



Standard Test Method for Vinyl and Trans Unsaturation in Polyethylene by Infrared Spectrophotometry¹

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1. Scope

1.1 This test method covers most types of polyethylene, those ethylene plastics consisting of ethylene and α -olefin comonomers longer than propylene, and blends of the above in any ratio.

1.2 The values stated in SI units are to be regarded as the standard.

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—There is no similar or equivalent ISO standard.

2. Referenced Documents

2.1 ASTM Standards:

D 792 Test Method for Density and Specific Gravity (Relative Density) of Plastics by Displacement²

D 1505 Test Method for Density of Plastics by the Density-Gradient Technique²

D 1898 Practice for Sampling of Plastics²

D 3124 Test Method for Vinylidene Unsaturation in Polyethylene by Infrared Spectrophotometry³

E 131 Terminology Relating to Molecular Spectroscopy⁴

E 168 Practices for General Techniques of Infrared Quantitative Analysis⁴

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods⁵

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers⁴

¹ This test method 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 April 10, 1998. Published February 1999.

² *Annual Book of ASTM Standards*, Vol 08.01.

³ *Annual Book of ASTM Standards*, Vol 08.02.

⁴ *Annual Book of ASTM Standards*, Vol 03.06.

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

E 380 Practice for Use of the International System of Unit (SI)⁵

Proposed Methods for the Evaluation of Spectrophotometers

3. Terminology

3.1 *General*—The units, symbols, and abbreviations used in this test method appear in Terminology E 131 or Practice E 380.

4. Summary of Test Method

4.1 The band at 965 cm^{-1} is characteristic of the trans-vinylene substituted group. The band at 908 cm^{-1} is characteristic of the terminal vinyl group.

4.2 These bands are not seriously overlapped by interfering groups from the polymer. The vinyl absorbance at 908 cm^{-1} is close to the absorbance band from terminal methyl groups on chains longer than ethyl, at 895 cm^{-1} . This interference is minimal for most products. Inclusion of the bromination and spectral subtraction step from Test Method D 3124 may improve the results for very low density products.

4.3 Integrated absorbance is used in this test method. Integrated absorbance is found by integrating the spectrum over the absorbance band when the spectrum is plotted as absorbance versus frequency, in cm^{-1} . Most spectral manipulation software contains algorithms for adequately determining baseline corrected integrated absorbencies.

4.4 Calibration is performed using a solution of 1-octene for normal vinyl groups, and trans-3-hexene for trans-vinylene groups.

5. Significance and Use

5.1 There are three types of olefinic groups present in sufficient concentrations to warrant consideration, one or more of that can normally be found in any polyethylene. The three types are trans-vinylene, $\text{R-CH=CH-R}'$, sometimes referred to as trans-internal unsaturation; vinylidene or pendent methylene, $\text{RR}'\text{C-CH}_2$; and vinyl unsaturation, R-CH=CH_2 , also referred to as terminal unsaturation.

5.2 The type and quantity of these groups can influence the chemical and physical properties of the resin. Information concerning their presence may also be used to characterize or identify unknown resins or blends of resins.

5.3 Additives may interfere with unsaturation measurements. The use is cautioned to determine which additives are present and if there any absorbance bands caused by additive presence that overlap or interfere with unsaturation absorbance bands used in this test method in the range of 1050 to 850 cm^{-1} . If overlapping bands occur, the method is not applicable.

5.4 Interference fringes resulting from smooth sample surfaces can cause measurement errors. This test method requires the use of aluminum foil in the compression molding of samples to provide an adequately rough surface to minimize interference fringes.

6. Apparatus

6.1 *Infrared Spectrophotometer*, either double-beam, or a fourier transform (FTIR).

6.1.1 *Double-Beam Infrared Spectrophotometer*, capable of spectral resolution as defined in Condition C of Section III (Spectral Resolution) of the Proposed Methods for the Evaluation of Spectrophotometers. Also, see Practice E 275 for testing procedures. The instrument should be capable of scale expansion along the wavelength (or wave number) axis.

6.1.2 *Fourier Transform Infrared Spectrometer*, capable of 4 cm^{-1} resolution. The instrument should be capable of scale expansion along the wavelength axis.

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

6.3 *Two Metal Plates*, 150 by 150 mm or larger, of 0.5-mm or greater thickness with smooth surfaces.

6.4 *Brass Shims*, approximately 75 by 75 mm, of 0.5-mm thickness with an aperture in the center at least 25 by 38 mm for most samples. A thinner shim may be used with highly absorbing samples.

6.5 *Micrometer Calipers*, with thimble graduations of 0.001 mm.

6.6 *Infrared Liquid Cell*, with sodium chloride or potassium bromide windows.

6.7 *Film Mounts*, with apertures at least 6 by 27 mm, to hold the specimens in the infrared spectrophotometer.

7. Reagents and Materials

7.1 *Carbon Disulfide* (CS_2), reagent grade.

