



# Standard Test Methods for Absorbance of Polyethylene Due to Methyl Groups<sup>1</sup> at 1378 cm<sup>-1</sup>

This standard is issued under the fixed designation D2238; 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.

<sup>ε1</sup> NOTE—Reapproved with editorial changes in December 2012.

## 1. Scope

1.1 These test methods cover measurement by infrared absorption spectrophotometry of the 1378.4-cm<sup>-1</sup> (7.255-μm) band in polyethylene due to methyl groups. (1, 2, 3-6)<sup>2</sup> Two test methods are covered:

1.1.1 *Test Method A* uses compensation with a standard sample film or wedge of known methyl content.

1.1.2 *Test Method B* uses compensation with a wedge of polymethylene or a polyethylene of known low methyl content.

1.2 These test methods are applicable to polyethylenes of Types I (density 910 to 925 kg/m<sup>3</sup>), II (density 926 to 940), and III (density 941 to 965).

NOTE 1—For determination of density, see Specifications D1248.

NOTE 2—In cases of Type III polyethylene with densities greater than 0.950 g/cm<sup>3</sup>, different results are obtained with the two test methods.

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.4 *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 7.

NOTE 3—There is no known ISO equivalent to this standard.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>3</sup>

D618 Practice for Conditioning Plastics for Testing

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D20 on Plastics and are the direct responsibility of Subcommittee D20.70 on Analytical Methods (Section D20.70.08).

Current edition approved Dec. 1, 2012. Published December 2012. Originally approved in 1964. Last previous edition approved in 2004 as D2238 - 92 (2004). DOI: 10.1520/D2238-92R12E01.

<sup>2</sup> The boldface numbers in parentheses refer to the list of references at the end of these test methods.

<sup>3</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

D1248 Specification for Polyethylene Plastics Extrusion Materials for Wire and Cable  
D1505 Test Method for Density of Plastics by the Density-Gradient Technique  
D1898 Practice for Sampling of Plastics (Withdrawn 1998)<sup>4</sup>  
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  
IEEE/ASTM SI-10 Standard for Use of the International System of Units (SI): The Modern Metric System

## 3. Terminology

### 3.1 Definitions of Terms Specific to This Standard:

3.1.1 *absorbance*—the logarithm to the base 10 of the reciprocal of the internal transmittance:

$$A = \text{LOG}_{10}(1/T) = -\text{LOG}_{10}T \quad (1)$$

3.2 Units, symbols, and abbreviations used in this test method appear in Terminology E131 or Practice IEEE/ASTM SI-10.

## 4. Significance and Use

4.1 When interpreted with the aid of appropriate calibration data, either test method can be used to compare the total methyl contents of polyethylenes made by similar processes. Such information can be interpreted in terms of specific alkyl groups with the aid of data on infrared absorption at certain other wavelengths (7).

NOTE 4—The bias of determination of the concentration of total alkyl groups depends on knowing the concentrations of methyl and ethyl branches present, since these branches have anomalously high absorptivities per group at 1378 cm<sup>-1</sup> (7.25 μm).

4.2 Knowledge of total methyl groups in polyethylene, when combined with data on molecular weight and on reactive end groups such as vinyl, can lead to assignment of end-group structures and can shed light upon polymerization mechanisms.

<sup>4</sup> The last approved version of this historical standard is referenced on www.astm.org.

4.3 Data on total methyl groups in polyethylene can be correlated qualitatively with certain polymer properties such as melting point, density, stiffness, and other mechanical properties that are closely dependent on the degree of crystallinity of the polymer.

4.4 These test methods are especially suitable for research. They have not been tested for use in manufacturing control.

## 5. Interferences

5.1 Compensation minimizes interference from methylene group absorption bands at  $1368\text{ cm}^{-1}$  ( $7.31\ \mu\text{m}$ ) and  $1352\text{ cm}^{-1}$  ( $7.39\ \mu\text{m}$ ) with the  $1378\text{-cm}^{-1}$  ( $7.255\ \mu\text{m}$ ) methyl deformation band.

5.2 In Test Method A residual absorption is often present at  $1352\text{ cm}^{-1}$  after compensation, but this band is believed not to contribute appreciable interference in the measurement of the methyl peak at  $1378.4\text{ cm}^{-1}$  in samples with very low methyl content.

## 6. Apparatus

6.1 *Infrared Spectrophotometer*, double beam, with rock salt prism, and spectral resolution as defined by Condition C in Part III (Spectral Resolution) of the Proposed Methods for Evaluation of Spectrophotometers, or <sup>5,6</sup>

6.2 *Fourier Transform Instrument*, capable of a spectral resolution of at least  $2.0\text{ cm}^{-1}$ .

