Designation: D3677 – 10 (Reapproved 2015)

Standard Test Methods for Rubber—Identification by Infrared Spectrophotometry[1]

This standard is issued under the fixed designation D3677; 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 These test methods cover rubber identification and are based on infrared examination of pyrolysis products (pyrolyzates) and films.

1.2 These test methods are applicable to rubbers in the raw state and, when compounded, both in the cured and uncured state.

1.3 Since it is customary in infrared spectrophotometry to use wavenumbers (cm^{-1}) rather than Hertz (Hz), the unit for frequency in the SI system, the former is employed throughout this test method.

1.4 This test method assumes that specimens and infrared spectra are prepared and analyzed by experienced personnel and that the equipment is operated according to the manufacturer's direction for optimum performance. No details for operation of infrared spectrophotometers are included in this test method.

1.5 *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 precautionary statements are given in Section 17.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D297 Test Methods for Rubber Products—Chemical Analysis

D1418 Practice for Rubber and Rubber Latices—Nomenclature

D3452 Practice for Rubber—Identification by Pyrolysis-Gas Chromatography

E168 Practices for General Techniques of Infrared Quantitative Analysis (Withdrawn 2015)[3]

3. Significance and Use

3.1 For research, development, and quality control purposes, it is advantageous to determine the composition of rubbers in cured, compounded products.

3.2 This test method provides such composition analysis utilizing an infrared technique.

4. Reagents

4.1 *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.

4.2 *Acetone.*

4.3 *Alcohol,* ethanol, denatured.

4.4 *2-Butanone.*

4.5 *Chloroform.*

4.6 *Congo Red Paper.*

4.7 *Diatomaceous Filter Aid*—Some grades are quite unsatisfactory in that they will not sufficiently absorb carbon black.

4.8 *1,2-Dichlorobenzene*—A check on suitability may be made by evaporating 50 cm^3 to dryness and making an infrared spectrum of the residue. Any substantial absorbance at positions near those wavenumbers that will be used for rubber analysis, indicates that the 1,2-dichlorobenzene is unsuitable for use.

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[1] These test methods are under the jurisdiction of ASTM Committee D11 on Rubber and are 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.

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

[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 *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

4.9 *Dry Compressed Air and Nitrogen,* in cylinders, or provided as a laboratory service.

4.10 *Sodium Sulfate,* anhydrous.

4.11 *Toluene.*

TEST METHOD A QUALITATIVE ANALYSIS

5. Scope

5.1 This test method, based on infrared examination of pyrolysis products (pyrolyzates) and films, will identify the rubbers in 6.1 occurring alone or in binary blends in the range from 80 % major component to 20 % minor component. Exceptions to this will be found in 6.2.

5.2 This test method is applicable to rubbers in the raw state and, when compounded, both in the cured and uncured state.

5.3 This test method implies that sample preparation and infrared spectrum are prepared and analyzed by experienced personnel and that the equipment used for the production of the spectra is operated according to the manufacturer's directions for optimum performance. No details for operation of infrared spectrophotometers are included in these test methods.

6. Field of Application

6.1 Infrared examinations of pyrolyzates and films will identify mixtures of two of the following types of rubbers in the range from 80 % major component to 20 % minor component. (See the exceptions in 6.2.)

6.1.1 *Isoprene Rubbers* (see 6.2.1):

6.1.1.1 Natural rubber, synthetic polyisoprene, gutta percha, and balata are included.

6.1.1.2 Examination of the pyrolyzate will not distinguish between the different forms of polyisoprene.

6.1.1.3 Examination of a film will distinguish natural and synthetic polyisoprene from balata and gutta percha.

6.1.2 *Styrene-Butadiene Rubbers with Styrene Content of Approximately 23.5 % Styrene* (see 6.2.2):

6.1.2.1 For the purpose of this standard, all copolymers of styrene and butadiene and their oil-extended forms are included.

6.1.2.2 Examination of the pyrolyzate will not distinguish between emulsion and solution polymerized rubbers.

6.1.2.3 Examination of films may give some information about the monomer ratio and the polymerization system.

6.1.3 *Acrylonitrile-Butadiene Rubber with Acrylonitrile Content of Approximately 33 %:*

6.1.3.1 Examination of the pyrolyzate will not measure the ratio of acrylonitrile to butadiene.

6.1.3.2 Examination of a film may give some information about the acrylonitrile content.

6.1.4 *Chloroprene Rubber*—This test method will not distinguish between the different types of chloroprene rubbers.

6.1.5 *Butyl Rubber*— This test method will not distinguish between butyl rubber and its halogenated forms.

6.1.6 *Polybutadiene Rubber (High cis):*

6.1.6.1 Examination of the pyrolyzate will not distinguish between polybutadiene rubbers having different isomer ratios.

6.1.6.2 Examination of a film may give some information about the monomer ratio.

6.1.7 *Ethylene-Propylene Rubbers* (see 6.2.3)—This test method will not distinguish between rubbers having different ratios of ethylene to propylene nor between copolymers and terpolymers.

6.2 Exceptions to the rubbers listed in 6.1 are:

6.2.1 A blend of natural or synthetic isoprene (20 %) and chloroprene (80 %), or both, may present difficulties, and identification of the minor component may be achieved only when its content is equal to or more than 30 % in the blend.

6.2.2 A blend of butadiene-styrene rubber (80 %) and high *cis* polybutadiene rubber (20 %) may present difficulties, and identification of the minor component may only be achieved when it is equal to or more than 30 % in the blend.

6.2.3 Ethylene-propylene rubber in blends with other rubbers presents difficulties when its content is in the range from 20 to 40 %.

6.3 In difficult cases, examination of the gaseous products of pyrolysis by gas chromatography (Practice D3452) may give further information.

7. Summary of Test Method

7.1 *Identification from Pyrolyzates:*

7.1.1 A small quantity of extracted and dried rubber is pyrolyzed in a stream of nitrogen in a test tube held in a small electric, thermo-regulated furnace at 450 to 500°C, or alternatively, rapidly pyrolyzed in a small test tube held in the hot zone of a gas flame.

7.1.2 A test for chlorine is conducted during pyrolysis.

7.1.3 A few drops of the pyrolyzate are transferred to a salt plate and an infrared spectrum recorded over the 4000 to 666 cm^{-1} region.

7.1.4 The rubber is identified by comparison to standard reference spectra and by reference to a table of diagnostic absorptions (significant absorption frequencies).

7.1.5 Each laboratory employing this standard must prepare spectra of all rubbers they might be expected to identify. These spectra must be prepared in the same manner and using the same equipment as will be used for unknown samples.

7.2 *Identification from Films:*

7.2.1 A small quantity of extracted and dried rubber is dissolved in 1,2-dichlorobenzene, filtered, and a film cast on a salt plate. This film is used as in 7.1.4.

7.2.2 A small quantity of extracted and dried rubber is subjected to mild thermal degradation at 200 ± 5°C for a short time. The degraded sample is dissolved in trichloroethylene then chloroform, and a film cast on a salt plate. This film is used as in 7.1.4.

8. Apparatus

8.1 *Extraction Apparatus:*

8.1.1 The extraction apparatus used shall be of the general type and dimensions shown in Fig. 1.

8.2 *Test Tubes,* small, and other necessary glassware sufficient to carry out the test as written.

8.3 *Pyrolysis Apparatus* (Fig. 2)—The pyrolysis apparatus consists of a glass tube (*P*) having inward projections to prevent the sample from falling to the bottom of the tube and a lateral condenser tube. The tube (*P*) has a ground-glass standard taper (*S*) which carries a small glass adductor tube. A collecting tube (*T*) is placed under the condenser tube. An electric, thermoregulated furnace (*F*) accommodates an aluminum block (*H*) with holes for one or more tubes (*P*).

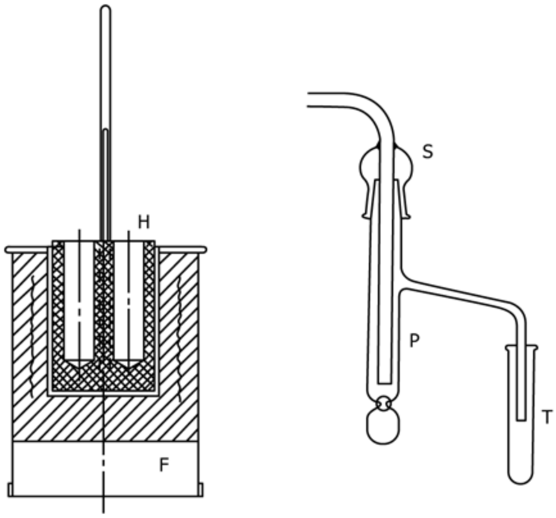
8.4 *Capillary Pipets.*

8.5 *Oven,* capable of maintaining a temperature of 200 ± 5°C for use in 10.2.

8.6 *Water Bath,* for use in 10.2.

8.7 *Salt Plates,* polished (sodium chloride or potassium bromide), 4 by 25 mm, to serve as windows for the spectrophotometer.

8.8 *Infrared Spectrophotometer, High-Resolution Scanning or Fourier Transform,* capable of recording a spectrum over the 4000 to 667 cm^{-1} region. (High resolution[5] requires that the spectral slit width should not exceed 2 cm^{-1} over 80 % of the wavenumber range and at no place should it exceed 5 cm^{-1}.) Any spectrophotometer complying with these requirements may be used. The equipment shall be operated by an experienced analyst according to the manufacturer's directions for optimum performance.



F	electric, thermoregulated furnace
H	aluminum block, bored to hold tubes
P	glass tube for sample container
S	ground-glass taper
T	collecting tube

FIG. 2 Temperature Controlled Pyrolysis Apparatus

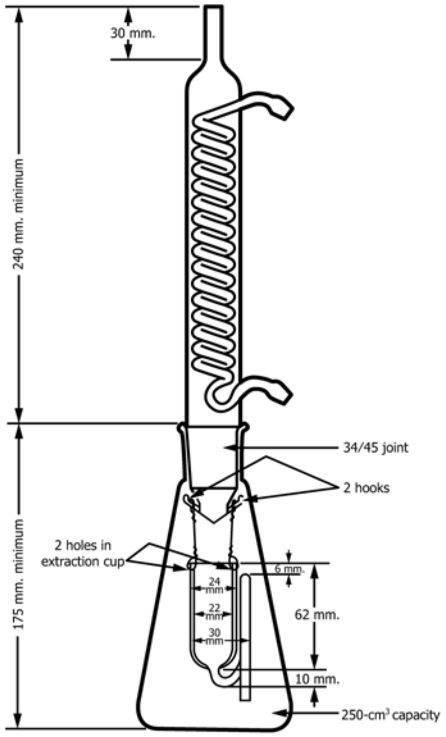


FIG. 1 Extraction Apparatus with Glass Condenser and Ground Glass Joint

9. Preparation of Test Portion

9.1 *Temperature Controlled Pyrolysis in a Stream of Nitrogen (*Fig. 2*; Preferred Method):*

9.1.1 Prepare the test portion by milling into a thin sheet on a laboratory mill or cutting into cubes about 2 mm wide and wrap approximately 0.5 g in filter paper or nylon cloth. Extract the wrapped test portion in an extraction cup in accordance with Section 19 of Test Methods D297, for a minimum of 4 h with methanol, ethanol, or 2-propanol. A vulcanizate may be extracted with acetone or 2-butanone, in addition to the above alcohols. Alternatively, the rapid reflux procedure may be used for 1 h in accordance with Section 26 of Test Methods D297.

9.1.2 Remove the extracted rubber from the apparatus and dry at 100°C until free of solvent. One to two hours is usually required.

9.1.3 Introduce a small amount of anhydrous sodium sulfate into the collecting tube (*T*) to absorb water produced during pyrolysis.

9.1.4 Place a strip of moistened Congo red paper across the mouth of the tube, as a test for chlorine (a change from red to blue).

9.1.5 If alternative chlorine determining methods are employed, this procedure must be suitably modified.

9.1.6 Bring the electrical furnace (*F*) to 450 to 500°C and hold at this temperature. This range is recommended to obtain

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[5] High resolution is defined in "Specification for Evaluation of Research Quality Analysis of Infrared Spectra," *Analytical Chemistry,* ANCHA, Vol 47, No. 11, p. 94A.

fast pyrolysis, without excessive degradation and carbonization. Temperatures below this range should be avoided.

