ASTM INTERNATIONAL

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Standard Test Methods for
Absorbance of Polyethylene Due to Methyl Groups[1] at 1378 cm^{-1}

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.

1. Scope

1.1 These test methods cover measurement by infrared absorption spectrophotometry of the 1378 cm^{-1} (7.25 μm) band in polyethylene due to methyl groups. (**1, 2, 3-6**)[2] Two test methods are covered:

1.1.1 *Test Method A* uses compensation with a standard sample film 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 0.910 to 0.925 g/cm^3), II (density 0.926 to 0.940 g/cm^3), and III (density 0.941 to 0.965 g/cm^3).

Note 1—For determination of density, see Specifications D1505.

Note 2—In cases of Type III polyethylene with densities greater than 0.950 g/cm^3, 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, health, and environmental 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.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D618 Practice for Conditioning Plastics for Testing

D883 Terminology Relating to Plastics

D1505 Test Method for Density of Plastics by the Density-Gradient Technique

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 For definitions of terms used in these test methods and associated with plastics issues refer to the terminology contained in Terminology D883.

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 is acceptable for use to compare the total methyl contents of polyethylenes made by similar processes. Data on infrared absorption at certain other wavelengths is potentially useful for information on 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^{-1} (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, is potentially useful so as to lead to

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assignment of end-group structures and to shed light upon polymerization mechanisms.

4.3 Qualitative correlations are possible between data on total methyl groups in polyethylene 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 cm⁻¹ (7.31 µm) and 1352 cm⁻¹ (7.39 µm) with the 1378 cm⁻¹ (7.25 µm) methyl deformation band.

5.2 In Test Method A residual absorption is often present at 1352 cm⁻¹ after compensation, but this band is believed not to contribute appreciable interference in the measurement of the methyl peak at 1378 cm⁻¹ in samples with very low methyl content.

6. Apparatus

6.1 *Infrared Spectrophotometer,* double beam, with NaCl prism, and spectral resolution as defined by Condition C in Part III (Spectral Resolution) of the Proposed Methods for Evaluation of Spectrophotometers, or

6.2 *Fourier Transform Instrument,* capable of a spectral resolution of at least 2.0 cm⁻¹.

6.3 *Compression-Molding Press,* small, with platens capable of being heated to 170°C.

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 graduations of 0.001 mm.

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. Preparation of Apparatus

8.1 The precision obtained using this test method depends very markedly upon the condition of the spectrophotometer. Instrument performance shall be at least equal to that cited in the manufacturer's specifications for a new instrument. Resolution shall be checked to assure conformance with 6.1 or 6.2. 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 to 1250 cm⁻¹ (7 to 8 µm) 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 (see Fig. 1 and Fig. 3).

9. Calibration and Standardization

9.1 Check the instrument for resolution and wavelength accuracy by checking against known wavelengths and absorbance for methyl absorbance bands in the 2851 cm⁻¹ (3.51 µm) range.

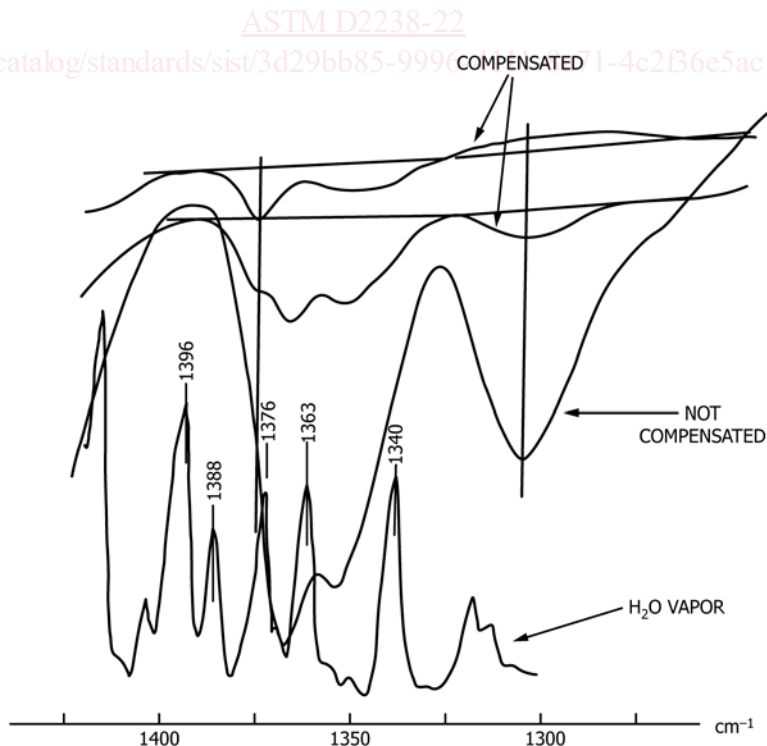FIG. 1 Example of Self-Compensation Spectrum of Type III Polyethylene (Method A)