6.3 *Compression-Molding Press*, small, with platens capable of being heated to  $170^\circ\text{C}$ .<sup>7</sup>

6.4 *Metal Plates*, approximately 150 by 150 by 0.5 mm with smooth surfaces.

6.5 *Brass Shims*, approximately 75 by 75 mm or larger with an aperture in the center at least 25 by 38 mm in a series of at least five thicknesses from 0.1 to 0.5 mm.

6.6 *Micrometer Calipers*, with thimble graduations of 0.001 mm.<sup>8</sup>

6.7 *Mounts*, for film specimens with aperture at least 6 by 27 mm.

## 7. Hazards

7.1 Caution must be used during molding to handle the hot plates and molds with appropriate gloves for hand protection.

## 8. Sampling

8.1 The polyethylene shall be sampled in accordance with Practice **D1898**.

## 9. Preparation of Apparatus

9.1 The precision obtained using this test method depends very markedly upon the condition of the spectrophotometer.

<sup>5</sup> *Proceedings*, ASTM, Vol 58, 1958, p. 472.

<sup>6</sup> The Perkin-Elmer Model 21 Spectrophotometer, Beckman IR-4 and IR-7, Hilger H-800, and Grubb-Parsons GS-2A Spectrophotometers are capable of this degree of resolution and have been found satisfactory for this purpose.

<sup>7</sup> Hydraulic presses that have been found satisfactory for this purpose are made by Pasadena Hydraulics, Inc., Pasadena, CA, and Fred S. Carver, Inc., Summit, NJ.

<sup>8</sup> Brown and Sharpe micrometer No. 223 RS has been found satisfactory for this purpose.

Instrument performance shall be at least equal to that cited in the manufacturer's specifications for the new instrument. Resolution shall be checked to assure conformance with **6.1**. The linearity of the photometric system shall be measured; linearity shall not deviate from absolute by more than 4 % of the transmittance range of interest. Frequency or wavelength in the  $1430\text{ to }1250\text{-cm}^{-1}$  ( $7\text{ to }8\text{-}\mu\text{m}$ ) region shall be calibrated.

NOTE 5—For wavelength calibration, it is helpful to record the spectrum of water vapor upon the spectra of the samples.

## 10. Calibration and Standardization

10.1 Check the instrument for resolution and wavelength accuracy by checking against known wavelengths and absorbance for methyl absorbance bands in the  $2851.4\text{ cm}^{-1}$  ( $3.507\ \mu\text{m}$ ) range.

## 11. Conditioning

11.1 *Conditioning*—Condition the test specimens at  $23 \pm 2^\circ\text{C}$  ( $73.4 \pm 3.6^\circ\text{F}$ ) and  $50 \pm 5\%$  relative humidity for not less than 40 h prior to test in accordance with Procedure A of Practice **D618**, for those tests where conditioning is required. In cases of disagreement, the tolerances shall be  $\pm 1^\circ\text{C}$  ( $\pm 1.8^\circ\text{F}$ ) and  $\pm 2\%$  relative humidity.

11.2 *Test Conditions*—Conduct tests in the standard laboratory atmosphere of  $23 \pm 2^\circ\text{C}$  ( $73.4 \pm 3.6^\circ\text{F}$ ) and  $50 \pm 5\%$  relative humidity, unless otherwise specified in the test methods or in this specification. In cases of disagreements, the tolerances shall be  $\pm 1^\circ\text{C}$  ( $\pm 1.8^\circ\text{F}$ ) and  $\pm 2\%$  relative humidity.

### TEST METHOD A—MEASUREMENT OF THE ABSORBANCE AT $1378\text{ cm}^{-1}$ ( $7.25\ \mu\text{m}$ ) BY A STANDARD SAMPLE COMPENSATION METHOD

## 12. Materials

12.1 *Aluminum Foil*.

12.2 *Crushed Ice*.

12.3 *Reference Wedge or Films*, prepared as described in **13.2.1**.

## 13. Calibration and Standardization For Test Method A

13.1 *Calibration of Reference Polymer by a Self-Compensation Method*—Mold a 0.5 mm film of annealed high-density polyethylene, as well as a series of thinner, shock-cooled films of the same polymer over a range of thickness from 0.1 to 0.4 mm (**Note 6**). Measure a series of difference spectra, with the annealed film in the sample beam of the spectrophotometer and each shock-cooled film, in turn, in the reference beam. From a graph of absorptivity of the  $\text{CH}_3$  band maximum at about  $1378\text{ cm}^{-1}$  ( $7.25\ \mu\text{m}$ ) as a function of absorptivity at  $1304\text{ cm}^{-1}$  ( $7.67\ \mu\text{m}$ ), obtain a corrected value of absorptivity at  $1378\text{ cm}^{-1}$  ( $7.25\ \mu\text{m}$ ) as well as the slope of the graph.