9.1.7 Pass a slow stream of nitrogen through the pyrolysis tube and introduce the tube into a hole of the aluminum block (*H*). The nitrogen serves to displace air, prevent oxidation, and facilitate transfer of the pyrolysis products to the collecting tube (*T*).

9.1.8 Carry on heating to complete distillation, which requires approximately 15 min.

9.1.9 Transfer a few drops of the pyrolyzate from the tube to a sodium chloride or potassium bromide plate, using a capillary pipet.

9.1.10 Place a spacer of suitable thickness in position, close the cell with a second plate of the same material, and mount the cell in the infrared spectrophotometer.

9.1.11 Record the spectrum over the wavelength range from 4000 to 666 cm^{-1}.

9.1.12 Spectra should be obtained immediately after pyrolysis to minimize further change in the pyrolysis products.

9.2 *Gas Flame Pyrolysis (Alternative Test Method):*

9.2.1 Prepare the extract, dry 2 g of test portion (9.1.1 and 9.1.2), and place 0.1 to 0.2 g of the test portion in the bottom of a small glass test tube. Place a strip of moistened Congo red paper across the mouth of the tube. Hold the tube horizontally, and quickly bring the lower end containing the test portion into the hot zone of a gas burner, so that the rubber is rapidly pyrolyzed and charring is kept to a minimum. Note any color change in the Congo red paper, from red to blue, indicating the presence of chlorine.

9.2.2 Maintain the heating until the pyrolyzate condenses in the cool end of the tube, withdraw the test tube from the flame, and cool while holding horizontally.

9.2.3 Alternatively, the sample may be placed in a small glass tube and the end of the tube drawn out to a "retort" shape with a blast lamp. Pyrolysis is carried out as described in 9.2.1. Care should be taken to keep the delivery end of the pyrolysis tube warm enough so that pyrolysis products do not condense and block the opening, causing the tube to explode. The condensate can be collected in a small test tube containing anhydrous sodium sulfate to remove moisture. Proceed as in 9.1.9 – 9.1.12.

9.2.4 If alternative chlorine detecting methods are employed, this procedure must be suitably modified.

10. Sample Preparation for Films

10.1 *Dissolution for Vulcanizates:*

10.1.1 Prepare a test portion in accordance with 9.1.1 and 9.1.2.

10.1.2 Pyrolyze and test for chlorine in accordance with 9.1.4 and 9.1.5 or 9.2.1 – 9.2.4.

10.1.3 Place 1 g of the prepared rubber (9.1.1 and 9.1.2) and 50 cm^3 of 1,2-dichlorobenzene in a 100 cm^3 flask fitted with a reflux condenser. Boil until the rubber is dispersed or dissolved.

10.1.3.1 The time required for dissolution varies with the rubber. Natural rubber requires 3 to 4 h, while chloroprene requires more than 24 h. Some rubbers never completely dissolve.

10.1.3.2 Discontinue refluxing at the end of 48 h to minimize the risk of altering the molecular structure of the rubber.

10.1.3.3 Even though complete dissolution is not affected in 48 h, enough rubber has usually dissolved to provide a good spectrum.

10.1.4 Cool the mixture and transfer to a beaker with 50 cm^3 of toluene.

10.1.5 If the compound does not contain carbon black, centrifuge to eliminate mineral fillers.

10.1.6 If the compound contains carbon black, add 10 to 20 g of filter aid (4.7) to facilitate filtration through filter paper.

10.1.7 If the filtrate from 10.1.6 still contains carbon black, repeat the filtration with additional filter aid.

10.1.8 Concentrate the centrifuged or filtered solution to a small volume under vacuum in a stream of nitrogen.

10.1.9 Evaporate a few drops of the concentrated solution on a salt plate to give a film thickness with 10 to 20 % transmittance at 1449 cm^{-1}.

10.1.10 Record the spectrum over the 4000 to 666 cm^{-1} region.

10.2 *Mild Thermal Degradation for Vulcanizates:*

10.2.1 Prepare, extract, and dry about 2 g of rubber in accordance with 9.1.1 and 9.1.2.

10.2.2 Place the dried rubber in a test tube capped with glass wool and heat to 200 ± 5°C in the oven (8.5) for approximately 10 min.

10.2.3 Transfer the rubber to a beaker and add 50 cm^3 of trichloroethylene.

10.2.4 Allow the beaker and contents to stand on a water bath for approximately 30 min with occasional stirring to effect dissolution of the degraded rubber.

10.2.5 Filter the mixture (10.2.4) through filter paper to remove any undissolved vulcanizate or fillers.

10.2.6 If free carbon is released by the vulcanizate (sometimes found with polyisoprene and butyl rubbers), add a small amount of filter aid (4.7) to the solution before filtering.

10.2.7 Remove the trichloroethylene by evaporation, distillation, or by the use of a rotary evaporator with vacuum. In no case should the solution be heated to over 80°C.

10.2.8 Dissolve the residue in a small amount of chloroform.

10.2.9 If the analyst suspects that the filtrate from 10.2.6 contains material other than rubber, which might interfere in interpretation of the final infrared spectrum, the polymer should be precipitated from the solution of 10.2.5 or 10.2.6 by methanol. Filter the recovered polymer and dissolve in chloroform.

10.2.10 Cast a film having 10 to 20 % transmittance at 1449 cm^{-1}, on a salt plate (see 8.7). Record the infrared spectrum over the 4000 to 666 cm^{-1} region, using the infrared spectrometer (8.8).

10.3 *Dissolution for Raw Rubbers:*

10.3.1 Prepare a test portion in accordance with 9.1.1 and 9.1.2, pyrolyze, and test for chlorine in accordance with 9.1.4 and 9.1.5 or 9.2.1 – 9.2.4.

10.3.2 Place 1 g of the prepared rubber (9.1.1 and 9.1.2) and 50 cm^3 of chloroform in a 100 cm^3 flask fitted with a reflux condenser. Boil until the rubber dissolves.

10.3.3 Cool and transfer to a beaker.

10.3.4 Concentrate the solution to a small volume under vacuum in a stream of nitrogen.

10.3.5 Cast a film on a salt plate and record the infrared spectrum over the 4000 to 666 cm^{-1} region, taking care that the film has a thickness sufficient to give approximately 10 to 20 % transmittance at 1449 cm^{-1}.

11. Interpretation of Spectra

11.1 *Reference Spectra:*

11.1.1 Because of the different modes of presentation of spectra, it is strongly recommended that a set of reference spectra on the same instrument should be prepared before proceeding to unknown samples.

11.1.2 Reference spectra must be produced from test pieces of known composition following either Section 9 or 10.

11.1.3 Spectra of mixtures are not given because it is preferable for each laboratory to prepare its own set from test pieces of known composition.

11.1.4 Small, but unavoidable, variations in experimental conditions and instrument characteristics may give rise to slight differences in spectra. Spectra produced at different times may not be identical in terms of peak height (intensity of absorption) or absorption wavelength. The experienced spectroscopist will recognize this.

11.1.5 Vulcanizates may give slightly different liquid pyrolyzate and film spectra than those prepared from corresponding raw rubber, and the interpretation of such spectra requires particular care, when strong characteristic features are lacking.

11.1.6 The precautions of 11.1.4 and 11.1.5 are cited to alert the spectroscopist to difficulties that may arise from the use of this method and to encourage the practice of maintaining a reference file of films and pyrolyzates of all the rubbers that may require identification.

11.1.7 In all cases, spectra must be interpreted in the light of the test for chlorine. If the test for chlorine is negative, then the rubber is characterized as a hydrocarbon or nitrile type.

11.2 *Diagnostic Absorptions:*

11.2.1 The tables of diagnostic absorptions (Sections 12 and 13) should be used only in conjunction with the reference spectra. Their purpose is to indicate the principal absorptions by which the spectra may be related to films and pyrolyzates, such as the specific nature of certain peaks, their relationship with neighboring peaks or other regions of the spectrum, etc.

11.2.2 The tables also serve to augment the reference spectra by drawing attention to absorptions that are absent, thereby eliminating certain rubbers when ambiguity might arise.

11.2.3 In Sections 12 and 13, diagnostic absorptions are arranged in order from strong to weak. By "diagnostic value" is meant those features of the absorption, subjectively assessed, which a practiced spectroscopist recognizes as of significance in rubber identification. Such absorptions are not necessarily specific nor necessarily very intense. They are, however, identifiable with certain compositional or structural features of the liquid pyrolyzates and films, and reproducible in the sense that they are not seriously influenced by moderate variations in pyrolysis and dissolution conditions.

11.2.4 In general, it can be assumed with confidence that, apart from exceptions stated, all the absorptions listed in Sections 12 and 13 will appear in the spectrum of the corresponding pyrolyzate or film, and if absent, it is inferred that the rubber sought is absent.

12. Diagnostic Absorptions for Pyrolyzates

12.1 The following absorptions, when they occur, are of no diagnostic value and should not be used for rubber identification:

Wavenumber, cm^{-1}	Wavelength, µm
3330	3.0
2860	3.5
1700	5.9
1450	6.9

12.2 The principal absorptions in order of diagnostic value are as follows:

12.2.1 *Isoprene Rubber* (see Figs. 3 and 4):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
885	11.3	very strong
1370	7.3	strong
800	12.5	medium
1640	6.1	medium
909	11.0	shoulder

In vulcanizates the absorption at 800 cm^{-1} may sometimes decrease in intensity with the appearance of a broader, less intense absorption at 813 cm^{-1}.

12.2.2 *Styrene-Butadiene Rubber* (see Figs. 5 and 6):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
699	14.3	very strong
775	12.9	strong
1490	6.7	medium
909	11.0	strong
990	10.1	fairly strong
962	10.4	medium

The relative intensities of absorptions at 909 cm^{-1} , 990 cm^{-1}, and 962 cm^{-1} depend on the ratio of isomers in the polybutadiene component and, therefore, may vary.

12.2.3 *Acrylonitrile-Butadiene Rubber* (see Figs. 7 and 8):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
2220	4.5	medium strong
962	10.4	medium
1610	6.2	medium
1590	6.3	medium
909	11.0	medium

12.2.4 *Chloroprene Rubber* (see Figs. 9 and 10):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
820	12.2	medium
747	13.4	weak, sometimes absent
769	13.0	weak, sometimes absent
885	11.3	medium
699	14.3	medium

The pyrolyzate of chloroprene rubber can give a variable spectrum that also tends to be lacking in characteristic features. The most useful absorption is that at 820 cm^{-1}, but this is rather broad and often not very intense. A weak absorption at 747 cm^{-1} sometimes fails to appear, while the stronger absorptions at 885 cm^{-1} and 699 cm^{-1} are common in some degree to all the other polymers.

12.2.5 *Butyl Rubber* (see Figs. 11 and 12):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
1370	7.3	strong
1390	7.2	strong
885	11.3	strong
1250 to 1220	8.0 to 8.2	medium doublet, sometimes absent
727	13.8	very weak, sometimes absent

12.2.6 *Polybutadiene Rubber* (see Figs. 13 and 14):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
909	11.0	strong
962	10.4	strong
990	10.1	medium
813	12.3	weak
695	14.4	weak

12.2.6.1 Some of the principal absorptions in the spectrum obtained from the pyrolyzate of polybutadiene rubber are closely similar both in frequency and intensity to those found in the spectrum of chlorosulfonated polyethylene pyrolyzate and the result of the test for chlorine should be taken into account when deciding between these two rubbers (see also 12.2.8). Particular care should be exercised in the interpretation of spectra from vulcanizates, and the 833 to 667-cm^{-1} region should be well scrutinized for small, but diagnostically significant absorptions.

12.2.6.2 Polybutadiene rubbers having different isomer ratios may, on pyrolysis, show absorptions of differing relative intensities, notably those at 962 and 909 cm^{-1}.

12.2.6.3 The spectrum of the polybutadiene pyrolyzate differs from that of the styrene–butadiene pyrolyzate in that the absorptions due to aromatic constituents are absent or much reduced.

