



Designation: D 3124 – 98

Standard Test Method for Vinylidene Unsaturation in Polyethylene by Infrared Spectrophotometry¹

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1. Scope

1.1 This test method is applicable to all types of polyethylenes, those ethylene plastics consisting of ethylene and α -olefin copolymers 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 Methods 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
- E 131 Terminology Relating to Molecular Spectroscopy³
- E 168 Practices for General Techniques of Infrared Quantitative Analysis³
- 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 Spectrophotometers³
- E 380 Practice for Use of the International System of Units (the Modernized Metric System)⁴
- Proposed Methods for Evaluation of Spectrophotometers⁵

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 (Section D20.70.08).

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

³ *Annual Book of ASTM Standards*, Vol 03.06.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

⁵ *Proceedings*, Am. Soc. Testing Mats., ASTEA, Vol 58, 1958, pp. 472–494.

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 888 cm^{-1} ($11.26\text{ }\mu\text{m}$) is characteristic of vinylidene groups (**1**, **2**).⁶ It is the strongest vinylidene band and is due to the deformation vibrations of the C - H bonds in the CH_2 group.

4.2 This band is overlapped by absorption at 11.25 to $11.07\text{ }\mu\text{m}$ (889 to 903 cm^{-1}) from vibrations of terminal methyl groups on alkyl groups longer than ethyl. By using a brominated sample in the reference beam of a double-beam spectrophotometer along with an untreated sample in the sample beam, the methyl absorption is cancelled out. For spectrometers with computerized spectral manipulation capabilities, the same effect may be accomplished by subtraction of the brominated spectra from the untreated spectra. The bromination destroys the vinylidene unsaturation in the sample (**1**) in the reference beam but leaves the methyl absorption intact. Thus, the methyl absorption is eliminated because it appears in both the sample and reference beams. The vinylidene absorption is then seen without interference in the difference spectrum.

4.3 Integrated absorbance, instead of the usual absorbance at the band peak, 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} . A very good approximation to integrated absorbance is obtained by multiplying the absorbance at the band peak by the band half-width, the width of the band in cm^{-1} at an absorbance equal to 50 % of the peak absorbance. This approximation may be used for this test method if integrated absorbance is not available. Most spectral manipulation software contains algorithms for adequately determining baseline corrected integrated absorbances. Integrated absorbance is used because it is more nearly constant for a series of materials containing the same absorbing group in different environments, or in different states of aggregation. It

⁶ The boldface numbers in parentheses refer to the list of references at the end of this test method.



is independent of changes in line shape. Peak absorbances are quite dependent on line shape factors, especially line width, which depends on the state of aggregation. Calibration with a liquid sample for measurements on solid-state samples is not satisfactory using peak absorbances but is satisfactory using integrated absorbances (1, 3).

4.4 Calibration is performed using a solution of 2,3-dimethyl-1,3-butadiene in a liquid cell of known thickness. This liquid has two vinylidene groups per molecule. Three different solutions are prepared and their measurements averaged to obtain greater accuracy.

5. Significance and Use

5.1 There are three types of olefinic groups present in sufficient concentrations to warrant consideration, one or more of which can normally be found in any polyethylene (4). The three types are: trans-vinylene, $R - CH = CH - R'$, sometimes referred to as transinternal unsaturation; vinylidene or pendent methylene, $RR'C = CH_2$; 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 Vinylidene unsaturation represents the major portion of the unsaturation present in most low-density polyethylenes.

5.4 Infrared spectroscopy can be used for the determination of unsaturation in polyethylene (1, 3, 5). The values determined by infrared agree with those determined by IC1 uptake (5).

6. Apparatus

6.1 *Infrared Spectrophotometer, Either Double Beam or Fourier Transform (FTIR):*

6.1.1 Double-beam infrared spectrophotometer, capable of spectral resolution as defined by Condition C of Section III (Spectral Resolution) of the Proposed Methods for 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.⁷

6.1.2 Fourier transform infrared spectrometer, capable of 4-cm^{-1} resolution and scale expansion along the wavelength axis.⁸

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 thickness with smooth surfaces, preferably chromium plated.

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.

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

6.6 *Infrared Liquid Cell*, with sodium chloride or potassium bromide windows, 0.1-mm spacing, calibrated.

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

6.8 *Glass Stoppered Flasks*, 150-mL.

6.9 *Vacuum Oven*.

7. Reagents and Materials

7.1 *Bromine*, reagent grade.

7.2 *Carbon Disulfide (CS₂)*, reagent grade.

7.3 *Poly(ethylene terephthalate) or Aluminum Sheets*, 80 by 80 mm, or slightly larger to cover brass shims.

7.4 *Standard Compound*, 2,3-dimethyl-1,3-butadiene (liquid) of high purity, five 1-mL vials.⁹

8. Hazards

8.1 Bromine is toxic and corrosive. Bromine treatment should be carried out in a hood or other ventilated space. Neoprene gloves should be worn and adequate eye protection employed. Bromine-treated samples should be exposed to a stream of air for 24 h or more to remove surplus bromine before measurement in order to protect the operator and equipment. Samples previously treated with bromine should never be stored with materials which will be damaged by bromine.

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 the standard compound in CS₂ at closely the same known concentration near 0.18 mol/L (14.8 g/L). Calculate the exact vinylidene concentrations (two times the molar concentrations) and record the values.

10.2 Set the controls of the infrared spectrometer for quantitative conditions with a good signal to noise ratio and satisfactory reproducibility. Use a sufficiently expanded chart scale such that line width can be measured accurately. 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. Record the instrument conditions used. For a FT-IR, 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 935 to 847 cm^{-1} (10.70 to $11.80\text{ }\mu\text{m}$) in the 0.1-mm sodium chloride cell which has been calibrated by interference fringes or other adequate method. For a FT-IR, expand the scale of the transformed and converted absorbance spectra from 935 to 847 cm^{-1} .

NOTE 2—Practice E 275, paragraph 21.5, describes the interference fringe method of calibrating the thickness of infrared cells.

10.4 For the FTIR, calculate the baseline corrected integrated absorbance of the 888-cm^{-1} ($11.26\text{-}\mu\text{m}$) band. For a double-beam IR without integration capability, measure the

⁷ Perkin-Elmer Models 21, 125, 221, and 421 spectrophotometers and Beckman IR-4 and IR-9 spectrophotometers have been found satisfactory for this purpose.

⁸ FT-IR instruments made by a variety of manufacturers that have spectral resolutions of at least 2 cm^{-1} have been found adequate for these purposes. Among those used have been the Nicolet, Digilab, and Perkin-Elmer series of Fourier Transform spectrometers.

⁹ Obtainable from Chemical Sales Co., 4692 Kenny Rd., Columbus, OH 43221.