NOTE 6—The polyethylene used for preparation of reference films should have very low methyl group content, preferably less than 0.3 for each 100 carbon atoms. Essentially linear Type III polyethylene with

density approximately 0.96 g/cm<sup>3</sup> has been found satisfactory for this purpose (Note 1).

13.2 Procedure:

13.2.1 From the reference polyethylene, mold three or four shock-cooled films about 0.5 mm in thickness and a number of films with thicknesses varying from 0.1 to 0.4 mm. The films shall be smooth and free of voids. Prepare the shock-cooled films in the following way: Place the desired brass shim on the aluminum foil on top of one of the metal plates. Place sufficient polymer in the aperture of the shim to fill completely this aperture after pressing. Cover the preparation with a second aluminum foil and metal plate. Heat the press to 170°C. Insert the mold assembly between the press platens. Preheat for 15 s, then apply pressure slowly until after 30 s the pressure has reached 30 000 lb. Hold the preparation at this pressure for an additional 30 s. Release the pressure, grasp the assembly with pliers, and quickly plunge it into a bucket containing a slurry of ice and water. Carefully remove the film and dry it with a cloth or tissue.

13.2.2 Anneal several 0.5-mm shock-cooled films by a suitable press or oven technique to obtain an increase in density at 23°C of at least 0.020 g/cm<sup>3</sup>.

13.2.3 Mount each film on a suitable holder. Measure the thickness in millimeters at three places in the aperture and record the average thickness on the sample holder. Measure the density of small clippings made close to but not in the aperture of the holder. Measure the density according to Test Method D1505.

13.2.4 Scan the spectrum between 11 and 13 μm and reject any film showing interference fringes.

13.2.5 Measure spectra in the range from 1430 to 1250 cm<sup>-1</sup> (7 to 8 μm) and record the absorbance of the 1368-cm<sup>-1</sup> (7.31-μm) band on each sample as follows: Place an annealed

sample in the sample beam of the spectrophotometer. Place a shock-cooled film in the reference beam. Set the spectrophotometer to achieve the resolution specified in 8.1 (Note 7, Note 8). Set the speed at 0.1 μm/min or 17 cm<sup>-1</sup>/min. Set the gain to produce overshoot of 1 division (1 % of full scale) at 1368 cm<sup>-1</sup> (7.31 μm). Adjust the electrical balance so that there is no drift. Adjust the balance control so that no part of the spectrum between 1430 and 1250 cm<sup>-1</sup> (7 and 8 μm) has more than 90% transmittance. Adjust the 0 % transmittance. Adjust the abscissa scale to at least 75 mm/200 cm<sup>-1</sup> (1.1 μm).

NOTE 7—The 1378-cm<sup>-1</sup> (7.25-μm) methyl band has a half-width less than 6 cm<sup>-1</sup> (0.03 μm) and is thus very sensitive to slit width in prism instruments. Close control of slit width is essential for precise measurements.

NOTE 8—For the Perkin-Elmer Model 21 Spectrophotometer, the following settings are generally satisfactory: Response 1 (electrical and mechanical), Suppression 2, Resolution 3 (960 program), electrical balance to give no drift. For the Beckman Model IR-4 or IR-7 Spectrophotometer, slits 0.40 mm, gain to give single beam/double beam ratio about 1 to 1368 cm<sup>-1</sup> (7.31 μm), Response 2 s.

13.2.6 Run the spectrum from 1430 to 1250 cm<sup>-1</sup> (7 to 8 μm) (see Fig. 1).

13.2.7 Return to 1430 cm<sup>-1</sup> (7 μm) at full speed without releasing the drum or paper lock. Record a spectrum of water vapor on the paper below the polyethylene trace.

13.2.8 Repeat 13.2.5, 13.2.6, and 13.2.7 for the remaining shock-cooled films.

13.3 Calculations:

13.3.1 Draw a base line to each curve from 1396 to 1330 cm<sup>-1</sup> (7.17 to 7.52 μm). Draw a second base line from 1330 to 1270 cm<sup>-1</sup> (7.52 to 7.87 μm) on each spectrum.

