Designation: D2702 – 05 (Reapproved 2016)

Standard Practice for
Rubber Chemicals—Determination of Infrared Absorption Characteristics[1]

This standard is issued under the fixed designation D2702; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 This practice covers a simple, rapid practice to prove the identity of a rubber chemical before incorporation into a rubber mix by comparison of its infrared absorption spectrum with that of a reference specimen.

1.2 This technique can also be used to detect gross contamination or large differences in rubber chemicals. Thus, it can provide a basis for producer-consumer agreement.

1.3 Wherever "infrared spectrophotometer" is used, "Fourier Transform Infrared Spectrometer (FTIR)" may also be understood.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E131 Terminology Relating to Molecular Spectroscopy
E168 Practices for General Techniques of Infrared Quantitative Analysis
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

3. Terminology

3.1 *Definitions:* For definitions of terms used in this practice refer to Terminology E131.

4. Summary of Practice

4.1 A method of specimen preparation is selected that is compatible with the physical and chemical properties of the rubber chemical that will provide the desired spectral information.

4.2 The specimen is placed in the specimen beam of the spectrophotometer and scanned to obtain a spectrum over the region of interest under specified instrument parameters.

4.3 The spectrum is compared with that of a reference specimen. It is understood that the reference specimen was prepared and scanned in an identical manner and preferably on the same infrared spectrophotometer.

5. Significance and Use

5.1 This procedure can be used for a variety of applications, including identifying unlabeled material, process control, raw material acceptance, product evaluation, and compositional change during environmental testing.

5.2 Rubber chemicals vary widely in their chemical and physical properties. Infrared spectrophotometers vary in the presentation of a spectrum (some are linear with absorbance, others with transmittance, some use grating for energy dispersion, others use a sodium chloride prism, some obtain a spectrum through a mathematical Fourier Transform, and the like). For these reasons, a single universal method of specimen preparation and set of instrument parameters is not possible.

5.3 By using a specific sampling procedure and operating conditions, a given spectrophotometer will give an absorption curve that is characteristic of the rubber chemical or mixture under investigation.

5.4 The ability to superimpose the infrared spectrum of the test specimen upon that of a reference specimen, obtained under the same conditions, is evidence that the two are identical.

5.5 The presence of additional absorption bands in either the test specimen or the reference specimen indicates the presence of one or more additional components.

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[1] This practice is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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[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.

6. Apparatus

6.1 *Initial Specimen Preparation*—The diverse physical nature of rubber chemicals may require the use of one or more of the following:

6.1.1 *Agate Mortar and Pestle,* small.

6.1.2 *Wig-L-Bug Amalgameter.* [3]

6.1.3 *Mold and Press for KBr Pellets*—The die size will depend on the disk holder available with the user's infrared spectrophotometer. The hydraulic press should be capable of exerting 140-MPa (20 000-psi) pressure.

6.1.4 *Vacuum Pump,* operating at 250 Pa or less.

6.2 *Infrared Spectrophotometer:*

6.2.1 The spectral region from 2.5 to 15 µm (4000 to 667 cm^{-1}) is the region most often used for rubber chemical identification, although inorganic chemicals may have useful bands down to 250 cm^{-1}.

6.2.2 If the performance of the spectrophotometer must be evaluated, refer to Practice E275.

6.3 *Demountable Cells*—Liquid cells ranging from 0.025 to 1.0 mm in specimen path length and KBr pellet holder should be available. On occasion, a variable-path cell is useful.

6.4 *KBr or NaCl Plates,* of suitable size for spectrophotometer.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Observe all health and safety recommendations for handling the chemicals in this practice.

7.3 Any of the following reagents may be required depending on the method chosen for sample preparation:

7.3.1 *Carbon Disulfide,* spectro quality.

7.3.2 *1,2-Dichlorobenzene.*

7.3.3 *Ether,* anhydrous.

7.3.4 *Hexachlorobutadiene.*

7.3.5 *Refined Mineral Oil.* [5]

7.3.6 *Perfluorocarbon Oil.*

7.3.7 *Potassium Bromide* (KBr), infrared quality.

7.3.8 *Tetrahydrofuran,* (without inhibitor).

7.3.9 *Acetone,* infrared quality.

8. Sampling and Sample Preparation

8.1 Generally, the physical nature of the specimen will determine the specimen preparation procedure. In some cases, where alternative procedures could be used, agreement between the chemical producer and consumer would be required. In choosing a specimen preparation procedure, certain potential sources of error should be considered. These are listed in the preparation procedures 8.2 – 8.5. The techniques are also described in Practices E168.