12.2.7 *Ethylene Propylene Rubber* (see Figs. 15 and 16):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
1370	7.3	strong
909	11.0	strong
885	11.3	strong
962	10.4	medium
725	13.8	medium

12.2.8 *Chlorosulfonated Polyethylene* (see Figs. 17 and 18):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
909	11.0	strong
962	10.4	medium
990	10.1	medium
813	12.3	weak
741	13.5	medium
720	13.9	weak
695	14.4	weak

Some of the principal absorptions in the spectrum obtained from the pyrolyzate of chlorosulfonated polyethylene are closely similar both in frequency and intensity to those found in the spectrum of polybutadiene pyrolyzate, and the result of the test for chlorine should be taken into account when deciding between these two polymers. The table above includes some absorptions common to both, but the bands at 813 and 741 cm^{-1} although not particularly strong, are indicative of chlorosulfonated polyethylene. Particular care should be exercised in the interpretation of spectra from vulcanizates.

13. Diagnostic Absorptions for Films

13.1 The following absorptions, when they occur, are of no diagnostic value and should not be used for rubber identification:

Wavenumber, cm^{-1}	Wavelength, µm
3330	3.0
2860	3.5
1700	5.9
1450	6.9

13.2 The principal absorptions in the order of diagnostic value are as follows:

13.2.1 *Isoprene Rubber* (see Figs. 19 and 20):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
833	12.0	strong
1370	7.3	strong
1665	6.0	medium
885	11.3	weak

Reported diagnostic absorptions and related spectra for natural rubber and synthetic polyisoprene are tabulated above. Gutta percha and balata have different diagnostic absorptions and spectra.

13.2.2 *Styrene-Butadiene Rubber* (see Figs. 21 and 22):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
699	14.3	very strong
758	13.2	strong
1490	6.7	medium
909	11.0	strong
962	10.4	very strong

Reported diagnostic absorptions and related spectra refer to styrene-butadiene rubber with a styrene content of about 23.5 %, produced by emulsion polymerization. Other copolymers having different monomer ratios or copolymers produced by solution polymerization may have slightly different diagnostic absorption and spectra.

13.2.3 *Acrylonitrile-Butadiene Rubber* (see Figs. 23 and 24):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
2220	4.5	strong
962	10.4	very strong
909	11.0	medium

Reported diagnostic absorptions and related spectra refer to acrylonitrile-butadiene rubber with an acrylonitrile content of about 33 %.

13.2.4 *Chloroprene Rubber* (see Figs. 25 and 26):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
1665	6.0	very strong
1315	7.6	medium
1110	9.0	strong
820	12.2	strong

13.2.5 *Butyl Rubber* (see Figs. 27 and 28):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
1370	7.3	very strong
1390	7.2	very strong
1235	8.1	very strong

13.2.6 *Polybutadiene Rubber* (see Figs. 29 and 30):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
741	13.5	very strong
909	11.0	medium
962	10.4	medium
990	10.1	medium

Reported diagnostic absorptions and related spectra refer to polybutadiene rubber with high *cis* content. Relative intensities of absorptions depend on the ratio of isomers in vulcanizates.

13.2.7 *Ethylene-Propylene Rubber* (see Figs. 31 and 32):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
1370	7.3	strong
1145	8.7	medium
760 and 710	13.0 and 14.0	medium

13.2.8 *Chlorosulfonated Polyethylene* (see Figs. 33 and 34):

Wavenumber, cm^{-1}	Wavelength, µm	Intensity
1370	7.3	strong
1265	7.9	medium
1150	8.6	strong
730	13.7	medium

In vulcanizates, the absorption, depending on the chlorosulfonic groups, strongly decreases.

TEST METHOD B SEMI-QUANTITATIVE ANALYSIS

14. Scope

14.1 These test methods describe the semiquantitative detection of certain rubbers in blends.

14.1.1 Polyisoprene (IR and NR), BR, and SBR are estimated when di-blends or tri-blends are present. The percentage of a single component of the blend is accurate to approximately ±5 % of the total rubber content. See 15.1 and Sections 16 – 22.

14.1.2 Saturated rubbers (IIR or EPDM) (see Note 4) are detected in the presence of unsaturated rubbers (NR, IR, BR, SBR, and CR). Approximately 3 to 6 % of EPDM or IIR alone can be found in blends of unsaturated rubbers. When both EPDM and IIR are present, the minimum detection limit is approximately 12 % of either rubber. See 15.2 and Sections 23 – 25.[6]

NOTE 1—For use in these test methods, the term "saturated rubbers" will be used to describe rubber containing no, or a small number of, double bonds in the main rubber chain. For example, isobutylene rubber (IIR) containing a small amount of an unsaturated material—isoprene. The term "unsaturated rubbers" will be used to describe those rubbers containing substantial numbers of double bonds in the main rubber chain, for example, IR, NR, SBR, BR, and CR.

14.1.3 References to IIR include chlorinated (CIIR) and brominated (BIIR) versions of these rubbers.

15. Summary of Test Methods

15.1 For estimation of NR, IR, BR, or SBR, or all of these, in di-blends or tri-blends:

15.1.1 A milled, extracted test portion is ground to 420-µm (40-mesh) size, digested in hot 1,2-dichlorobenzene, and filtered to remove the carbon black. An infrared spectrum is made on a film prepared from this solution.

15.1.2 Absorbance ratio measurements at 1450 cm^{-1} and other significant peaks found in the absorbance spectrum of the rubbers listed in 14.1 are obtained next.

15.1.3 When the ratio values in accordance with 15.1.2 are compared to those obtained from calibration data prepared from all possible blends that the analyst expects to encounter of NR, IR, BR, and SBR rubbers listed in 14.1.2, the composition of blends may be assessed.

15.2 For detection of EPDM or IIR in NR, IR, BR, SBR, or CR:

15.2.1 A milled vulcanizate is digested with a hot solution of sulfuric and chromic acid and the residue is dissolved in boiling dichloromethane. An infrared spectrum of a film, cast on a salt plate from dichloromethane, provides a means of determining the presence or absence of saturated rubbers in unsaturated rubbers.

15.2.2 The acid mixture decomposes unsaturated rubbers such as NR, IR, BR, and SBR. Because EPDM and IIR are highly saturated, they are virtually unattacked by the acid mixture. Furthermore, IIR and EPDM are only partially vulcanized in the presence of high levels of unsaturated rubbers and may therefore be soluble in chlorinated solvents.

15.2.3 Any saturated polymer or rubber resistant to the acid mixture, and also soluble in hot dichloromethane will appear in the residue and consequently in the spectrum. Examples would be low molecular mass polyethylene and polystyrene.

16. Apparatus

16.1 See Section 8 in addition to the following:

16.1.1 *Grinding Mill,* capable of grinding vulcanized rubber to 420 µm (40 mesh).

16.1.2 *Magnetic Stirring Hot Plate,* with controlled stirring rates, capable of holding several 50 cm^3 conical flasks.

16.1.3 *Magnetic Stirring Bars,* covered with a chemical-resistant coating (see Note 2), approximately 25 mm long.

NOTE 2—Polytetrafluoroethylene has been found satisfactory.

16.1.4 *Büchner Funnel,* for use with 5.5 cm filters.

16.1.5 *Glass Fiber Filters,* 5.5 cm in diameter.

16.1.6 *Vacuum Filtering Device.*

16.1.7 *Vacuum Oven.*

16.1.8 *Conical Flasks,* 50 cm^3 and 250 cm^3 capacity, of heat-resistant glass.

NOTE 3—Borosilicate glass has been found satisfactory.

16.1.9 *Pipet,* Pasteur type, disposable (or equivalent).

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[6] Based upon Anderson, M., Uniroyal Tire Co., "Detecting Traces of EPDM or IIR in Blends," *Elastomerics*, October 1978, p. 40.

16.1.10 *Usual Laboratory Glassware,* necessary for carrying out the test method as written.

17. Safety Precautions

17.1 Because of the toxicity of the solvents used in this test method, a well-ventilated fume hood shall be used and the skin and eyes suitably protected during this analysis.

17.2 Although not outlined in this test method, all recognized health and safety precautions shall be observed when following this test method.

18. Preparation of Test Portion

18.1 If the test portion is vulcanized, sheet it out on a cool mill and weigh approximately 2.2 g.

18.2 If the test portion is unvulcanized, vulcanize it and sheet it out on a cool mill. Weigh approximately 2.2 g.

18.2.1 Test portions must be vulcanized; otherwise, the intensity of the unsaturation bands will be variable.

18.3 Extract the vulcanized sheet overnight with alcohol (4.3), using the apparatus in accordance with 8.1.

18.4 Extraction for 2 h with acetone or 2-butanone may also be effective.

18.4.1 The object of extraction is to remove, as much as possible, all the additives in the compound. The choice of solvent is left to the discretion of the analyst, whose prior knowledge of the vulcanizate composition will dictate the most suitable solvent for extraction.

19. Calibration

19.1 Prepare sets of standard, vulcanized compounds containing blends of the rubbers of interest over ranges of expected ratios (for example, 80/20 NR/BR, 70/30, 60/40, 50/50) with blends of two or three rubbers.

19.1.1 Prepare separate standard blends for emulsion SBR, solution SBR, and high-styrene SBR, and for *cis*-BR and high-*trans* emulsion BR.

19.1.2 NR and IR give essentially the same values; therefore, one set of standards with either IR or NR should be sufficient.

19.2 Carry out the preparation and procedure as outlined in Sections 18 and 20 for all blends. Use the same infrared instrument for sample measurement as for standard calibration measurements.

19.3 On linear graph paper, plot the absorbance ratios for each peak in each blend against the known rubber content of each rubber, in percent of total rubber.

19.3.1 For BR blends at 735 cm^{-1}, make separate calibration curves for high SBR and high NR content.

19.4 Use the following peak absorbance and that at 1450 cm^{-1} to obtain the necessary ratios:

For NR/BR: 1375, 965, 910, 835, and 735 cm^{-1}
For NR/SBR: 1375, 965, 910, 835, 735, and 699 cm^{-1}
For NR/BR/SBR: 1375, 835, 735, and 699 cm^{-1}
For BR/SBR: 910, 735, and 699 cm^{-1}

19.5 Inaccurate results will be obtained if absorbance ratios from di-blends are compared to ratios from tri-blends.

20. Procedure

20.1 Dry the extracted test portion thoroughly and grind in the mill (16.1.1) to 420 µm.

20.2 Divide the test portion into approximately equal portions and place in three 50 cm^3 conical flasks.

20.3 Place a stirring bar in each of the flasks, fill it nearly full with 1,2-dichlorobenzene, and cover with a watch glass.

20.4 Place the flasks on the stirring hot plate, set for a temperature a few degrees below boiling (approximately 175°C), and stir vigorously for 2 to 8 h, until digestion is complete.

20.4.1 It is imperative that digestion be complete so that all of the rubber is in solution. Completeness of digestion is evident when the flask is shaken, held up to a strong light, and the solution exhibits a deep purplish-brown color with no undigested particles floating on the surface.

20.5 Prepare a filter bed by placing a glass fiber filter in a Büchner funnel, wetting it with chloroform, then filling the funnel with diatomaceous filter aid (4.7), and saturating this with chloroform from a wash bottle.

20.6 With the Büchner funnel in place on the vacuum filtering device (16.1.6) and a 250 cm^3 beaker placed to receive the filtrate, pour the hot solution from the flask into the funnel, and at the same time turn on the vacuum.

20.7 Wash the solution through the funnel with boiling chloroform until the filtrate comes through colorless.

20.7.1 Filtering requires some experience. If a black filtrate comes through the filter (or anything darker than a golden-yellow) it will be necessary to refilter the solution, while hot, through the filter until the filtrate is clear.

20.7.2 Stirring the filter bed with a spatula during filtration can improve the intimate contact between the filter aid and the liquid.

20.8 Evaporate the liquid in the beaker to near dryness on an electric hot plate, at the same temperature as in 20.4, using a stream of dry air.

20.9 Add a few drops of toluene to the dried residue of 20.8, and with a Pasteur pipet (16.1.9), transfer a few drops of the solution to the sodium chloride or potassium bromide plate (8.7) that has been placed on a watch glass.