7.2 *Aluminum Foil Sheets*.

8. Hazards

8.1 Carbon disulfide is flammable and toxic.

9. Sampling

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

10. Calibration

10.1 Prepare at least three different solutions of each of the standard compounds in CS_2 at closely the same known concentration near 0.18 mol/L.

10.2 Set the controls of the infrared spectrometer for quantitative conditions with a good signal to noise ratio and satisfactory reproducibility. Use a scanning speed sufficiently slow to give good reproducibility of line shape. Set the slit width narrow enough that there is little distortion of the true line shape. For a FTIR, a spectral resolution of 4 cm^{-1} should be used. An apodization function that gives good quantitation should be used. Beer-Norton medium and Happ-Genzel have been found to be appropriate.

10.3 Scan the solutions from 1050 to 850 cm^{-1} in a 0.1-mm path length cell which has been calibrated by interference fringes or other methods. Cell windows made of either NaCl or KBr are suitable.

10.4 Determine the integrated peak areas, A , for each standard at the wavelength specified for the appropriate end group. The baseline shall be drawn from valley to valley for the peak centered at or near the specified wave number for each type of unsaturation.

10.5 Calculate the molar absorptivity, B for each solution using the known concentrations from 10.1 and the following equation:

$$B = (A/C \times T) \quad (1)$$

where:

B = molar absorptivity, L/mol-cm,

A = integrated absorbance, measured or estimated as defined in 10.4,

C = concentration of end group, Mol/L, and

T = cell thickness, cm.

10.6 For each type of unsaturation, calculate the average of the molar absorptivities determined in 10.5.

11. Procedure

11.1 *Sample Preparation:*

11.1.1 Preheat the press to 140 to 150°C.

11.1.2 Place a brass shim on an aluminum foil sheet, dull side up, that in turn covers a metal plate.

NOTE 2—Placing the dull side of the aluminum foil next to the polymer gives the sample film some texture and reduces fringe effects.

11.1.3 Add sufficient polymer so that the shim aperture will be completely filled when the polymer is pressed.

11.1.4 Cover with another sheet of aluminum foil, dull side down, and another metal plate.

11.1.5 Insert the mold assembly between the press platens and apply a slight pressure.

11.1.6 Allow the sample to preheat for 30 s. Apply a press clamping pressure of 70 000 to 210 000 kPa (approximately 10 000 to 30 000 psig) at 140 to 150° C for 1 min or until all exudation ceases. Use the lower pressure for 150 × 150 mm plates, and the higher pressure for 300 × 300 mm plates.

11.1.7 Remove the mold from the press and allow it to cool to room temperature. The cooling may be assisted by immersion in cold water.

11.1.8 Using the micrometer, measure the thickness of the sample to ± 0.01 mm at three places within the sample beam area. Calculate an average of the three measurements and record the result in centimetres.

NOTE 3—The thickness is given here in cm in order to agree with the molar absorptivity term.

11.2 Spectral Measurements:

11.2.1 Scan each sample slowly from 1050 to 850 cm⁻¹.

11.2.2 Measure the integrated peak area for the each peak in the normalized spectrum at the wavelengths used to measure the standard solutions. The integrated area baseline shall be drawn from valley to valley for the peak centered at or near the specified wave number for each type of unsaturation.

11.3 Density Measurement—Measure the density of the polyethylene sample by displacement, or gradient column technique.

12. Calculation

12.1 Calculate the end-group concentrations using appropriate molar absorptivity for each end group, using the following equation:

$$C = (A/B \times T) \quad (2)$$

where:

B = average molar absorptivity of the standard compound of interest as defined in 10.6, L/mol-cm,

T = sample thickness, cm, and

A = integrated absorbance, measured or estimated, as defined in 11.2.2.

12.2 Calculate the number of end groups per 1000 carbon atoms, *V* for each sample by the following equation:

$$V = 14 \times C/D \quad (3)$$

where:

C = end group concentration, mol/L, calculated in 12.1, and
D = density of the polyethylene sample, g/cm³, measured in 11.3.1.

13. Report

13.1 Report the following information:

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

13.1.2 Date of test,

13.1.3 Density of the material tested,

13.1.4 Number of vinyl groups per 1000 carbon atoms for each sample,

13.1.5 Number of trans-vinylene groups per 1000 carbon atoms for each sample, and

13.1.6 Any sample or spectral anomalies seen during the measurements.

14. Precision and Bias

14.1 The repeatability standard deviation (2σ) has been determined to be ± 0.0176 trans-vinylene carbon atoms per 1000 total carbon atoms, and ± 0.029 vinyl carbon atoms per 1000 total carbon atoms. The reproducibility of this test method is being determined.

14.2 No information can be presented on the bias of the procedure in this test method because no material having an accepted reference value is available.

15. Keywords

15.1 FTIR; infrared spectrophotometry; polyethylene; trans-vinylene unsaturation; vinyl unsaturation

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