8.2 *Liquids*—Fixed-thickness absorption cells of 0.025 to 0.5 mm are used for the analysis of low-viscosity liquids. Demountable cells are used with more viscous liquid specimens. Spacers can be used to adjust specimen thickness, but the usual practice is to spread a film of viscous liquid over one salt plate, overlay a second plate, and squeeze out the excess until the desired film thickness has been reached. Initially, the desired thickness may be obtained by trial and error. A specimen thickness of 0.02 to 0.1 mm usually gives a good spectrum. The experienced spectroscopist can usually judge an adequate film thickness with minimum effort.

8.3 *Solids*—Specimens that are solid (amorphous, polymeric, or crystalline) may be handled by one or more of several techniques:

8.3.1 *Mulling Techniques:*

8.3.1.1 Perhaps the most common method for infrared study of solid powders is to grind a few milligrams of powder in an agate mortar and add a suspending agent to make a mull (see Practices E168). Scan the resultant paste in a demountable cell.

8.3.1.2 *Mineral Oil*[5] is a mulling agent, which in the thickness used, is quite transparent in the infrared, except for the CH absorption frequencies at 3.3, 6.9, 7.3, and 13.9 µm (3000, 1450, 1375, and 720 cm^{-1}). If information is desired in these regions, alternative mulling materials are hexachlorobutadiene or perfluorocarbon oil.

8.3.1.3 It is desirable to grind the specimen thoroughly with mortar and pestle before adding the mulling agent to minimize light scattering and reduce window scratching. A minimum of mulling agent should be used to wet the powder.

8.3.1.4 Polymeric specimens are usually better handled by other techniques because of the grinding difficulty. Freezing this type of specimen with dry ice or the use of a freezer mill may help, but it can also introduce water condensate contamination.

8.3.2 *Melted Film Technique:*

8.3.2.1 This method can be used for polymeric or highly viscous materials. It consists of melting the specimen and spreading a thin film across the face of a salt plate.

8.3.2.2 Advantages are that no solvent or mulling agent interference bands are introduced. Possible disadvantages are thermal or oxidation breakdown, loss of volatile components, or spurious bands due to crystal orientation in the case of crystalline materials.

8.3.3 *Solution Technique:*

8.3.3.1 Dissolving the specimen in a suitable solvent and scanning the solution in a fixed path cell is a technique that is frequently used.

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[3] The sole source of supply of the apparatus known to the committee at this time is Crescent Dental and Manufacturing, 7750 W. 47th St., Lyons IL 60534. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[5] Nujol has been found satisfactory for this purpose.

8.3.3.2 The solution technique is used in resolving OH and NH bands in the 3.3 to 2.5-µm (3000 to 4000-cm^{-1}) region. Hydrogen-bonding effects in this region are reduced by dissolving the rubber chemical in a solvent.

8.3.3.3 One problem with this technique is that no single solvent is completely transparent in the infrared region. Two or more solvents are thus necessary to provide "windows" across the infrared region so that solvent interference peaks do not occur.

8.3.3.4 Minor solvent interference bands can often be cancelled by use of a variable-path reference cell containing pure solvent. However, if major solvent bonds are compensated in this manner, there is little or no available energy left in the spectrophotometer. Therefore, little or no useful information can be obtained in these wavelength regions.

8.3.3.5 Another problem is that solubility of polar rubber chemicals is very limited in the better nonpolar solvents, such as carbon disulfide. Some rubber chemicals will also react with carbon disulfide.

8.3.4 *Film Cast from Solution:*

8.3.4.1 In this technique, the specimen is dissolved in a suitable volatile solvent. The solution is poured on a salt plate leaving a film, or, on a glass plate, where the dried film may be lifted from the surface and placed in a specimen holder for subsequent infrared analysis.

8.3.4.2 Difficulties with this method may be incomplete solvent removal or spurious bands due to crystal orientation.

8.3.5 *KBr Pellet Technique:*

8.3.5.1 The specimen is intimately mixed with KBr powder and pressed into a pellet for measurement of the infrared spectrum.

NOTE 1—The Wig-L-Bug is useful in intimately mixing the specimen with KBr using a vial and pestle and a vibrating motion.

8.3.5.2 This technique is described in Practices E168.

8.3.5.3 This technique should be used only when there is agreement between the producer and the consumer because the spectrum obtained by this means may contain extra crystalline bands or the specimen may react with KBr to produce spurious bands.