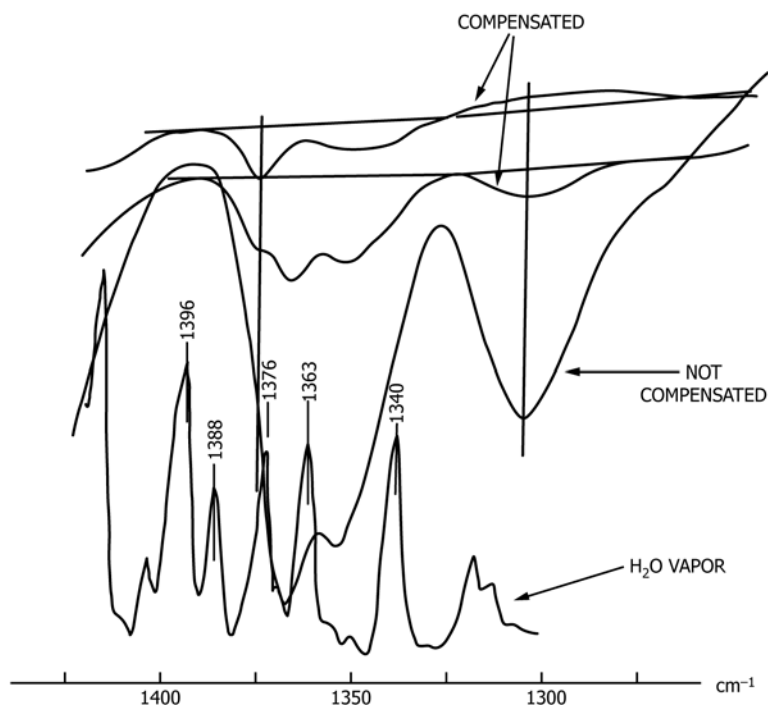


FIG. 1 Example of Self-Compensation Spectrum of Type III Polyethylene (Method A)

13.3.2 Measure the absorbance of the methyl band at 1378.4 cm<sup>-1</sup> (7.255 μm). Measure the absorbance at 1304 cm<sup>-1</sup> (7.67 μm).

NOTE 9—Type I polyethylene may show weak bands between 7.3 and 8.0 μm which interfere slightly in this measurement.

13.3.3 Calculate the following quantities for each pair of films:

$$\alpha = A_{1378} / (d_s t_s - d_r t_r) \quad (2)$$

$$\beta = A_{1304} / (d_s t_s - d_r t_r) \quad (3)$$

where:

$A_{1378}$  = absorbance at 1378 cm<sup>-1</sup> (7.25 μm),

$A_{1304}$  = absorbance at 1304 cm<sup>-1</sup> (7.67 μm),

$d_s$  = density of sample film, g/cm<sup>3</sup>,

$d_r$  = density of reference film, g/cm<sup>3</sup>,

$t_s$  = thickness of sample film, cm, and

$t_r$  = thickness of reference film, cm.

13.3.4 Plot the quantity  $\alpha$  as ordinate against  $\beta$  as abscissa on graph paper for each pair of films.

13.3.5 Draw the best straight line through the points on the graph (see Fig. 2). The intercept on the ordinate is the absorptivity,  $K'_{1378}$ , in square centimeters per gram, due to the methyl band at 1378.4 cm<sup>-1</sup> (7.255 μm). Let  $R$ , the slope of the line, =  $\Delta\alpha/\Delta\beta$ . A value of 0.5 for  $R$  at 1378.4 cm<sup>-1</sup> is recommended.

NOTE 10—Provided that the 1378.4-cm<sup>-1</sup> (7.255-μm) band is normal, the proportionality factor  $R$  for the correction is the same for all polyethylenes.

NOTE 11—The center of the 1378-cm<sup>-1</sup> (7.25-μm) methyl band is normally found between 1379.3 and 1378.0 cm<sup>-1</sup> (7.250 and 7.257 μm). Variation in position of the band center within this range will give a value of  $R$  between about 0.40 and 0.52, in direct proportionality.

13.3.6 For each reference film, correct the measured absorbance at 1378.4 cm<sup>-1</sup>,  $A_{1378}$ , for absorption by amorphous bands at the same frequency by use of the equation

$$A_{1378} \text{ (due to methyl groups)} = A_{1378} - R \times A_{1304} \quad (4)$$

Record  $R$  and the corresponding  $A_{1378}$  (due to methyl groups) on each reference film mount.

