Designation: D 5576 – ~~94~~00

Standard Practice for
Determination of Structural ~~Entities~~ Features in Polyolefins and Polyolefin Copolymers by ~~Fourier Transform~~ Infrared Spectros~~co~~photometry (FT-IR)[1]

This standard is issued under the fixed designation D 5576; 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 practice ~~describes~~ covers infrared procedures for determining the molecular structural ~~entities~~ features in ~~the polyolefin chains (their quantitative levels with internal (Procedure A)~~ polyolefins and ~~external (Procedure B) evaluation for sample thickness are suggested in Appendix X1).~~ polyolefin copolymers. The structural ~~entities~~ features of primary concern are the types and ~~distribution~~ numbers of branches. Although this practice centers its attention on polyolefins and polyolefin copolymers, the techniques, with proper modification, can be used for some other polymers as well.

~~1.2 Often these structural entities are at a level of less than 2 %. Higher concentration of branching systems may be treated in other methods that address a specific problem associated with entities between 2 and 49 %.~~

~~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.* Specific hazards statements are given in Section 8.~~

NOTE 1—Quantitative determinations require either an internal or an external evaluation of sample thickness. ASTM test methods available for specific features are listed in Tables 1 and 2.

1.2 *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 to determine the applicability of the regulatory limitations prior to use.*

NOTE 2—There is no similar or equivalent ISO standard.

2. Referenced Documents

2.1 *ASTM Standards:*

---

[1] This practice is under the jurisdiction of ASTM Committee D~~-~~20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.
Current edition approved ~~June 15, 1994.~~ March 10, 2000. Published ~~August 1994.~~ June 2000. Originally published as D 5576 – 94. Last previous edition D 5576 – 94.

***A Summary of Changes section appears at the end of this standard.**

~~E~~D ~~1~~883~~1~~ Terminology Relating to ~~Molecular Spectroscopy~~ Plastics[2]
~~E 168 Practices~~
D 1505 Test Method for ~~General Techniques~~ Density of Plastics by the Density-Gradient Technique[2]
D 1600 Terminology of Abbreviated Terms Relating to Plastics[2]
D 2238 Test Methods for Absorbance of Polyethylene Due to Methyl Groups at 1378 cm^{-1} [2]
D 3124 Test Method for Vinylidene Unsaturation in Polyethylene by Infrared ~~Quantitative Analysis~~ Spectrophotometry[3]
~~E 177 Practice~~
D 3594 Test Method for ~~Use of the Terms Precision and Bias~~ Copolymerized Ethyl Acrylate in Ethylene-Ethyl A~~S~~crylate[3]
D 5594 T~~M T~~est Method for Determination of Vinyl Acetate Content of Ethylene-Vinyl Acetate (EVA) Copolymers by Fourier Transform Infrared Spectroscopy (FT-IR)[4]
~~E 380 Practice for Use of the International System of Units (SI) (The Modernized Metric System)~~[4]
D 6248~~8~~ Test Method for Vinyl and Trans Unsaturation in Polyethylene by Infrared Spectrophotometry[4]
E 131 Terminology Relating to ~~Plastics~~ Molecular Spectroscopy[5]
~~D 1600 Terminology~~
E 168 Practices for General Techniques of ~~Abbreviated Terms Relating to Plastics~~ Infrared Quantitative Analysis[5]
E 932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrophotometers[5]
E 1421 Practice for Describing and Measuring Performance of Fourier Transform Infrared (FT-IR) Spectrometers: Level Zero and Level One Tests[5]

---

[2] *Annual Book of ASTM Standards*, Vol ~~03.06.~~ 08.01.

[3] *Annual Book of ASTM Standards*, Vol ~~14.01.~~ 08.02.

[4] *Annual Book of ASTM Standards*, Vol ~~14.02.~~ 08.03.

[5] *Annual Book of ASTM Standards*, Vol ~~08.01.~~ 03.06.