20.10 Place the prepared plate in a vacuum oven under strong vacuum with a slight intake of air at about 50°C for 1 h to dry the film completely. Make the film even by smoothing it with a rotating motion of the side of the Pasteur pipet. The thickness of the film shall be such that when placed in the sample beam of the spectrophotometer and measured against air in the reference beam, an absorbance of 0.04 to 0.10 is obtained at 4000 cm^{-1}, and 0.35 to 0.45 absorbance at the peak around 1450 cm^{-1}. This corresponds to about 80 to 90 % and 35 to 45 % transmittance respectively.

20.11 Scan the spectrum of the prepared film (20.10) from approximately 4000 to 600 cm^{-1} with an instrument setting suitable for quantitative analysis, in the absorbance mode, if possible.

20.11.1 The spectrophotometer shall be adjusted according to the manufacturer's directions for optimum performance. Since instruments vary widely in settings and display, the optimum settings are left to the discretion of the analyst. Refer to Practice E168 for further recommendations on the use of infrared spectrophotometers.

20.11.2 If only a transmittance mode is possible with the instrument being used, the spectrum shall be scanned in that mode.

20.12 Draw baselines with a straightedge, preferably to approximately the following wavenumbers (all values are in reciprocal centimetres):

1390–1510 for the 1450 peak
1340–1390 for the 1375 peak
930–990 for the 965 peak
790–870 for the 835 peak
650–790 for the 735 peak
660–710 for the 699 peak

20.12.1 Although other baselines can be used, experience has shown that short baselines are preferred. In any case, the analyst must draw the baselines for the standards in the same manner as was done for the samples.

20.13 On the spectrum, subtract the absorbance at a point on the baseline directly below each peak of interest, from the peak absorbance, to give the corrected absorbance.

20.13.1 When the percent transmittance mode is used, divide the percent transmittance at a point on the baseline directly above the peak by the percent transmittance of the peak and take the $\log_{10}$ of the quotient.

20.14 Obtain absorbance ratios by dividing the corrected absorbance of each of the peaks at 1375, 965, 910, 835, 735, and 699 cm^{-1} as are of interest, by the corrected absorbance at 1450 cm^{-1}.

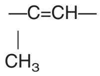
20.15 Take the mean for the three test portions as the absorbance ratio in each case.

20.16 Using the data obtained in 20.14 and 20.15, refer to the calibration curves prepared in accordance with Section 19 and determine the percent of each rubber in the mixture.

20.17 If the readings from different peaks disagree, give precedence to the 1375 and 699 cm^{-1} peaks as the most accurate, 835 and 735 cm^{-1} peaks as second in accuracy, and 965 and 910 cm^{-1} peaks as the least accurate.

21. Absorbance Peaks and Their Assignments

21.1 The absorbance peaks and their assignments are:

cm^{-1}		
1450	methylene	$—CH_2—$
1375	methyl	$—CH_3$
965	trans	C=C
910	vinyl	C=C
835	propenyl	 $\underset{\displaystyle CH_3}{—\overset{}{C}}=CH—$
699	5 adjacent hydrogens of monosubstituted benzene ring (for example, phenyl) of styrene	
735	*cis*	C=C

22. Precision and Bias

22.1 *Precision*—No work has been done to test the precision of this test method, however, the results obtained by this test method have been verified on an NR/SBR blend, using Test Methods D297, Section 52, for Polyisoprene Content, and Section 56, for SBR Content, and the results have been found to be consistent within ±5 %.

22.2 *Bias*—Under the best conditions, accuracy is ±5 % of the rubber content for detection of EPDM or IIR in NR, IR, BR, SBR, or CR. For example, in a 70/30 NR/BR blend, the outlined procedure would give 70 ± 5 % NR and 30 ± 5 % BR.

23. Apparatus

23.1 Usual laboratory glassware necessary for carrying out the test method as written and in addition to apparatus in 8.7 and 8.8 are the following:

23.2 *Stainless Steel Sieve,* [7,8] 420 µm (40 mesh) or finer.

23.3 *Electric Hot Plate.*

24. Reagents

24.1 *Chromic Acid Digestion Mixture*—Dissolve 200 g of chromic acid (CrO_3) in 500 cm^3 of water, *Cautiously* add 150 cm^3 of H_2SO_4 (density 1.84 mg/m^3), and mix well.

24.2 *Acetone, Reagent Grade.*

24.3 *Dichloromethane, Reagent Grade,* with a residue on evaporation not over 0.0002 %.

24.4 *Wetting Agent*—A saturated solution of dioctyl sodium sulfosuccinate (aerosol OT) is satisfactory.

25. Procedure

25.1 Weigh about 1 g of milled vulcanizate and place in a 400 cm^3 beaker, then add about 200 cm^3 of acetone. (Uncured compounds should be vulcanized by any appropriate method, before milling.)

25.2 Heat the beaker on a hot plate, so that it boils for about 1 min, then decant the acetone. This short solvent treatment will remove most of the compounding and extender oils, should any be present.

25.3 Dry the beaker and contents until all of the acetone has evaporated, then add 50 cm^3 of the acid digestion solution (see 24.1) and one drop of wetting agent (see 24.4).

25.4 Cover the beaker with a watch glass and place on a steam plate or steam bath (not an electric hot plate) and observe the start of the reaction, as evidenced by bubbles. Remove the beaker just 15 min after bubbles start to appear.

25.5 Pour the warm solution through the sieve (see 23.2), wash the residue copiously with hot water, then with a few cubic centimetres of acetone.

25.6 If there is no rubber residue on the sieve at this point, then IIR or EPDM is absent, and the test should be discontinued.

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[7] The sole source of supply of the stainless steel sieve known to the committee at this time is W. S. Tyler Co., Mentor, OH 44060.

[8] 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.

TABLE 1 Determination of Saturated Rubbers in the Presence of Unsaturated Rubbers

Sample	Known	Results found by laboratory			
		Lab. 1	Lab. 2	Lab. 3	Lab. 4
A424	29 % CIIR, 3 % EPDM, 13 % NR, 10 % SBR	IIR	IIR	IIR	IIR
A425	12 % CIIR, 12 % EPDM, 15 % NR, 15 % SBR	IIR + EPDM	IIR + EPDM	IIR + EPDM	IIR + EPDM
A426	5 % IIR, 10 % NR, 5 % BR, 29 % SBR, 5 % CR	IIR + EPDM	IIR + EPDM	IIR	IIR + EPDM
A427	5 % EPDM, 10 % NR, 5 % BR, 29 % SBR, 5 % CR	EPDM	...	IIR + EPDM	EPDM
A428	3 % IIR, 13 % NR, 5 % BR, 29 % SBR, 5 % CR	IIR	EPDM	IIR	IIR + EPDM
A429	3 % EPDM, 13 % NR, 5 % BR, 39 % SBR, 5 % CR	EPDM	EPDM	IIR + EPDM	EPDM

25.7 If there is residue on the sieve, collect it in a beaker, dry off most of the acetone and add 30 cm^3 of dichloromethane, cover the beaker with a watch glass and boil the dichloromethane on a hot plate at high heat until a volume of about 10 cm^3 is reached.

NOTE 4—If a large amount of solid particles are present, filter the solution into a beaker through a loose filter such as a glass fiber pad or glass wool. However, this filtration may not be necessary.

25.8 Pour the solution into a 50-cm^3 beaker and evaporate to 1 to 2 cm^3.

25.9 Apply enough drops of the solution from 25.8 to a salt plate window to make a good film. Evaporate the dichloromethane with gentle heat (for example in a vacuum oven at 50°C). If the residue was quite small, apply all of it to the salt plate.

25.10 With the salt plate in the sample beam of the infrared spectrophotometer and air in the reference beam, scan the spectrum from 4000 to 600 cm^{-1} or lower. If the spectrum is weak, expand it 5 or 10 times in the ordinate direction, if the instrument permits.

25.11 Compare the spectrum obtained with Fig. 28 and Fig. 32 or preferably to one's own spectra of purified IIR or EPDM.

NOTE 5—Purified rubbers may be prepared by pouring a hot toluene solution of the rubber into about four times as much methanol to coagulate it, then dissolving it in dichloromethane and scanning in the same manner as for the unknowns.

25.12 Note the following diagnostic bands and their configurations: 1390, 1370, and 1230 cm^{-1} for IIR and 1380 and 721 cm^{-1} for EPDM. Since the 1380-cm^{-1} band might be caused by NR contamination, look for the accompanying NR band at 836 cm^{-1} to verify this contamination.

26. Precision and Bias

26.1 See 14.1.2.

26.2 A task group composed of four laboratories, testing six vulcanizates (both black and white stocks) obtained the following results with this test method: see Table 1.styrene-butadiene rubber

27. Keywords

27.1 acrylonitrile-butadiene rubber; balata; butyl rubber; chloroprene; ethylene-propylene rubber; ethylene-propylene-diene rubber; gutta percha; infrared spectrometry; polybutadiene; polyisoprene; nitrile rubber