8.4 *Reflectance Measurements:*

8.4.1 A variety of reflectance apparatuses are available for use with IR and FTIR spectrometers. The most common is Attenuated Total Reflectance (ATR), but several other configurations are available, including Horizontal ATR (H-ATR). The sample must be such that it can be pressed into intimate contact with the reflectance crystal, either by a holder, or by pressing the sample into the crystal.

8.4.2 The use of reflectance spectroscopy may cause distortion of the shape of the bands or of the shape of the baseline, or both. Care must be taken in the interpretation of reflectance spectra when comparing them with spectra generated by other sampling techniques.

8.5 *Special Handling:*

8.5.1 Some specimens require pretreatment before examination by the infrared technique. For example:

8.5.1.1 Specimens containing water, carbon, or other highly active infrared absorbers must be treated to remove the interference.

8.5.1.2 Some rubber chemicals are dispersed on inert materials such as diatomaceous earth or clay. In this case, solvent extraction and subsequent evaporation of the solvent may separate the rubber chemical from the inert material.

9. Test Specimen

9.1 The specimen thickness normally chosen is one in which two or three of the stronger bands fall within about 10 % transmittance range.

9.2 For FTIR spectrometers, the spectrum is obtained from a minimum of 32 scans (interferograms).

9.3 Sometimes this does not provide complete information on the very weak or very strong bands, and a second spectrum at 5 to 10 times or ⅕ to ⅒ the original thickness is run through portions of the spectrum.

10. Procedure

10.1 Scan the spectrum at median values of the operating range, resolution, and signal to noise ratio of the particular instrument employed.

10.2 For detailed instrument operation, refer to the instrument manual of the spectrophotometer used.

11. Interpretation of Results

11.1 The objective of this practice is to determine whether the test specimen is the same as a reference specimen. If the spectrum of the two can be superimposed over each other, the materials are identical.

11.2 If the spectra are not superimposable, compare the location, shape, and relative absorbance of every absorption band in each of the spectra. If the materials are identical, these factors should agree. Furthermore, there should be no extraneous bands in either spectrum. However, crystallinity, sample oxidation, specimen path length, or solution concentration differences may cause the absorbance of the absorption bands in one spectrum to be different from those in the other. If the materials are identical, these differences will be proportional throughout the spectra.

11.3 If discrepancies exist between the spectrum of the test specimen and that of the reference specimen, one of the following conclusions may be drawn:

11.3.1 If one or more major bands in the spectrum of the reference specimen is missing from the spectrum of the test specimen, the probability is that the two are not the same material.

11.3.2 If extra absorption bands appear in the spectrum of either the reference or test specimen, the presence of one or more extra components in that specimen is indicated.

11.4 If the reference and test specimens are found to be essentially the same, but one or the other has been found to contain extra components, one or more of the following factors may be the cause:

11.4.1 The components were added to improve the product. Examples: dedusting oils, stabilizers, coloring agents, anticaking agents, and the like.

11.4.2 These components may be the result of the decomposition due to aging, thermal breakdown, and the like.

11.4.3 These components may be the result of improper or incomplete processing.

11.4.4 Specimens of the same technical grade material from different manufacturers may contain different impurities because of differences in raw materials and processing.

11.4.5 These components may be present because of gross contamination of the specimen with foreign materials.

11.5 If the test specimen is not identical to the reference specimen, there must be agreement between the producer and consumer on the type and amount of extra material that must be added (or removed) as criterion for acceptance or rejection of the lot of rubber chemical. This may require quantitative determinations as described in Practices E168.

12. Report

12.1 Report the following information:

12.1.1 Description of the material tested: that is, the name, manufacturer, lot number, and other pertinent data,

12.1.2 Description of method of specimen preparation,

12.1.3 Description of spectrophotometer used and operating parameters, such as time of scan, slit program, amplifier gain, attenuator speed, or the use of computer-assisted techniques,

12.1.4 A statement on whether the test specimen was identical with the reference specimen or whether it fell within the specifications agreed to by the producer and consumer,

12.1.5 Notation on any differences that had not been previously agreed upon,

12.1.6 Indication of possible interferences, such as crystal orientation, moisture, or solvent contamination, and

12.1.7 Date of test.

13. Precision and Bias

13.1 No statement is made about either the precision or the bias for Practice D2702 since this practice is intended as a qualitative procedure.

14. Keywords

14.1 FTIR; infrared (IR) analysis; rubber chemicals