IEEE/ASTM SI–10 Standard for Use of the International System of Units (SI): The Modern System[6]

3. Terminology

3.1 *Definitions*— For definitions of plastics terms used in this practice~~,~~ see Terminology D 883 and ~~Terminology~~ D 1600.

~~3.2 *Terminology*—Units, symbols,~~

3.2 Units, symbols and abbreviations used in this practice appear in Terminology E 131 or ~~Practice E 380.~~ IEEE/ASTM SI-10.

4. Summary of ~~Test Method~~

~~4.1 Suitable infrared~~ Practice

4.1 Infrared absorption bands ~~useful~~ suitable for quantitative analysis by FT-IR are listed in Tables 1~~.~~ and 2. These are only typical bands and are not to be construed as exhaustive.

4.2 ~~S~~For quantitative determinations, sample specimen thickness is measured internally ~~(Procedure A—see Appendix X1)~~ at some band representing the basic chain structure, such as ~~1465~~ 2019 cm^{-1} for polyethylene, or externally ~~(Procedure B—see Appendix X1)~~ using a micrometer~~. C~~ **(see Ta~~u~~bles 1 and 2 for ASTM t~~i~~est methods).**

NOTE 3—**Warning:** Molding can cause carbonyl formation due to oxidation~~; t~~. This should be checked in the 1700 to 1750 cm^{-1} range.

~~4.3 Absorbance for structural features per unit thickness, determined by suitable standards covering the analytical range, usually with five points, should be plotted versus the known structural feature expressed in percent. A typical resulting calibration curve can be used to determine the structural content of subsequent samples. See Table 2 for modified structures other than simple polyolefins.~~

5. Significance and Use

5.1 The structural features expressed by these determinations affect the ultimate polymeric properties and are useful in showing correlations with many performance properties.

6. Apparatus

6.1 *Infrared Spectrophotometer*, either double beam or a Fourier transform (FT-IR).

6.1.1 Double-beam infrared spectrophotometer capable of a 4 cm^{-1} spectral resolution as defined in Practice E 932. The instrument should be capable of scale expansion along the wavelength axis.

6.1.2 *Fourier Transform Infrared ~~(FT-IR) Spectrophotometer~~ Spectrometer*, ~~with nominal 4-cm^{-1}~~ capable of 4 cm^{-1} resolution. The instrument should be capable of scale expansion along the wavelength axis. Also, see Practice E 1421 for testing procedures.

6.2 *Hot Plate* ~~(Procedure A only).~~ .

6.3 *Microscope Slides* ~~(Procedure A only).~~ .

TABLE 1 ~~Fundam~~Polyolefin~~tal~~ Structural Features~~A~~ Determined by FT-IR~~Note 1—All values in wavenumbers.~~

Structure	~~Effective~~Absorption Band~~s~~	~~Internal~~ ~~Thi~~, c~~kness Band~~m^{-1}
~~Ethylene (C-C)~~	~~1465~~	~~2019~~
Ethylene (C-C)	~~1465~~	~~2019~~ASTM Test Method
~~Methyl group~~	~~1378~~	~~...~~
Methyl group (polyethylene)	1378	D 2238
~~Linearityofpolyethylene~~	~~735~~	~~...~~
	~~723~~	~~...~~
Methyl group (eth-prop copol)	1380	
~~Propylene~~	~~1380~~	~~4325~~
Pendant methyl	935	
~~Terminal vinyl~~	~~908~~	~~...~~
Terminal vinyl	908	D 6248
~~Pendant methyl~~	~~935~~	~~...~~
Trans-vinylene	965	D 6248
~~Trans unsaturation~~	~~955~~	~~...~~
Vinylidene	888	~~...~~
~~Pendant unsaturation (pendant methylene)~~	~~888 (LDPE)~~	~~...~~
Pendant unsaturation (pendant methylene)	888 (LD~~PE)~~	~~...~~ 3124

~~[A] Interference may occur depending on the branching of the polyolefin being measured.~~