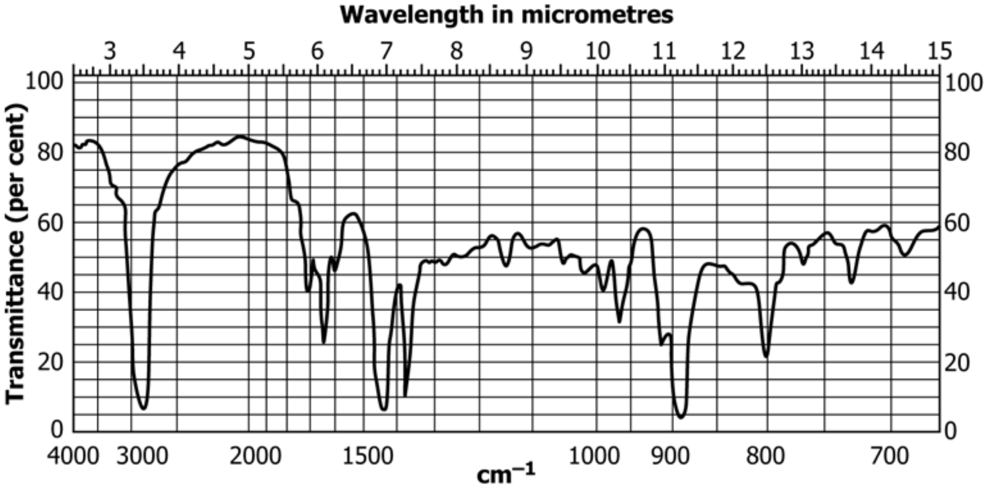

FIG. 3 IR Pyrolyzate from Raw Rubber

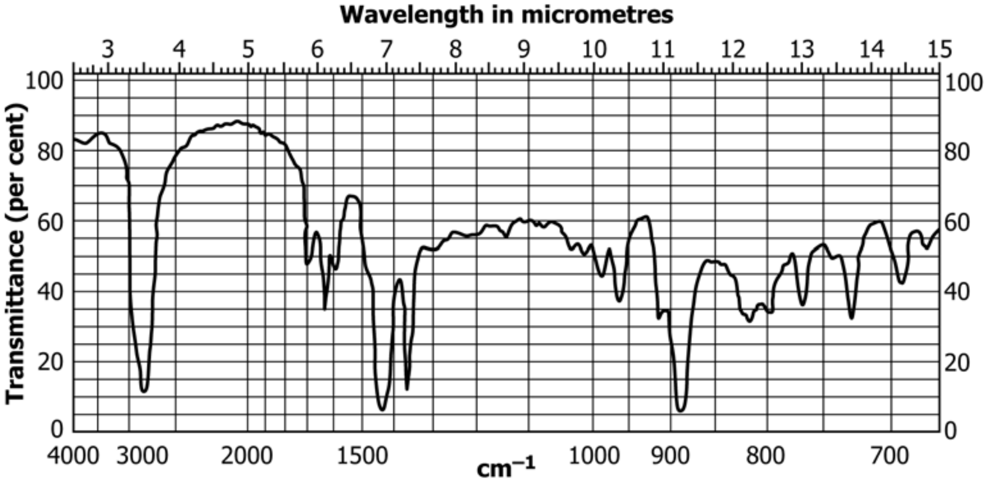

FIG. 4 IR Pyrolyzate from a Vulcanizate

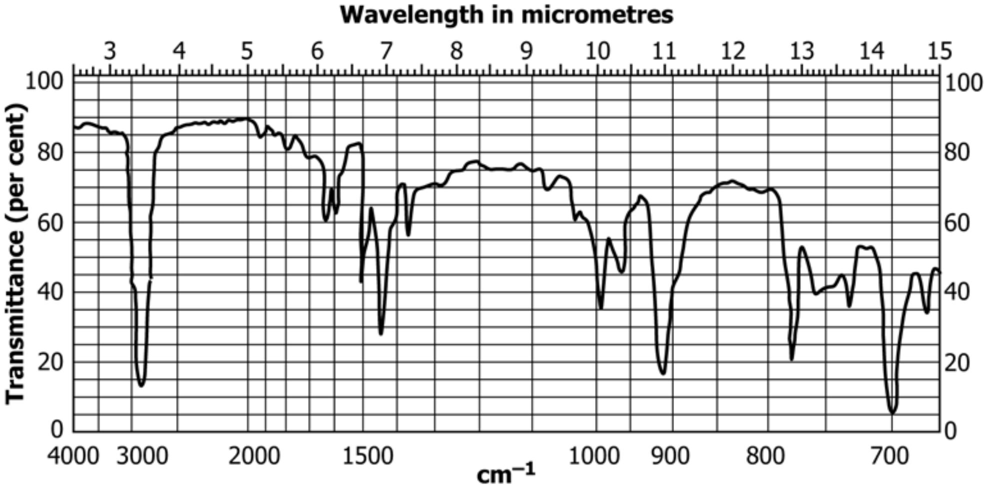

FIG. 5 SBR Pyrolyzate from Raw Rubber

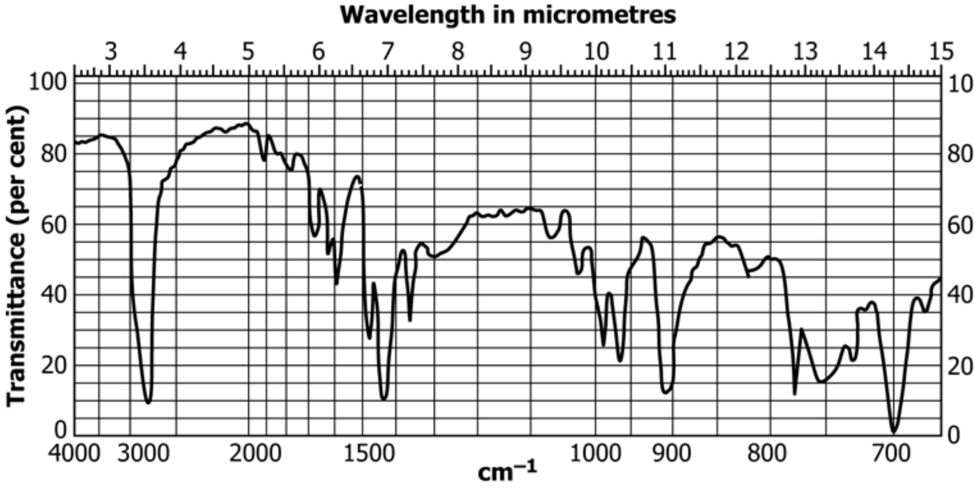

FIG. 6 SBR Pyrolyzate from a Vulcanizate

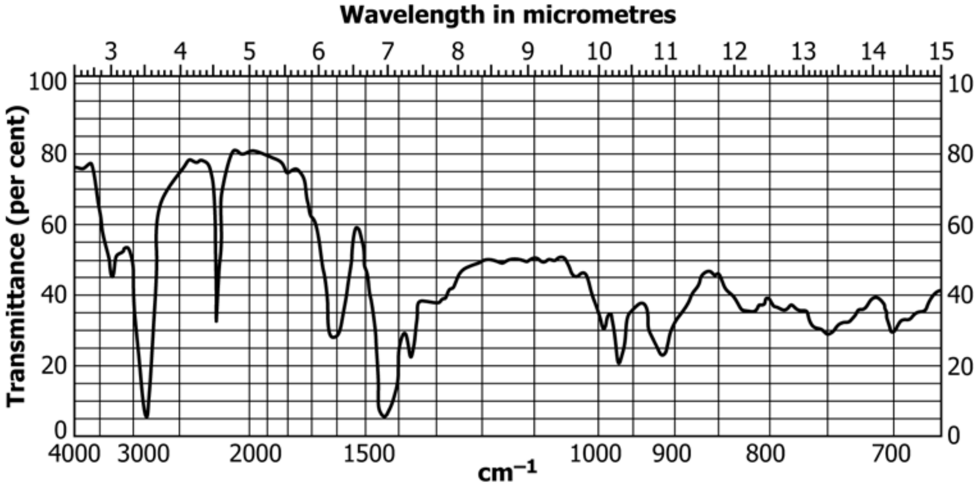

FIG. 7 NBR Pyrolyzate from Raw Rubber

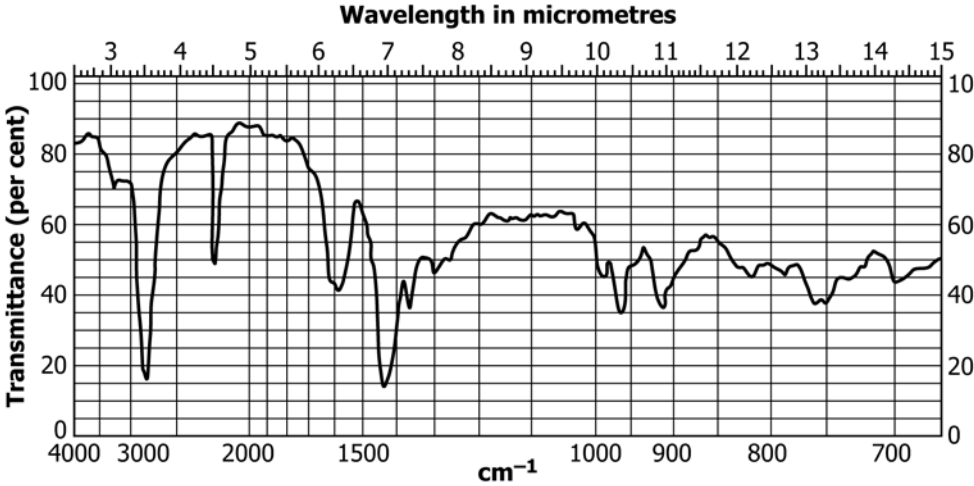

FIG. 8 NBR Pyrolyzate from a Vulcanizate

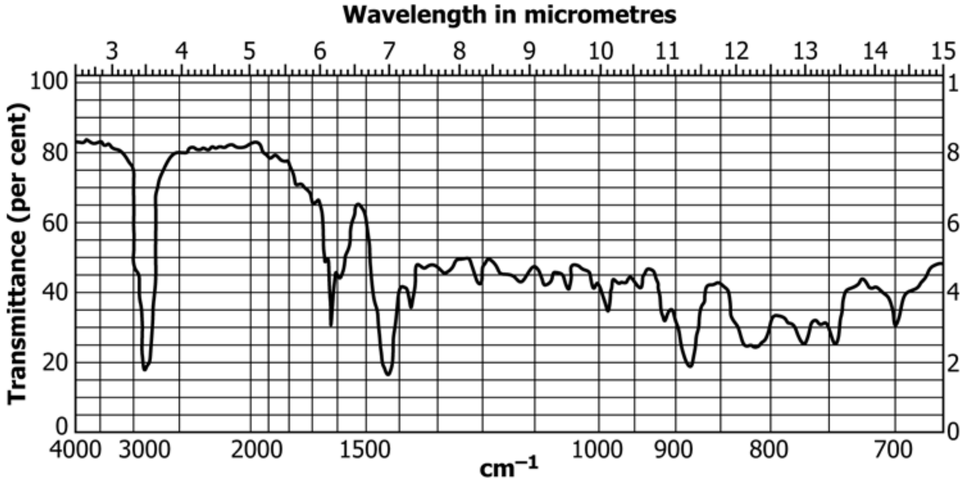

FIG. 9 CR Pyrolyzate from Raw Rubber

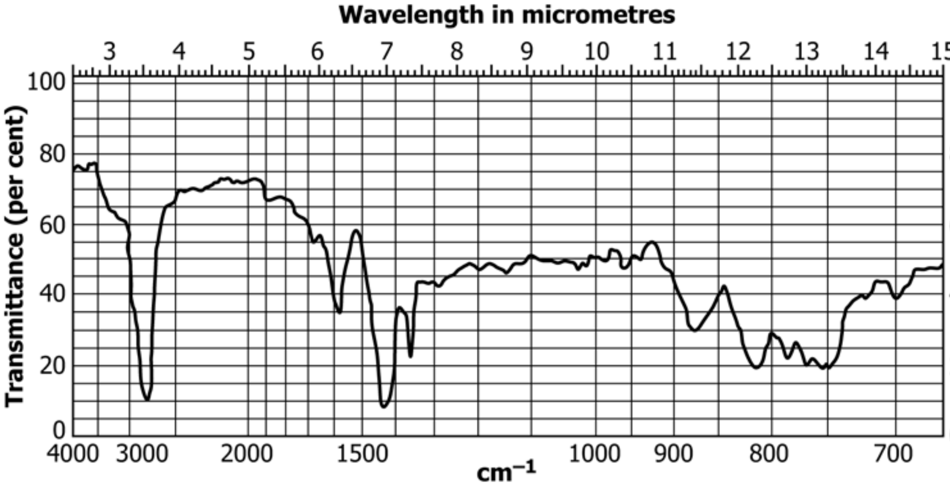

FIG. 10 CR Pyrolyzate from a Vulcanizate

