Designation: D2238 – 22

# 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

[1] 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).

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

[3] 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.

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.

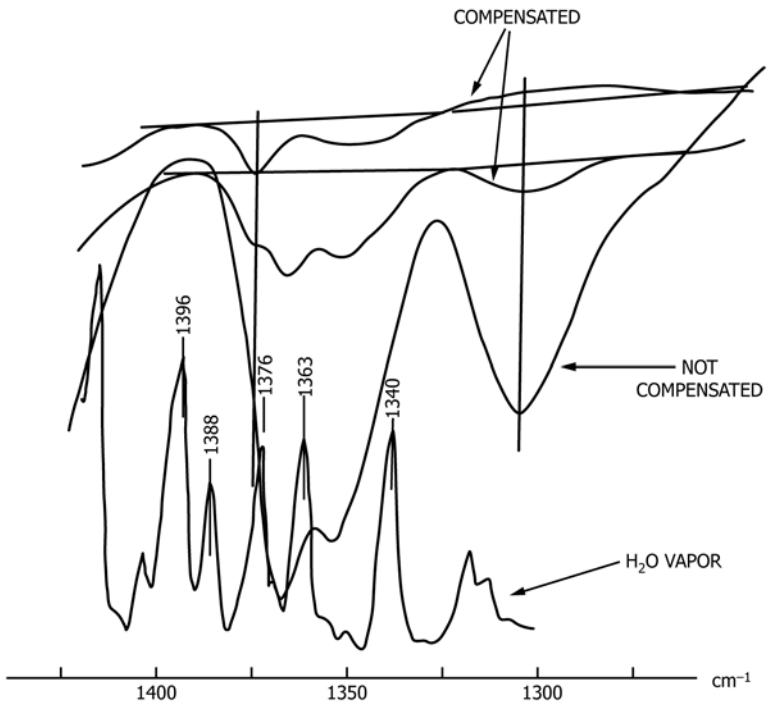


**FIG. 1 Example of Self-Compensation Spectrum of Type III Polyethylene (Method A)**

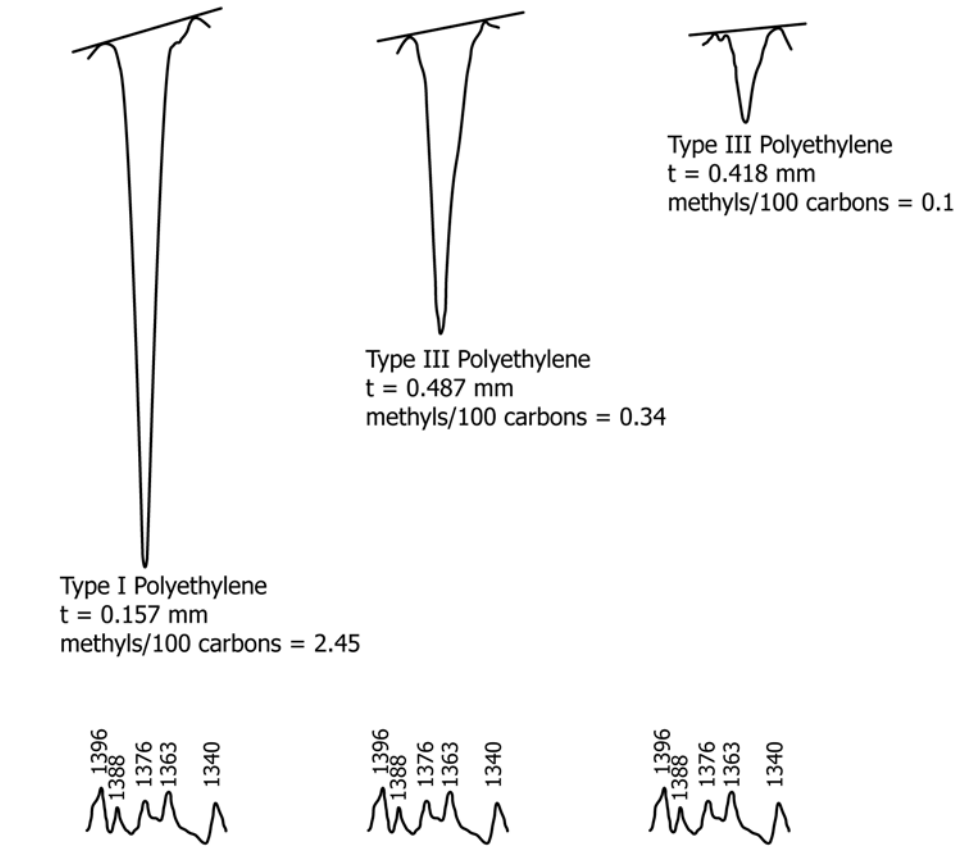


**FIG. 3 Examples of Measuring Absorbance at 1378 $cm^{-1}$ (7.25 µm) (Method B)**

## 10. Conditioning

10.1 *Conditioning*—Condition the test specimens at 23 ± 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 D618, for those tests where conditioning is required. In cases of disagreement, the tolerances shall be ±1°C (±1.8°F) and ±2 % relative humidity.

10.2 *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 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 $g/cm^3$ 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