Standard Test Method for Vinylidene Unsaturation in Polyethylene by Infrared Spectrophotometry[1]

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 known ISO equivalent to this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D792 Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement
D1505 Test Method for Density of Plastics by the Density-Gradient Technique
D1898 Practice for Sampling of Plastics (Withdrawn 1998)[3]
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
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers
IEEE/ASTM SI 10 Standard for Use of the International System of Units (the Modernized Metric System)
Proposed Methods for Evaluation of Spectrophotometers[4]

3. Terminology

3.1 *General*—The units, symbols, and abbreviations used in this test method appear in Terminology E131 or Standard IEEE/ASTM SI 10.

4. Summary of Test Method

4.1 The band at 888 cm^{-1} (11.26 μm) is characteristic of vinylidene groups (**1, 2**).[5] 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 μm (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

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[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods (Section D20.70.08).

Current edition approved Feb. 1, 2011. Published March 2011. Originally approved in 1972. Last previous edition approved in 2003 as D3124 – 98(2003). DOI: 10.1520/D3124-98R11.

[2] 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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

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

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

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 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 E275 for testing procedures. The instrument should be capable of scale expansion along the wavelength (or wave number) axis.[6]

6.1.2 Fourier transform infrared spectrometer, capable of 4-cm^{-1} resolution and scale expansion along the wavelength axis.[6,7]

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* (CS_2), 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.[8]

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 D1898.

10. Calibration

10.1 Prepare at least three different solutions of the standard compound in CS_2 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 $4\ \text{cm}^{-1}$ 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.

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

[7] FT-IR instruments made by a variety of manufacturers that have spectral resolutions of at least $2\ \text{cm}^{-1}$ have been found adequate for these purposes.

[8] Obtainable from Chemical Sales Co., 4692 Kenny Rd., Columbus, OH 43221.

10.3 Scan the solutions from 935 to 847 cm^{-1} (10.70 to 11.80 µm) 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 E275, 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-µm) band. For a double-beam IR without integration capability, measure the absorbance maximum intensity of the same band using the baseline technique. Then, measure the band width, in cm^{-1}, at half intensity of the band. Multiply the two measurements to get an estimate of the integrated area.

NOTE 3—Practice E168 describes a suitable procedure for measuring the absorbance.

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

$$B = (A/C \times L) \tag{1}$$

where:

B = molar absorptivity, L/mol-cm,
A = integrated absorbance, measured or estimated as defined in 10.4,
C = concentration of vinylidene group, mol/L, and
L = cell thickness, cm.

10.6 Calculate the average molar absorptivity from the values obtained 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 a polyethylene terephthalate or aluminum sheet, which in turn covers a metal plate.

11.1.3 Add polymer in sufficient quantity to completely fill the shim aperture during pressing.

11.1.4 Cover with another sheet of polyethylene terephthalate or aluminum 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 the full press pressure at 140 to 150°C for 1 min or until all exudation ceases.

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 Release the pressure and remove the sample.

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

11.1.10 Repeat 11.1.1-11.1.9 until two pairs of samples have been obtained such that for each pair the members do not differ by more than 2 % in thickness. Use one member of each pair for bromination in 11.2. Set the other member of each pair aside for use in 11.3 without bromination.

11.2 *Bromination:*

11.2.1 Two alternate bromination test methods, solution or vapor phase, may be employed. The solution test method uses a solution of bromine in carbon tetrachloride. The vapor-phase test method uses the vapor above liquid bromine.

NOTE 4—The vapor-phase test method is recommended for any samples that show solubility in carbon tetrachloride.

11.2.2 *Solution Test Method:*

11.2.2.1 Place the samples in a 5 % by volume solution of bromine in carbon tetrachloride for 3 h. This reaction should be performed in the dark or in a flask which has been blackened to exclude light.

11.2.2.2 Remove the samples from the bromine solution. Suspend freely and dry in a vacuum oven at room temperature overnight. The films should then have a pale yellow color.

11.2.3 *Vapor Phase Test Method:*

11.2.3.1 Cut a portion of the sample film to fit snugly in the mouth of a 150-cm^3 glass stoppered flask.

11.2.3.2 Hold one end of the film with forceps and push it into the neck of the flask containing a few cubic centimetres of liquid bromine so that the greater part of the film is suspended in bromine vapor in the body of the flask. The film should be held by the edges at the narrow part of the neck.

NOTE 5—The following method of suspending the film above the bromine seems preferable. Find a ground glass joint which will fit the flask. Form it into a stopper with a hook drawn out from the bottom. Perforate the film at one end and attach to the hook before closing the flask with this stopper.

11.2.3.3 Stopper the flask with a short ground stopper and leave this assembly at room temperature (23°C) for 2 h. After 2 h, remove the film using forceps.

11.2.3.4 Place the bromine-treated film on a watch glass and allow it to remain in the draught of the hood until most of the absorbed bromine has been removed and the film is pale yellow in color.

11.3 *Spectral Measurements:*

11.3.1 Use samples of brominated and unbrominated materials in pairs such that the thickness does not differ by more than ±2 %. Errors in the true integrated vinylidene absorbance will result if thickness differences are larger or if bromination is incomplete.

11.3.2 Place the unbrominated sample in the sample beam and its brominated counterpart in the reference beam.

11.3.3 Scan the samples slowly from 935 to 847 cm^{-1} (10.70 to 11.80 µm), employing the instrument conditions recorded previously in 10.2 and 10.3. For a FT-IR, the instrument conditions described in 10.2 and 10.3 should be used.

11.3.4 For the peak at 888-cm^{-1} (11.26 µm) measure the integrated absorbance, or estimate the integrated area employing the procedure used in 10.4.

11.3.5 Repeat 11.3.1-11.3.4 for replicate samples.

11.3.6 Measure the density of the polyethylene sample by displacement or gradient column technique.

12. Calculation

12.1 Calculate the vinylidene concentrations using the following equation:

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

where:

B = average molar absorptivity of the standard compound as defined in 10.5, L/mol-cm,
L = sample thickness, cm, and
A = integrated absorbance, measured or estimated, as defined in 11.3.4

12.2 Calculate the number of vinylidene groups per 1000 carbonations, V, for each sample pair by the following equation:

$$V = 14\,C/D$$

where:

C = vinylidene concentration, mol/L, calculated in 12.1, and
D = density of the polyethylene sample prior to bromination, g/cm^3.

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 Bromination method used,

13.1.4 Density of material,

13.1.5 Number of vinylidene groups per 1000 carbon atoms for each sample, and

13.1.6 Any sample or spectral anomalies seen during the measurements.

14. Precision

14.1 The precision of the analysis method has been calculated by an analysis of variance of round-robin data from nine laboratories on three samples by ASTM Subcommittee D20.13 on Statistical Methods.[9] For the number of vinylidene groups per 1000 carbon atoms, the intralaboratory precision is ±0.0352 (D2S) vinylidene groups/1000 C atoms and the interlaboratory precision is ±0.0667 (D2S) vinylidene groups/1000 C atoms, as defined in Practice E177. Thus, the following statements can be made with 95 % confidence:

14.1.1 Two measurements made by a single laboratory on one type of material should not differ by more than 0.0352 vinylidene groups/1000 C atoms.

14.1.2 Two laboratories should not differ by more than 0.0667 vinylidene groups/1000 C atoms in measuring one type of material.

15. Keywords

15.1 FTIR; infrared spectrophotometry; polyethylene; vinylidene unsaturation

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[9] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D20-1029.

REFERENCES

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