13.4 Factors:

13.4.1 Factors,  $f_{1378}$ , in methyl groups for each 100 carbon atoms, in grams per square centimeter, are used to convert absorptivity data to methyl groups for each 100 carbon atoms by the following relationship:

$$\text{Methyl groups (calculated as methyl in alkyl groups)} > C_3 = \quad (5)$$

$$f_{1378 (>C_3)} \times K'_{1378}$$

13.4.2 The conversion factors,  $f_{1378}$ , must be determined for each spectrophotometer.

NOTE 12—In the calculations, the Beer-Lambert law is assumed to apply, that is, the absorptivity at 1378 cm<sup>-1</sup> (7.25 μm) is proportional to the concentration of methyl groups.

NOTE 13—The conversion factor,  $f_{1378}$ , has been derived from measurements of homopolymers of 1-olefins. In the laboratory of origin, using a Perkin-Elmer Model 21 Infrared Spectrophotometer,  $f_{1378 (>C_3)}$  has been determined to be equal to 0.110. In the absence of suitable polymers for calibration, this factor may be adopted for use with other instruments by means of standard reference samples. For example, *n*-cetane (*n*-hexadecane) of certified purity (NBS or equivalent) is scanned in an 0.025-mm cell as directed in the procedure.  $K'_{1378}$  for cetane is then calculated, and  $f_{1378}$  is determined as follows:

$$f_{1378} = (114/K'_{1378} \text{ for cetane}) \times 0.110 \quad (6)$$

here 114 is the value of  $K'_{1378}$  for cetane in the reference instrument.

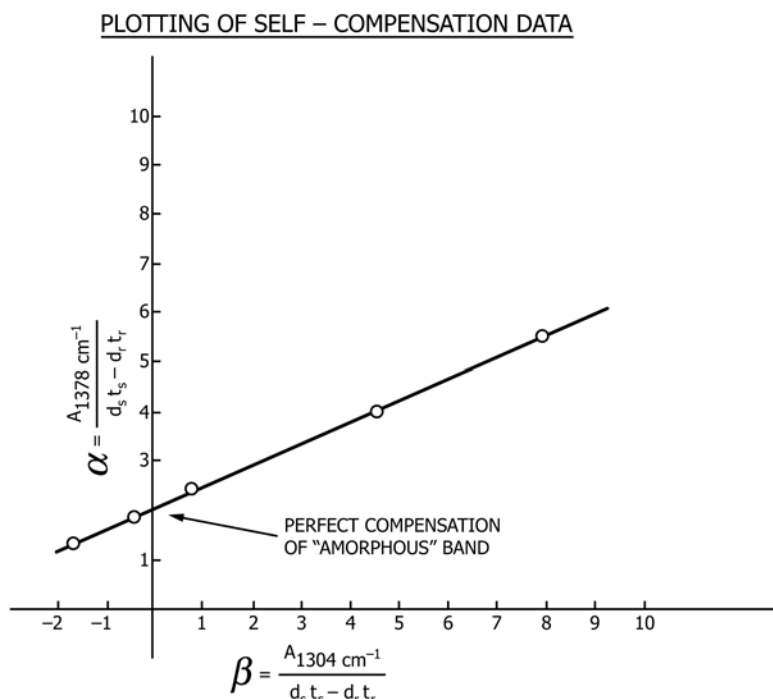


FIG. 2 Plotting of Self-Compensation Data for Absorptivity of Reference Polymer Type III Polyethylene (Method A)

## 14. Procedure

14.1 Mold the polyethylene sample into shock-cooled films about 0.3 mm thick, as directed in 13.2.1.

14.2 Mount the films, measure thickness and density, and look for interference fringes, as directed in 13.2.4 and 13.2.5.

14.3 Place the sample film in the sample beam of the spectrophotometer and in the other beam a reference film chosen so that  $A_{1304}$  is less than 0.05 (Note 14). Set the spectrophotometer to the operating conditions listed in 13.2.6. Record the spectrum between 1430 and 1250  $\text{cm}^{-1}$  (7 and 8  $\mu\text{m}$ ).

NOTE 14—Instead of flat reference films, a wedge molded from the reference polymer may be used if desired. Such a wedge is typically 100 mm long, tapering from 0.4 to 0.2 mm, and is mounted in a holder which allows continuous transverse adjustment of its position in the reference beam. Trial scans are performed to establish a wedge position that gives  $A_{1304} < 0.05$ , before recording the final spectrum.

## 15. Calculation

15.1 Draw base lines and measure absorbances as directed in 13.3.1 and 13.3.2.

15.2 Correct the 1378.4- $\text{cm}^{-1}$  (7.255- $\mu\text{m}$ ) absorbance for incomplete compensation by subtracting  $R \times A_{1304}$ . At 1378.4  $\text{cm}^{-1}$  (7.255  $\mu\text{m}$ ),  $R = 0.5$  (see 13.3.5).

