Designation: D 2238 – 92 (Reapproved 1999)

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

This standard is issued under the fixed designation D 2238; 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 1378.4-cm^{-1} (7.255-μm) band in polyethylene due to methyl groups. **(1, 2, 4-7)**[2] 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^3), II (density 926 to 940), and III (density 941 to 965).

NOTE 1—For determination of density, see Specifications D 1248.

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 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 similar or equivalent ISO standard covering the subject matter of these test methods.

2. Referenced Documents

2.1 *ASTM Standards:*

D 618 Practice for Conditioning Plastics and Electrical Insulating Materials for Testing[3]
D 1248 Specification for Polyethylene Plastics Molding and Extrusion Materials[3]
D 1505 Test Method for Density of Plastics by the Density-Gradient Technique[3]
D 1898 Practice for Sampling of Plastics[3]
E 131 Terminology Relating to Molecular Spectroscopy[4]
E 168 Practices for General Techniques of Infrared Quantitative Analysis[4]
E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[5]
E 380 Practice for Use of the International System of Units (SI)[5]

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:

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

3.2 Units, symbols, and abbreviations used in this test method appear in Terminology E 131 or Practice E 380.

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 **(3).**

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

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[1] These test methods are under the jurisdiction of ASTM Committee D-20 on Plastics and are the direct responsibility of Subcommittee D20.70 on Analytical Methods (Section D20.70.08).

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[2] The boldface numbers in parentheses refer to the list of references at the end of these test methods.

[3] *Annual Book of ASTM Standards*, Vol 08.01.

[4] *Annual Book of ASTM Standards*, Vol 14.01.

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

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 cm^{-1} (7.31 µm) and 1352 cm^{-1} (7.39 µm) with the 1378-cm^{-1} (7.255 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 1378.4 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[6,7]

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.[8]

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.[9]

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 platens and molds with appropriate gloves for hand protection.

8. Sampling

8.1 The polyethylene shall be sampled in accordance with Practice D 1898.

9. Preparation of Apparatus

9.1 The precision obtained using this test method depends very markedly upon the condition of the spectrophotometer. Instrument performance should be at least equal to that cited in the manufacturer's specifications for the new instrument. Resolution should be checked to assure conformance with 6.1. The linearity of the photometric system should be measured; linearity should 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 should 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 cm^{-1} (3.507 µm) range.

11. Conditioning

11.1 *Conditioning*—Condition the test specimens at 23 ± 2°C (73.4 ± 3.6°F) and 50 ± 5 % relative humidity for not less than 40 h prior to test in accordance with Procedure A of Practice D 618, for those tests where conditioning is required. In cases of disagreement, the tolerances shall be ±1°C (±1.8°F) and ±2 % relative humidity.

11.2 *Test Conditions*—Conduct tests in the standard laboratory atmosphere of 23 ± 2°C (73.4 ± 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 ±1°C (±1.8°F) and ±2 % relative humidity.

TEST METHOD A—MEASUREMENT OF THE ABSORBANCE AT 1378 cm^{-1} (7.25 µm) 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 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.

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^3 has been found satisfactory for this purpose (Note 1).

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[6] *Proceedings*, ASTM, Vol 58, 1958, p. 472.

[7] 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.

[8] 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.

[9] Brown and Sharpe micrometer No. 223 RS has been found satisfactory for this purpose.

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. The shock-cooled films may be prepared 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^3.

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 D 1505.

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^{-1} (7 to 8 μm) and record the absorbance of the 1368-cm $^{-1}$ (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^{-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} (1.1 μm).

NOTE 7—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.

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^{-1} (7.31 μm), Response 2 s.

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

13.2.7 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.

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^{-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.

13.3.2 Measure the absorbance of the methyl band at 1378.4 cm^{-1} (7.255 μm). Measure the absorbance at 1304 cm $^{-1}$ (7.67 μm).

NOTE 9—Type I polyethylene may show weak bands between 7.3 and

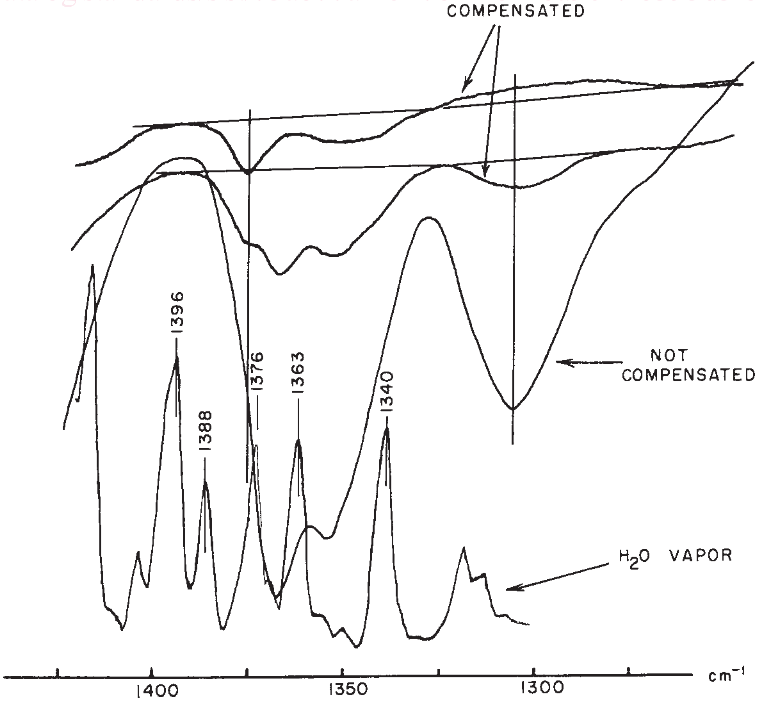

FIG. 1 Example of Self-Compensation Spectrum of Type III Polyethylene (Method A)