~~[B] Overtone bands frequently used for thickness measurements.~~

TABLE 2 ~~Other~~Structural Features in Polyolef~~ l~~int Copolymer Dest~~Note 1—All values~~rmin ~~wavenum~~d ~~bers.~~y FT-IR

Structure	~~Effective~~Absorption Band~~s~~, cm^{-1}	~~Internal~~ AST~~hickn~~M Tes~~s Band~~	~~Bas~~t Me~~line Range~~thod
~~Vinyl acetate~~	~~1020 (0 to 8%)~~	~~20191099 to 982~~	
Vinyl acetate	609	D 5994	
	~~609 (5 to25 %)~~	~~665 to 580~~	
	1020	D 5994	
	~~3270 (overtone) (20 to 40 %)~~	~~3200 to 3350~~	
	3270	D 5994	
~~Styrene~~	~~1600 1500~~	~~...~~	~~1450 to 1250~~
Styrene	770–700	~~...~~	~~1450 to 1250~~
	~~770 700~~	~~...~~	~~850 to 600~~
	1600–1500	~~...~~	~~850 to 600~~
~~Ethyl acrylicacid~~	~~1640 1730~~	~~...~~	
Ethyl acrylate	1640–1730		
	~~1800 to 162~~	~~D 3550~~	
	862	D 3594	
~~Ethylene acrylate~~	~~1280 1200~~	~~...~~	~~1300 to 1160~~
Ethylene acrylate	1280–1200	~~...~~	~~1300 to 1160~~
	~~1640 1625~~	~~...~~	~~1700 to 1600~~
	1640–1625	~~...~~	~~1700 to 1600~~

6.4 ~~*Laboratory Press,*~~[6]Compression-Molding Press, capable of ~~4.8 MPa (25 000 lbf) and 225°C (Procedure B only).~~ 200°C.

6.5 ~~*Backing*~~*Metal Plates,* ~~steel~~ two, 150 by 150 mm or ~~aluminum (Procedure B only).~~ larger, of 0.5–mm thickness with smooth surfaces.

6.6 *Brass ~~Shim Stock (Roll)~~ Shims,* ~~0.125-mm (5-mil) thick, 0.25-mm, and 0.50-mm, and 152.4-mm (6 in.) wide (Procedure B only).~~ approximately 75 by 75 mm, of 0.5-mm thickness with an aperture in the center at least 25 by 38 mm.

~~[6] Wabash Model 50-12-1TMAC, available from Wabash Metal Products, Inc., 1569 Morris St., Wabash, IN 46992, or equivalent, has been found satisfactory for this purpose.~~

[6] *Annual Book of ASTM Standards*, Vol 14.02.

6.7 ~~*Polyester Film*, textured TFE-fluorocarbon cloth,[7] or heavy-gage aluminum foil (Procedure B only).~~

~~6.8 *Metal Template (Mold)*, with 152.4 by 152.4 mm (6 in. by 6 in.) pieces of brass shim stock containing six 1.27 mm (0.5 in.) cavities (Procedure B only).~~

~~6.9~~ *Micrometer*~~, capable~~ (optional), with thimble graduations of ~~measuring~~ 0.001 mm.

6.8 *Film Mounts*, with apertures at least 6 by 27 mm, to ~~±0.0025 mm (0.0001 in., 0.1 mil) (Procedure B only).~~ hold the specimens in the infrared spectrophotometer.

7. Materials

~~7.1 The structural feature may be quantified using standards covering the entire range of measurements (see Appendix X1).~~

~~7.2 Although a minimum of three points is required to detect curvature in the standard curve, seven to ten points are ideal. If the standard curve has any curvature in it, more points may be necessary.~~

7.1 *Polyethylene Terephthalate, Aluminum or Matte Finished Teflon-Fiberglass Sheets*.

8. Hazards

~~8.1 For Procedure B in Appendix X1, wear~~

8.1 Wear gloves when plaques are prepared using a heated ~~press. Take care to avoid burns when handling heated microscope slides and the hot plate, as outlined in Procedure A.~~ press.