Type III Polyethylene
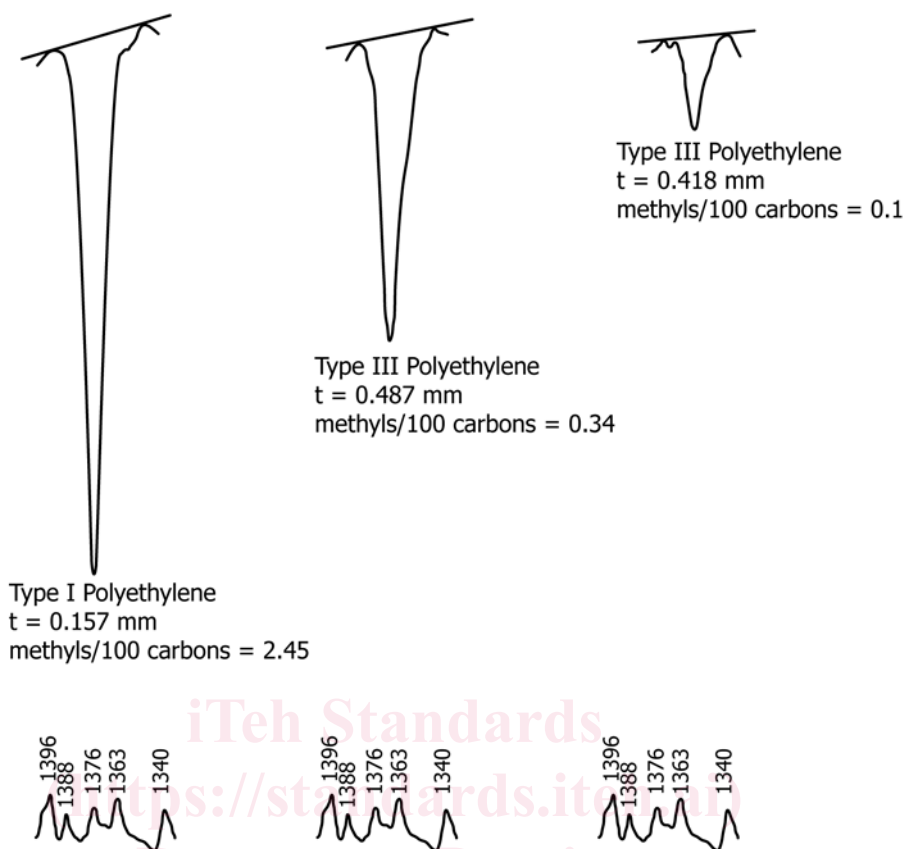t = 0.418 mm
methyls/100 carbons = 0.1

Type III Polyethylene
t = 0.487 mm
methyls/100 carbons = 0.34

Type I Polyethylene
t = 0.157 mm
methyls/100 carbons = 2.45

FIG. 3 Examples of Measuring Absorbance at 1378 cm⁻¹ (7.25 µm) (Method B)

10. Conditioning

10.1 *Conditioning*—Condition the test specimens at $23 \pm 2°C$ ($73.4 \pm 3.6°F$) and 50 ± 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 $\pm 1°C$ ($\pm 1.8°F$) and ± 2 % relative humidity.

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

TEST METHOD A—MEASUREMENT OF THE ABSORBANCE AT 1378 cm⁻¹ (7.25 µm) BY A FILM COMPENSATION METHOD

11. Materials

11.1 *Aluminum Foil.*

11.2 *Crushed Ice.*

11.3 *Reference Films,* prepared as described in 12.2.1.

12. Calibration and Standardization For Test Method A

12.1 *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. 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 CH_3 band maximum at about 1378 cm⁻¹ (7.25 µm) as a function of absorptivity at 1304 cm⁻¹ (7.67 µm), obtain a corrected value of absorptivity at 1378 cm⁻¹ (7.25 µm) as well as the slope of the graph. Use polyethylene, for preparation of reference films, having a 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/cm³ has been found satisfactory for this purpose (Note 1).

12.2 *Procedure:*

12.2.1 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

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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 20.7 MPa (3000 psi). 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.

12.2.2 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^3.

12.2.3 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.