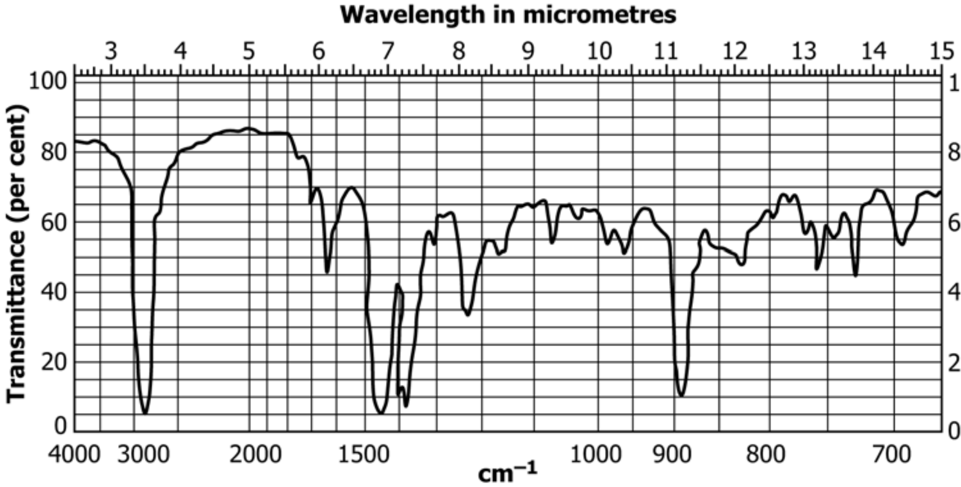

FIG. 11 IIR Pyrolyzate from Raw Rubber

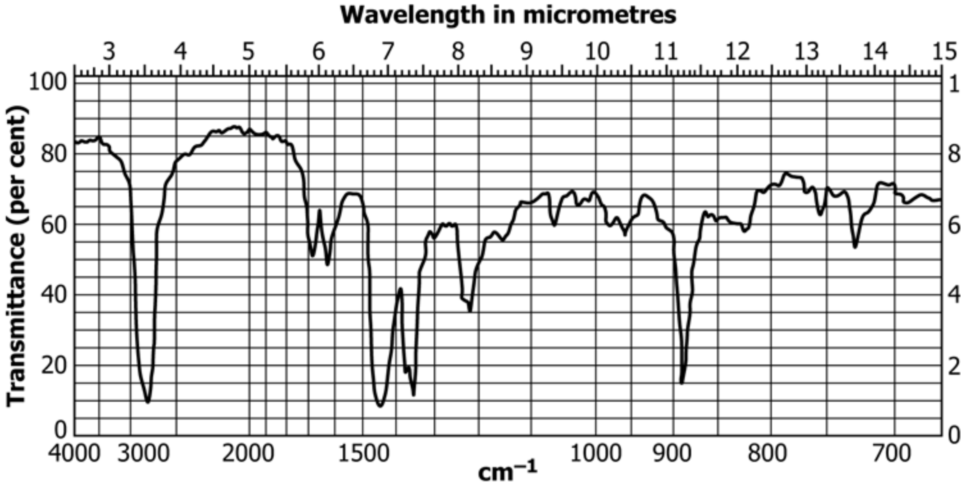

FIG. 12 IIR Pyrolyzate from a Vulcanizate

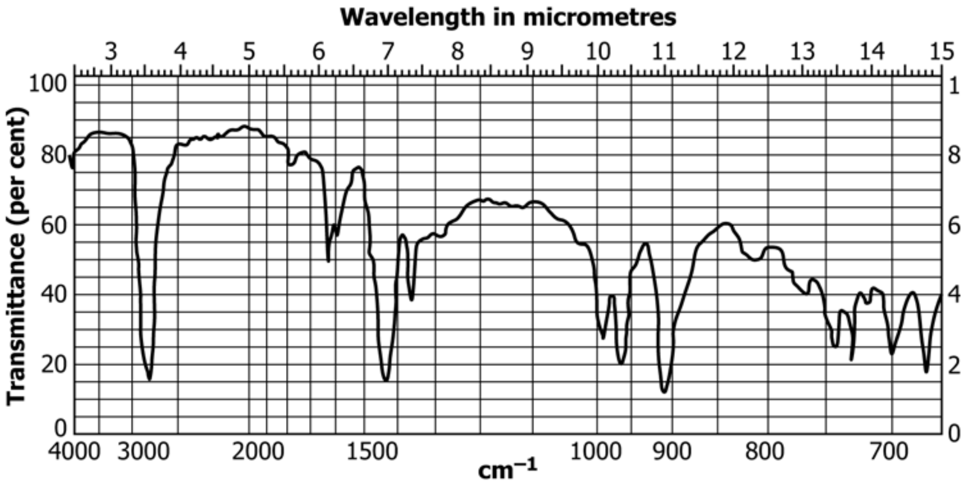

FIG. 13 BR Pyrolyzate from Raw Rubber

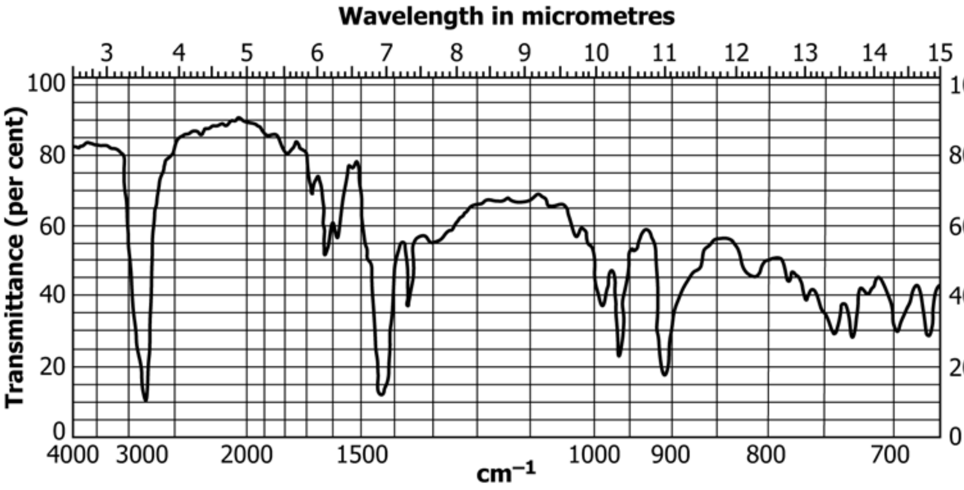

FIG. 14 BR Pyrolyzate from a Vulcanizate

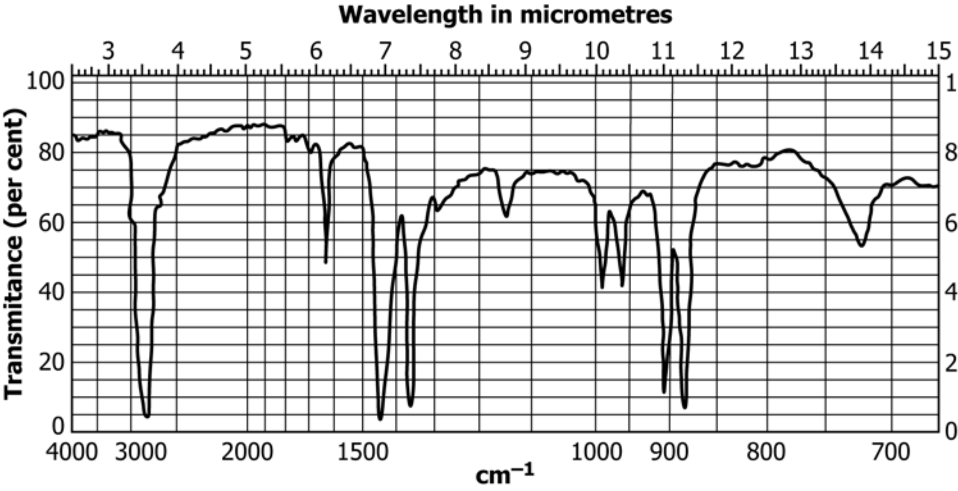

FIG. 15 EPM Pyrolyzate from Raw Rubber

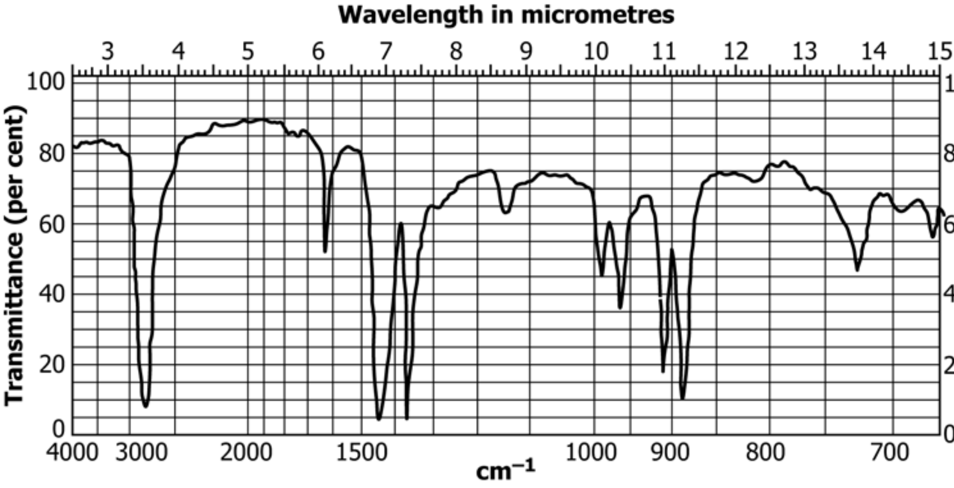

FIG. 16 EPM Pyrolyzate from a Vulcanizate

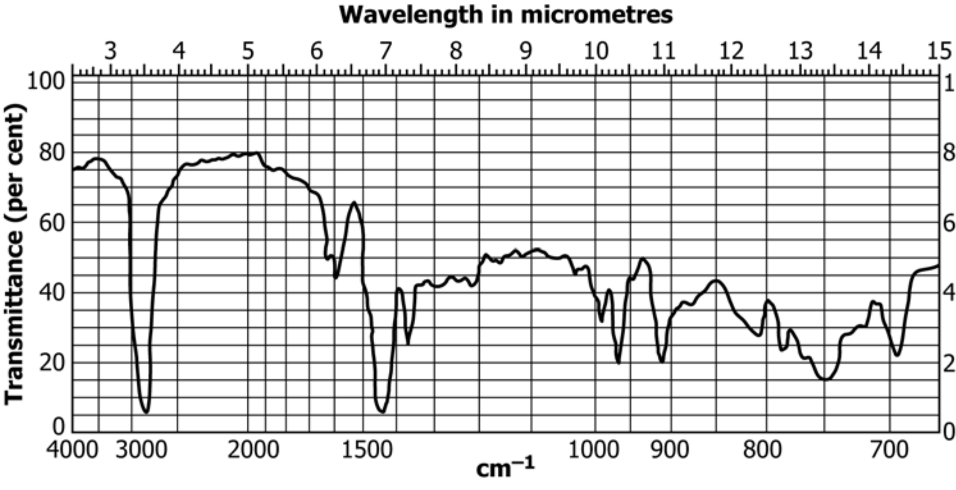

FIG. 17 CSM Pyrolyzate from Raw Rubber

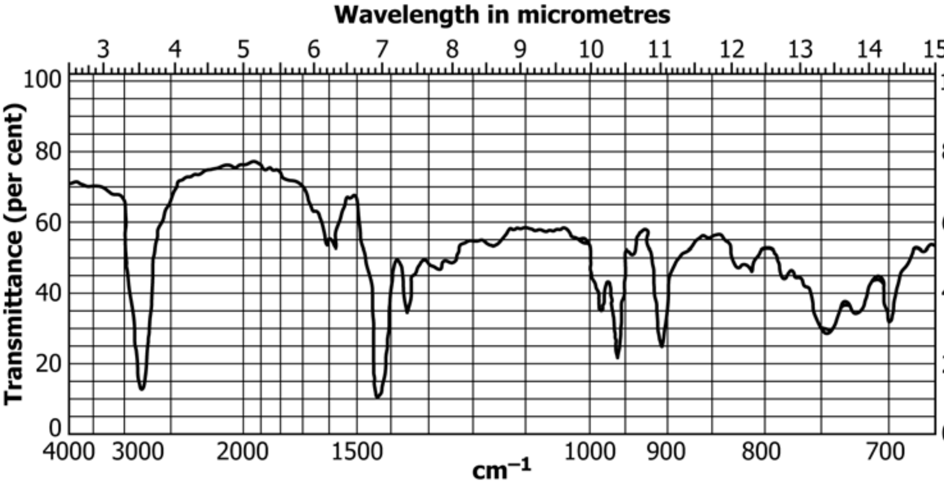

FIG. 18 CSM Pyrolyzate from a Vulcanizate