8.2 The optical bench of the FT-IR ~~spectrophotometer~~ spectrometer contains a laser. To avoid eye injury, do not look directly into the laser beam.

9. ~~Specimen Preparation~~ Procedure

9.1 ~~*Procedure A*~~*Sample Preparation*:

~~9.1.1 Control the hot plate temperature at 100 ± 10°C above the appropriate melting temperature of the polymer.~~

~~9.1.2 Place a portion of a sample (or standard) pellet on a microscope slide on the hot plate.~~

~~9.1.3 Cover the sample with another slide and press with a wooden pestle. Use firm circular motions to press a uniform film.~~

~~9.1.4 To quench the pressed polymer film, dip the two slides carefully into a beaker of cold water. Remove the film and blot dry.~~

~~9.2 *Procedure B*:~~

~~NOTE 2—Omit 9.2.1-9.2.9 for analysis of a blown film or cast film 0.1 mm or less.~~

~~9.2.1 Place polyester sheet (or TFE-fluorocarbon cloth) and then 0.125 mm (5 mil) brass mold on a backing plate.~~

~~9.2.2 Place the sample in the center of the mold using approximately 1.5 g of sample in each opening. Do not overfill the mold openings. If flashing occurs, clean the mold and backing plates using a nylon scrubbing pad.~~

~~9.2.3 Place another piece of polyester sheet (or TFE-fluorocarbon cloth) and a backing plate on top of the sample.~~

~~9.2.4 Place the resulting composite in the press with the platens heated to a temperature 50°C above the melting point of the polymer.~~

~~9.2.5 Close the press until the top platen barely touches the top plate and leave for 2 min to permit the sample to soften.~~

~~9.2.6 Close the press completely and apply 4.8 MPa (25 000 lbf) for 1 min.~~

~~9.2.7 Release pressure and remove the molding assemblage from the press.~~

~~9.2.8 Cool the molding assemblage to room temperature with cold water on press, separate the backing plates, and remove plaques from the mold.~~

~~9.2.9 Select plaques that are clear and of uniform thickness for the FT-IR analysis. Care should be taken to avoid interference fringes if the film surfaces are too perfectly parallel.~~

~~10. Calibration~~

~~10.1~~

9.1.1 *Procedure A*:

~~10.1.1 Place film, prepared as described in 9.1, in~~

9.1.1.1 Control the ~~sample beam~~ hot plate temperature at 100 ± 10°C above the melting temperature of the ~~FT-IR spectrophotometer.~~

~~10.1.2 Record the infrared spectrum from 5000 to 450 cm $^{-1}$ at nominal resolution~~ polymer.

9.1.1.2 Place a portion of ~~4.0 cm^{-1}~~.

~~10.1.3 Measure~~ the ~~absorbance peak height (area) for~~ sample on a microscope slide on the ~~bands representing~~ hot plate.

9.1.1.3 Cover the ~~structural feature of interest. The baselines for~~ sample with another slide and press with a wooden pestle. Use firm circular motions to press a uniform film.

9.1.1.4 To quench the ~~peaks must be established. Both~~ pressed polymer film, dip the ~~peaks and baseline are listed in Table 1 for corresponding structural features.~~

~~10.1.4 Calculate any ratios~~ two slides carefully into a beaker of ~~structural features from these peak heights (areas).~~

~~NOTE 3—If quantitative relations are needed, check Appendix X1. (Plot height (area) ratios from 10.1.4 versus known concentrations of~~ cold water. Remove the ~~structural feature to prepare a calibration curve. All absorbances to be used should be below 1.0 absorbance units (Beers-Lambert)).~~

~~10.2~~ film and blot dry.

9.1.2 *Procedure B*:

~~10.2.1 Place standard plaques, prepared as described in 9.2, in~~

9.1.2.1 Preheat the ~~sample beam~~ press to about 50°C above the melting point of the ~~FT-IR spectrophotometer.~~

~~10.2.2 Scan~~ polymer.