15.3 Add the corrected value of the observed 1378.4  $\text{cm}^{-1}$  (7.255- $\mu\text{m}$ ) absorbance to the absorbance of the methyl band in the reference film (from 13.3.6) (Note 15). The result is the corrected absorbance of the sample film. Divide this value by the density in grams per cubic centimeter and by the thickness in centimeters to obtain the absorptivity,  $K'_{1378}$ , for the sample.

NOTE 15—If a wedge is used as reference, use as the absorbance of the methyl band in the reference the wedge correction,  $d_w t_w K'_w$ .

where:

- $d_w$  = density of wedge,  $\text{g}/\text{cm}^3$ ,  
 $t_w$  = wedge thickness, cm at center of beam, and  
 $K'_w$  = absorptivity of the reference polymer,  $\text{cm}^2/\text{g}$  (13.3.5).

## 16. Report

16.1 Report the following information:

16.1.1 Complete identification of the material tested, including name, manufacturer, lot code number, and physical form when sampled,

16.1.2 Date of test,

16.1.3 Method used,

16.1.4 Densities of the films used in the measurements,

16.1.5 Absorptivity values at 1378.4  $\text{cm}^{-1}$  (7.255  $\mu\text{m}$ ),

16.1.6 Total methyl groups (calculated as methyl in alkyl groups greater than  $\text{C}_3$ ), and

16.1.7 Any unusual absorption bands noted in the spectra.

## 17. Precision and Bias

17.1 In a single laboratory, the measurement of the absorptivity of the 1378.4- $\text{cm}^{-1}$  (7.255- $\mu\text{m}$ ) band is precise to 0.1  $\text{g}/\text{cm}^2$  or 4 % of  $K'_{1378}$ , whichever is greater, using dispersive equipment.

17.2 In an interlaboratory study by six laboratories, the coefficient of variability was 4 % for two samples of Type III polyethylene, 2 % for a sample of Type II, and 15 % for a sample of Type I.

## TEST METHOD B—MEASUREMENT OF THE ABSORBANCE AT 1378 $\text{cm}^{-1}$ (7.25- $\mu\text{m}$ ) BY A WEDGE COMPENSATION METHOD

## 18. Apparatus

18.1 See Section 6.

18.2 *Wedge Holder*—Framework which can be mounted transversely in the reference beam of the spectrophotometer and adjusted continuously to place any thickness of the wedge in the beam.

## 19. Materials

19.1 *Aluminum Foil*.

19.2 *Wedge*:

19.2.1 *Preparation*—A wedge is prepared from the reference polymer by pressing in a special mold (6). Typical wedge dimensions are 100 mm long, tapering from 0.4 to 0.2 mm.

19.2.2 *Calibration*—Measure the thickness of the wedge at small intervals (about 3 mm apart) and mark the thickness on the holder.

NOTE 16—If it is suspected that the reference polymer contains significant methyl group absorptivity at 1378  $\text{cm}^{-1}$  (7.25  $\mu\text{m}$ ), it should be determined using the principle of self-compensation (13.1) but with the base line and wedge adjustment of Test Method B. An annealed film of reference polymer should therefore be prepared as the “sample film” and the procedure of 20.1 – 20.5 and the calculations of 21.1 and 21.2 used, modifying the calculation of 21.3 to read

$$K'_{1378} = A_{1378} / (d_s t_s - d_r t_r), \quad (7)$$

where subscripts  $s$  and  $r$  refer to sample and reference films respectively.

## 20. Procedure

20.1 Mold the polyethylene sample into films having the following thicknesses:

20.1.1 *Types I and II*—Thickness about 0.10 to 0.15 mm.

20.1.2 *Type III*—Thickness about 0.30 to 0.40 mm. (Use a procedure similar to that in 13.2.1 except, after the pressure is released on the press, shut off the heat and leave the preparation in the press. When the platen temperature has fallen below the melting point of the polymer, remove the preparation and separate the film.)

20.2 Mount the film, measure its thickness, scan the spectrum, and reject any film showing interference fringes, as directed in 13.2.4 and 13.2.5.

NOTE 17—For the Perkin-Elmer Model 21 and the Beckman Model IR-4 or IR-7 Spectrophotometer, use the settings given in Note 8. For the Hilger H-800 Spectrophotometer, the following settings have been used: slits 0.1 mm at 3  $\mu\text{m}$  and program 40, speed 132  $\text{min}/\mu\text{m}$ , gain and damping adjusted to provide optimum servo response for the particular sample. For the Grubb-Parsons GS-2A Spectrophotometer, the following settings have been used: slits program 10, speed 4  $\text{min}/\mu\text{m}$ , gain and damping adjusted to optimum as above.