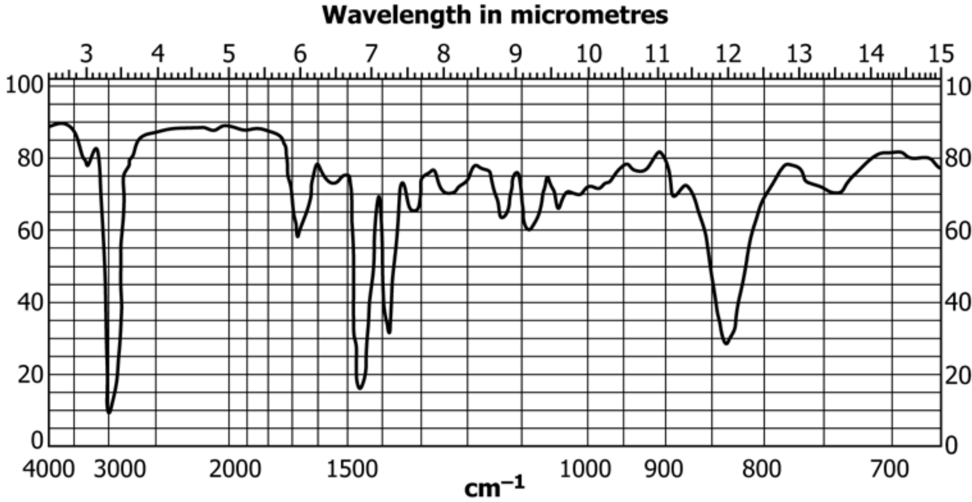

FIG. 19 IR Film from Raw Rubber

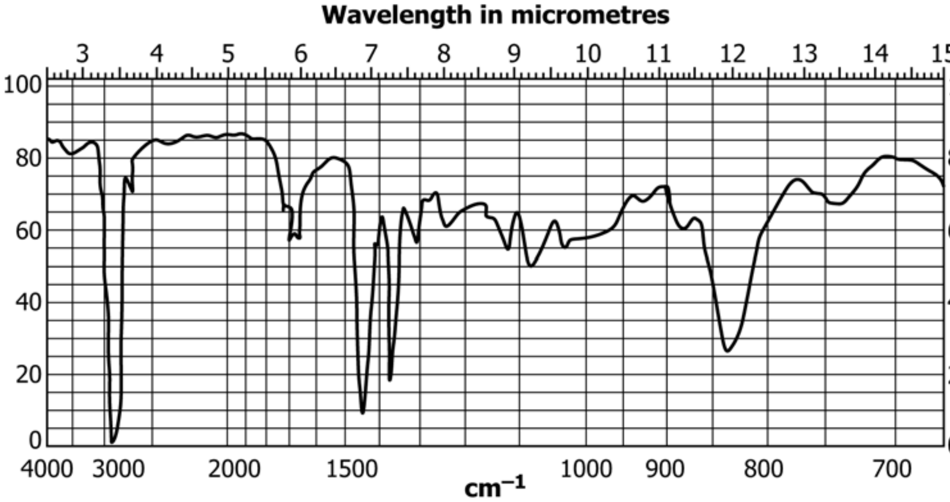

FIG. 20 IR Film from a Vulcanizate

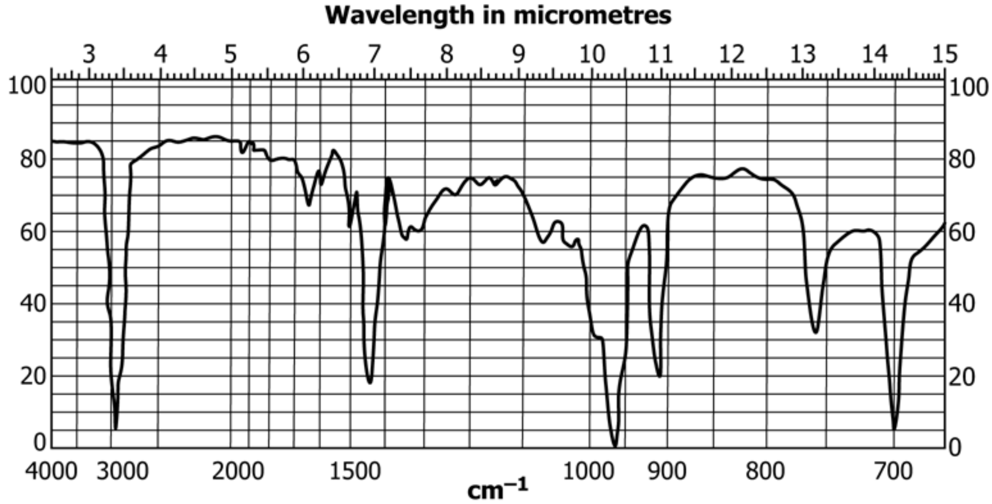

FIG. 21 SBR Film from Raw Rubber

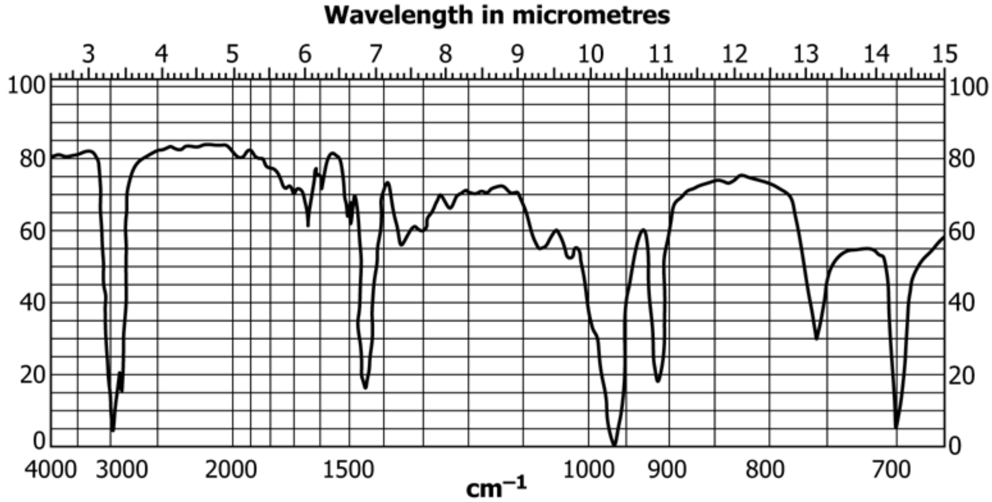

FIG. 22 SBR Film from a Vulcanizate

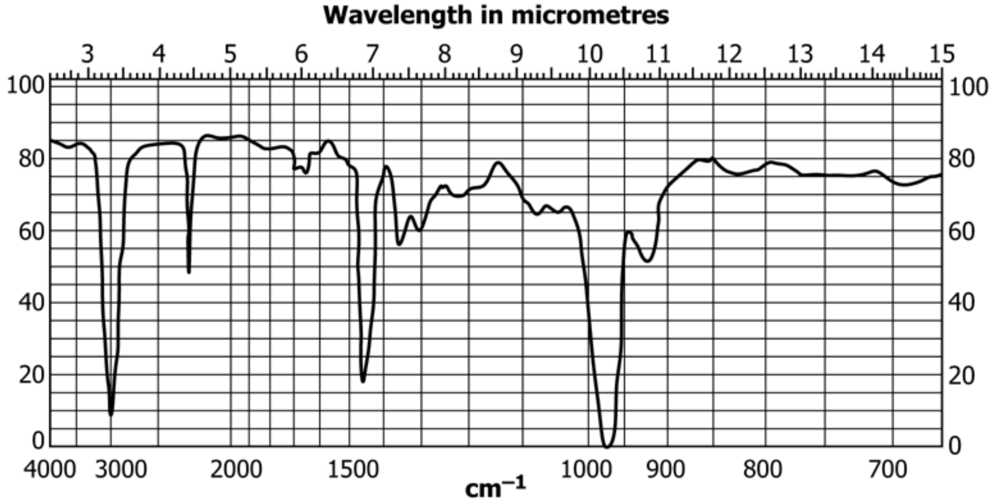

FIG. 23 NBR Film from Raw Rubber

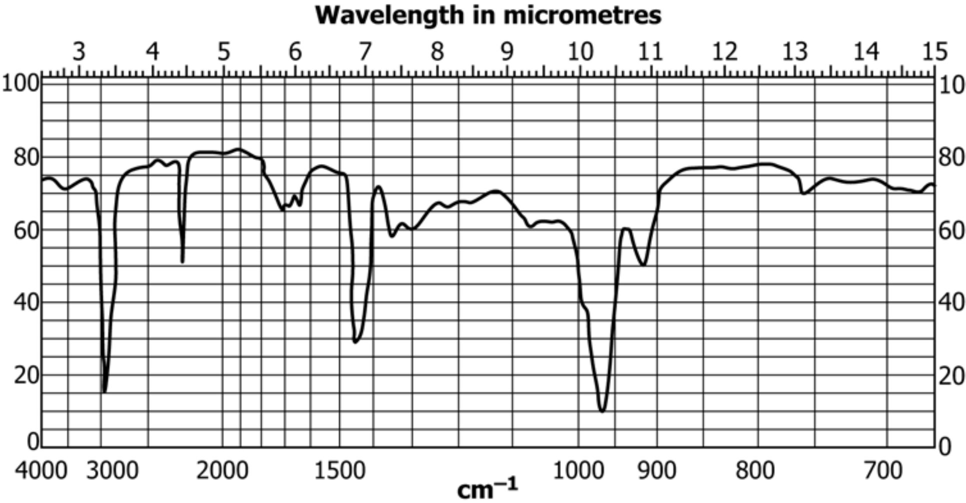

FIG. 24 NBR Film from a Vulcanizate

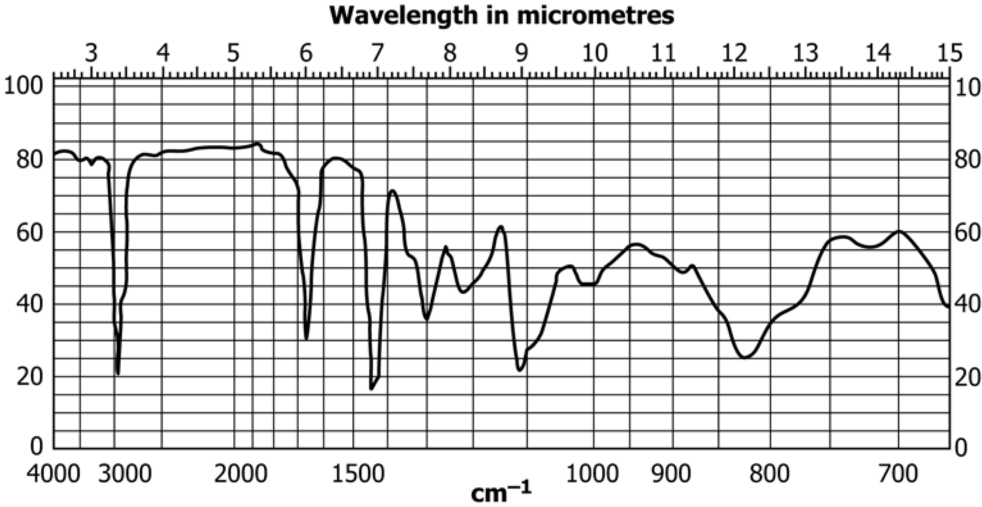

FIG. 25 CR Film from Raw Rubber

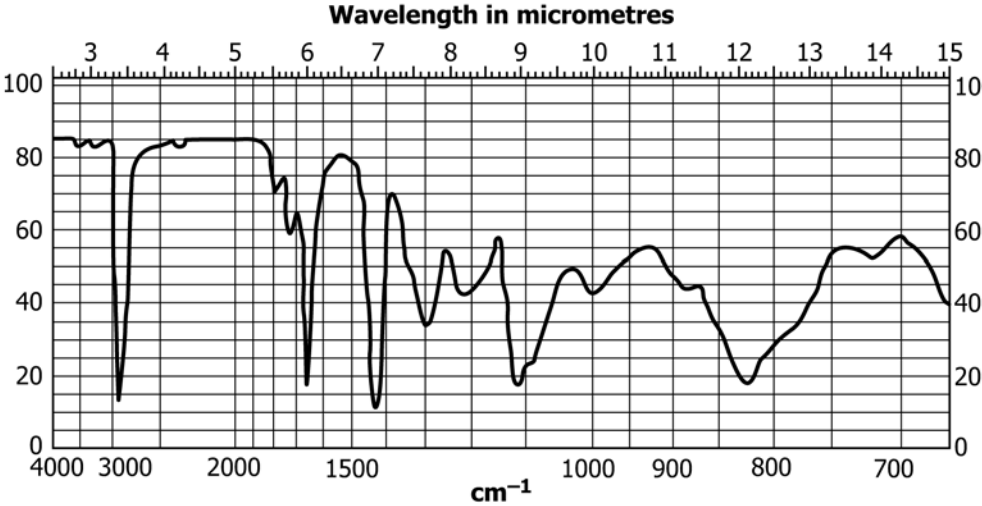

FIG. 26 CR Film from a Vulcanizate