9.1.2.2 Place a brass shim on the ~~infrared spectrum with no sample~~ sheet material chosen (see 7.1) that, in ~~the beam 32 times at 4.0 cm^{-1} resolution and~~ turn, covers a ~~gain setting of 1.0 to obtain a background spectrum.~~

~~10.2.3 Repeat 10.2.2 with each standard~~ metal plate.

9.1.2.3 Add polymer in sufficient quantity to completely fill the ~~beam. Determine the ratio~~ shim aperture during pressing.

9.1.2.4 Cover with another piece of sheet (see 7.1) and another metal plate.

9.1.2.5 Insert the ~~sample spectrum to~~ mold assembly between the ~~background spectrum~~ press platens and ~~convert~~ apply a slight pressure.

9.1.2.6 Allow the ~~data~~ sample to preheat for about 30 s. Apply the ~~absorbance mode.~~

~~10.2.4 Determine~~ full press pressure at a temperature approximately 50°C above the ~~absorbance~~ melting point of the ~~structural feature at the appropriate wavelength selected from Table~~ polymer for 1 ~~by subtracting~~ min or until all exudation ceases.

9.1.2.7 Turn off the ~~peak absorbance from~~ heat, turn on the ~~baseline absorbance.~~

~~10.2.5 Using a micrometer, measure~~ cooling water, and allow the ~~thickness (mils) of standard plaques.~~

~~10.2.6 Calculate~~ sample to press quench at full pressure until the ~~absorbance~~ temperature drops below 50°C (or cool enough to ~~thickness ratios for~~ remove the ~~structural feature, using~~ mold assembly by hand).

9.1.2.8 Release the ~~appropriate values of 10.2.4~~ pressure and ~~10.2.5.~~

~~NOTE 4—If quantitative relations~~ remove the sample.

9.1.2.9 Select plaques that are ~~needed, check Appendix X1. (Plot peak height ratios~~ clear and of ~~10.2.6 versus known structural feature concentrations~~ uniform thickness for the ~~standards to prepare a calibration curve. Be sure to use absorbances less than 1.0 (Beers-Lambert Law)).~~

~~11. Procedure~~

~~11.1 *Procedure A*~~ *FT-IR analysis. To avoid interference fringes in the spectrum, the plaque/film surfaces must be slightly dimpled.*

9.2 *Spectral Measurements*:

~~11.1.1 Prepare~~

9.2.1 Place the sample ~~films as described~~ in ~~9.1, then place films in~~ the ~~FT-IR sample beam.~~

~~11.1.2 Record~~ infrared spectrophotometer.

9.2.2 Set the controls of the infrared spectrophotometer for quantitative conditions with a good signal to noise ratio and satisfactory repeatability. For a FT-IR, a spectral resolution of 4 cm^{-1} and an apodization function (Beer-Norton medium and Happ-Genzel have been found to be appropriate) that gives good quantitation should be used.

9.2.3 Record the infrared spectrum from 4000 to ~~450~~ 500 cm^{-1} at a nominal resolution of 4.0 cm~~$^{-1}$~~$^{-1}$.

~~11.1.3 Measure the absorbance for all~~

9.2.4 Determine which structural ~~features using appropriate baselines, as listed in Table 1.~~

~~NOTE 5—If quantitative relations~~ feature(s) are ~~needed, calculate~~ present and select the ~~peak height ratios, if appropriate,~~ appropriate ASTM method for quantitative determination.

10. Calculation

10.1 If no standard method is available and an estimate of the ~~structural features in 11.1.3. For further details, see Appendix X1.~~

~~11.2 *Procedure B*:~~

~~11.2.1 Prepare sample plaques as described in 9.2.~~

~~11.2.2 Using a micrometer, measure~~ concentration of the ~~thickness (mils)~~ feature of ~~sample plaques.~~

~~11.2.3 Scan~~ interest is sought, the ~~infrared spectrum 32 times with no sample~~ approach in 10.1.1-10.1.3 is suggested.