20.3 Place the sample film in the sample beam of the spectrophotometer and the wedge (the thinnest part) in the reference beam.

20.4 Adjust the wedge in progressive steps with manual scanning until the desired degree of compensation is achieved. This is achieved by alternately setting the wavelength to 1368 cm<sup>-1</sup> (7.31 μm) and to 1400 cm<sup>-1</sup> (7.14 μm). When the absorbance is the same at these wavelengths, the wedge is correctly placed.

20.5 Record the spectrum of the 1378-cm<sup>-1</sup> (7.25-μm) band from 1343 to 1400 cm<sup>-1</sup> (7.45 to 7.14 μm).

**21. Calculation**

21.1 Draw a baseline tangent to the recorded curve over the interval from 1343 to 1400 cm<sup>-1</sup> (7.45 to 7.14 μm) (see Fig. 3).

21.2 Measure the absorbance at the center of the methyl band, A<sub>1378</sub> (Note 18).

NOTE 18—If a wedge correction is necessary, add to the absorbance of the 1378-cm<sup>-1</sup> (7.25-μm) methyl band the wedge correction, t<sub>w</sub>K<sub>w</sub>,

where:

- t<sub>w</sub> = wedge thickness, cm, and
- K<sub>w</sub> = absorptivity of the reference polymer, 13.1, 13.2, and 13.3.1 – 13.3.5.

21.3 Calculate the absorptivity at 1378 cm<sup>-1</sup> (7.25 μm), K'<sub>1378</sub>, in square centimeters per gram as follows:

$$K'_{1378} = A_{1378}/(t \times d) \tag{8}$$

where:

- A<sub>1378</sub> = absorbance at 1378 cm<sup>-1</sup> (7.25 μm) from 21.2,
- t = thickness of the sample film, cm, and
- d = density of the polymer, g/cm<sup>3</sup>.

21.4 Calculate the total methyl content (calculated as methyls in alkyl groups > C<sub>3</sub>) as follows:

$$\text{Methyl groups per 100 carbon atoms} = K'_{1378} \times f_{1378} \tag{9}$$

where:

- K'<sub>1378</sub> = absorptivity, as calculated in 21.3, and
- f<sub>1378</sub> = conversion factor, which must be determined for each spectrophotometer.