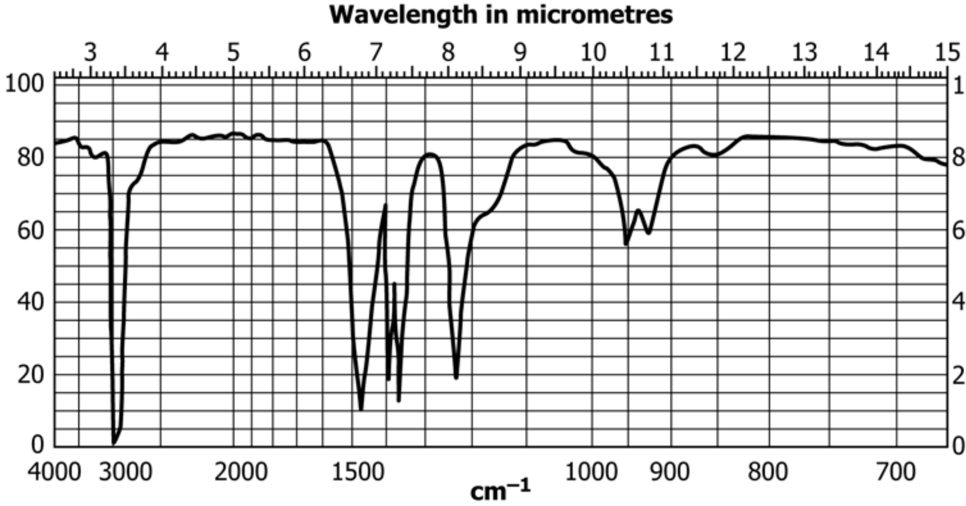

FIG. 27 IIR Film from Raw Rubber

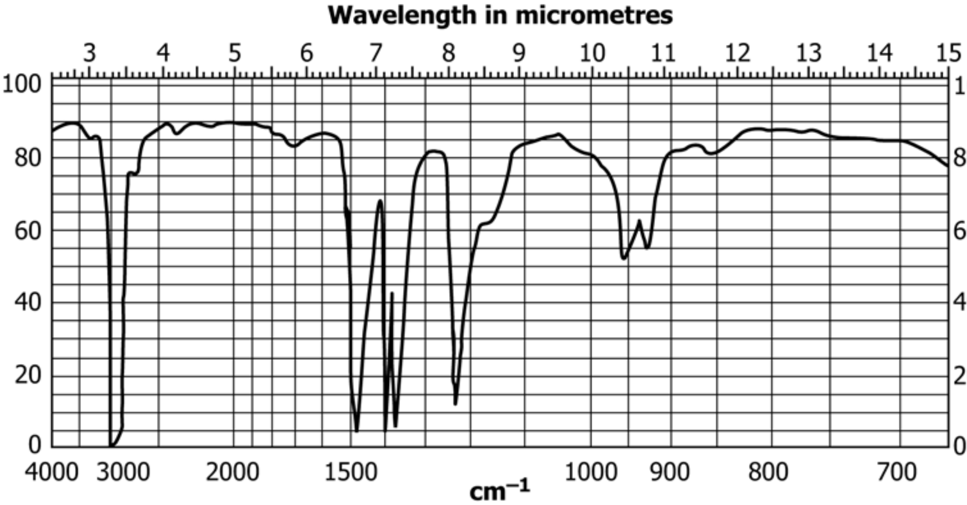

FIG. 28 IIR Film from a Vulcanizate

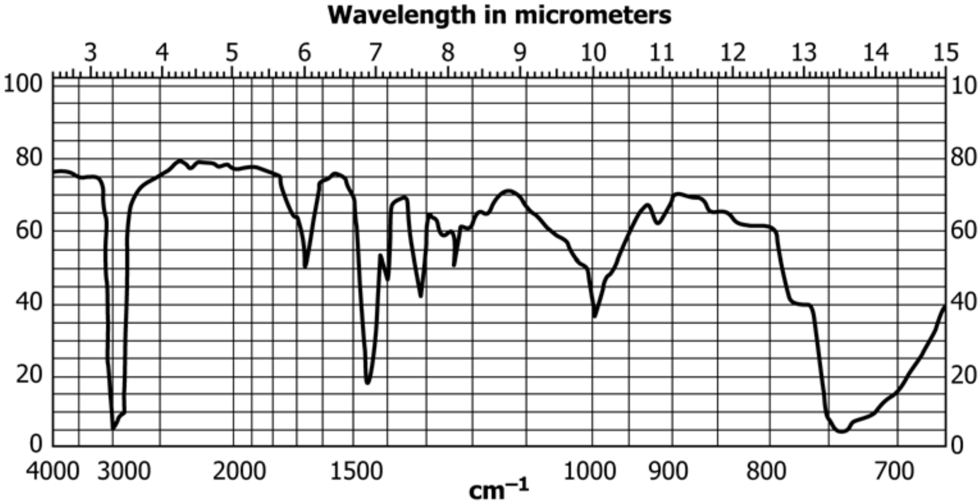

FIG. 29 BR Film from Raw Rubber

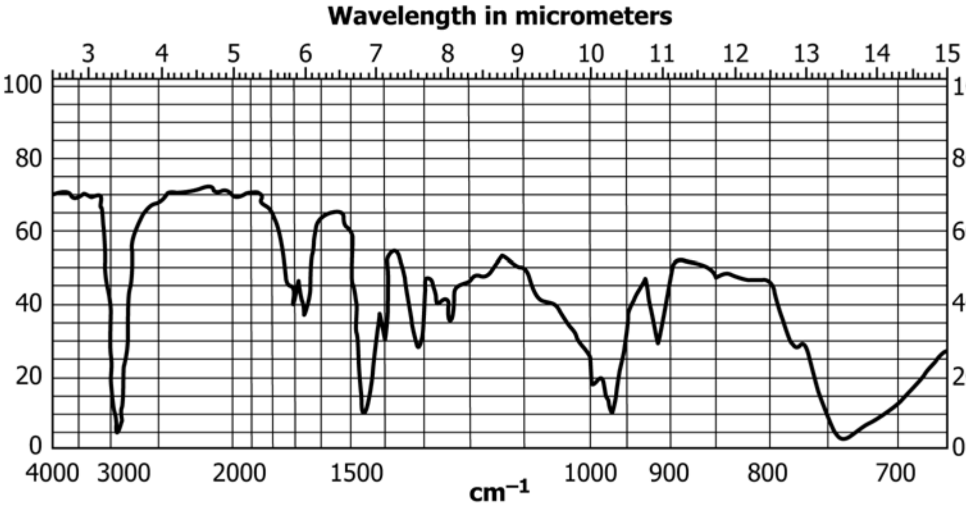

FIG. 30 BR Film from a Vulcanizate

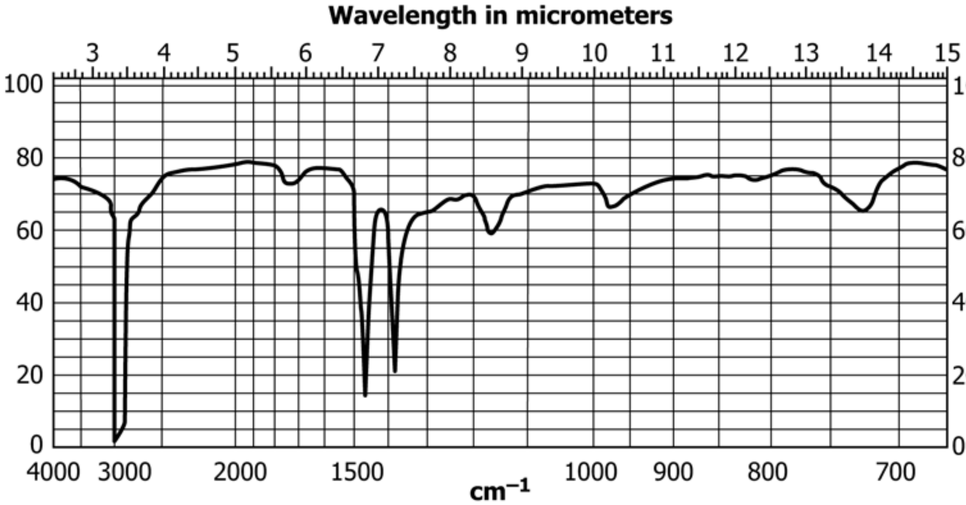

FIG. 31 EPM Film from Raw Rubber

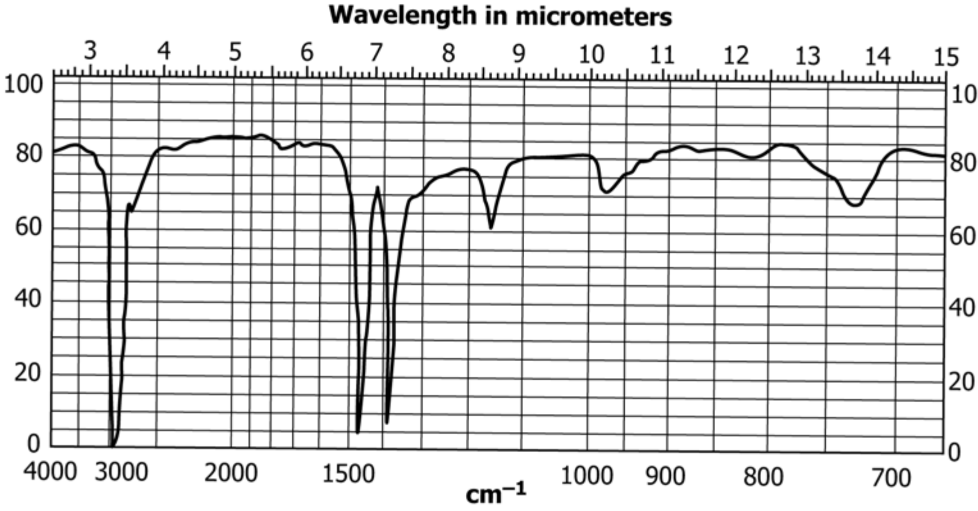

FIG. 32 EPM Film from a Vulcanizate

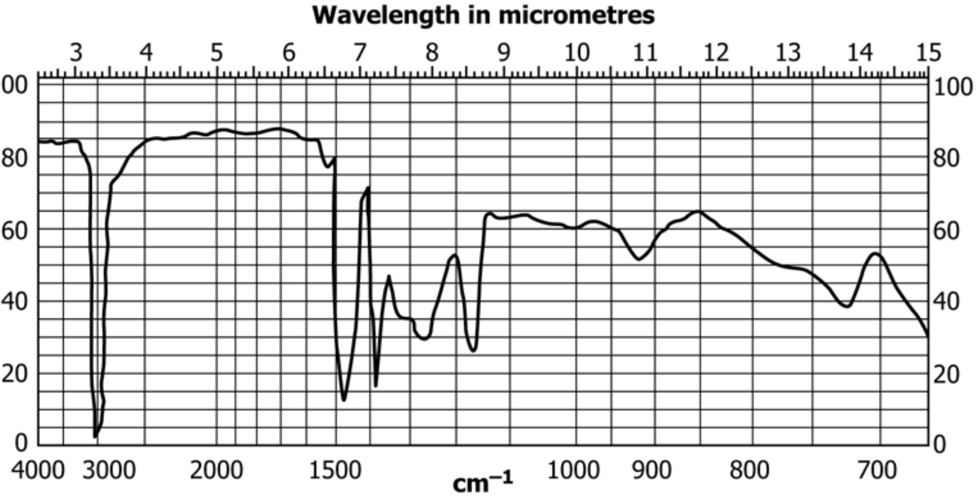

FIG. 33 CSM Film from Raw Rubber

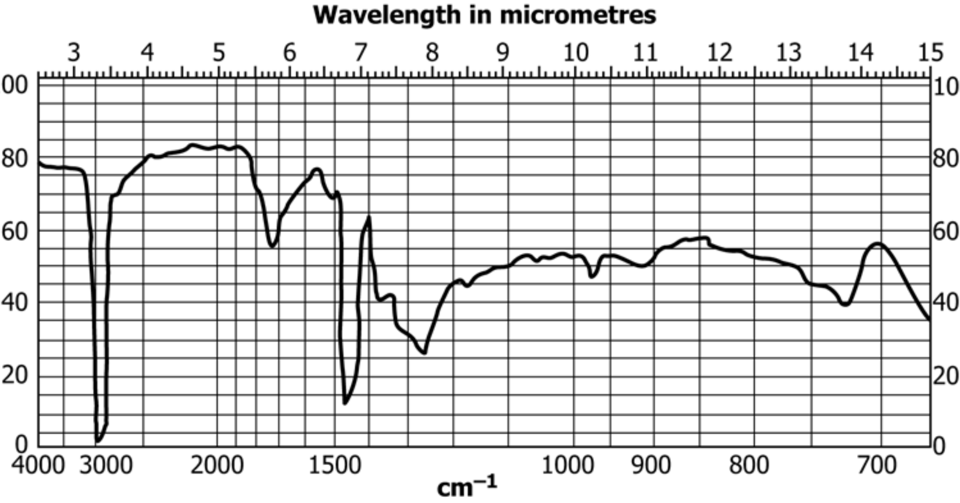

FIG. 34 CSM Film from a Vulcanizate

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