12.2.4 Scan the spectrum between 909 and 769 cm^{-1} (11 and 13 μm) and reject any film showing interference fringes.

12.2.5 Measure spectra in the range from 1430 to 1250 cm^{-1} (7 to 8 μm) and record the absorbance of the 1368 cm^{-1} (7.31 μm) band on each sample as follows: for prism instruments, place an annealed sample in the sample beam of the spectrophotometer. Place a shock-cooled film in the reference beam: for FTIR instruments, the shock-cooled film represents the background or reference films. Set the spectrophotometer to achieve the resolution specified in 8.1. For prism instruments, the following parameter settings have been found to achieve this: set the speed at 0.1 μm/min or 17 cm^{-1}/min. Set the gain to produce overshoot of 1 division (1 % of full scale) at 1368 cm^{-1} (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^{-1} (7 and 8 μm) has more than 90 % transmittance. Adjust the 0 % transmittance. Adjust the abscissa scale to at least 75 mm/200 cm^{-1} (75 mm/50 μm). The 1378 cm^{-1} (7.25 μm) methyl band has a half-width less than 6 cm^{-1} (0.03 μm) and is thus very sensitive to slit width in prism instruments. Close control of slit width is essential for precise measurements.

12.2.6 Run the spectrum from 1430 to 1250 cm^{-1} (7 to 8 μm) (see Fig. 1).

12.2.7 Return to 1430 cm^{-1} (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 (Note 5).

12.2.8 Repeat 12.2.5, 12.2.6, and 12.2.7 for the remaining shock-cooled films.

12.3 *Calculations:*

12.3.1 Draw a base line to each curve from 1396 to 1330 cm^{-1} (7.17 to 7.52 μm). Draw a second base line from 1330 to 1270 cm^{-1} (7.52 to 7.87 μm) on each spectrum.

12.3.2 Measure the absorbance of the methyl band at 1378 cm^{-1} (7.25 μm). Measure the absorbance at 1304 cm^{-1} (7.67 μm).

12.3.3 Calculate the following quantities for each pair of films:

$$\alpha = A_{1378}/(d_s t_s - d_r t_r) \tag{1}$$

$$\beta = A_{1304}/(d_s t_s - d_r t_r) \tag{2}$$

where:

A_{1378} = absorbance at 1378 cm^{-1} (7.25 μm),
A_{1304} = absorbance at 1304 cm^{-1} (7.67 μm),
d_s = density of sample film, g/cm^3,
d_r = density of reference film, g/cm^3,
t_s = thickness of sample film, cm, and
t_r = thickness of reference film, cm.

12.3.4 Plot the quantity α (Eq 1) as ordinate against β (Eq 2) as abscissa on graph paper for each pair of films.

12.3.5 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 cm^{-1} (7.25 μm). Let R, the slope of the line, $= \Delta\alpha/\Delta\beta$. A value of 0.5 for R at 1378 cm^{-1} is recommended.

NOTE 6—Provided that the 1378 cm^{-1} (7.25 μm) band is normal, the proportionality factor R for the correction is the same for all polyethylenes.

NOTE 7—The center of the 1378 cm^{-1} (7.25 μm) methyl band is normally found between 1379 and 1378 cm^{-1} (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.

12.3.6 For each reference film, correct the measured absorbance at 1378 cm^{-1}, A_{1378}, for absorption by amorphous bands at the frequency by use of the equation

$$A_{1378} \text{ (due to methyl groups)} = A_{1378} - (R \times A_{1304}) \tag{3}$$

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

12.4 *Conversion Factors:*

12.4.1 Factors, f_{1378}, in methyl groups for each 100 carbon atoms, in g/cm^2, are used to convert absorptivity data to methyl groups for each 100 carbon atoms by the following relationship:

$$\text{Methyl groups, as methyl in alkyl groups of} > C_3 = f_{1378\,(>C3)} \times K'_{1378} \tag{4}$$

12.4.2 The conversion factors, f_{1378}, must be determined for each spectrophotometer. In the calculations, the Beer-Lambert law is assumed to apply, that is, the absorptivity at 1378 cm^{-1} (7.25 μm) is proportional to the concentration of methyl groups.

NOTE 8—The conversion factor, f_{1378}, has been derived from measurements of homopolymers of 1-olefins. In the laboratory of origin, $f_{1378\,(>C3)}$ has been determined to be equal to 0.110. In the absence of suitable polymers for calibration, this factor will be adopted for use with other instruments by means of standard reference samples. For example, *n*-cetane (*n*-hexadecane) of certified purity 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:

$$f_{1378} = 114/(K'_{1378} \text{ for cetane}) \times 0.110 \tag{5}$$

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