular Spectroscopy](#)

[E168 Practices for General Techniques of Infrared Quantitative Analysis](#)

[E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods](#)

[E932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers](#)

[E1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared \(FT-MIR\) Spectrometers: Level Zero and Level One Tests](#)

[IEEE/ASTM SI-10 Standard for Use of the International System of Units \(SI\): The Modern System](#)

## 3. Terminology

3.1 *Terminology*—The units, symbols, and abbreviations used in this test method appear in Terminology [E131](#) or [IEEE/ASTM SI-10](#).

3.2 *comonomer*— $\alpha$ -olefin monomer. In this test method, comonomer refers to 1-butene, 1-hexene, and 1-octene only.

## 4. Summary of Test Method

4.1 The band located between  $1377 \text{ cm}^{-1}$  and  $1379 \text{ cm}^{-1}$  is due to a deformation vibration of the  $-\text{CH}_3$  group. Bands at approximately  $772 \text{ cm}^{-1}$  (branch methylene rocking mode),  $895 \text{ cm}^{-1}$  (methyl rocking mode), and  $785 \text{ cm}^{-1}$  (branch methylene rocking mode) are characteristic of ethyl (that is, butene copolymer), butyl (that is, hexene copolymer), and hexyl (that is, octene copolymer) branches, respectively.<sup>4</sup>

4.2 This test method determines the methyl (that is, comonomer) content of a polyethylene copolymer based on the IR absorbance at  $1378 \text{ cm}^{-1}$  from a pressed plaque. The comonomer type has to be known and a calibration curve has to be available prior to the analysis. If the comonomer is not known a priori, the presence of bands at  $772 \text{ cm}^{-1}$ ,  $895 \text{ cm}^{-1}$ , and  $785 \text{ cm}^{-1}$  can be used to identify ethyl (minimum of 1 branch per 1000 carbons), butyl (minimum of about 5 branches per 1000 carbons), and hexyl (minimum of about 5 branches per 1000 carbons) branches, respectively. A more sensitive and

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.

Current edition approved Jan. 1, 2010. Published January 2010. Originally approved in 2001. Last previous edition approved in 2001 as D6645 - 01. DOI: 10.1520/D6645-01R10.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

<sup>4</sup> Blitz, J. P., and McFadden, D. C., "The Characterization of Short Chain Branching in Polyethylene Using Fourier Transform Infrared Spectroscopy," *J. Appl. Pol. Sci.*, 51, 13 (1994).

less ambiguous identification is obtained by C13 NMR spectroscopy. The latter technique is also used as a reference technique to provide polymer standards for the generation of calibration curves.

NOTE 2—For comonomer identification, it is recommended, for maximum sensitivity, to view the second derivative of the IR spectrum.

4.3 The method is calibrated by plotting absorbance at 1378  $\text{cm}^{-1}$  per unit area of the methylene combination band at 2019  $\text{cm}^{-1}$  (that is, internal thickness correction approach) or per unit of spectral cross-section (that is, the reciprocal of the product of plaque thickness and density) versus number of branches per 1000 carbons as determined by C13 NMR spectroscopy. Although both approaches give equivalent results, the one using internal thickness correction is recommended in this test method since it is considerably simpler to execute.

## 5. Significance and Use

5.1 This method determines the number of branches (that is, comonomer content) in copolymers of ethylene with 1-butene, 1-hexene or 1-octene. This information can be correlated with physical properties such as melting point, density, and stiffness, all of which depend on the degree of crystallinity of the polymer. Differences in the comonomer content thus may have a significant effect on the final properties of products made from these resins.

## 6. Interferences

6.1 A conformational  $\text{CH}_2$  wagging absorbance at 1368  $\text{cm}^{-1}$  overlaps the methyl absorbance at 1378  $\text{cm}^{-1}$ , but does not cause significant interference in this test method since its intensity is not significantly affected by the comonomer content, but rather by the plaque thickness. The result of not correcting for this overlap is a positive ordinate intercept for the calibration curve (see 10.4). Another conformational  $\text{CH}_2$  wagging absorbance at 1352  $\text{cm}^{-1}$  does not significantly overlap the 1378  $\text{cm}^{-1}$  absorbance.

6.2 The presence of most pigments will interfere with this method.

6.3 The presence of low molecular weight hydrocarbons will produce high results in this method due to absorbance by their end methyl groups at 1378  $\text{cm}^{-1}$ .

6.4 The secondary antioxidant Irgafos 168<sup>5</sup> shows an absorbance at 768  $\text{cm}^{-1}$  which interferes with the identification of low levels (that is, typically less than 5 branches per 1000 carbons or less) of ethyl branches.

6.5 Vinylidene groups absorb at 888  $\text{cm}^{-1}$  and thus may interfere with a conclusive identification of a hexene copolymer from its 895  $\text{cm}^{-1}$  resonance, depending on the relative intensities of the two peaks.

## 7. Apparatus

7.1 *Infrared Spectrophotometer*, either double beam or a Fourier transform (FTIR).

7.1.1 *Dispersive Infrared Spectrophotometer*, capable of achieving a spectral bandwidth of 4  $\text{cm}^{-1}$  (see Practice E932). The instrument should be capable of scale expansion along the wavenumber axis.

7.1.2 *Fourier Transform Infrared Spectrometer*, capable of 4  $\text{cm}^{-1}$  resolution (see Practice E1421). The instrument should be capable of scale expansion along the wavenumber axis.

7.2 *Compression Molding Press*, with platens capable of being heated to 180°C.

7.3 *Two Metal Plates*, 150 by 150 mm or larger, of 0.5-mm thickness with smooth surfaces.

7.4 *Brass Shims*, approximately 75 by 75 mm, of 0.3 mm thickness with an aperture in the center at least 25 by 38 mm.

7.5 *Micrometer (optional)*, with thimble graduations of 0.001 mm.

7.6 *Film Mounts*, with apertures at least 6 by 27 mm, to hold the specimens in the infrared spectrophotometer.

## 8. Materials

8.1 *Polyethylene Terephthalate, Aluminum Foil or Matte Finished Teflon-Fibreglass Sheets*.

## 9. Hazards

9.1 Caution must be used during plaque preparation to handle the hot platens with appropriate gloves for hand protection.

## 10. Procedure

10.1 *Preparation of Polymer Plaque:*

10.1.1 Preheat the press to about 50°C above the melting point of the polymer.

10.1.2 Place a 0.3-mm thick brass shim on the sheet material chosen (see 8.1) which in turn covers a metal plate.

NOTE 3—When using aluminum foil, place the dull side next to the polymer to give the sample film some texture, thereby reducing fringe effects in the infrared spectrum.

10.1.3 Add polymer in sufficient quantity to completely fill the shim aperture during pressing.

10.1.4 Insert the mold assembly between the press platens and apply a slight pressure.

10.1.5 Allow the polymer to preheat for about 30 s. Apply the full press pressure at a temperature approximately 50°C above the melting point of the polymer for 1 min or until all exudation ceases.

10.1.6 Turn off the heat, turn on the cooling water, and allow the polymer to press quench at full pressure until the temperature drops below 50°C (or cool enough to remove the mold assembly by hand).

10.1.7 Select plaques that are clear for the FTIR analysis. To avoid interference fringes in the spectrum, the plaque surfaces must be slightly dimpled.

10.2 *Spectral Acquisition:*

10.2.1 Place the polymer plaque in the infrared spectrophotometer.

10.2.2 Set the controls of the infrared spectrophotometer for quantitative conditions with a good signal to noise ratio and a

<sup>5</sup> Trademark of the Ciba Specialty Chemicals Co.