10.1.1 Determine the ~~beam, resolution~~ thickness of ~~4.0~~ the plaque or, preferably, its spectral cross-section, *b*, in cm~~$^{-1}$,~~^{2}/g, by measuring the thickness and ~~gain set at 1.0 to obtain~~ density or alternatively the mass and surface area of a ~~background spectrum.~~

~~11.2.4 Place sample plaque in~~ uniformly thick portion of the plaque

10.1.2 Measure the ~~FT-IR beam and scan 32 times with resolution~~ absorbance of ~~4.0 cm^{-1} and gain at 1.0.~~

~~11.2.5 Measure~~ the peak ~~height~~ of interest. Choose a baseline between valleys on either side of the ~~structural feature at~~ peak in a manner to produce the ~~appropriate wavelength by subtracting~~ most accurate and repeatable representation of the ~~absorption maximum from~~ actual background absorbance

10.1.3 Calculate the ~~absorption minimum.~~

~~NOTE 6—If quantitative relations are needed, calculate~~ concentration, *c*, of the ~~peak height ratios, if appropriate, for the structural features relative to the sample thicknesses~~ feature using either the ~~d~~ Beer-Lambert Law ($A = a \cdot b \cdot c$) with the appropriate molar absorptivity, *a*, or an appropriate calibration curve. If a calibration curve is used, it should have a minimum of ~~11.2.2~~ 5 data points, and ~~11.2.5. For further details, see Appendix X1.~~

~~12.~~ the unknown should be within the high and low limits of the standards.

11. Report

1~~2~~1.1 Report the following information:
~~12.1.1 Structural entity,~~
~~12.1.2 Identify the material,~~
~~12.1.3 Identify which procedure is used in preparing the sample,~~
~~12.1.4 Internal thickness band used if Procedure A is employed,~~
~~12.1.5 Infrared spectrum range used, and~~
~~12.1.6 Date~~
11.1.1 Complete identification of material tested including name, manufacturer, lot number and physical form when sampled,
11.1.2 Date of test, and
11.1.3 Any sample or spectral anomalies observed during the ~~t~~ measurement.

1~~3~~2. Keywords

~~13.1 branching; fourier transform infrared spectroscopy;~~
12.1 copolymers; FT-IR; infrared spectro~~sc~~photometry; polyethylene; structural ~~entities~~ features ~~APPENDIX~~

~~(Nonmandatory Information)~~

~~X1. CALCULATIONS~~

~~X1.1 If quantitative results are needed,~~

SUMMARY OF CHANGES

This section identifies the ~~following techniques are suggested:~~

~~X1.1.1 Using linear regression analysis, determine equations for calibration lines obtained in Note 3 or Note 4. Check the equation~~ location of selected changes to ~~ensure that it has~~ this practice. For the ~~ability to predict~~ convenience of the ~~structural entity with statistical significance.~~

~~X1.2 Enter~~ user, Committee D-20 has highlighted those changes that may impact the ~~appropriate sample-area~~ use of this practice. This section may include descriptions of the changes or ~~peak-height ratios from Note 5 or Note 6 into~~ the ~~appropriate equation to calculate~~ reasons for the ~~weight percent of~~ changes, or both.
D 5576-00:
(*1*) Changed title.
(*2*) Added ASTM test methods for the ~~structural feature needed.~~

~~NOTE X1.1—With an instrument capable~~ determination of ~~determining quantitative functions, the software will employ linear regression analysis~~ referenced features added to ~~fit unknown spectra~~ Section 2.
(*3*) Rewrote procedures section to make it consistent with the ~~infrared spectra of standards. See Practices E 168 and E 177 for assistance.~~

~~NOTE X1.2—The operation of some FT-IR spectrophotometers can be controlled by macro programs that are used to calculate~~ equivalent sections in the ~~structural content being studied.~~ newly referenced test methods.