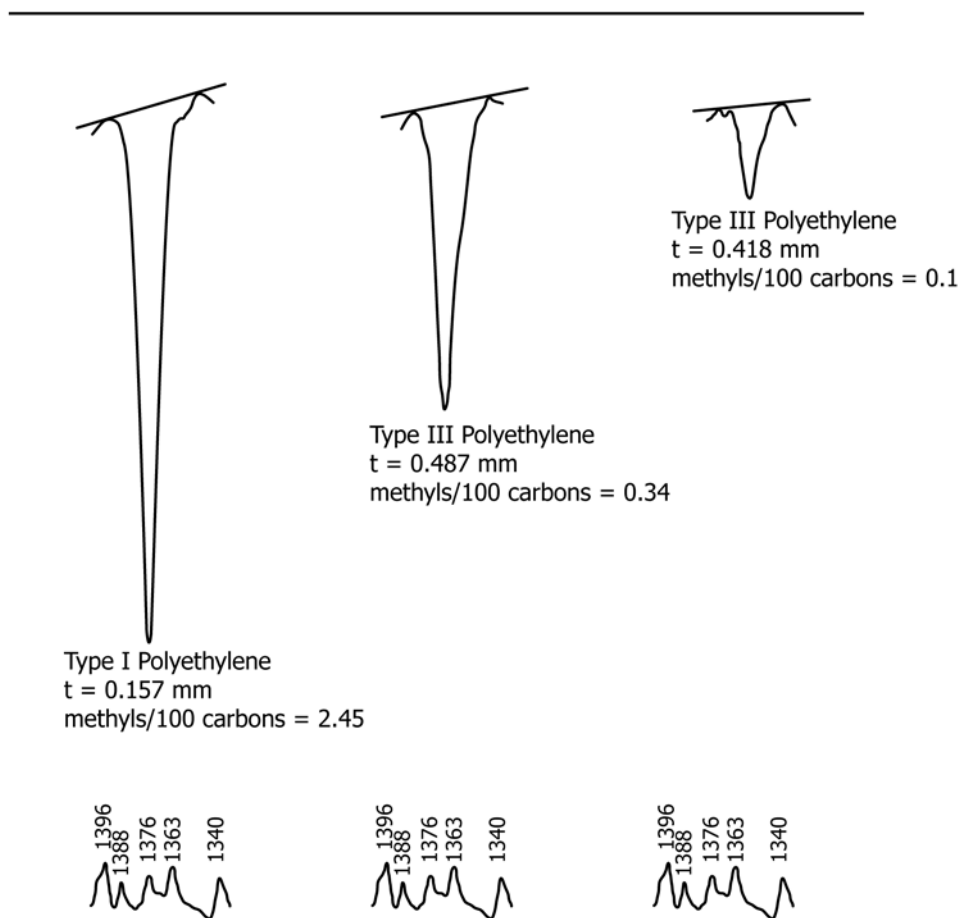


FIG. 3 Examples of Measuring Absorbance at 1378 cm<sup>-1</sup> (7.25 μm) (Method B)

NOTE 19—An absolute calibration of an infrared method for methyl group determination is described in Reference (4). This method involves the preparation of branched deuterated polymethylenes. The calibration obtained in this way is expressed by the equation:

$$\text{Number of methyl groups} \quad (10)$$

(calculated as alkyl groups  $>C_3$ )

$$\text{per 100 carbon atoms} = 0.0765 K'_{1378}$$

Instead of the calibration with the branched deuterated polymethylenes a value of 0.0765 may be adopted for use with other instruments by means of standard samples. For example, *n*-cetane (*n*-hexadecane) of certified purity (NBS or equivalent) is scanned in an 0.075-mm cell as directed in the procedure.  $K'_{1378}$  for *n*-cetane is then calculated, and  $f_{1378}$  is determined as follows:

$$f_{1378} = [120/(K'_{1378} \text{ for } n\text{-cetane})] \times 0.0765 \quad (11)$$

where 120 is the value of  $K'_{1378}$  for *n*-cetane in the reference instrument.

## 22. Report

22.1 See 16.1.1 – 16.1.3 and 16.1.5 – 16.1.7. In addition, report whether methyl group absorptivity at  $1378 \text{ cm}^{-1}$  has been determined and corrected for Note 16.

## 23. Precision and Bias

23.1 Precision in one laboratory is estimated to be about  $\pm 2\%$  relative for methyl content = 3/100 carbon atoms and up to  $\pm 5\%$  relative for methyl content = 0.3/100 carbon atoms, using dispersive equipment.

23.2 In an interlaboratory study by ten laboratories, the coefficient of variability was 30 % for one sample of Type III polyethylene, 13 % for another sample of Type III, 16 % for a sample of Type II, and 18 % for a sample of Type I, using dispersive equipment.

## 24. Keywords

24.1 Fourier transform spectroscopy; infrared spectroscopy; methyl groups; polyethylene; quantitative analysis

## REFERENCES

- (1) Bryant, W. M. D., and Voter, R. C., "The Molecular Structure of Polyethylene. II. Determination of Short-Chain Branching," *Journal of the American Chemical Society*, Vol 75, 1953, pp. 6613–6118.
- (2) Reding, F. P., and Lovell, C. M., "The Effect of Various Branch Lengths on the Crystallinity of Polyethylenic Resins," *Journal of Polymer Science*, Vol 21, 1956, pp. 157–159.
- (3) Boyd, D. R. J., Voter, R. C., and Bryant, W. M. D., "Identification and Measurement of Alkyl Groups in Branched Polyethylenes by Infrared Spectrometry," paper presented at 132nd Meeting, Am. Chemical Soc., New York, NY, Sept. 9, 1957.
- (4) Willbourn, A. H., "Polymethylene and the Structure of Polyethylene: Study of Short-Chain Branching, Its Nature and Effects," *Journal of Polymer Science*, Vol 34, 1959, pp. 569–597.
- (5) Oetgen, R. A., Kao, Chao-lan, and Randall, H. M., "The Infrared Prism Spectrograph as a Precision Instrument," *Review of Scientific Instruments*, Vol 13, 1942, p. 515.
- (6) Harvey, M. C., and Peters, L. L., "Polymer Wedge for the Infrared Determination of Methyl Groups in Polyethylene," *Analytical Chemistry*, Vol 32, 1960, p. 1725.
- (7) Silas, R. S., "Bond Intensities of Methyl and Olefin Groups in Polyethylenes," Presented at Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, OH, June 11–15, 1956; abstract in *Spectrochimica Acta*, Vol 8, 1956, p. 313.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/